Energy Conversion Application of Chemicurrents Induced in

Metal-Semiconductor Nanostructured Devices

BY

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THESIS

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TABLE OF CONTENTS

1	INTRODUCTION	
2	LITERATURE REVIEW	ļ
	2.1 Hydrogen Sensing and Monitoring.	Ģ
	2.2 Solid State Energy Conversion Devices	13
	2.3 Wide Bandgap Semiconductors	17
	2.3.1 Silicon Carbide	18
	2.3.2 Gallium Phosphide	19
	2.4 Non-Semiconductor Materials (Metal Substrates)	2
	2.5 Schottky Contacts	22
	2.5.1 Schottky Barrier Construction.	23
	2.5.2 Schottky Contact Under External Bias	26
	2.5.3 Current Transport Mechanisms in Schottky Contacts	27
	2.5.4 Application of Schottky Diodes.	33
	2.6. Ohmic Contacts	3
	2.6.1 Ohmic Contact Fabrication Thoery	30
	2.6.2 Criteria for Ohmic Contact Formation	39
3	EXPERIMENTAL WORK	4
5	3.1 Materials	42
	3.2 Experimental Equipment	4
	3.2.1 Electrochemical Cell	4
	3.2.2 E-beam Evaporator	4
	3.2.3 Ultra High Vacuum System	4
	3.2.4 Mass-Spectrometer	4
	3 2 5 Ohmic Contact Fabrication Procedure	4
	3 2 5 1 Ohmic Contacts on Semiconductor Substrates	4
	3 2 5 2 Ohmic Contacts on Metallic Substrates	5(
	3 2 6 Characterization Techniques	5(
	3.2.6.1 X-Ray Diffraction (XRD)	5
	3 2 6 2 Scanning Electron Microscopy	52
	3.3. Experimental Procedure	5
	3.3.1 Ohmic Contact Fabrication procedure for Semiconductor and Metallic	~ •
	Substrates	5
	3 3 2 Shoottky Barrier Contacts Fabrication Technique	5
	3.3.3 Chemicurrent and Diode Characteristic Measurement and Sample	5
	Characterization	5
		-

4	IN-SITU MEASUREMENT AND CONTROL OF TEMPERATURE OF PLATINUM				
	NANOFILMS ON SILICON SUBSTRATES				
	4.1 Introduction				
	4.2 Experimental Procedure				
	4.3 Results and Discussion				
	4.3.1 Direct In-situ Resistive Nanofilm Thermometry Method				
	4.3.2 Resistive Heating Method				
	4.4 Conclusion				
5	EFFECT OF CHEMICURRENT PROPERTIES OF Pt/SiC PLANAR				
	NANOSTRUCTURES BY HYDROGEN ADSORPTION AT AMBIENT				
	CONDITIONS				
	5.1 Introduction				
	5.2 Experimental Work				
	5.3 Results and Discussion				
	5.3.1 Measuring Thermal Stability, Ideality Factor and Schottky Barrier Height				
	5.3.2 Chemicurrent Measurements				
	5.4 Conclusions				
6	SEPARATION AND ANALYSIS OF ELECTRIC CURRENT COMPONENTS ON				
	Pt/n-GaP PLANAR NANOSTRUCTURE				
	6.1 Introduction				
	6.2 Experimental Procedure				
	6.3 Results and Discussion				
	6.3.1 Electrical Properties				
	6.3.2 Calibration Curve				
	6.3.3 Chemicurrent Studies				
	6.3.3.1 Chemicurrent Component Separation Technique				
	6.4 Conclusions				
_					
1	CHEMICAL TO ELECTRICAL ENERGY CONVERSION APPLICATION OF				
	$METAL-UXIDE (Pt/TiO_2) COMPOSITE CATAYLSTS$				
	7.1 Introduction				
	7.2 Experimental Procedure				
	7.3 Results and Discussion				
	7.3.1 Sample 11; Anodized at 1.20 A and 150 V				
	7.3.2 Sample 01; Anodized at 1.69 A and 175 V				
	7.3.3 Sample 10 and Sample 30				
	7.3.4 Effect of Hydrogen Pressure on Schottky Barrier Height and Ideality Factor				

	Measurements	150
	7.3.5 Effect of Anodization Parameters on the Oxide Layer Structure and Surface	
	Morphology	153
	7.4 Conclusions	159
		168
8	CONCLUSIONS	
9	CITED WORK	170
	VITA	186

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
I.	PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN AND OTHER FUELS	10
II.	COMPARISON OF ELECTRICAL, MECHANICAL AND THERMAL PROPERTIES OF GaP AND SiC	20
III.	METAL WORK FUNCTIONS AND SEMICONDUCTOR ELECTRON AFFINITIES	41
IV.	TITANIUM ANODIZATION PARAMETERS	56
V.	ALUMINUM ANODIZATION PARAMETERS	57

LIST OF FIGURES

PAGE

FIGURE

1.1. U.S. Energy consumption and energy production (Energy Information Administration 2010)..... 2 1.2. U.S. energy expenditure (Energy Information Administration 2010).... 2 1.3. Primary Energy production by source in U.S. 3 1.4. Carbon dioxide emission content in atmosphere from fuel source...... 4 2.1. Architecture of the energy conversion device used to detect chemicurrents induced by surface chemical reactions..... 15 2.2. Schottky contact between n-type semiconductor and metal (a); and creation of a barrier along with band bending (b)..... 24 2.3. Depicts the detailed spillover mechanism; hydrogen desorption, ionization and spillover (1&2), $2H^+ + 2e^- + 1/2O_2 = H_2O$ process on TiO2 (3), product desorption process (4)..... 33 2.4. Energy band diagram for an n-type metal-semiconductor Ohmic contact system in separation (a) and in contact (b) (A. K. Singh., (2008))..... 37 2.5. Illustration of the Ohmic contact formation in a n-type semiconductor system. (a) $q\phi_m < q\phi_s$ (b) band alignment after the formation of contact..... 39 3.1. Schematic of the Anodization cell..... 44

3.2.	High vacuum chamber for V-I measurements. (1) vacuum/ gas mixture handling components. (2) mass spectrometer, (3) signal conditioning unit, (4) multi channel temperature Control, (5) analytical chamber, (6) main flange for sample mounting and (7) precision current/voltage source	47
3.3.	Schematic of brazing assembly for 4H-SiC Systems	54
3.4.	Schematic of Brazing assmbly for n-GaP System	54
3.5.	Final schematic of the fabricated system	58
3.6.	Sample holder assembly	59
4.1.	Nanofilm with buses as CV prototype cathode; thin support wires attached to ohmic contact (top). Electrical circuit used for R(T) measurement, direct resistive heating and temperature measurement studies (bottom).	63
4.2.	Resistance-temperature dependence for Pt nanofilm on Si and SiC substrates	65
4.3.	Wheatstone bridge circuit for ultrasensitive in-situ temperature control of nanocathod temperature. Potentiometer sets up a required temperature, I- Current generated by the novel cell	67
4.4.	Initial heating rate and final temperature of 20nm Pt film on a SiC substrate as a function of the voltage applied for heating. Inset: Electric powere dissipated as a function of voltage applied	68
5.1.	Charge carrier transport in the metal-semicondcutor heterojunction system; (1) thermionic emission, (2) recombination current (electrons from metal to semiconductor), (3) electron diffusion	73
5.2.	Stable resistance to temperature behavior of Pt nanofilm (Pt/n-SiC system) after annealing at 250°C for about 30 hrs	78

5.3.	Electrical diode out-of-plane properties (current-voltage behavior) of Pt/n-SiC nanostructure system after annealing at 250C for about 30 hrs		
5.4.	Shows the LN(I) versus Voltage (I-V curve at 240C); used to find the slope of the line for calculating ideality factor	80	
5.5.	Ideality factor and Schottky barrier height; Diode characteristics of Pt/n-SiC nanostructure system	81	
5.6a.	Temperature kinetics. The inset shows the long term kinetics of the process in presence of H2 and N2 in two different cases	83	
5.6b.	Chemicurrent kinetics for the two scenarios studied for Pt/n-SiC nanostructure system	83	
5.7.	Chemicurrent peak value dependence on the ratio of O_2 and N_2 partial pressures in 760 Torr mixture	85	
6.1.	Transportation of hot electrons (chemically excited) over Schottky barrier in metal-semicondcutor nanostructure system. Barrier potential separates electric charge, and nanofilm cathode performs as catalyst for the reaction (hydrogen oxidation). Schematics on the right depict the sample mounting without the help of a sample mount or holder	89	
6.2.	Front view and the electrical wiring schematic. The sample is heated resistively at nanofilm terminals a and b. Chemical induced current I and leakage current Io is measured at terminals b and c	92	
6.3.	Electrical diode out-of-plane properties (current-voltage behavior) of Pt/n-GaP nanostructure system	94	
6.4	Variance of electrical properties with temperature for Pt/GaP Schottky structure	95	

6.5.	Shows the variation of Resistance fraction with increasing temperature. Ratio of the diose resistance measured at 1.15V forward and reverse biases		
6.6.	Variation of diode characteristics with temperature	97	
6.7.	Dependence of resistance on temperature at Pt nanofilm. Resistance measured after 25 and 60 hrs of sample annealing in vacuum at 530 K.	99	
6.8.	Current component separation technique. Resistively heated Pt/n-GaP sample at 393 K nanocathode temperature, exposed to 2:1 oxyhydrogen mixture (black) and oxynitrogen mixture (red). For the nanofilm under bias, any leakage current is recorded as a constant instrumental compliance current. The generated current is identified upon elimination of the leakage component by switching off the nanofilm bias. Difference in the peak values represents the contribution from the diabatic component of the current.	101	
6.9.	Dependence of total current magnitude on the nanocathode temperature at various oxy-hydrogen mixture pressures. Inset plot shows dependence of individual components of current at 120 Torr case (log scale)	103	
6.10.	Temperature dependence of the diabatic current fraction, I_d/I , at various stoichiometric oxy-hydrogen mixture pressures	104	
6.11.	Contribution from each current component to the total current generated in the system with increase in temperature at 120 Torr of oxyhydrogen pressure	105	
6.12.	Effect of dilution with nitrogen gas on the chemicurrent at two different temperatures	106	
6.13.	Dependence of quantum efficiency with temperature at 90 Torr of reactive gas mixture pressure	107	
7.1.	(a) Older electrolyte free chemical energy to electrical energy conversion system by thermoelectric effect in a narrow bandgap		

	semiconductor system, (b and c) e-h pair and hot electron nonadiabatic mechanisms respectively, in a wide band gap semiconductor system	1		
7.2.	New architecture of the Pt/TiO2 system	1		
7.3.	Schematic of the Pt/TiO2 system with the electrical connections. (1) TiO2 porous oxide layer, (2) Ti support, (3) Electrical contacts and (4) Ti base metal/ Ohmic contact	1		
7.4.	Anodization kinetics, Voltage to time dependence for the three samples fabricated			
7.5	The oxygen-hydrogen mixture kinetics for sample 11	1		
7.6.	Chemicurrent kintics for Sample 11, showing fast and slow reaction regimes	1		
7.7.	Surface temperature kinetics as for Sample 11	1		
7.8.	Shows the long term kinetics of the residual hydrogen pressure	1		
7.9	XRD spectra showing the two oxide forms of titania; Anatase and Rutile. For sample 11 higher rutile phase was observed	1		
7.10	Shows the nanomesh layer of the platinum metal deposited on top of TiO2 layer	1		
7.11	I-V dependence between the Ti and one of the Pt terminals; positive bias is applied to the Pt terminal	1		
7.12	Total pressure kinetics monitored for about 4 hours; Sample 01	1		
7.13.	Long term chemical induced current generated during the fast and slow reaction regimes	1		
7.14	Long term temperature kinetics for Sample 01 during fast and slow reaction modes	1		

7.15.	15. Hydrogen partial pressure kinetics for fast and slow reaction modes fo Sample 01		
7.16.	XRD spectra for sample 01; anodized at 1.69 A and 175 V		
7.17.	Pt coated TiO2 layer for sample 01; Nanomesh support structure		
7.18	Out-of-plane I-V dependence between Ti and one the Pt terminal in vacuum and oxyhydrogen mixture for Sample 10(a) and Sample 30 (b)		
7.19	Long term Total pressure kinetics for the fast and slow reaction regimes for Sample 10 (a) and Sample 30 (b)		
7.20	Mass spectroscopy for H2 pressure for Sample 10 (a) and Sample 30 (b)		
7.21	Long term chemically induced current kinetics for both fast and slow reaction regimes for Sample 10 (a) and Sample 30 (b)		
7.22.	Temperature kinetics for fast and slow reaction modes for Sample 10 (a) and Sample 30 (b)		
7.23	XRD spectra for Sample 10 (a) and Sample 30 (b); Sample 10 showed higher trace amounts of anatase phase compared to Sample 30		
7.24	Pt deposited TiO ₂ surface for Sample 10 and Sample 30; Nanomesh support structure		
7.25.	Chemicurrent kinetics for sample 10; with varying load resistance regime		
7.26.	Variance of the chemicurrent, voltage and electrical power output (inset) with load resistance		
7.27.	Schottky barrier height dependence on Hydrogen gas pressure		
7.28.	Dependence of ideality factor on the hydrogen pressure for the three samples		

7.29.	XRD spectra showing increase in the rutile phase fraction in TiO_2 for a greater final anodizing voltage or film thickness at a constant supplied current of 0.85 A (increasing voltage from top to bottom)	155
7.30.	XRD spectra showing increase in the rutile phase fraction in TiO_2 for a greater final anodizing voltage or film thickness at a constant supplied current of 1.20 A (increasing voltage from top to bottom)	156
7.31.	XRD spectra showing increase in the rutile phase fraction in TiO_2 for a greater final anodizing voltage or film thickness at a constant supplied current of 1.69 A (increasing voltage from top to bottom)	157
7.32	SEM imaging of the samples fabricated at different anodizing parameters. Finer features observed at lower voltages at all three current densities.	158

SUMMARY

Hydrogen is one the most attractive and suitable energy systems for generation of power in the future with high efficiencies and renewable properties. Nanoscale materials, because of their surface and physical properties are the promising candidates for the development of high performance energy conversion devices, essential components to ensure the efficient operation of the infrastructure and to facilitate the wide spread implementation of hydrogen technologies.

This work realizes the use of solid state energy conversion concept to develop metalsemiconductor, metal-oxide architecture devices for electrolyte free conversion of chemical energy to electrical energy by hydrogen oxidation process. This investigation addresses the synthesis of these nanostructure devices by selection of suitable system material combinations, electrical and surface morphological characterization leading to the successful implementation in generation of chemicurrents. Also, the hydrogen oxidation process on each nanostructure device is elucidated with the help of corresponding mechanisms and the performance of each system developed was evaluated based on the resulting output efficiency.

The two systems (metal-semiconductor and metal-oxide) realized, showed excellent chemical to electrical energy conversion abilities. Compared to metal-semiconductor nanostructure devices, metal-oxide systems exhibited better energy conversion abilities for indefinitely long duration of time at room temperature. The electron yield observed in considered metal-oxide systems can be sufficient for their use in practical applications. A

xvi

continued realization of these metal-oxide systems with different material combinations would lead to more ecologically friendly and sustainable energy economics.

1. INTRODUCTION

From supporting our everyday lives to promoting most advanced technologies, fossil fuels have played an important role. As these finite amounts of fossil fuel reserves are being depleted at a rate so rapid that they will not last longer to support the needs of the continuously growing population. Hence, increasing the need for development of more affordable, advanced and alternative sources of energy has become more prominent. Renewable energy sources like wind, hydro and solar powers are abundant and can be harnessed and used without further polluting our green planet. Analysts predict the transition from non-renewable energy sources or fossil based sources to some superior and renewable energy technology to occur long before the humankind consumes all the available oil and coal supplies, arguing that "the stone age did not come to an end because of lack of stones" (P. McGinniss., (2007)). However, the well established infrastructure for the extraction and distribution of fossil fuel derived power allows the cost to remain relatively low, making more expensive alternate energy harvesting methods less attractive.

Department of Energy study reports in United States show an increase in energy consumption by 300% in the last 60 years (U.S. Energy Information Administration / Annual Energy Review 2010) as shown in Figure 1. The study also showed the dependence on the increase in the energy imports from foreign countries at a rate greater than the U.S. production of energy.

Also the cost for producing this energy is also on the rise as shown in the studies and can be seen in the plot in Figure 2. Also it is expected that the energy consumption all over the world would be increased by at least 57% as the whole in the next 20 years.



Figure 1.1 U.S. Energy consumption and energy production (Energy Information Administration 2010)



Figure 1.2. U.S. energy expenditure (Energy Information Administration 2010)

Figure 3 shows the dependence on fossil fuel consumption for primary energy production in the United States in the last 60 years. Majority of the energy produced is from non-renewable/fossil fuel sources that are finite in quantity.



Figure 1.3. Primary Energy production by source in U.S.

The increasing dependence on foreign imports to meet energy needs, exploration of alternative means of producing energy and rightful consumption of the energy have all been in constant discussion on the political and the social front in the United States. These issues are not just limited to the United States but also address the other countries of the World. Initiatives based on the environmental, social, economic factors are attempting to reduce energy consumption and are being motivated among others by an increase in government regulations, energy prices and environmental awareness. All these factors are motivating the private and academic industries to look into novel energy harvesting techniques. Combustion of these fossil fuels has a deleterious effect on the environment. The carbon dioxide produced during these processes is a major contributor to the harmful effects on environment, the total amount of carbon dioxide byproduct produced has steadily increased in the last 15 years up to the year 2005 and after there is a slight decrease in the carbon dioxide emission due to the newer regulations and methods developed to maintain the environment as can be seen in Figure 4. These drawbacks or factors play a major role in contributing to a serious thought to look in to the advanced and alternative energy sources and technologies.



Figure 1.4. Carbon dioxide emission content in atmosphere from fuel source.

The two main concerns of the energy crisis are demand and supply. In this thesis, investigation on novel solid state electric generator devices designed for functional applications in direct power generation is discussed.

Solid state energy conversion devices that are typically know in the form of thermoelectric, thermionic and photovoltaic devices. These devices represent wellestablished concepts with very long histories (R. S. Ohl., (1946); M. Riordan et al., (1997); S. Benzer., (1947)). And also, two broad categories of non-fossil and non-nuclear technologies are known to us. They can be summarized as, the first being the conversion of mechanical energy into electric energy and the second covers the solid state electric generators. The first category is limited to utilization of wind, tidal and geothermal forms of energies for conversion to electric energy and the second uses the solar, chemical and thermal energy for the conversion process. The three major types of solid-state devices that are being investigated intensively upon are: (a) Electrochemical cells, (b) Solar cells, (c) Thermoelectric generators (A. S. Arico et al., (1998); M. A. Green., (2003)). These solid state devices use an external energy source for the generation and separation of the electric charge in the device body. Also they differ from each other by the type of energy source utilized: photonic, chemical, and thermal energy for the solar and thermoelectric cells. They also rely on different physical mechanisms of the electric charge generation and separation. The high cost of solar cells and limited efficiency and lifetime of fuel cells constrain their massive implementation. While the thermoelectric generators demonstrate better lifetimes, they do not provide satisfactory efficiency and energy density in order to successfully compete with traditional portable sources of power. The main drawback is that the researchers working on these technologies independently are confined to only these focused areas. However, the question arising is, is it possible to come up with a more efficient solution utilizing the principles of multiple device types? Are there other useful mechanisms

that are being overlooked? This current research also focuses on answering some of these broader scientific questions.

There is one possibility that needs attention at this point. In order to better understand this, let us consider the photovoltaic effect. Photovoltaic effect comprises of two physical processes i.e., photoinduced electron excitation and transport of energetic electron over internal potential barriers in a heterogeneous material [M. A. Green., (2003); R. J. Komp (1995) J. Nelson., (2003)). The external photovoltaic (emission into vacuum) effect was used in vacuum photoelements (V. K. Zworykin et al., (2005)). The vacuum gap between the collector anode and emitter cathode made with a low work function metal serves as a potential barrier separating the charge. If we consider that the cathode is heated rather than illuminated, the hot electrons proceed to the thermal equilibrium with the lattice structure, and the electron distribution will take the standard Fermi-Dirac form (C. Kittel., (2005)). And the internal thermionic emission is inherent to heterogeneous semiconductor structures with intrinsic potential barriers. By introduction of heterojunction potential barriers, researchers could selectively pass the energetic electrons and constrain the transport of phonons and lower energy electrons which contribute for the heat transfer. This effect is most utilized in pn junction, Schottky diodes and bipolar transistors. This effect was used by many researchers to improve the efficiency of the thermoelectric devices (A. Shakouri et al., (1998); A. Shakouri, (2004)).

In this investigation, metal-semiconductor diodes and metal-oxide-metal systems are used as the solid state energy conversion devices. These devices are capable of converting chemical energy directly into a more useful form of energy i.e. electrical energy. An exothermic chemical reaction such as hydrogen-oxidation can be initiated on the nanofilm of platinum or palladium and is capable of producing hot electrons. These electrons are able to travel ballistically over the Schottky barrier towards the Ohmic contact. They collect in the form of an electric current in the external circuit. This is also the basic working principle of a catalothermionic power generator (E. Karpov et al., (2009)) and requires materials with a unique combination of high bandgap and low thermal conductance. The generation of an electric current referred to as "chemicurrent" due to a surface chemical reaction is often used as an indication for the detection of gas molecules (C.K. Kim et al., (2001)). These chemical reactions usually require the presence of an external energy source for the continued production of hot electrons. This problem can be overcome by the room temperature working regimes which do not require an additional heating source. This will also ensure the presence of a self-sustainable energy regime.

These studies are focused on performing experimental and theoretical studies leading to the formulation of basic principles and practical guidelines for an efficient chemovoltaic generator (CVG). To be more exact, during the course of this study, specific questions like: (a) principles of collection and separation of the chemically induced electric charge in catalytic metal-semiconductor nanostructures will be answered. This will help to understand the physical processes responsible for the nonadiabatic energy transfer between the adsorbate and metallic catalyst; and also the ballistic electron transport in nanofilms. Also, new device type's metal-oxide (Pt/TiO2) systems are studied. The mechanisms involved (like hydrogen spillover mechanism) are highlighted during this study. (b) Universal efficiency parameter will be introduced and investigation of specific architectures, gas phase and other conditions leading to the efficient and self sustainable working regimes of the CVG generation operation will also be studied. (c) Possibility of a reverse polarity CVG will also be investigated.

In the following chapters, principles required to carry out this investigation are explained (Chapter 2) in detail along with the experimental procedure and the fabrication techniques employed to manufacture these specific sample systems (Chapter 3). And finally, the findings of this investigation for each individual type of system can also be found under the results and discussion section divided into multiple chapters. Chapter 4 and Chapter 5 discuss the electrical and chemicurrent analysis along with the new techniques developed to resistively heat the nanofilm cathode layer on and the method developed to accurately separate the two current components on Pt/SiC nanostructure device is discussed. Chapter 6 discusses the studies carried out on Pt/GaP energy conversion device and finally Chapter7 discusses the findings of the electrical and chemicurrent analysis on higher efficiency Pt/TiO₂-Ti device systems. This thesis is then concluded by a few concluding remarks.

2. LITERATURE REVIEW.

2.1. Hydrogen Sensing and Monitoring.

With growing concern all over the world about the depleting energy reserves, with increase in population, number of automobiles is leading to the demand for newer renewable sources is also rising significantly. Alternative sources of energy are being developed to meet the demands of environmental issues and also to support the depleting natural reserves. Hydrogen is becoming a popular fuel that has a great potential for use in most energy related applications. Atomic hydrogen is crucial for several purposes such as passivation of semiconductor defects, production of synthetic diamond, cleaning of semiconductor surfaces, ultra high vacuum compatible beams and fuel cell applications (H. Neinhauss et al., (1999)).

Safety is a major concern and represents a potential barrier to the introduction of hydrogen technologies. Being colorless and odorless, it is impossible to perceive an unwanted release of hydrogen. Hydrogen is one of the cleanest and most abundant fuels known to mankind. But the disadvantage associated with this fuel if that it has low ignition point. It is highly flammable and explosive leading to difficulties in its storage, transportation and handling. Hydrogen is also a highly diffusive and even a small leak into the atmosphere can lead to catastrophic outcomes. These issues along with many other emphasize the importance of monitoring hydrogen in industrial processes such as petroleum refineries, fuels cells, hydrogen storage and distribution systems (A. Salehi et al., (2006)). Table 1 depicts the physical and chemical properties of hydrogen, methane and petrol.

Property	Hydrogen (H ₂)	Methane (CH ₄)	Petrol (-CH ₂ -)
Lower heating value (kWh.kg ⁻¹)	33.33	13.9	12.4
Self ingnition temperature (°C)	585	540	228-501
Flame temperature (°C)	2045	1875	2200
Ignition limits in air (Vol%)	4-75	5.3-15	1-7.6
Minimal Ignition energy (mW.s)	0.02	0.29	0.24
Flame propagation in air (ms ⁻¹)	2.65	0.4	0.4
Diffusion coefficient in air (cm ² .s ⁻¹)	0.61	0.16	0.05
Toxicity	No	No	High

 TABLE I

 PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN AND OTHER

 FUELS (L. Schlapbach et al., (2001))

Furthermore, safety is the major physiological and sociological issue from the stand point of commercialization and public acceptance of hydrogen technologies (P.P. Edwards et al., (2007)). The use of hydrogen sensors is a necessity not only to ensure the efficient and safe operation of the infrastructure but also to facilitate the public acceptance of hydrogen energy systems. In the last couple of decades, different detection principles, methods and materials have been utilized to fabricate these hydrogen sensors. These are generally classified as catalytic bead sensors, electrochemical sensors, hydrogen field effect transistors and Schottky diodes and semiconductor metal oxide sensors (V.M. Aroutiounian., (2005); V.M. Aroutiounian., (2007)). Although most of these technologies are used in industrial environments, they could not be implemented in fuel cells, household, biomedical and transportation applications. This is due to the size, complexity, slow response time, cost and energy input. For complete acceptance and implementation of a fully intedrated hydrogen economy requires the development of sophisticated hydrogen sensors with superior sensitivity, fast response, IC compatibility, ability to work at ambient temperatures and low cost and low power consumption.

Most of the existing sensor technologies based on silicon are faced with challenges to function effectively at high temperatures (C.K. Kim et al., (2006)). Sensors based on the metal-semiconductor layered structures with a noble metal coating are inexpensive and reliable. These sensors reflect a change in their electrical properties when in contact with hydrogen gas. But, these changes take a longer time as the gas has to diffuse through multiple layers. Also there is a chance that these sensors may show a permanent change in electrical properties when exposed to hydrogen for longer durations (H. Neinhauss et al., (1999)). Another issue encountered is the formation of metal hydrides, hydrocarbons and carbon monoxide which may block the metal surface (I. I. Nedrygailov et al., 2010). Hence, there is an immediate demand for sensors with increased sensitivity, faster response time and stability at higher temperatures so that hydrogen monitoring is efficient even in aggressive environments.

In the recent past, Schottky diodes have been successfully used in the sensors for efficient and reliable hydrogen detection and monitoring (S. P. Nehra et al., (2010); I. I. Nedrygailov et al., (2010); H. Neinhauss et al., (1999); W. P. Kang et al., (1994)). In these systems the hydrogen-metal interaction is a surface phenomenon rather than the diffusion process involved in the layered structures. The detection of hydrogen gas is based in the observation of a chemicurrent or change in voltage-current behavior. The use of the catalyst metal layer increases the dissociation and chemisorption of the gas molecules followed by a

solid state diffusion process of atomic hydrogen through the film which finally leads to adsorption of the atomic hydrogen, which occurs at the metal-semiconductor interface. Once the hydrogen atoms reach the interface, they become trapped and form a polarized layer with a dipole moment approximately equal to $2-4D/m^3$ of hydrogen atoms (J. Fogelberg et al., (1995); M. Löfdahl et al., (2002)). The presence of the dipole layer causes a change in the work function of the metal. This in turn affects the Schottky barrier height thereby leading to a shift in the current-voltage characteristics. Parameters such as ideality factor and series resistance are also affected because of this shift. The adsorbed hydrogen decreases the metal work function and also decreased the barrier height, resulting in increase in the current flow. The Schottky barrier height is exponentially dependent on the current through the diode that means a small change in the barrier height can lead to a significant change in the current and is explained in detail in section 2.5. The adsorption of hydrogen on the metal surface creates energetic electron-hole pairs due to transfer of non-adiabatic energy. These electrons then ballistically transport over the Scottky barrier and are collected as "chemicurrent" in the external circuit via the Ohmic back contacts. It was observed that the presence of molecular oxygen in the host environment increase the sensitivity of the device. This is due to that exothermic reaction leading to the formation of water molecule on the surface of the nanofilm (H. Neinhauss et al., (2002)).

Factors that lead to the effective functioning of these systems are type of semiconductor material used, the thickness and type of metallic nanofilm used. The response time is dependent on the type of interactions between hydrogen and the catalyst film. The type of chemical reaction occurring on the substrate surface, extent of mass transport or diffusion and the amount of sites available for hydrogen adsorption are other important factors that influence sensitivity. And also, depending on the type of metal nanofilm used the sensitivity to hydrogen varies, for example palladium has higher hydrogen sensitivity compared to platinum metal (W.P. Kang et al., (1994); H. Neinhauss et al., (1999)b).

2.2. Solid State Energy Conversion Devices.

There are different technologies in use currently for the production of the greener and sustainable energy such as conversion of mechanical energy to electrical energy using windmills, geothermal turbines etc and conversion of chemical, solar and thermal energy to electrical energy using fuel cells, solar cells, thermo electric generators etc. Of all, the latter technologies like conversion of solar energy to electric energy proved more efficient and reliable as it is abundantly available and energy can be produced continuously and also accessibility to numerous sources to convert the chemical or thermal energy more useful and user friendly energy attracted every ones attention. These devices are useful especially in applications requiring mobility and usage of heavy mechanical systems for producing energy can be avoided such as automobiles and portable electronic devices. However, these devices have a few setbacks; like the high cost of production, low power to weight ratio combined with the limited lifetime of fuel cells, poor efficiency and energy density of thermoelectric devices (E. Karpov et al., (2009); E. Karpov et al., (2009)b); F. Rumiche., (2009) F. Rumiche et al., (2008)).

These setbacks encountered can be eliminated by using Schottky barrier heterojuntion structures in thermoelectric power generators. Some of the advantages of these novel devices can be summarized as; longer lifetimes, higher energy densities, efficiency and robustness. The working principle of these devices is based on the chemically induced electron excitation and ballistic transportation of electrons over the Schottky barrier. Any exothermic chemical reaction on the metal catalyst surface is bound to produce energetic electron-hole pairs since there is no defined gap between the vacant and occupied energy levels in a metal. When the reaction is initiated on a metal surface with high work function, a considerable amount of energy is transferred to as hot or ballistic electrons. This mechanism was first observed during oxygen adsorption on cesium metal surface and chlorine adsorption on a thin potassium film (X. Ji et al., (2005); J.Y. Park et al., (2006)). Hot electrons and holes were also observed during the adsorption studies of atomic hydrogen and deuterium on catalyst silver and copper surfaces that were a part of the Schottky device (H. Nienhaus et al., (1999)). Apart from the studies based on the adsorption of atomic hydrogen and deuterium, hydrogen oxidation, carbon monoxide oxidation and chemisorption or physisorption of monoatomic or polyatomic gasses such as O, Xe, NO, C2H4CO2 etc are also studied (X. Ji et al., (2005); J.Y. Park et al., (2006); J. Y. Park et al (2006)b; A. Hervier et al., (2009); B. Gergen et al, (2001)). These chemical reactions can lead to both adiabatic and nonadiabatic processes. Where the adiabatic process implies generation of heat which causes the metallic film to heat up, the non-adiabatic process leads to the transfer of chemical energy to the electron subsystem resulting in the ballistic transport of electrons.

The typical architecture of an electrolyte free solid state energy conversion device where a chemical reaction is initiated on the thin film of metal which forms the Schottky contact is shown in Figure 2.1. The reaction being exothermic generates hot electron hole pairs. These energetic electrons are able to pass over the Schottky barrier and move over towards the semiconductor anode. Once the electrons reach the anode, they diffuse through the Ohmic contact and towards the cathode surface via external circuit. They appear in the form of electrical current and which are known as the "chemicurrent". The chemicurrent generated is attributed to the nonadiabatic process, which is due to the generation of the hot electrons from the exothermic reaction on the metal catalyst surface. During this process few electrons attain additional energy to cross over the Schottky barrier from the heating of the metallic film as a result of the surface reactions and undergo the thermionic emission process (E. Karpov et al., (2009)). These electrons detected attribute to the adiabatic portion of the chemicurrent generated and recorded.



Figure 2. 1. Architecture of the energy conversion device used to detect chemicurrents induced by surface chemical reactions.

In these systems the energy conversion process requires the presence of an external power source for the continued generation of the current. The electron flux developed in the device depends on factors such as thickness of the nanofilm, reaction turnover rate, Schottky barrier parameters and the presence of the oxide layer and many more (X. Ji et al., (2005)). For these devices the turnover rate is defined as the number of product molecules per noble metal site per second and can be increased by changing the flow rate of the gas and the temperature of operation. Also, the catalytic diode materials may be suitably chosen depending upon the chemical reaction occurring and the nature of the heterogeneous junction material used.

These devices depend mainly on the nonadiabatic processes for the generation of electrical energy. The nonadiabatic process not only minimizes the heat losses but also increases in the efficiency and energy densities of these devices. In the past these devices have incorporated semiconductor materials like silicon, gallium phosphide and other materials to increase the performance of the device. Also, high quantum yields of about 1.4% have been reported using these devices at elevated temperatures (E. Karpov et al., (2009)b). For these devices, low thermal conductivity along with high bandgap structures is preferred as the heat produced during this process is solely used in maintaining the metal cathode nanofilm temperature. The low thermal conductivity helps in directing the heat flux away from the cold anode (Ohmic contact) because of the thermal gradient that is generated. This would also help in attaining the self-sustainable energy regime for the device. Apart from these semiconductor materials mentioned, other oxide films grown on top of a metallic substrate are also being studied currently by many researchers for use in these device systems (J. M. Herrmann et al., (1982); A. Hervier et al., (2009); J. Y. Park et al., (2007)). In

following sections of this chapter; the material selection criteria for these devices, importance of the Schottky barrier and the Ohmic contact, different mechanisms that could lead to the generation of chemicurrents or electron transport mechanisms, would be discussed.

2.3. Wide Bandgap Semiconductors.

Silicon based technologies are being limited these days as they can no longer be used for high temperature and power applications as the theoretical limit is approached. Most of these applications require high switching frequencies, good thermal stability, high breakdown voltage and low on-state conduction losses. In order to meet these requirements semiconductor materials known as wide bandgap semiconductors (WBG) are used. For these materials the gap between the valence band maximum and the conduction band minimum is more than 2 eV. Due to this high bandgap, these materials have superior properties which make them suitable for high power electronics, transportation, nuclear instrumentation and aerospace applications.

Wide bandgap material based devices are generally used at higher temperatures making them suitable for power electronics (A. Elasser et al., (2002)). Due to this, the electrons excited need sufficiently highly thermal energy to move to the conduction band from the valence band (B. Ozipenci et al., (2003). Hence electrical characteristics are retained even at higher temperatures. The higher thermal conductivity of these materials allows for heat conduction to the surroundings thereby resulting in slower increase of device temperature. This eliminates the need for expensive, efficient and large cooling systems in order to maintain device temperature. This is particularly useful in the transportation industry because lighter vehicles with lower fuel consumption can be manufactured. Some of the other useful properties of these materials are; higher electron ballistic transport probabilities, large heterojunction offset potentials and negative electron affinity for materials with higher bandgaps. The other advantages of WBG materials lie in their lower intrinsic carrier concentration, higher electric breakdown field, lower on-impedance and higher saturated drift velocity. Hence it is evident that replacement of silicon by wide bandgap semiconductors would result in devices with higher efficiency and lower losses and reduced sizes.

2.3.1. Silicon Carbide.

Silicon carbide is one of the widely used WBG semiconductor material. It has high dielectric strength and thermal conductivity when compared to simple silicon. It exhibits one dimensional polymorphism called "polytypism" and has over 150 polytypes. The three basic and commonly known polytypes are cubic (C), hexagonal (H) and rhombohedral (R). These polytypes differ in the stacking arrangement of the tetrahedrally bonded Si-C layer. In this study, 4H-SiC polytype has been used. This and 6H polytypes are the only two forms of SiC that are commercially available in both epitaxial layers and bulk wafers. Both the polytypes have n-type doping and are indirect bandgap semiconductors. 4H-SiC has an equal number of cubic and hexagonal bonds and the bandgap for 4H-SiC is 3.23eV. 4H-SiC has superior electrical properties and is used widely in electronic devices. The anisotropic electronic mobility of 4H-SiC is higher, indicating that the mobility along the two planes of the semiconductor is the same. Another attractive feature of SiC is its ability to form an oxide layer upon heating. This oxide layer is a critical component in the development of promising technologies in the area of metal/oxide-semiconductor based electronic devices (H. Morkoc, et al., (1994)).

2.3.2. Galium Phosphide.

Gallium phosphide (GaP) is a compound semiconductor with indirect bandgap energy of 2.26 eV. It is popular for its use in light-emitting diodes and other opto-electronic devices. Diodes made from GaP are particularly suited for high temperature operations. The reverse leakage in these diodes is about four times less than conventional silicon diodes. The efficiency of these diodes is slightly on the lower side because of the reduced minority carrier lifetimes. This is attributed to the indirect bandgap in these conductors. GaP has a cubical zinc blende crystal structure. Crystals of GaP can be grown by ion implantation, metal organic chemical vapor deposition, liquid phase epitaxy etc (R.M. Biefield., (1982)). It is stable in air till a temperature of 750°C but begins to vaporize in vacuum at 1000°C. The intrinsic region in gallium phosphide develops only at high temperatures of about 500°C. The electron and hole mobilities in GaP are pretty low. For the purpose of this study, n-type gallium phosphide has been used. Commercially available wafers are orange in color and tend to be brittle. Table 1 provides further the other important properties of these two materials selected for the current investigation (J. B. Casady et al., (1996); N. M. Yoder., (1996); L. M. Tolbert et al., (2003)).

TABLE II

COMPARISON OF ELECTRICAL, MECHANICAL AND THERMAL PROPERTIES OF

Property	GaP	4H-SiC
Crystal structure	Zinc Blende	Wurtzite
Melting point (⁰ K)	1743	3103 ± 40
Bandgap (eV)	2.2	3.23
Thermal Conductivity (W/cm-K)	1.1	4.9
Specific heat (J g ⁻¹ °C ⁻¹)	0.43	0.69
Thermal diffusivity (cm ² s ⁻¹)	0.62	1.7
Electron Affinity (eV)	3.8	3.7
Saturation Velocity (x10 ⁷ m/s)	1.25	2
Electron Mobility (cm ² /V.s)	<=250	<=900
Hole Mobility (cm ² /V.s)	<=150	<=120
Electric breakdown field (kV/cm)	1000	600
Bulk Modulus (x 10 ¹² dyne/cm ²)	88	2.2
Intrinsic carrier concentration (cm ⁻³)	7.7 x 10 ⁻¹	8.2 x 10 ⁻⁹
Dielectric constant	11.1	9.7

GaP AND SiC
2.4. Non-semiconductor Materials (Metal Substrates).

In this investigation, semiconductor substrate materials were replaced by titanium dioxide grown on titanium substrate and alumina grown on aluminum substrate. The oxide layer grown on these substrates act as the semiconductor layer helping the formation of the Schottky barrier required for these solid state energy conversion devices.

Titanium dioxide (TiO₂) is an important commercial material which is widely used in many applications. This material being a typical n-type semiconductor material, it is commonly used applications for photocatalysis (M. E. Kurtoglu et al., (2011); Fujishima, Akira et al., (1972)) dye sensitized solar cells (D. Martineau., (2007); B, O'Regan et al., (1991)) and gas sensors. In nature it occurs as the well-known naturally occurring minerals rutile, anatase (both tetragonal) and brookite (orthorhombic). Rutile is found to be the most thermodynamically stable phase of titanium dioxide. And the anatase phase is stable up to temperatures around 800°C, above this temperature it changes into rutile phase. Researchers have reported that anatase structure formed influences the photo catalytic activity of titanium dioxide thin films (C. Su et al., (2004)). Also the electron affinity of titania is of the order of 1.1 to 1.2 eV.

Aluminum oxide (Al_2O_3) is commonly referred to as alumina or corundum in its crystalline form. Due to a number of polymorphs, hydrates and incorporated ions, Al_2O_3 can exist in various forms, e.g Al_2O_3 (H₂O)_n where n ranges from 0 to 3. Corundum is the most thermodynamically stable form among alumina oxides and is generated above 1100°C. apart from the regular use of alumina as abrasive and refractory material, it is also used widely as electrical insulating material (M. K. Olsson et al., (1998); J. M. Schneider et al., (1999)).

Alumina also finds use as a catalyst or a catalyst support material. Owing to these properties of alumina, it is being used widely in the energy conversion devices.

In this research we apply the technique of anodic oxidation to titanium and aluminum foils hoping to see higher current densities when exposed to hydrogen and oxugen mixtures in comparison to the semiconductor substrates used, as the anodization process is carried out at large anode voltages, which leads to the formation of a porous oxide layer with high surface area. This process is also called Plasma electrolytic oxidation (PEO).

2.5. Schottky Contacts.

Schottky contacts are metal-semiconductor junctions, which allow the flow of current in a single direction due to their rectifying nature. The rectifying property is due to the presence of an electrostatic barrier between the metal and the semiconductor. This barrier is referred to as the Schottky barrier and its height is dependent on several factors such as metal work function, bandgap energy, type and concentrations of the dopants in the semiconductor. The barrier indicates the mismatch between the Fermi levels of the metals and the semiconductor material. These Schottky contacts are widely used in microwave detectors, power rectifiers, solar cells and wireless devices. The important characteristic of these contacts are the low forward voltage drop and the high switching speeds. The voltage drop for a Schottky diode is only 0.15 to 0.45 V in comparison to a silicon diode whose voltage drop is about 0.6 to 1.7 V. The only limitation of these diodes is their high reverse leakage current which can be eliminated by using wide bandgap semiconductor materials.

Unlike the p-n junction diodes, the Schottky diodes are majority carrier devices. In case of the n-type semiconductors, the electrons are solely responsible for flow of current

through the device. This enhances the speed of the device as there is no time lag involved for the re-combination of holes and electrons like in the previous conventional diodes. There is also no reverse recovery time in case of Schottky diodes. This is particularly suited for radio frequency and integrated circuit applications where higher switching speeds are preferred. The lower forward voltage drop allows for higher current density which makes these diodes ideal for power rectifying, voltage clamping and prevention of transistor saturation.

2.5.1. Schottky Barrier Construction.

When a metal and a semiconductor are brought in contact with each other, electrons flow from one material to the other depending upon the position of their Fermi levels. This occurs in order to maintain equilibrium. For typical n-type semiconductor the work function of the metal is higher than electron affinity of semiconductor resulting in the flow of electrons from semiconductor material to the metal. And for p-type seminconductor systems the work function of the metal is lower than the electron affinity of the p-type semiconductor then the electrons will flow from the metal into the semiconductor. This leads to the creation of a dipole that comprises of a negatively charged space region within the semiconductor which is balanced by an equal density of positively charged space region in the metal (M. Shur et al., (2006)). Either ways in both the cases, there is bending of the conduction and valence bands of the semiconductor. A potential barrier is created at the metal-semiconductor interface because of the curvature of the bands which is explained in detail in the following section about Ohmic contacts. Figure 2.2 presents the above discussed formation and band bending in a n-type semiconductor.



Figure 2. 2. Schottky contact between n-type semiconductor and metal (a); and creation of a barrier along with band bending (b)

The barrier created between the metal and semiconductor is given by the energy needed for an electron or hole to enter the semiconductor material from the metal side. The barrier height for an n-type semiconductor is given by;

$$q\Phi_b = q\Phi_m - q\chi_s \tag{2.5.1}$$

Where, E_g is the bandgap energy, $q\Phi_m$ is the metal work function, $q\Phi_s$ is the semiconductor work function and $q\chi_s$ is the electron affinity of the semiconductor. The conditions under which a Schottky barrier is formed can be defines as: (1) $\phi_m > \phi_s$ for an n-type semiconductor wherein bands are bent upwards and (2) $\phi_m < \phi_s$ for a p-type semiconductor wherein the bands are bent downwards.

The Schottky barrier height is about one-third of the bandgap energy for p-type semiconductors and two-thirds of the bandgap energy for n-type semiconductors (F.P. McCluskey et al., (1997); D.K. Schroder., (2006)). This barrier extends to a distance "W" within the semiconductor as shown in Figure 2.2. This region is called the depletion layer and it represents the area within the semiconductor that has been depleted off the majority charge carriers i.e. electrons in case of n-type semiconductor and holes in case of p-type semiconductor. The width of depletion layer is influenced by the concentration of dopants in the semiconductor. It can be seen from eq. 2.5.1 that the barrier height depends on the semiconductor bandgap, electron affinity and the metal work function. Since electron affinity and bandgap of the semiconductor remain constant, the only quantity that can be varied in order to alter the barrier height is the metal work function. However this is an ideal case where the effects of interface states have been ignored. The dependence of the barrier height on the metal work function is very rare. Usually, there are large numbers of interface energy states present in the forbidden gap of the semiconductor (T.V. Blank et al., (2009); S.J. Pearton., (2000); M. Shur et al., (2006)). These changes occur due to the disruption of the semiconductor crystal lattice because of chemical defects such as surface oxidation, adsorbed impurities, dangling bonds etc. A neutral level is often defined for this distribution such that the states below it are neutral if they are filled and the states above it are neutral if they are empty. If the density of these surface states is high enough, then they can act as acceptors or donors and hence affect the barrier height (E.H. Rhoderick., (1982)). The Fermi level is pinned at the interface by surface states close to the neutral level. Even a slight movement of the Fermi level would be enough for transferring sufficient charge to equalize the Fermi levels. This mechanism is yet to be understood completely. If there is Fermi level pinning,

then the barrier height does not depend on the metal work function. This phenomenon is more likely to occur in covalently bonded semiconductors. Though many metalsemiconductor contacts have interface states, their density is not high enough to cause pinning down of the Fermi Level. In this case, the influence of metal work function cannot be ignored. Thus the barrier height is dependent on the semiconductor type, metal work function, interfacial chemistry of metal-semiconductor junction and the condition of the semiconductor surface prior to deposition of the contact.

2.5.2. Schottky Contact Under External Bias.

In an n-type semiconductor material when no bias is applied the electrons movement in the metal is opposed by the electrons movement in the semiconductor material over the Schottky barrier. Thus, resulting a state of equilibrium with no flow of electrons when no bias is applied to the device. Once a bias is applied, the chemical potential of the electrons over the barrier is changed and the current flow is initiated. A forward bias means application of positive voltage on the metal film. When a positive voltage is applied the electrons in the semiconductor side acquire enough energy to cross-over the Schottky barrier and the electron movement from semiconductor to metal increases. And the barrier potential for electrons moving into the metal is decreased as the band bending is reduced (M. Shur et al., (2006); J. Zhang et al., (2003)). The current flowing under forward bias condition can be given by the ideal diode equation 2.5.2.1 where V_a is the applied bias, k is the Boltzmann constant, T is the absolute temperature, q is the electronic charge and I_s is the saturation current arising from the thermionic emission type transport of electrons. I_s depends on the barrier height and the semiconductor intrinsic properties. Apart from the current flow due to

the movement of electrons, there is also a small fraction of current due to the movement of holes from metal to semiconductor during forward bias. However this fraction of current is small as holes are minority carriers and this current can be ignored.

$$I = I_s (e^{\frac{qV_a}{kT}} - 1)$$
(2.5.2.1)

When the bias is reversed, the barrier height for the transfer of electrons from semiconductor to metal is increases significantly. The reverse saturation current depends on the probability of an electron acquiring sufficient energy to overcome the increased barrier height, leading to no transfer of electrons and the current produced is zero. This characteristic of the Schottky diode is used in applicatons requiring rectification mechanism (G.P. Neudeck et al., (2002)).

2.5.3. Current Transport Mechanisms in Schottky Contacts.

As mentioned above the current flow in the Schottky diode occurs due to the flow of majority carriers (electrons) over the barrier. And this flow is governed by four main mechanisms. They are (B. Ghosh., (2009); M. Shur et al., (2006); F.P. McCluskey et al., (1997); D.K. Schroder., (2006); S.M. Sze., (1969)):

- a. Thermionic emission over the barrier
- b. Quantum mechanical tunneling through the barrier
- c. Carrier recombination in the depletion layer
- d. Carrier recombination in the neutral region or minority carrier injection

The first mechanism deals with the thermionic emission of electrons in slightly doped semiconductors with carrier concentrations usually lower than 10^{18} /cm³ (F.P. McCluskey et

al., (1997)). The thickness of the depletion is wide in this case making the electron tunneling through it difficult. The depletion layer width under no bias is given by equation 2.5.3.1, where ε_s is the semiconductor permittivity, V_{bi} is the built-in potential due to the presence of a barrier, N_d is the carrier concentration and q is the electronic charge.

$$W_d = \sqrt{\frac{2\varepsilon_s V_{bi}}{qN_d}} \tag{2.5.3.1}$$

From the above equation it can be clearly seen that when the carrier concentration is low, the depletion layer is wide. In order for the electrons to cross the barrier, they need to be excited thermally. Thus, electrons with energies greater than the Schottky barrier height $q\phi_{bn}$ can surmount the barrier and enter the metal. However, before the electron can overcome the barrier it has to pass through the depletion region towards the metal-semiconductor interface. This would require the diffusion of electrons in the semiconductor which can be explained by the diffusion theory proposed by Schottky (E.H. Rhoderick., (1982); S.M. Sze., (1969)). This theory states that the current flow is limited by the diffusion and drift process of electrons in the depletion layer. This is based on the assumption that barrier height is much greater than kT. It is also assumed that the electrons in the conduction band adjacent to the metal are in equilibrium with the metal electrons. Hence the two processes of emission and diffusion compete against each other and the current flow depends on the ease with which these processes can occur. J. Zhang et al., reported that for Al/4H-SiC Schottky diodes the thermionic emission is the dominating charge transport mechanism up to voltages of 0.3 Vafter this range the space charge dominates.

In lightly doped semiconductor systems, the carrier mobility is limited, refraining the current flow to diffusion process alone. From the above discussion is it evident that thermionic emission is prominent at higher temperatures because the number of energetic carriers is more at higher temperatures. This will increase the rate at which the electrons cross over the barrier. Also, the barrier height can be lowered by chemically changing the interface at the semiconductor surface to enhance electron emission (B. Ghosh., (2009); V.T. Blank et al., (2007); P.H. Holloway et al., (1997); A.A. Illadis et al., (2002); V.L.Rideout., (1975)). For a Schottky diode with a forward bias and voltage greater than 3kT, the current is given by equation 2.5.3.2. Where n is the ideality factor and I₀ is the saturation current given by eq. 2.5.3.3. The ideality factor term, 'n', has been included in the equation because it introduces the dependence of the barrier height on the voltage.

$$I = I_0 \exp(\frac{qV}{nkT})$$
(2.5.3.2)
$$I_0 = AA^{**}T^2 \exp(-\frac{q\phi B}{kT})$$
(2.5.3.3)

The ideality factor is used to determine the quality of the schottky diode. In an ideal condition the diode under thermionic emission should have an ideality factor value equal to unity. In most cases the ideality factor is greater than unity. One of the reasons that increase the ideality factor above unity is the presence of an interfacial layer between the metal and the semiconductor.

The quantum tunneling mechanism for current transport is seen in heavily doped semiconductors, where the doping density is much greater than 10^{18} /cm³. The higher the dopant the higher is the probability of electron tunneling through the barrier. This is due to the fact that as the dopant concentration is increased the depletion layer thickness is

decreased allowing the electrons to tunnel through it. During this process the barrier also becomes extremely thin allowing for tunneling through it, and a certain limit exists for the dopant concentration after which the tunneling mechanism becomes dominant. The current densities obtained via this mechanism can be much higher in comparison to thermionic emission mechanism. This mechanism is also called field emission when applied to the degenerate semiconductors with small effective masses, the electrons tunnel through the barrier near the Fermi level in presence of an electric field (F.P. McCluskey et al., (1997); E.H. Rhoderick., (1982)). The electric field causes the potential energy in the vicinity of the semiconductor to decrease. This in turn reduces the barrier width. At a certain value of field strength, the electrons begin to tunnel out of the semiconductor. The emitted electrons have energies close to the Fermi level similar to those in the n-type semiconductors. If the temperature is raised, due to thermal excitation of the electrons the tunneling increases making tunneling possible from the top. Only the electrons having energies greater than energy at the bottom of the conduction band will contribute towards the current (M. Shur et a., (2006)). This mechanism is called thermionic field emission.

The third mechanism, carrier recombination occurs in semiconductor systems with large bandgap energies and low carrier concentrations at low temperatures and bias voltages (E.H. Rhoderick., (1982)). In this mechanism, the electrons present in the mid gap energy levels take part. This participation is due to the presence of crystalline defects and impurities in the semiconductor materials. When a forward bias is applied, the respective carrier concentration is exceeded in both metal and semiconductor and the recombination occurs in the depletion layer to maintain equilibrium leading to current generation. When a reverse bias is applied, electron-hole pairs are formed in the depletion layer leading to additional current component in the leakage current.

Minority carrier injection mechanism is observed in semiconductor with high dopant concentration, low resistivity and small intrinsic carrier concentration (S.M. Sze., (1969)). This mechanism is dominant when the barrier height is more than half of the semiconductor bandgap energy. For this mechanism to occur the concentration of the holes is greater than that of a electrons in an n-type semiconductor. The minority carriers diffuse into the neutral part of the semiconductor under forward bias. Injection mechanism is defined terms of an injection ratio. The injection ratio is small in terms of n-type semiconductors because the barrier height for holes is much greater than that for electrons. Minority carrier injection and recombination mechanisms are rare in semiconductors and occur under special conditions. While recombination mechanism does not play a significant role in deriving the I-V characteristics of a Schottky diode, minority carrier injection becomes important in power rectifiers wherein it contributes to the conductivity modulation.

Another mechanism observed but not recognized widely yet in systems containing metal-oxide (Pt/TiO₂) interfaces is the spillover mechanism. Emmett discovered this phenomenon for the first time during the synthesis and decomposition of NH_3 . The spillover mechanism involves the movement of the active species adsorbed or formed on the first surface onto another surface that is not under the same conditions for adsorption or generation of the active species (W. Curtis et al., (1995)), causing the adsorbed species to move to the other surface in contact with the original adsorbing surface. Spillover is an important mechanism in adsorption and also in heterogeneous catalysis. This is not limited to

just the surface immediately next to the activating surface; it can be extended to other surfaces in contact with accepting nature.

Spillover is only just another mechanism occurring during the adsorption process. Figure 2.3 shows the spillover mechanism by showing adsorption and activation of a diatomic molecule (H₂) onto a catalytic surface. During this process, hydrogen dissociates on the metal surface into atomic H, which then spills over onto the other (oxide) surface. The movement of the dissociated species occurs by forming equivalent bonds with similar neighboring surface atoms. This leads to the effective exchange of bonds between the adsorbed atoms and the surface, allowing the adsorbed surface to reach the interface between the activating and the accepting surface. Spillover can occur in different combinations of systems, like metal to an oxide, from one metal to another metal, from metal oxide to metal or also from one metal oxide to the other. Hydrogen spillover process is the fastest spillover process and also, hydrogen adsorption process is a well known measure of the surface area of the metal catalyst (W. Curtis et al., (1995)).



Figure 2.3. Depicts the detailed spillover mechanism; hydrogen desorption, ionization and spillover (1&2), $2H^+ + 2e^- + 1/2O_2 = H_2O$ process on TiO2 (3), product desorption process (4).

2.5.4. Applications of Schottky Diodes.

The Schottky Diodes are most commonly used in gas-sensing and energy conversion devices. These devices work on the principle of detection of molecular hydrogen or hot electrons generated by a chemical reaction occurring on the surface of a semiconductor material surface. The energetic electrons produced are utilized for converting into more useable form of energy like electricity. Much literature is available in terms of use of these Schottky diodes for detection of gas molecules, hydrogen sensing and also their use as solid state energy conversion for power generation (H. Neinhaus et al., (1999); B. Gergen et al., (2001); E. Karpov et al., (2009 to 2010); C. K. Kim et al., (2001); S. Roy et al., (2003)).

In these studies, Schottky diode structures are selected to develop the energy conversion devices. One of the main reasons for this selection is that the semiconductor material in abundance of oxygen gas does not degrade. Hence a nobel metallic film is needed on the surface to prevent it from degradation and which also helps in the catalyses of the surface chemical reaction process. This leads to formation of a Schottky barrier structure. The presence of excited electrons or electron-hole pairs is manifested by a chemicurrent in the circuit and this current is detectable by Schottky structures only. This forms the working basis of sensors and energy conversion devices. Also, the electrical circuit for a Schottky contact in devices like sensors is relatively simple and easy to operate (S. Roy et al., (2003)).

Reactive metals like platinum, nickel, silver etc are the most commonly used catalysts in the hydrogen oxidation processes which give out the hot electron-hole pairs that referred to as chemically induced charge carriers. The thickness of the nanofilm formed on the semiconductor surface by these metals is lower than the ballistic mean free path of the electrons thereby facilitating their transport over the Schottky barrier (H. Neinhaus et al., (1999); E. Karpov et al., (2010)). This is necessary to see the chemicurrent generation in the external circuit. Also a barrier with greater height is preferred because it allows for efficient charge separation and high temperature operation by decreasing the reverse thermal current. However, too large a barrier also makes the transportation of these hot electrons difficult, leading to smaller magnitudes of the chemicurrent generation. Compound semiconductors may be a good choice for this purpose as their bandgap varies with the chemical composition.

2.6. Ohmic Contacts.

Ohmic contacts are metal-semiconductor contacts in which the voltage drop across the contact is negligible compared to the bulk of the device. These contacts show linear I-V characteristics and follow the Ohm's law. The Ohmic contacts display little or no resistance to the movement of majority carriers in and out of the semiconductor. An ideal contact should not interfere in the regular functioning of the device in any manner. Good contacts should possess high thermal stability, low resistance, uniformity and durability even under harsh environments. Fabrication of a good quality Ohmic contact has been a challenege for the micro-fabrication industry. This issue is more profound in case of the wide bandgap semiconductors where the fabrication of good Ohmic contacts becomes even more difficult due to the higher bandgap energies.

Ohmic contacts are usually made up of a metallic layer on top of a heavily doped semiconductor material. Depending on the material used they can be either rectifying or Ohmic depending on the metal and semiconductor used (V. T. Blank et al., (2007); H. Morkoc et al., (1994)). This contact is similar to that of a Schottky contact, except that the Schottky barrier height is zero or negative (A.Y.C. Yu., (1970)). And also Ohmic contacts allow the flow of current in and out of the semiconductor with little voltage drop. At the interface, an electrostatic potential barrier exists. This barrier is extremely high for wide bandgap semiconductor materials like SiC, GaP, diamond etc. In one case where gold was deposited on top of a diamond a barrier height of 1.73 eV was reported by K. L. Moazed (1990). In most cases due to the fabrication techniques used, the Ohmic contact made on the semiconductor material shows high resistance and the purpose of the contact is lost.

Commonly used methods to fabricate Ohmic contacts are; e-beam deposition, sputtering, thermal evaporation, soldering, electroless and electrolytic-plating (V. L. Rideout., (1975); A. Piotrowska et al., (1983)). Generally an alloying element is added to these metal contacts in order to minimize the resistance and increase the durability. And it is also possible to convert a rectifying contact into Ohmic contact by carrying out rapid thermal processing treatments (T. V. Blank et al., (2009)). Diffusion process plays an important role in the manufacturing of an Ohmic contact.

2.6.1. Ohmic Contact Formation Theory.

The Ohmic contact formation depends on several factors; like bandgap energies, electron affinity of the metal used, type and amount of dopant in the semiconductor material. By controlling these factors the type of contact can be determined. Figure 2.4 depicts the energy band diagrams for a metal-semiconductor (n-type) combination before and after the contact is fabricated. The energies of electrons in the conduction band Ec and the energies of the electrons in valence band Ev appear flat before the contact is made because there are no surface states in the gap between these two bands. E_F refers to the energy needed to remove an electron from the Fermi level in the metal into vacuum where it is in an unbound or free state. Similarly, 'q ϕ_s ' or work function of the semiconductor to vacuum level. ' χ_s ' or electron affinity is defined as the energy needed to remove an electron from the Fermi level in a semiconductor to vacuum level. ' χ_s ' or electron affinity is defined as the energy needed to remove an electron from the Fermi level in a semiconductor to vacuum level. ' χ_s ' or electron affinity is defined as the energy needed to remove an electron from the Fermi level in a semiconductor to vacuum level. ' χ_s ' or electron affinity is defined as the energy needed to remove an electron from the Fermi level in a semiconductor to vacuum level. ' χ_s ' or electron affinity is defined as the energy needed to remove an electron from the Fermi level in a semiconductor to vacuum level. ' χ_s ' or electron affinity is defined as the energy needed to remove an electron from the Fermi level in the wacuum level. For an n-type semiconductor as shown in Figure 2.4 (a), the Fermi level lies above the metal Fermi level. This is observed when the

metal and semiconductor are separated from each other and the complete system is not in equilibrium.



Figure 2.4. Energy band diagram for an n-type metal-semiconductor Ohmic contact system in separation (a) and in contact (b) (A. K. Singh., (2008)).

To obtain a good Ohmic contacts the Fermi levels of the two (metal and semiconductor) materials should align with each other in order to obtain state of equilibrium. This usually happens when the electrons flow from the material with low work function to the material with higher work function until the levels are in equilibrium. In an n-type semiconductor material the work function is lower than the metal, hence the electrons flow from conduction band in the semiconductor material towards the metal. And also the electron flow is always from higher Fermi level to the lower Fermi level. Due to this flow of electrons the semiconductor material attains a positive charge while the metal attains a negative charge. As the metal is a good conductor, it cannot support any potential difference across it and also there is no band bending in the metal (K.F. Brennan., (1999)). The negative charge attained by the metal is evenly distributed because of the number of free electrons that are present. Due to this the Fermi level in the metal does not change once it comes in contact with the semiconductor material but, the bands in the semiconductor bend near the surface as the electric field is developed. This region where the bending occurs is called the depletion layer as the major charge carriers are depleted in this region. During this process the Fermi level in the semiconductor is lowered and become equal to the difference in the work function of the metal and semiconductor ($q\phi_m - q\phi_s$). A potential is developed and is termed as the contact potential (qV_{Bi}) and a Schottky barrier is also created at a height ' $q\phi_{Bn}$ '.

In a rectifying type contact in a n-type semiconductor, the expression for barrier height in terms of work function of metal and electron affinity of semiconductor is given by equation 2.6.1.1. The relationship between barrier height and the built-in-voltage is then given by equation 2.6.1.2. and this built-in potential stops the movement of electrons from the metal to semiconductor while the Schottky barrier restricts the flow of electrons from the semiconductor to the metal.

$$q\phi_{Bn} = q\phi_m - q\chi \tag{2.6.1.1}$$

$$q\phi_{Bn} = qV_{Bi} + (E_c - E_{FS}) \tag{2.6.1.2}$$

For an Ohmic contact to be formed the work function of metal should be smaller than the work function of the semiconductor material $q\phi_m < q\phi_s$, under these conditions the metal will give out electrons to the semiconductor. The accumulated electrons at the interface build a positive charge over the metal surface leading to a buildup of an electric field which in turn gives rise to an electric potential. This potential causes the downward bending of the bands in the semiconductor (seen in Figure 2.5). This system does not give rise to a depletion layer to be formed. This implies that the electrons can freely move in and out of the semiconductor.



Figure 2.5. Illustration of the Ohmic contact formation in a n-type semiconductor system. (a) $q\phi_m < q\phi_s$ (b) band alignment after the formation of contact.

2.6.2. Criteria for Ohmic Contact Formation.

Ohmic contact fabrication for wide bandgap semiconductors have to meet certain criterion, them being;

- a. Use of a metal with a lower or equal work function than the electron affinity of GaP and SiC such that there is no barrier present at the interface of the metal and the semiconductor.
- b. Introducing a narrow layer of highly doped semiconductor layer near the contact interface so as to decrease the width of the barrier resulting in tunneling
- c. Altering the chemical composition of the semiconductor near the interface so as to reduce the barrier height
- d. Surface alteration of the semiconductor by methods like sand blasting thereby introducing large density of crystal defects which may recombine resulting in a conduction mechanism for electrons.

Off the above mentioned criterion, the first criterion is difficult to meet as the work function of most metals is larger than the electron affinity of the semiconductor as can be seen in Table 2. Except for indium most other metals have higher work function values in comparison to the semiconductor materials. Because of this, they all tend to form Schottky barrier when brought in contact with the semiconductor. This dependence on the work function of a metal for the formation of a high quality Ohmic contact can be eliminated by using a heavily doped semiconductor or by altering the chemical composition of the semiconductor near the contact interface (criterion 2 and 3) (V.T. Blank et al., (2009)).

TABLE III

METAL WORK FUNCTIONS AND SEMICONDUCTOR ELECTRON AFFINITIES (M. Shur et al., (2006); A. Piotrowska et al., (1983))

Metal	Work Function (eV)	
Silver (Ag)	4.6	
Copper (Cu)	4.3	
Titanium (Ti)	4.33	
Gold (Au)	5.1	
Nickel (Ni)	5.15	
Platinum (Pt)	5.65	
Aluminum (Al)	4.28	
Tin (Sn)	4.43	
Semiconductor	Electron Affinity (eV)	
GaP	3.8	
4H-SiC	3.7	
6H-SiC	3.3	

3. EXPERIMENTAL WORK.

This chapter describes the experimental work performed to create nanostructured energy conversion devices which convert chemical energy to electrical energy in the current investigation. Firstly, the materials used in the research are mentioned. And, the following sections provide description of the techniques used to fabricate and characterize the samples.

3.1. Materials

Single crystals of 4H-SiC used for this study have been purchased from University Wafer or MTI Corp. All GaP single crystals have been purchased from MTI Corp. Silver foil required for Ohmic contact preparation was purchased from Sigma Aldrich. The foil was of 0.1mm thickness. TiCuSil was used as a brazing material for obtaining ohmic back contact joining SiC wafer to Ag from Wesgo Metals. The TiCuSil foil has a thickness of 0.05mm and the composition of Ag-26.7%Cu-4.5%Ti with a liquidus temperature of 900^oC. For the fabrication GaP samples, Tin foil was used as the brazing material for obtaining the back ohmic contact between GaP substrate and Ag. And this was of 0.1mm thickness. Indium is also used as another brazing material for GaP samples. Indium was obtained in the form of pellets which was rolled into thin foil of 0.008mm thickness using a cold rolling mill. Also, sheets of Titanium and Aluminum were purchased from McMaster-Carr Inc. of 0.5mm and 0.75mm thickness respectively for the anodization process in order to grow the oxide layer required for the Schottky junction. Platinum pellets are used in the e-beam deposition process for making Schottky contacts.

3.2. Experimental Equipment

3.2.1. Electrochemical Cell

An electrochemical cell was developed to anodize Titanium and Aluminum samples by using Micro-arc Oxidation process (MAO, also named as Plasma Electrolytic oxidation or Anodic Spark oxidation) and simple Anodization process in sulfuric acid solutions respectively. Micro-arc oxidation process is a novel technique used to deposit ceramic coatings on the surface of valve metals and their alloys (A. A. Voevodin et al., (1996); W. Xue et al., (1998); S.V. Gnedenkov et al., (1999)). Commonly used valve metals include Al, Mg, Ta, W, Zn, and Zr. These metals in their natural state are protected by a thin, self healing dielectric oxide film which resists the flow of current in the anodic direction. If a valve metal is used as an anode, higher potentials are required to pass significant amounts of current through the anode. In the MAO process, the metal is immersed in an aqueous solution and the high alternating currents are applied between the electrodes (anode and cathode). The MAO process is typically characterized by an electric discharge phenomenon on the anode surface. These coatings are widely used in many application fields such as, automotive, aerospace, medicine and textile engineering.

MAO process was chosen for the current studies, as the oxide layer grown is thick (tens of hundreds of micrometers is possible), porous and uniformly coated on metal surface. The oxide layer also, has excellent adhesion to the substrate metal, high hardness, excellent wear resistance. Titanium and Aluminum were anodized in this electrochemical cell by passing few Amperes of current through them until a specific voltage value is reached. Graphite reference electrode is used as the cathode and the Ti or Al strips are used as an anode to complete the circuit. The process is carried out at room temperature conditions. The power supply used for this process is Sorensen XHR 300-3.5 DC Power Supply. The schematic of this setup is shown in Figure 3.1.



Figure 3.1. Schematic of the Anodization cell.

3.2.2. E-beam Evaporator

Prior to the electrical characterization, Schottky contacts are deposited on the front face of the semiconductor/oxide-metal substrate. This is done by physical vapor deposition technique using VARIAN e-beam depositor equipment at the Nanocore Facility of UIC. The electron beam evaporator is used to deposit solid dielectric materials onto solid substrates. Evaporation is done under high vacuum in a water cooled bell jar chamber. Evaporation is achieved by heating a source with an electron beam. As the source material evaporates, it forms a thin film on the samples. In the current study the Schottky contact is obtained by depositing a 15nm platinum layer on the semiconductor (SiC and GaP) and oxide-metal (Ti and Al) surfaces. During the deposition process, the surface temperature is maintained at approximately about 100°C.

3.2.3. Ultra High Vacuum System

The electrical characterization of the fabricated device is done in an ultra high vacuum system (Figure 3.2). The vacuum system is connected to hydrogen, oxygen and nitrogen cylinders for measuring hydrogen sensitivity or recording chemicurrents upon passage of the oxygen-hydrogen or synthetic air mixture.

The electrical set up comprises of a BK Precision high current DC regulated power supply, SRS operational amplifier. The analog to digital data logger equipment, PICO high resolution data logger is connected to record the changes in pressure, temperature and the Chemicurrent generated during the H_2 oxidation process. A Keithley 2400 source meter is

used for recording the current-voltage (I-V) characteristics of the diode structure under varying conditions. It converts all the analog data from the fabricated device into an understandable digital format and sends it to an attached computer. Lab Tracer software is used in combination with the Keithley 2400 power supply to record the I-V characteristics of the sample in test. A Stanford Research System (SRS) PTC 10 Thermocouple system is used to monitor the change in temperature inside the vacuum chamber and in the vicinity of the sample surface being tested via a temperature sensor Pt100 RTD. Also, to monitor the H₂ oxidation process a Mass-Spectrometer is attached to the ultra high vacuum chamber which aids in the efficiency parameter calculations.



Figure. 3.2. High vacuum chamber for V-I measurements. (1) vacuum/ gas mixture handling components. (2) mass spectrometer, (3) signal conditioning unit, (4) multi channel temperature Control, (5) analytical chamber, (6) main flange for sample mounting and (7) precision current/voltage source.

3.2.4 Mass-Spectrometer

The mass-spectrometer is an instrument that measures the masses of individual molecules that have been converted into ions, i.e., molecules that have been electrically charged. A mass-spectrometer does not actually measure the molecular mass directly, but rather measures the mass-to-charge (m/z) ratio of the ions formed from the molecules. The

mass spectrometry is a non-destructive technique and requires only a few nanomoles of sample to obtain its characteristic information (Stanford Research Systems; M. A. Duncan., (2000); NASA KSC WebPages).

The first step in the mass spectrometric analysis of compounds involves the production of gas-phase ions of the compound, e.g. by electron ionization:

$$M + e \rightarrow M^+ + 2e$$

This molecular ion may further undergo fragmentation giving new radical cations and neutral molecules. All these ions are separated in the mass-spectrometer according to their m/z ratio and are detected in proportion to their abundance.

Any typical mass spectrometer always contains the following functional units:

1. A device to introduce the compound that is analyzed, e.g. a direct insertion probe or a gas chromatograph.

2. A source to produce ions from the sample.

3. An analyzer(s) to separate the various ions according to their m/z ratio.

4. A detector to count the ions emerging from the analyzer and to measure their abundance.

5. A computer to process the data, which produces the mass spectrum in a suitable form and controls the instrument through feedback.

3.2.5 Ohmic Contact Fabrication Procedure

3.2.5.1 Ohmic Contacts on Semiconductor Substrates:

For the fabrication of Ohmic contact on semiconductor substrates of SiC and GaP, Vacuum Brazing Technology was used. These wideband gap semiconductors need sophisticated ohmic metallization techniques which may involve up to four steps of metallization. The two basic properties employed during this process are: (1) a diffusive layer should be formed between the alloy and the semiconductor substrate and should have a low work function and (2) the 'capping' layer should be wettable by the metal/alloy present in the diffusive/intermediate layer. The most commonly used metals for the intermediate layer are In, Sb, Ti etc and for capping layer Ag, Cu, Zn etc are widely used.

For these studies with the semiconductor substrate Silver (Ag) capping layer is chosen. The work function of silver is in the range of 4.52-4.74 eV (M. Shur et al., (2006)). Even though, the work function is high, Ag has high diffusivity and wettability compared to Copper. Also, it is easily available, which makes the fabrication process easy and also, the mechanical strength of these contacts is good.

For Silicon Carbide samples, the intermediate layer chosen was an alloy of titanium, silver and copper and it is commercially popular as TiCuSil. And in case of GaP samples two different intermediate layer metals (Tin and Indium) are used. The reason for the selection is, their ability to help wetting. Wetting is an important property for a brazed joint as it ensures the strength and integrity. In turn help the formation of Ohmic contacts in the case of current study.

Vacuum brazing technique is well known for brazing metals and semiconductors. This process employs high temperature reactions for forming low resistance back/ohmic contacts. As the process is carried out at high temperatures, it ensures diffusion of metal into semiconductor substrate ensuring excellent bonding.

3.2.5.2. Ohmic Contacts on Metallic Substrates:

The Ohmic contact in case of the Titanium and Aluminum substrates was obtained by removing the oxide layer from the edges of the sample exposing the metallic substrate. As mentioned earlier that a metallic layer or component is necessary for forming an Ohmic contact. The work function of Titanium and Aluminum are in 4.33eV and 4.06-4.26eV. Even though, they have high work functions they were chosen for the studies keeping in mind the catalytic properties and the ease of fabricating nano diode structures. The contact is made by attaching the sample to a metallic copper clamp at the places where the oxide layer was removed. The process is much simpler and economical in case of metallic substrates than compared to semiconductor substrates.

3.2.6. Characterization Techniques:

3.2.6.1 X-Ray Diffraction (XRD)

X-ray diffraction is a versatile, non-destructive technique that is used to collect detail information about the chemical composition and crystallographic structure of various materials etc. The generated electromagnetic waves of the X-rays are several thousand electron volts, usually originating from the interaction of high energy electrons with a copper target (8.05keV, 0.154nm) (H.K. Kammler et al., (2005)). This radiation penetrates surfaces and interacts with the solids internal structure. Constructive interference occurs when the incident beam interacts with the crystalline plane at angle θ . The detector receives a set of interference signals at different angles θ , which correspond to the lattice spacing based on Bragg's law:

$$n \lambda = 2d \sin\theta, n=1,2,3...$$

Where, *d* is the distance between two atomic planes (lattice spacing), n is an integer called the order of reflectance, λ is the wavelength of the electromagnetic radiation, and θ is the angle between the incident beam and normal to the reflectance crystalline plane. The lattice spacing *d*, is the characteristic and therefore can be used to identify the crystal structure and atomic composition. For crystallite sizes smaller than about 1µm, destructive intereference in the scattering direction occurs due to the lack of long range order in crystal structure. Crystallite size can be calculated by the Scherrer relation (P. Scherrer et al., (1939)) for sub-micron size particles or crystallites:

$$d = K \lambda \left(\cos \beta \right)^{-1}$$

where, *d* is the mean crystalline size, K the shape factor, λ the wavelength, and β the line broadening at half of maximum intensity. This derivation is based on the assumption of a Gaussian shape profile.

In the current studies XRD analysis was adapted in order to study the changes in the crystal structure of the oxide layer formed in Titanium and Aluminum substrates with change in anodization parameters. It is know that with increasing anodization potential the thickness of the oxide layer increases thus changing the oxide layer structure. In titanium samples, changes in the crystal TiO₂ phases (specifically, anatase and rutile) are studied and in the case of aluminum substrates changes in the Al₂O₃ phases are studied. The surface morphology is investigated by Electron Microscopy technique. A Siemens D5000 XRD Diffraktometer was used to carry out the analysis.

3.2.6.2 Scanning Electron Microscopy

A Scanning Electron Microscope (SEM) use an electrons to generate images, thus the resolution is limited by the wavelength of electrons, which at the standard energy of 5keV is 0.55nm (J. Bindell., (1992)). A SEM works by focusing a source of electrons into a fine point that can be scanned over the surface of the object being viewed. This way the SEM provides a high magnification image of the surface of a material that is very similar to what one would see if optical microscope had such high resolution at small length scales. The features that needed to be imaged in this study are a few micrometers in width, making them slightly small to be accurately resolved with an optical microscope. Hence, the improved resolution of an SEM was needed to generate good quality images.

Also, it is necessary to understand the subtle differences in the images to reality that could be misleading, as the images are not optically generated. For example, the reason for obtaining sharper, three dimensional images in an SEM is because of the number of secondary electrons reaching the detectors. Also, sometimes it can lead to the "edge effect" in which the sharp edges of a sample appear abnormally brighter than the rest of the sample. Also, in some other cases unlike optical imaging, SEM imaging can damage the sample surface being viewed due to the interactions between the incident electrons and the sample surface.

The instrument used is part of the Research Resource Center equipment at UIC. The SEM is a Hitachi make and 3000-N model which has an attachment for Back-scattered diffraction elements.

3.3. Experimental Procedure

3.3.1. Ohmic Contact Fabrication procedure for Semiconductor and Metallic Substrates

These contacts were fabricated by Jyotsna Mohan as part of her Master's thesis research (J. Mohan., (2011). In case of semiconductor substrates the single crystal GaP and SiC wafers were cut into rectangular pieces of $18 \times 12 \text{mm}^2$ and $36 \times 12 \text{mm}^2$ by means of a precision diamond saw. The brazing material TiCuSil and silver foil were also cut into the same dimensions. The substrates and foils were thoroughly cleaned using alcohol. In order to keep these foils and substrates in place two stainless steel blocks were used, they provide additional pressure required during brazing process. Figure 3.3 shows the schematic of the assembly used for brazing of SiC. The brazing was done at a maximum temperature of 900°C and at vacuum levels of 10^{-4} to 10^{-6} Torr.



Figure 3.3. Schematic of brazing assembly for 4H-SiC Systems (J. Mohan., (2011)).

Schematic in Figure 3.4 shows the assembly used for fabrication of GaP systems. The maximum temperature used in this case is about 500C.



Figure 1.4. Schematic of Brazing assmbly for n-GaP System (J. Mohan., (2011)).

Samples of Ti and Al were cut into rectangular pieces of 12 x 36 x 0.5 mm. These pieces were cleaned thoroughly using ethanol and placed in the sample holder constructed for carrying out the anodization process. 3M sulfuric acid solutions were used for anodization process. Anodization process was carried out by controlling the current in some cases and by controlling the voltage in some cases. The parameters used can be summarized from the two tables, Table IV and Table V for titanium and aluminum respectively.

In case of Titanium samples the current was set at a predetermined value and waited for the voltage to rise to a fixed cell potential. The final cell potential is selected such that potential exceeds the dielectric breakdown potential of the growing oxide film. During this process the cell voltage increases steadily to a value greater than breakdown voltage allowing the microarcs to be formed on the surface of the titanium sample producing a perforated or porous sample surface, which in turn increases the surface area for catalysis process. The sample is then taken out and rinsed in de-ionized water and blow dried in air at room temperature. Table IV shows the parameters used and the no of samples prepared. For each set of current and voltage parameters two samples are prepared, one for the chemicurrent analysis and the other for the purpose of characterization. In case of samples anodized at 3molar solution and 175 V at the different currents could not reach the final voltages, the final cell potential the sample could reach is indicated in the parenthesis. This potential can be said to be the saturation potential in case of these samples, that is the oxide layer does not grow beyond this potential.

Table V shows the parameters used for anodization of Aluminum samples. As mentioned earlier, two samples of each set are produced. For these samples the anodization

process is carried by setting up a finite current value in the system and making time a parameter instead of the voltage as compared to the earlier case. The voltage in this cell was stable at a low fixed value and does not grow continuously to a value larger than the dielectric breakdown voltage of the oxide layer due to the limitations of the power supply used. Thus, making time an important parameter in fabrication. These samples are then taken out and rinsed in de-ionized water and blow dried in air at room temperature. The chemicurrent studies on Al samples are not discussed in this thesis; they will be studied in the future.

TABLE IV

TITANIUM ANODIZATION PARAMETERS

I	V	3M Electrolyte		
		125(V)	150(V)	175(V)
0.85	5 (A)	Sample 26	Sample 10	Sample 30 (155V)
1.20) (A)	Sample 19	Sample 11	Sample 14 (162V)
1.69	9 (A)	Sample 2	Sample 5	Sample 1 (168V)
I (A)	t (min)	1 M Electrolyte		
----------	---------	-----------------	---------------	------------------
		10 min	34 min	100 min
0.21 (A)		Sample 11	Sample 12	Sample 10
0.85 (A)		Sample 13	Sample 9	Sample 8
1.69 (A)		Sample 14	Sample 5	Sample 6

Table V.ALUMINUM ANODIZATION PARAMETERS

3.3.2. Schottky Barrier Contacts Fabrication Technique.

After the fabrication of the Ohmic contacts, the samples were prepared for the Schottky contact preparation. Platinum source was used to deposit the Schottky contact and this was deposited using an electron beam deposition technique. The deposition is carried out in VARIAN under a vacuum of about 10⁻⁷ torr. A deposition rate of 0.02 nm /sec was used and the total thickness of the metallic nanofilm was controlled to 20 nm and 15 nm for semiconductor and metallic substrate systems respectively, keeping in mind the mean free path of the hot electrons in metals, which is on the order of tens of nanometers (K. W. Frese et al., (1992); M. P. Seah et al., (1979)). On the fabricated samples the electrical contacts are made using silver paste and platinum wire on either ends of the Schottky contact. These

contacts also play the role of supports when the sample is suspended into the vacuum chamber for the analysis. Figure 3.5 shows the typical architecture of the final fabricated system.



Figure 3.5. Final schematic of the fabricated system

3.3.3. Chemicurrent and Diode Characteristic Measurement and Sample Characterization:

The fabricated sample is placed on a sample holder and inserted inside the main chamber of the vacuum system. Electrical connections to the sample are made with the help of copper rods inserted through the flange lid. A PTC-10 thermocouple was placed next to the sample surface to monitor the changes in temperature during the analysis process. This assembly can be seen in Figure 3.6 below. These copper rods are connected to the signal generator, power supply unit, data logger system and a thermocouple reader. Once placed inside the ultra high vacuum chamber (seen in Figure 3.2.) the system is evacuated and diode properties (V-I characteristics) are characterized in vacuum and also in various concentrations of the hydrogen, nitrogen and oxygen mixtures concentrations and pressures. Keithley 2400 source meter was used to study the V-I characteristics by passing current or voltage through the diode within a fixed range. The chemicurrent generated was recorded using Pico logger system connected to the computer and the changes in the hydrogen and oxygen partial pressures was monitored using a Mass-spectrometer system connected to the ultra high vacuum chamber from the top. The experimental procedure varies slightly for each individual sample studied during the course of this investigation. The procedure will be explained in detail while discussing that particular sample in the following chapters. Once the electrical properties and chemicurrent analysis were performed on each sample they are characterized using XRD to analyze the oxide layer structure in order to correlate the relation between the oxide layer structure and the magnitude of chemicurrent generated during hydrogen oxidation process. And the surface morphology was studied using a Scanning Electron Microscope.



Figure 3.6. Sample holder assembly

In the following Chapters detailed discussions about the electrical diode properties, chemicurrent analysis, characterization techniques mentioned here are discussed in detail for the Pt/SiC, Pt/GaP and Pt/TiO₂/Ti systems.

4. IN-SITU MEASUREMENT AND CONTROL OF TEMPERATURE OF PLATINUM NANOFILMS ON SILICON SUBSTRATES.

4.1 Introduction.

As described earlier, when thermal gas particles come in contact with the metal surfaces chemical excitation of the e^{-}/h^{+} pairs occur and these are subsequently transported into the bulk of the metal. This process can be quantitatively characterized if a nanometer thick metal layer is used a sample, as in the top layer of the metal-semiconductor, metal-oxide-semiconductor and metal-insulator-metal structures (B. Gergen et al., (2004); B. Roldan Cuenya et al., (2004); B. Mildner et al., (2006)). Using these devices a chemicurrent has been successfully measured. The working principle of such devices is based in the ability of chemically induced energetic electrons and holes to come over or under (for energetic holes) an internal potential barrier between the catalytic metal nanofilm and a substrate and be detected.

As mentioned in section 1, a component of thermal current also arises in these systems along with the chemicurrent due to spurious heating of the metal nanofilm by the chemical energy released at the surface (E. G. Karpov et al., (2009)). Two band tunneling model suggests a high sensitivity metal-insulator-metal systems to the local heating induced by the interaction of low energy particle beams with the top electrodes of the device (D. Diesing et al). These thermal effects hinder the experimental measurement of the chemicurrent unless a highly reliable and accurate monitoring of the nanofilm temperature is established. The traditional temperature sensors and resistance temperature detector (RTD)

attached to the surface are inadequate for the nanometer thickness films due to the high heat capacity of the sensor compared to that of nanofilms.

In this chapter a Pt/SiC planar nanostructure system is realized. It is shown that these systems provide a highly accurate method for noninvasive measuring and controlling the temperature of the nanofilm with the direct resistive heating technique. Accuracy of this method for the measurement is shown to be appreciably better than that of a usual approach using a Pt resistive temperature detector attached to the nanofilm.

Section 4.2 illustrates the experimental work done. Section 4.3 contains the results and discussion. The concluding remarks are drawn in section 4.4.

4.2. Experimental Procedure.

The metal-semiconductor system of Pt/SiC system was prepared as mentioned in chapter 3 section 3.3.1. Figure 4.1 shows the improvised device architecture of the fabricated sample. The electrical resistance R of the film was measured using the contact pads on top of the fabricated metal-semiconductor system in the temperature range of 273 to 600 K to measure the temperature dependence. This temperature was obtained by heating the sample using a boron nitride substrate heater. The resistance was measured by using a constant voltage bias of 100 mV to the contact pads. A Pt1000 RTD sensor was placed closely at the middle of the Pt nanofilm, was used to measure the reference temperature. All measurements were carried out in the UHV chamber (refer to Figure 3.2).



Figure 4.1. Nanofilm with buses as CV prototype cathode; thin support wires attached to ohmic contact (top). Electrical circuit used for R(T) measurement, direct resistive heating and temperature measurement studies (bottom).

4.3. Results and Discussion.

4.3.1. Direct In-Situ Resistive Nanofilm Thermometry Method.

This method is based on the temperature dependence of in-plane resistance of a nanofilm on semiconductor substrate. As mentioned earlier at this stage the entire sample is slowly heated or cooled by external means. Figure 4.2 shows the temperature dependence of the Pt film resistance for the Pt-Si and Pt-SiC nanostructure systems. As seen, both the systems show a linear temperature dependence of the Pt nanofilm resistance. At higher temperatures a strong deviation from the linear behavior is seen as the resistance drops after reaching a temperature, T_{drop}. This effect can be explained by the understanding of the growing contribution from a current through the semiconducting substrate, to which an increasing conductance across the Pt substrate interface may give rise. This value of the Pt film resistance can be reversibly monitored as the function of temperature for each system of samples and has been observed that it does not change under repeated heating conditions. Thus, it can be inferred that the appearance of T_{drop} is not caused by an irreversible change of the Pt-substrate interface. Instead, the value of T_{drop} clearly depends on the interface conditions, being around 350 or 500 K for Pt-Si and Pt-SiC structures respectively. It can be noted that the presence of silicide, which forms at the Pt-Si interface after annealing at 250 °C, (G. Majni et al., (1985) or also, defects present in oxide would increase the leakage currents through the silicon substrate and significantly affect the value of T_{drop}.



Figure 4.2. Resistance-temperature dependence for Pt nanofilm on Si and SiC substrates

As the relationship between the film resistance and temperature is understood, the film itself can act as the sensor of its own temperature. In order to do this, the linear fit of the dependence R(T) at $T < T_{drop}$ can be inverted to determine the temperature T=T(R). This technique in the further cases will be referred as *in-situ thermometry*. This technique

eliminates the specious effects of the traditional technique of using a standard RTD or thermocouple sensor attached or placed close to the surface of the nanofilm. This effect can be accounted for in the following ways:

- Large response time due to the much larger heat capacity of the sensor compared to that of the nanostructure.
- 2. Uneven temperature distribution at the area of contact between the sensor and the surface of interest, and
- 3. Heat transfer problems surface and the sensor.

4.3.2. Resistive Heating Method.

Resistive Joule heating can be obtained by passing a significant amount of dc current through the nanofilm, which is however not conflicting the process of measuring the temperature as the resistance is monitored. The resistance dependence on temperature obtained earlier provides a versatile method for controlling the temperature (seen in Figure 4.2). In order to do this, the setup uses a wheatstone bridge circuit assembly (seen in Figure 4.3) used to maintain a constant voltage to current ratio, i.e., resistance is maintained constant and therefore the temperature of the nanofilm. This method is novel in the field of catalysis and surface science, though it has been widely used in the field of hydro and aerodynamics for the constant temperature hot wire anemometry method. Using this technique very clean experimental condition could be achieved, as the direct heating would deposit the current directly into the platinum layer of the systems developed as long as the T < T_{drop} . Also

contamination from the sample holder or the heating elements via degassing can be avoided. We also confirm that the initial and final temperature of the nanofilm is linearly dependent on the voltage applied to the film, which makes it easier to monitor and control the final temperature of the film by adjusting the current passing through the platinum nanofilm. Figure 4.4 shows the final temperature and the initial heating rate, when Pt film if resistively heated under UHV conditions by applying various voltages. And the inset in the figure shows the electric power dissipated in the Pt nanofilm as a function of voltage applied.



Figure 4.3. Wheatstone bridge circuit for ultrasensitive in-situ temperature control of nanocathod temperature. Potentiometer sets up a required temperature, I-Current generated by the novel cell.



Figure 4.4. Initial heating rate and final temperature of 20nm Pt film on a SiC substrate as a function of the voltage applied for heating. Inset: Electric powere dissipated as a function of voltage applied

The dependence of temperature as a function of voltage can be fitted using a line,

$$\Gamma_{\text{final}} = \Gamma_0 + k U_{\dots}$$
 (4.3.2.1)

Where T_0 is the initial temperature and *k* is the slope of the line.

It is an unexpected behavior of final temperature as it would be expected to see a linear dependence with power and not with voltage applied. However it can be understood

that if the resistance of the film is taken into account i.e. it does not stay constant which can be seen in Figure 4.2. This results in acknowledging the dependence of T_{final} as a function of dissipated power may deviate from the expected U² dependence.

$$P = U^2/R = U^2/(R_0(1+\alpha T_{\text{final}})).....$$
 (4.3.2.2)

This suggests the weaker dependence on U^2 . For these conditions of testing the dependence of P scales close to linear with U for U > 2V, which explains the scaling observed in case final temperature T_{final} with U.

Also during testing it was observed that as the temperature reached T_{drop} the resistance decreases rapidly and the dissipated power increases rapidly resulting in damage to the sample systems developed. And it was also observed that even a small amount of dc current, such as that used for the in-situ thermometry, will also heat the Pt film. From the data obtained (from Figure 4.4) it can be calculated that $\Delta T/U = 39.3$ K/V, where ΔT is the change in the temperature due to internally dissipated electric power when the voltage U is applied. As mentioned earlier the voltage step size used in these studies is of the order of 0.1V which results in the change of temperature due to effect of self heating to 3.93K. Also, the current could be reduced to a value less than 1 mA, which will lead to a ΔT of less than 1 K. This change in temperature due to self heating can be considered as tolerable for the current experimental situations.

4.4. Conclusions

Noninvasive thermometry technique using Pt nanofilm on Si supports has been presented. This method is based on the temperature dependence of the nanofilm's resistance under the thermal equilibrium conditions.

The accuracy of the present technique have been found to be of significantly better than that compared to the standard approach of using a commercial RTD sensor under fast heating rate of the Pt nanofilm.

A novel technique in the field of surface science, could be used in the studies of temperature programmed desorption processes.

At higher temperatures a nonlinear behavior is observed for resistance as a function of temperature. This can explained by the increasing influence of the current from the semiconductor substrate i.e. increasing conductance of the Pt-substrate interface may give rise. And the T_{drop} observed during this behavior also depends on the conductive properties of the Pt-substrate interface.

5. EFFECT ON CHEMICURRENT PROPERTIES OF Pt/SiC PLANAR NANOSTRUCTURES BY HYDROGEN ADSORPTION AT AMBIENT CONDITIONS.

5. 1. Introduction

The basic understanding on the charge transfer processes at solid interfaces with reactive gas mixture leads to a path towards technologies of advanced sensing, novel catalysts and energy conversion applications. In the past few years there has been extensive interest in the field of catalyst surface reactions producing currents in Schottky barrier structures (B. Mildner et al., (2006); D. Diesinget al., (2011); E. Hasselbrink, (2009); E. Karpov et al., (2009); E. Karpov et al., (2010)). The physical nature of these currents is very fascinating as these systems contain no unequivocal ion conductive layers resembling more to a photovoltaic cell than a conventional electrochemical cell/device. For this reason the current induced due to chemical reactions is termed as "chemicurrent" in correspondence to the photocurrents produced by the photovoltaic devices. In these devices the chemical energy released at the surface is transferred directly to the electron subsystems of the metal nanofilm to produce hot mobile electrons which are able to travel over the potential barrier at the metal-semiconductor (MS) or metal-oxide-semiconductor (MOS) interfaces, see Figure 5.1. The potential barrier formed at the interface of metal-semiconductor contact acts as the charge separator, similar to that seen in the photovoltaic devices. Upon in depth analysis, these currents could provide direct insight into the charge transfer process in the heterogeneous catalysis process. Also, other authors (J. Creighton et al., (2012)) indicate that production of these currents may be due to the thermoelectric effect, at least for the stationary

currents on devices with both Schottky and Ohmic contacts fabricated on the same side of the semiconductor substrate, this is explained by the fact that a thermal gradient could be developed between the catalytic Schottky contact, heated by the surface reaction, and the ohmic contact which is chemically inert to these reactions.

This chapter provides details of the nonthermal nature of the reaction induced currents in the metal-semiconductor systems (Pt/n-SiC/Ag). Chemicurrents were observed at ambient surface and gas phase conditions during H₂ adsorption on O₂ pretreated Pt surface of the heterogeneous structure i.e. H₂ + O₂ atmospheres. The thermal effect was studied by admitting N₂ instead of H₂ to the O₂ pretreated Pt surface i.e. N₂ + O₂ as N₂ gas has distinctive adsorptive properties. When N₂ was admitted instead of H₂ gas, showed the same or greater thermal effect on the surface as during the process with hydrogen. From this data obtained, slope and magnitude of the thermal effect was measured. Even though, the thermal effect was similar in both the cases the chemicurrent was observed only during the admission of hydrogen to the pretreated surface, therefore it could be said that this current doesn't account for the thermal current generated in the other cases.



Figure 5.1. Charge carrier transport in the metal-semicondcutor heterojunction system; (1) thermionic emission, (2) recombination current (electrons from metal to semiconductor), (3) electron diffusion.

Section 5.2 illustrates the experimental work done. Section 5.3 contains the results and discussion. The concluding remarks are drawn in section 5.4.

5.2. Experimental Work

The sample was prepared as described in chapter 3 section 3.3.1 and section 3.3.2. The sample was then suspended into a 4.5L ultra high vacuum chamber for chemicurrent studies. The sample was suspended using three 20mm silver wires of 0.5mm diameter attached to the copper rods of the electrical feed through flange. Thus no particular sample holder was utilized to minimize the heat flow effects. The sample was heated for outgassing and characterization of electrical properties in vacuum was performed using two internal 100 W halogen bulbs with controlled intensity. Sample surface temperature was also measured by using a 2x2x0.8 mm ceramic body RTD sensor attached with an SRS SIM918 unit connected to PicoTech ADC-24 data logger as mentioned earlier in chapter 3.

5.3. Results and Discussion

5.3.1. Measuring Thermal Stability, Ideality Factor and Schottky Barrier Height.

The fabricated samples were measured for their out of plan electrical diode characteristics (I-V dependence) as to check for the structural stability of the developed system. Resistance of the freshly deposited Pt nanofilm was measured to be independent of the excitation current in the range of 10⁻⁵ to 10⁻² A under 10⁻⁷ Torr of vacuum pressure. The resistance showed a nonlinear dependence on the surface temperature of the metallic cathode. Also, it was noticed that during multiple heating cycles the resistance varied (mainly decreased) in the temperature range of 26°C to 250°C. But after treatment for 30 hrs at 250°C, the resistance to temperature curve stabilized and became fully reproducible. Figure 5.2 shows the final stable resistance to temperature dependence curve, where each data point

collected represents the systems thermal stability at that particular heating current and the ambient. Figure 5.3 shows the out of plane current dependence as a function of voltage in vacuum for this system after achieving stability, this data was also completely reproducible at this point. The data in Figure 5.3 shows a well preserved non-linear diode like voltage to current characteristics throughout the temperature range. Further analysis of this diode structure characteristics lead to calculations of its ideality factors and the Schottky barrier height measurements and they were found to be between 4 to 10 and 0.6 to 1.05eV respectively depending on the temperature the sample was heated to. These values can be seen in the plot in Figure 5.4. These values of ideality factor and Schottky barrier height are measured by using the following method.

The quality of an ohmic contact can be determined by depositing Schottky structures on the semiconductor substrate. A Schottky diode has two main attributes; ideality factor and Schottky barrier height. While ideality factor reflects the goodness of the diode, Schottky barrier height is a measure of the electrostatic potential between the metal and the semiconductor. These parameters can be obtained by analyzing the voltage-current characteristics of the diode. Since the semiconductors used for this study are moderately doped, we assume that the current flow across the diode occurs by thermionic emission and we use the following equations (C.K. Kim et al., (2000); W.P. Kang et al.,(1994)).

$$I = I_0 \exp(\frac{qv}{nkT}) \tag{5.3.1.1}$$

$$I_0 = AA^{**}T^2 \exp\left(-\frac{q\phi B}{kT}\right)$$
(5.3.1.2)

Eq. 5.3.1.1 relates the current (I) flowing through a Schottky diode to the applied voltage (V) for forward bias condition. I_0 is the saturation current which is relatively high when compared to the saturation current in p-n junction diodes. The ideality factor 'n' can be obtained from the slope of the Ln (I) versus V_{appl} . Figure 5.3 shows the voltage-current curve of sample Pt/n-SiC. It is evident from the curve that the fabricated diode has excellent electrical characteristics because of the high reverse voltage and low forward voltage. The reverse leakage current is also extremely low and tends to decrease further on increasing the reverse voltage.

Once the plot of Ln (I) versus V_{appl} was obtained, only the linear portion of the plot was considered for further calculations. A straight line equation of the form ln I = ln I₀ + qV/nkT can be written for the linear plot where 'q' is the elementary charge, 'k' is the Boltzmann constant and 'T' is the applied temperature. The slope of the line, q/nkT, is used to determine the ideality factor at the given temperature. Since the slope and the ideality factor vary inversely with each other, the higher the slope the lower will be the ideality factor. The lower the ideality factor, the better is the quality of the fabricated diode. Ideality factor was calculated for all other samples in the same manner for varying hydrogen pressures. Figure 5.4 shows a plot of Ln (I) versus V for the same sample and is used to evaluate ideality factor.

The saturation current (I₀) can be obtained by extrapolating the linear plot to zero applied voltage. Once the saturation current is obtained, the Schottky barrier height can be calculated using eq. 5.3.1.2. In this is equation, 'A' represents the area of the Schottky contact which in our case was equal to 17.34 mm^2 . A^{**} is the effective Richardson's constant and can be represented by eq. 5.3.1.3. where 'h' is Planck's constant, 'k' is Boltzmann's

constant, 'q' is electronic charge and 'm^{*}' is effective electron mass whose value depends on the semiconductor type. 'm^{*}' is 0.35 m_0 for GaP and 0.36 m_0 for 4H-SiC.

$$A^{**} = 4\pi k^2 q m^* / h^3 \tag{5.3.1.3}$$

These preliminary examinations of the sample lead us to believe that the sample was suitable for carrying out the chemicurrent measurements. Chemicurrent analysis along with the surface thermal outgassing procedures were carried out at temperatures upto 140°C, i.e. 100°C below the highest temperature point which could be repeatable for additional assurance. Figure 5.5 depicts the changed in Schottky barrier height and ideality factor for this sample system as a function of temperature.



Figure 5.2. Stable resistance to temperature behavior of Pt nanofilm (Pt/n-SiC system) after annealing at 250°C for about 30 hrs.



Figure 5.3. Electrical diode out-of-plane properties (current-voltage behavior) of Pt/n-SiC nanostructure system after annealing at 250C for about 30 hrs.



Figure.5.4. Shows the LN(I) versus Voltage (I-V curve at 240C); used to find the slope of the line for calculating ideality factor.



Figure 5.5. Ideality factor and Schottky barrier height; Diode characteristics of Pt/n-SiC nanostructure system.

5.3.2. Chemicurrent Measurements

Before each chemicurrent measurement experiment with admission of gasses is carried out, the sample surface is cleaned by outgassing at 140°C for about 10 min in vacuum pressures of 10^{-7} Torr followed by cooling down to room temperature. The cooling down usually takes about 25mins. Once cleaned, pure synthetic air mixture of 79% N₂ and 21% O₂ at 760 Torr total pressure was allowed into the analytical chamber. During this process the surface temperature would generally increase by about 3 to 4°C, this we assume is due to the adsorption of nitrogen gas onto the Pt cathode surface. The sample was again allowed to cool down to room temperature and attain equilibrium with the surrounding atmosphere.

Once the sample surface is cleaned, chemicurrent measurements are carried out for two different cases: (1) 57 Torr of hydrogen gas was admitted to chamber with the sample present inside it at fast rate of about 110 Torr/s and the (2) 85 Torr of nitrogen gas was admitted into the chamber at a rate of 130 Torr/s rate. During the first scenario i.e. during admission of hydrogen gas, the surface temperature of the sample increased and also it showed a peak for the chemicurrent measurements. While in the second scenario i.e. when nitrogen gas was admitted the surface temperature of the sample rose at a similar rate compared to previous case but lead to a greater magnitude of the temperature and did not lead to any chemicurrent formation. Figure 5.6 (a) and Figure 5.6 (b) depict the description given above. Figure 5.6(a) present the important chemicurrent measurements that serve a key role in the current investigation. In spite of the higher rise in temperature observed in the case of N2 admission compared to H2 admission, H2 admission lead to a chemicurrent peak of the order of 93 nA (Figure 5.6 (b)) and this result was reproducible multiple no of times for this sample system.



Figure 5.6 (a). Temperature kinetics. The inset shows the long term kinetics of the process in presence of H2 and N2 in two different cases.



Figure 5.6 (b). Chemicurrent kinetics for the two scenarios studied for Pt/n-SiC nanostructure system.

These results do not have a particular order to be followed, as in no particular sequence needed to be followed one after the other for the two scenarios. Thus, it could be inferred that the chemicurrent observed during the oxy-hydrogen interaction with the Pt nano cathode is not due to a thermal effect of the interactions, but due to the elementary charge transfer phenomenon as explained earlier in chapter 2. The recorded chemicurrent kinetics is a clear representation of these charge transfer processes.

The chemicurrent peak magnitude was studied as a function of oxygen fraction in the oxygen-nitrogen mixture prior to hydrogen admission. Statistical averaging over multiple experiments using identical procedures with the same sample gives us the data in Figure 5.7. It can be seen that with increase in oxygen fraction the chemicurrent peak value tends to increase and saturate for highly oxygen rich mixtures. And also, a non-zero current was observed at 0% oxygen environments i.e. in pure nitrogen environments upon admission of the hydrogen gas. From this observation it could be said that, chemicurrents could be excited with adsorption process on metal-semiconductor planar nanostructure systems exposed to either vacuum as reported by others (E. Karpov et al., (2009); E. Karpovet al., (2010)) and E. Hasselbrink, (2009)) or in an inert gas mixture atmosphere.



Figure 5.7. Chemicurrent peak value dependence on the ratio of O_2 and N_2 partial pressures in 760 Torr mixture

5.4. Conclusions.

Adsorption of molecular hydrogen and nitrogen gases on Pt/SiC planar nanostructure at normal atmospheric conditions leads to generation of detectable chemicurrents, but of a higher magnitude in the presence of hydrogen.

Nitrogen admission conditions were selected to imitate an equal or greater thermal effect of adsorption as observed during admission of hydrogen gas. Therefore the recorded chemicurrent is a result of physio-chemical processes on the sample surface that can be associated with the generation and transport of hot electrons and electron-hole pairs in the catalytic nanostructure.

Chemicurrents due to adsorption of hydrogen can arise not only for surfaces at prevacuum conditions as proved earlier, but also for surfaces exposed to pure nitrogen or synthetic air mixture at normal atmospheric pressures.

6. SEPARATION AND ANAYLSIS OF ELECTRIC CURRENT COMPONENTS ON Pt/n-GaP PLANAR NANOSTRUCTURE

6.1. Introduction

As mentioned in the previous chapter 5 and also from the findings of the other authors (B. Mildner et al., (2006); D. Diesing et al., (2011); E. Hasselbrink, (2009); E. Karpov et al., (2009); E. Karpov et al., (2010); Nedrygailov et al., 2010; and B. Gergen et al., (2001); B. Gergen et al., (2001)b; B. R. Cuenya et al., (2004); H. Nienhaus et al., (1999); H. Nienhaus et al., (1999); H. Nienhaus et al., (2002); D. Krix et al., (2007)) on the flow of chemically induced hot electrons over Schottky barrier in nanolayer planar structures provide greater possibilities of developing electrolyte free conversion of chemical energy to electrical energy, also which could be used in novel analytical tools and sensor applications. The concept of a nonadiabatic and diabatic process (E. Hasselbrink et al., (2009); B. Gergen et al., (2001); Hermann Nienhaus et al., (2002); T. Greber, (1997); J. R. Schmidt et al., (2007)) is appropriate for the generation of above hermal electron states in the course of chemical events on solid surfaces. They also include the elementary acts of chemisorption from the gas phase and surface radical recombination, when the chemical energy released on precursory states of the newly formed adsorbate species is further dissipated by electron system of the solid, rather than by the phonons. Phonon dissipation on the contrary corresponds to the usual adiabatic phenomenon associated with the Born-Oppenheimer approximation (BOA) for the heterogeneous chemical reactions. According to BOA the energy gap should be significantly large between the ground state and the excited electron states and therefore implies more strict conditions on the dissipation via electron channel for semiconductor surfaces than for

metal surfaces. The chemical excitation was found in the solids by the phenomenons of chemiluminescence and adsorboluminescence from non-metal samples (T. Greber, (1997); M. Breysse et al, (1974)) and in case of metallic samples these phenomenon have been argued about based on the short life times (\approx 10fs) and mean free path values of \approx 20 nm for hot electrons (K. Frese et al., (1992)). The experimental studies on metals were difficult due to the evasive nature of the diabatic process on metals. Until the 90's it was difficult to study the chemically induced exoelectron emission experiments on metal samples due to their high activation barrier (A. Bottcher et al., (1990); M. Cox et al., (1983)), until new Schottky heterojunction structures with nanometer thickness metallization were introduced as hot electron devices (B. Gergenet al., (2001); H. Nienhaus et al., (1999)). For a more pronounced effect these structures used internal emission of the chemically induced hot electrons over the Schottky barrier that is several times smaller than a typical electron work function in metals.

For efficient hot electron harvesting based on internal emission requires a continuous nanofilm of a chemically stable metal, whose chemoexcitation is of interest, deposited on a planar semiconductor substrate to form a wide area Schottky junction as seen in Figure 6.1. Thickness of the nanofilm has to be smaller than the hot electron mean free path for that particular metal system which is usually about < 20 nm. For the current studies as already explained in chapter 2, low resistance Ohmic contacts are fabricated on the reverse side of the substrate. The ultrathin cathode layer on the top provides a catalytic action to the reactive gas phase mixture, while its nanometer thickness enables the short lived electron induced in chemical acts on the surface to travel ballistically towards and over Schottky barrier. The current magnitude observed in the external circuit reflects the intensity of the internal

emission and therefore provides an extensive characteristic to the process of chemically induced excitation of hot electrons on the catalytic metal surface.



Figure 6.1. Transportation of hot electrons (chemically excited) over Schottky barrier in metal-semicondcutor nanostructure system. Barrier potential separates electric charge, and nanofilm cathode performs as catalyst for the reaction (hydrogen oxidation). Schematics on the right depict the sample mounting without the help of a sample mount or holder.

For these systems to be considered as the energy conversion devices, they should be able to completely oxidize the hydrogen to water or any other conventional fuel on the nanocathode surface. This process of producing electric current via diabatica physicochemical process in the course of a complex surface reaction with stable products and reactants can be referred as the chemivoltaic effect, due to the similar post-excitation electronic mechanism with those barrier layer photovoltaic's. As mentioned earlier these currents are referred to as "chemicurrent". Electrochemical mechanism, in addition to the hot electron mechanisms outlines above, are also advocated to contribute significantly towards electromotive force generation in porous microlayered Schottky structures (K. Schierbaum et al., (2011)).

For the hydrogen to get oxidized completely higher cathode surface temperatures are needed, in older systems a substrate heater was attached to the backside of the sample and this was popularly famous among other researchers too (E. Karpovet a., (2009); E. Karpov et al., (2010); K. Schierbaum et al., (2011)). Hence, the diabatic chemicurrent is associated with the usual thermal currents of the thermionic and thermoelectric nature in the Schottky structure due to the external heating and the heat produced in phonon dissipation of surface released chemical energy. Thus, the total current measured in the external circuit Figure 6.1, is comprised of both the thermal and diabatic current components. Separating these two components is a greater challenge. But the separation of the two components is important in order to study the basic mechanisms involved during the chemical energy dissipation at nanostructured surfaces and also for developing analytical, sensor and energy conversion applications of the chemicurrents. The use of the substrate heater in the earlier work could also cause a reverse flow of thermal and diabatic currents causing complications for developing current separation techniques even further.

This chapter provides information about a simple and reliable method for the separation and analysis of the diabatic component in the total measured current. The separation is based on the in-situ resistive heating of the cathode layer on the Schottky structure (technique first described in chapter 4). This method provides a versatile temperature control and ensures a positive temperature gradient in samples around the cathode area, and therefore thermal and diabatic currents flow in the same direction. This technique is simple to use in the current studies as the temperature range is between (68 to 160C) for the Pt/GaP sample systems. This analysis is performed for stoichiometric oxyhydrogen mixtures of 60-150 Torr of total pressure.

6.2. Experimental Procedure

The Pt/GaP sample is prepared as described earlier in chapter 3, section 3.3. The final fabricated sample was suspended into the analytical vacuum chamber on three silver wires of 0.5 mm diameter and 20 mm in length each (Figure 6.1). This setup reduces the conductive heat exchange with any inner components of the chamber. As already mentioned in the previous chapters, these wires also act as electrical connections between the sample and the chambers electrical feed through: two wires attached to the nanofilm terminals a and b and one wire to the Ohmic contact terminal c, see Figure 6.1 and 6.2. At the terminals b and c VAC measurements are carried out. Electric current is passed to the terminals a and b in the range of 10's of amperes, which leads to the heating of the nanocathode layer. The heating of the nanofilm is measured using a Pt100 RTD sensor placed in a ceramic housing, which is mounted approximately in the middle of the sample surface. After the VAC measurements

were carried out, electrical resistance of the nanofilm was measured at terminals a and b as a function of temperature, R(T). Finally technique to separate the two current is investigated along with the chemicurrent analysis.



Figure 6.2. Front view and the electrical wiring schematic. The sample is heated resistively at nanofilm terminals a and b. Chemical induced current I and leakage current Io is measured at terminals b and c.
6.3. Results and Discussion

6.3.1. Electrical Properties

The final fabricated Pt/n-GaP nanostructure showed essential nonlinear diode like voltage-ampere characteristics (VAC) measured at different temperatures with a Keithlev 2400 Sourcemeter. The VAC measurements are shown in Figure 6.3. The data shows a non linear diode like structure characteristics throughout the temperature range selected for the studies using this sample. Further analysis of this data is done to find out the ideality factor and the Schotkky barrier height values. These values were calculated using the procedure explained in the previous chapter 5 in section 5.3.1. This method was first used by these authors (C.K. Kimet al., (2000); W.P. Kanget al., (1994)). The ideality factor and the Schottky barrier height measurements at different temperatures are shown in Figure 6.4. These calculations were carried out in the temperature range of 297-457 K for one specific sample selected for the studies described in this chapter. Figure 6.5 and 6.6 also show the asymmetry of the voltage-current characteristics at various temperatures, as a ratio the resistance measured at 1.15 V forward and reverse biases. The nanostructure showed satisfactory electrical diode properties until about 440 K. preliminary mass-spectrometry experiments were also carried out to determine the minimal surface temperatures of about 340 K that is sufficient for a reproducible initiation of the catalytic oxidation of molecular hydrogen on the Pt nanofilm cathode. The temperature range of 341-433 K was finally selected for the chemicurrent studies.



Figure 6.3. Electrical diode out-of-plane properties (current-voltage behavior) of Pt/n-GaP nanostructure system.



Figure 6.4. Variance of electrical properties with temperature for Pt/GaP Schottky structure.



Figure 6.5. Shows the variation of Resistance fraction with increasing temperature. Ratio of the diose resistance measured at 1.15V forward and reverse biases.



Figure 6.6. Variation of diode characteristics with temperature.

6.3.2. Calibration Curve

The electrical resistance of the nanofilm is measured at terminals a and b as a function of temperature R(T). Figure 6.7 shows the dependence of resistance on temperature for Pt nanofilm. In the as fabricated condition the sample showed unstable or unsteady resistance dependence. But upon annealing for about 30 hours at 530K in vacuum a stable, steady and reproducible dependence was recorded. Further heating-cooling cycles mostly resulted in slow downward drift of the entire curve with fewer changes of its overall shape. This dependence was stabilized asymptotically after 60 hrs of the cumulative 530 K treatment. We note that the function of R(T) has a global minimum at some critical temperature T_c similar to that seen in chapter 4 in case of Pt/n-SiC sample systems. For temperatures significantly lower than T_c , dependence R(T) is close to linear as typical for Pt metal's resistance, and thus is dominated by the nanofilm in-plane resistance. In the vicinity of T_c , resistance of the semiconductor substrated drops significantly to influence R(T)dependence and becomes dominant at $T > T_c$. In order to avoid sample overheating, the resistive sample heating procedure should account for the shape of the R(T) dependence using voltage controlled power in the range of $T < T_c$ and a current control regime at $T > T_c$. Stabilization of the nanofilm in-plane electrical properties had completed sample preparation for the chemicurrent studies.



Figure 6.7. Dependence of resistance on temperature at Pt nanofilm. Resistance measured after 25 and 60 hrs of sample annealing in vacuum at 530 K.

6.3.3. Chemicurrent Studies.

6.3.3.1. Chemicurrent Component Separation Technique.

At lower temperatures it is difficult to separate the two current components (thermal and diabatic) that are observed during chemical excitation on the surface of a metallic nanofilm cathode due to the small amounts of surface reaction turnover rates. The approach here uses the novel technique of resistively heating the sample mentioned in the earlier chapters and sections. The nanofilm terminals a and b are first connected to a high precision voltage/current source as shown in the circuit diagram (see Figure 6.2) where the switch S is turned on. In order to carry out the experiments an oxy-hydrogen mixture is admitted diffusively into analytical chamber to a given pressure, and the nanofilm heating bias is adjusted to achieve a desired sample temperature. Mass-spectroscopic technique is used to observe the initiation and progress of the catalytic hydrogen oxidation to water on the heated nanofilm surface. Upon reaching a constant H₂O turnover rate, switch S is turned off, so the total current kinetics has a typical shape as shown in Figure 6.8. The positive bias at the nanofilm terminal a leads to the opposite flow of any leakage current I_o relative to the current I generated in the sample as shown in Figure 6.2. As a result the total current kinetics has a well defined peak of the sought magnitude I and the effect of the leakage current was limited with an instrumental compliance setting; that explains the flat shape of the current kinetics prior to disconnecting the nanofilm heating bias. Separation of the diabatic current I_d and the thermal current I_t components in the total generated current $I = I_d + I_t$ is performed by repeating this procedure for an inert mixture at the same total pressure, were hydrogen part of the mixture is replaced by adding equal amounts of nitrogen. The inert mixture current contains no contribution from the chemical reactions, and therefore can be said is due to pure

thermal effects and the current contains only the thermal current. Figure 6.8 shows the difference in the height of the two peaks, and this difference is attributed to the diabatic component of the total current produced.



This procedure was carried out at various total pressure and different temperatures,

Figure 6.8. Current component separation technique. Resistively heated Pt/n-GaP sample at 393 K nanocathode temperature, exposed to 2:1 oxyhydrogen mixture (black) and oxynitrogen mixture (red). For the nanofilm under bias, any leakage current is recorded as a constant instrumental compliance current. The generated current is identified upon elimination of the leakage component by switching off the nanofilm bias. Difference in the peak values represents the contribution from the diabatic component of the current.

the details of the procedure are as follows. Chemicurrents for the Pt/n-GaP sample were measured at various nanocathode surface temperatures in the range of 341-433K and total pressures of the oxyhydrogen gas mixtures ranging from 60 to 150 Torr, with a step size of 30 Torr. Firstly the sample surface is cleaned by outgassing at 10⁻⁷ Torr vacuum at 550 K for 20 min and then cooled down to room temperature before the mixture is admitted into the ultra high vacuum chamber holding the sample. Current magnitude is measured once the H2O production rate reaches a maximal level on the mass-spectrum at a given sample temperature and total mixture pressure by following the steps described earlier. Based on the sample surface temperature and mixture pressure, the minimal rate was observed normally within 2 to 4 min at the onset of the nanofilm resistive heating. Nanofilm heating was initiated only after the mixture admission was completed, i.e. this approach is slightly different to the chemicurrent measurement technique mentioned in the earlier chapter 5.

Figure 6.9 shows the results obtained for the total current at different pressures and temperature combinations. From this figure it can be seen that there is a strong dependence on temperature of the nanocathode surface and also it can be seen that there is no apparent dependence on the mixture pressure on the total current generated. Inset of Figure 6.9 shows the behavior of the two current components (diabatic and thermal currents) individually. From this inset it is clearly seen that the absolute magnitude of the diabatic current may have a stronger dependence on the temperature than the thermal current component. Earlier studies carried out by Dr. E. Karpov also show a similar behavior in case of the SiC and GaP based Schottky barrier structure systems at temperature above 450 K and 0.2 Torr of oxyhydrogen mixture pressures.



Figure 6.9. Dependence of total current magnitude on the nanocathode temperature at various oxy-hydrogen mixture pressures. Inset plot shows dependence of individual components of current at 120 Torr case (log scale).

Further analysis of the current components by studying the fraction of the diabatic current component in the total current, I_d/I dependence on temperature between 370 and 410 K can be seen in Figure 6.10. Furthermore the diabatic fraction dependence grows steadily with pressure at all temperatures, as can be seen from the plot. The diminishing effects of the thermal component at higher mixture pressures could be explained by a stronger heat dissipation of sample back surface into the gas phase of the surrounding environment, and therefore by smaller temperature gradients across the anode layer.



Figure 6.10. Temperature dependence of the diabatic current fraction, I_d/I , at various stoichiometric oxy-hydrogen mixture pressures.

Figure 6.11 gives us information on the amount of contribution from each individual component of the total current generated during the chemical excitation on the nanocathode surface at various temperatures for 120 Torr of oxyhydrogen pressure. Also at highest temperature the contribution of the diabatic current component is calculated to be about 15% of the total current. And the rest of it is contributed by the thermal component of the current.



Figure 6.11. Contribution from each current component to the total current generated in the system with increase in temperature at 120 Torr of oxyhydrogen pressure.

Figure 6.12 presents the effect of addition of nitrogen to the stoichiometric oxyhydrogen mixture. From the figure it can be learned that at lower temperatures dilution with nitrogen gas does not change the total chemicurrent behavior but the contribution by the diabatic component increases slightly. And at higher temperatures the contribution by both the total and the diabatic component increases with increase in dilution with nitrogen.



Figure 6.12. Effect of dilution with nitrogen gas on the chemicurrent at two different temperatures.

The quantum efficiency of the process is calculated for one such case at 90 Torr of oxyhydrogen pressure at different temperatures, see Figure 6.13. The quantum efficiency can be defined as the total no of electrons produced and delivered to an external short circuit per water molecule exhausted by the device. From this figure it can be seem that with increase in temperature the quantum efficiency increases at a particular total pressure of the reactive mixture. This observation is also in agreement with the understanding of obtaining higher total current at higher temperatures (refer Figure 6.9).



Figure 6.13. Dependence of quantum efficiency with temperature at 90 Torr of reactive gas mixture pressure.

6.4. Conclusions

The non-thermal nature of the diabatic chemicurrents over Schottky barriers in catalytic Schottky nanostructures was explored at low temperature (341-433 K) chemivoltaic effect of hydrogen on water oxidation on Pt/n-GaP trype structures. The chemicurrents were studied in 60-150 Torr stoichiometric oxyhydrogen mixtures.

Separation of the nonadiabatic component from the total generated current is performed with an accurate method based on resistive heating of the nanofilm cathode. This in-situ heating was possible by (a) eliminating the substrate holder, minimizing the conductive heat exchange with the surrounding and (b) maintaining a stable temperature dependence for the in-plane resistance of the nanofilm cathode in vacuum at 530K. The insitu technique in turn provided a positive temperature gradient in the sample towards the nanocathode layer to avoid mutual cancelling of the thermal and adiabatic current components. This helped in studying the chemicurrent analysis at lower temperatures.

Chemicurrent measurement results showed a stronger dependence of diabatic component with temperature than the thermal current component for the considered range of temperatures and pressures. And also the diabatic current fraction can reach up to 25% for temperatures as low as 341 K, then it decreased by a factor of about 2 and then recovered to about 30% at 430K. That is the diabatic fraction can be maximized at lower and higher temperatures, i.e. temperatures as low close to minimal for the initiation of the catalytic hydrogen oxidation on the Pt nanocathode surfaces.

This study unveils wider scope of opportunities for applications at normal ambient conditions.

7. CHEMICAL TO ELECTRICAL ENERGY CONVERSION APPLICATIONS OF METAL-OXIDE (Pt/TiO₂) COMPOSITE CATALYSTS.

7.1 Introduction.

The present day demand for newer and advanced technologies like "photocatalytic water splitting" method to efficiently convert chemical energy to electrical energy seem to be more logically viable technique in sustainable energetic (A. L. Linsebigler et al., 1995; K. Maeda et al., 2010; C. L. Muhich et al., 2012; D. Riassetto et al., 2009; F. E. Osterloh et al., 2011; M. G. Walter et al., 2010; B. K. Vijayan et al., 2010; A. Dermibas et al., 2004; G. P. Hammond et al., 2004; Paul McGinniss et al., 2007). In contrast to this thought, fuel cell technologies (W. R. Growe et al., 1839; S. P. S Badwal et al., 1996; A. F. Ghenciu et al., 2002; C. S. Spiegel., 2007; N. A. Hampson et al., 1979) that already existing in the market are struggling to meet their basic goals of performance, especially in automobile and electronic applications, and are subject to criticism (J. Gordon., 2012; L. E. Hall., 2012). Some of the factors limiting the fuel cell performance that needed to be addressed are; slowrate ionic diffusion and spurious electronic conduction in electrolytes or ionic-conductive solid layers along with high manufacturing costs and faster degradation of the electrolyte (T. Matushi et al., 2005; T. Suzuki et al., 2004; C. Huang et al., 2003; X. Huang et al., 2006; M. Inaba et al., 2006; A. S. Arico et al., 2008). However, we suggest that the modern energy conversion research should shift towards better technologies like electrolyte-free concepts based off of recent advancements in the field of surface science and nanocatalysis. All the known concepts so far have involved the reaction driven charge transfer at metal phase boundaries of composite catalysts, this is because such a charge transfer is the only known source generating the regular electromotive force to drive the process other than the well know galvanic effect. With this current research it is expected that broader heterogenous catalysis research is expected to be explored into greater depths along with novel findings and discoveries. One such effort towards the development of electrolyte free devices is the study of energy conversion applications of chemicurrents in metal-oxide systems.

For these studies the first system selected is a composite of catalyst platinum nanofilm deposited on the oxide layer grown on a titanium metallic substrate. This is different to the earlier systems consisting of narrow and wide bandgap semiconductor layer supporting an electrically continuous metal catalyst to maintain a catalytic oxidation of chemical fuel. In these older systems the electric potential was built up by thermal drift of the majority carriers in a direction opposite to the temperature gradient (Figure 7.1(a)) and with



Figure 7.1. (a) Older electrolyte free chemical energy to electrical energy conversion system by thermoelectric effect in a narrow bandgap semiconductor system, (b and c) e-h pair and hot electron nonadiabatic mechanisms respectively, in a wide band gap semiconductor system.

the additional advantage of charge separation function of the p-n junction along with the production of e-h pair production as seen in Figure 7.1 (b & c) analogous to earlier narrow bandgap systems. Figure 7.1 (c) presents the novel mechanism of hot electron excitation and internal emission induced by surface reactions, this system was proposed to explain the chemicurrent production. Using a nanometer thick metal film allowed the interface to be accessible by the hot electrons whose mean free path value in bulk metals vary in the range between 5 to 50 nm. These systems came into being when Dr. Neinhauss with others showed the generation of electricity was possible by adsorption of O2, H, D and H+H and D+D (D. Krix et al., 2007; H. Neinhauss et al., 2007) recombination processes on a Schottky type metal nanofilm and single crystal Si structures with large continuous inert metallic layer. These studies used the adiabatic Born-Openheimer approximation ignoring the electron excitations in the systems. During these studies the term chemicurrent was used based on the electro motive force of a nonadiabatic origin.

Figure 7.2 shows the schematic of a newer type of device architecture where the Schottky barrier is created between the oxide layer grown on the metal substrate and the metallic nanofilm deposited on top of it. These systems were first used by Dr. Somorjai, Park and co-workers at Berkley (A. Hervier et al., 2009), who used these systems to study chemicurrent production in Pt/TiO_2 systems by hydrogen oxidation. These studies showed a stable chemicurrent produced by catalytic oxidation of the H₂, a regular chemical fuel at lower temperatures and higher pressures. This property of this system attracted attention all over in the research community. The same group also demonstrated the use of this same system for steady state chemicurrent generation using carbon monoxide as the catalyst fuel.

As seen in the earlier chapters, various autonomous regimes of self heating were tried out, but it was realized that a major breakthrough should depend upon the room temperature operation based off of a better catalyst surfaces in oreder to minimize the thermal losses, maintain sample homogeneity. The system Pt/TiO₂ exhibits a variety of interesting properties: they being photocatalytic degradation of organic compounds, water splitting, gas sensing, resistive switching, heterogeneous catalysis and ultraviolet light sensing (J. Lee et al., (2005); A. Fujushima et al., (1972); J. Trimboli et al., (2004); D. S. Jeong et al., (2008); C. Zhang et al., (2006); T. Dittrich et al., (2005)). Our interest lies in the heterogeneous catalysis property of this particular system type, therefore high surface area Pt/TiO_2 structures are considered as promising systems. For this effect a nanometer thick platinum layers is required and is associated with hot electron effect (non-adiabatic reaction). During the reaction a fraction of the exothermal reaction heat of -2.5eV produced per water molecule in the oxidation event on the platinum surface is converted directly into the kinetic energy of metal electrons, generating electrons which are sufficiently fast to pass over the Schottky barrier formed between the platinum and the titanium oxide layer. And also under the short circuit conditions the electrons flow continuously from the Ohmic back contact to the platinum cathode with the help of an outer electronic circuit during the hydrogen oxidation process (see Figure 7.2).



Figure 7.2. New architecture of the Pt/TiO2 system.

In this chapter, microarc oxidation technique was used to develop the oxide layer on titanium foils, this process is performed at high anodization voltages V_{anode} . Due to this process porous titanium oxide layers are formed on the titanium metal strips. In following sections of this chapter the experimental procedure (Section 7.2), the chemicurrent studies and the structural characterization (Section 7.3), along with the concluding remarks (Section 7.4) can be found.

7.2 Experimental Procedure.

Detailed explanation on the sample preparation can be found in Section 3.3.1 and Section 3.3.2. In these, platinum catalyst was finely dispersed as an electrically continuous nanometer thickness mesh by the wide angle PVD system, supported by a microporous TiO2 layer (Figure 7.3). The samples were of (ASTM B265) 0.989 pure Ti, serving as the base support and the back Ohmic contact. For these samples, the Ohmic contact fabrication step will not be necessary as the titanium strip in itself acts as the Ohmic contact. Due to this the material costs is reduced by few orders of magnitude, compared to the earlier single crystal systems (Chapter 5 and Chapter 6). Once the sample was anodized the oxide layer thickness was measured using a micrometer with 0.1 μ m accuracy. The anodization process, voltage kinetics are shown in Figure 7.4. The oxide layer grown was measured to be between 4 and 10 µm thick depending on the anodization parameters (Table VI). Once the complete fabrication was completed, electrical contacts were applied to the Schottky contact and the Ohmic back contact and the sample was suspended into the chamber (see Figure 7.3) for its electrical properties and also to carry out the chemicurrent analysis in different oxy-hydrogen mixture pressures and temperatures, which are described in detail while explaining the results obtained. Finally these metal-oxide nanostructures were evaluated for their structural properties using XRD and SEM techniques.



Figure 7.3. Schematic of the Pt/TiO2 system with the electrical connections. (1) TiO2 porous oxide layer, (2) Ti support, (3) Electrical contacts and (4) Ti base metal/ Ohmic contact.

TABLE VI.ANODIZATION PARAMETERS AND THE MEASURED THICKNESS FORTITANIUM SAMPLES

Ι	V	3Molar Sulfuric Acid Solution		
		125(V)	150(V)	175(V)
0.85 (A)		Sample 26	Sample 10	Sample 30 (155V)
		Thickness 4 µm	Thickness 6 µm	Thickness 11 μm
1.20 (A)		Sample 19	Sample 11	Sample 14 (162V)
		Thickness 5 µm	Thickness 6 µm	Thickness 10 µm
1.69 (A)		Sample 2	Sample 5	Sample 1 (168V)
		Thickness 4 µm	Thickness 6 µm	Thickness 10 µm



Figure 7.4. Anodization kinetics, Voltage to time dependence for the three samples fabricated.

7.3. Results and Discussion.

The fabricated samples were analyzed for their diode characteristics as the preliminary studies. Of the 11 samples (2 samples not shown in the table) chosen for the studies (Table II), some of these samples fabricated did not show diode characteristics at room temperature and in vacuum. And some of the samples were short circuited at the time of placing/attaching the electrical contacts, this short circuit of the diode structure can be attributed to the thinner porous oxide layer grown on the titanium strip surfaces, leaving them unfit for the chemicurrent studies. Finally, four samples (samples 11, 1, 30 and 10) showed

diode characteristics, hence they were used to carry out further thorough analysis. These samples displayed Schottky n-type diode properties between platinum and titanium terminals in oxyhydrogen atmospheres and a stable 200-300 Ω resistance between the two Pt terminals. As the porous structure in itself could act as the catalyst on both Pt and porous TiO2 phases, additional current generation mechanisms are expected apart from that observed due to the hot electron transfer.

7.3.1. Sample 11; Anodized at 1.20 A and 150 V.

The first sample that was tested was sample 11, this particular sample was prepared by anodizing titanium strip at 1.2 A and 150 V in 3M H₂SO₄ solution. The other two samples; Sample 19 and Sample 14 could not be used to carry out further analysis as Sample 19 was short circuited and Sample 14 was over heated in the initial trials and lost diode characteristics. These tests were conducted in oxyhydrogen atmosphere containing 160 Torr of oxygen and different amounts of hydrogen. For this particular test, firstly 160 Torr of oxygen was added to an empty chamber containing the sample then at first 16 Torr of hydrogen was added then waited for half an hour and then 6 Torr of hydrogen was added thrice with an interval of half an hour between each steps. And after the final addition the total mixture was left in the chamber to diffuse out for about 10 hours. During this time the changes in total pressure, surface temperature, chemicurrent measurements and the mass spectrometer are recorded by the help of the equipment and the electrical setup explained in section 3.3.3. Figure 7.6 presents the above mentioned pressure kinetics.



Figure 7.5. The oxygen-hydrogen mixture kinetics for sample 11.

During this process two different reaction regimes are observed that is the fast reaction process (when the first 16 Torr of hydrogen is added to the 160 Torr of oxygen) and the second regime is the slow reaction regime (the next three steps of adding 6 Torr of hydrogen). And also it is to be noted that the sample was not heated to initiate the reaction regimes. The chemicurrents generated from these two reactions can be compared in magnitude but the reaction rate is different for the two processes. The steady state current recorded after addition of the first 16 Torr of hydrogen was recorded to be in the range of 3-15 μ A/cm² recorded over long periods of time at room temperatures (see Figure 7.6). Also,

during the slow reaction regimes the chemicurrent generated was in the reverse order compared to the fast reaction regimes or from that observed using singlecrystal semiconductor systems (Chapter 5 and 6). From this it could be inferred that the slow reaction current is neither dominated by the thermal or hot electron-hole pair transport processes. As proved earlier these mechanisms should accumulate a positive charge on the Pt surface in the absence of any external heat source. But from these observations Pt/TiO₂/Ti system yields a robust steady state current with a negative potential at the platinum nanofilm terminal. The current intensities measured here are a few hundred orders larger than seen in the earlier cases with different sample systems.

The steady current seen in Figure 7.6 in the Pt/TiO2/Ti system can be explained by



Figure 7.6. Chemicurrent kintics for Sample 11, showing fast and slow reaction regimes.

the mechanism of hydrogen spillover from Pt to TiO_2 support. In this system it is know that platinum has high electronegativity, which leads to the ionization of the excited hydrogen molecules causing fast surface diffusion and spilling onto the TiO₂ support in the form of protons. These protons also take part in the hydrogen oxidation reaction at the porous oxide surface following water desorption. Thus the Pt and TiO2 phases in themselves act as the anode and cathode in a close contact, distinguished only by the Schottky barrier for electrons. And the proton spillover is readily separates the electric charge. Also it is known that hydrogen oxidation process releases 76% of the reaction energy as the heat of hydrogen adsorption (W. R. Williams et al., (1992)), which is not an electrochemical mechanism and therefore cannot be converted to electrical energy by the usual fuels cells. But for these newer systems this energy is utilized in ionizing the hydrogen on the Pt surface. This is one possible reason for the high yield observed with these systems. In general, galvanic effect would have created a positive potential on the higher electronegative metal surface by diffusion of protons throughout the oxide layer between Pt and Ti. Thus, we can say that the current system does not provide a proton conductive layer. Also, a fuel cell used by (K. Schierbaum et al., (2011)) would have similarly provided a positive potential at the platinum surface layer which in general needs to attract protons rather than spilling them over.

The temperature kinetics recorded during the test showed a steep rise in temperature when 16 Torr of hydrogen was added to 160 Torr of oxygen and remained constant close to room temperature during the three steps when 5 Torr of hydrogen was added at each step. This also proves to show that a stable-steady state chemicurrent was generated at room temperature. This behavior/change in temperature behavior can be seen in Figure 7.7.



Figure 7.7. Surface temperature kinetics as for Sample 11

Figure 7.8 presents the changes in the partial pressure of hydrogen monitored using a mass-spectrometer during different reaction regimes. From the slow reaction regime of the plot, the electron yield was calculated to a 0.74 per one hydrogen molecule consumed (theoretical limit is 2) and the energy conversion efficiency was calculated to be between 0.2-0.7% at $1k\Omega$ load.



Figure 7.8. Shows the long term kinetics of the residual hydrogen pressure.

The hydrogen consumption rate (K_{H2}) can be calculated with the data obtained by the mass-spectrometer, which in turn helps in finding out the electron yield η_e , per hydrogen molecule consumed and also the energy conversion efficiency, η .

$$\eta_{\rm e} = I_{\rm sc} / e^{-} K_{\rm H2} \tag{7.3.1}$$

$$\eta = P / e \cdot Q \cdot K_{H2} = I^2 \cdot R / e \cdot Q \cdot K_{H2}$$
(7.3.2)

where I_{sc} is the short circuit current, e⁻ electron charge, I and P are current and power at the external load R, and Q = 2.52 eV is the energy effect of $H_2 + \frac{1}{2} O_2 = H_2O$ per hydrogen molecule (W. R. Williams et al., (1992)). During the slow reaction regime the K_{H2} was found to be $5.38E^{14}$ s⁻¹, the H₂ consumption rate is found out by;

$$K_{\rm H2} = - V x \, dp/dt / K_{\rm B} T$$
 (7.3.3)

The measured value of efficiency for this particular case is 0.0052. These values of the electron yield, hydrogen consumption rate and the energy conversion efficiency cannot be related to the thermal mechanism at room temperatures. These details, confirm the nonthermal origin the chemicurrents observed besides the reverse polarity current.

These systems were finally characterized by using XRD and SEM techniques to understand if there stands a relationship between the basic electronic properties of the chemicurrent generated in these systems to the morphological and electrical properties of the Pt/TiO₂/Ti structures. XRD analysis of the grown titanium oxide layer showed higher amounts of rutile phase in comparison to the anatase phase. It is known that anatase is a well know photocatalyst, it would be of interest to see if higher amounts of anatase phase in the oxide layer would help increase the generation of chemicurrents in other samples fabricated. For this a comparative studies would be carried out with the other samples. Also, the XRD studies would aid in understand the relation between the anodization parameters and the oxide layer structure/phase obtained on the titanium metal strips. Figure 7.9 presents the XRD pattern for sample 11. Also SEM imaging of this sample was done using Hitachi S-3000N at a resolution of 10-15 nm to understand the dependence of the anodization parameters on the porous oxide layer structure. SEM imaging of the other samples would help us understand the structural dependence on the anodization parameters and the concentration of the sulfuric acid electrolyte used for anodization. Imaging over the areas covered with the platinum and those not covered by the platinum layer showed no significant visible differences in the surface structure. Figure 7.10 shows the mesh like surface structure of the platinum coated titanium oxide layer.



Figure 7.9. XRD spectra showing the two oxide forms of titania; Anatase and Rutile. For sample 11 higher rutile phase was observed.



Figure 7.10. Shows the nanomesh layer of the platinum metal deposited on top of TiO2 layer.

Further analysis of the nanomesh layer in terms of determining the pore opening size, pore depth etc is required to understand clearly the spillover and overall reaction mechanisms.

7.3.2. Sample 01; Anodized at 1.69 A, 175V.

The next sample that was tested was Sample 01 from the set of sample that were fabricated at 1.69 A and different cell potentials, as the oxide thickness was larger compared to the other two (Table VI). And also, Sample 02 from this set was short circuited during the

application of the electrical contacts using silver paste and Sample 05 showed very minute chemicurrent when preliminary tests were carried out. For Sample 01, firstly the diode properties of the sample were tested as part of the preliminary examination to determine the stability and the integrity of the sample structure. The out-of-plane properties of the sample between the Pt and Ti terminals showed good diode characteristics in oxyhydrogen environments. These tests were carried out by admitting 160 Torr of oxygen to the chamber containing the sample, and then adding 16 Torr of hydrogen as the first step and the additional 5 Torr for each step for the next 5 steps. The change in diode characteristics behavior with addition of additional 5 Torr of hydrogen at each step is as shown in Figure 7.11. The I-V curve in vacuum displayed linear dependence of voltage on current or vice versa and when the oxyhydrogen mixture was added to the chamber in the step wise manner the diode characteristics changed and started to display non linear dependence while shifting the short circuit current I_{sc} value while presenting a well defined n-type diode like shape and characteristics. The shift in the overall curve to the left with addition of higher pressures of hydrogen signifies the level of sensitiveness of the diode to the hydrogen pressure. The nonlinear dependence of current on voltage showed that these structures worked in a different manner than the usual electrochemical device whose I-V dependence is a simple straight line shifting along the voltage axis (H. He et al., (2011)). This system also showed a different behavior than that observed in the previous single crystal systems which preserved that shape in any oxyhydrogen mixture environments. From Figure 7.11 it can be argued that the Pt/TiO₂ catalyst system was experiencing a reversible qualitative change in its energy band structure under the influence of the slow mode reaction on its surface. The slow reaction mode apparently converts the titanium oxide layer from an intrinsic to n-type

semiconductor by temporary enhancement with some donor species and creates a Schottky barrier type structure at Pt/TiO_2 interface.



Figure 7.11. I-V dependence between the Ti and one of the Pt terminals; positive bias is applied to the Pt terminal.

Once the integrity of the structure was defined, chemicurrent analysis was done on this sample. The analysis was carried out by passing oxyhydrogen mixtures of 160 Torr of oxygen and then to initiate the reaction process 16 Torr of hydrogen was added and for the next 5 steps the 5 Torr of hydrogen was added to the existing mixture. After the fast reaction
ample time was given for the surface temperature of the platinum film to cool down to room temperature and then the additional amounts of hydrogen is added with an interval of about half hour between each step, see Figure 7.12. While carrying out this procedure, simultaneous measurement of chemicurrents, mass-spectoscope and temperature variation is monitored and recorded.



Figure 7.12. Total pressure kinetics monitored for about 4 hours; Sample 01

During this process two reaction regimes are observed, similar to that seen in case of Sample 11. The only difference is the slow reaction regime was carried out for 5 steps in this case instead of 3 steps as in with Sample 11. The steady current measured after the five slow steps was in the range of 30 μ A (reverse polarity) before the chamber was evacuated to terminate the test. The magnitude of the chemicurrent for the current and the previous sample are of the same order. The samples tested after this point all follow a similar experimental approach with five steps in slow reaction reaction mode. The chemicurrent kinetics can be seen in Figure 7.13. The highest peak current was observed at the fourth step of hydrogen addition and at the fifth step, the chemicurrent magnitude tends to decrease. This point may probably indicate the saturation point or the complete consumption of the hydrogen gas from the oxyhydrogen gas mixture during the oxidation reaction on the catalyst surface. This observation of the chemicurrent can be attributed to the hydrogen spillover mechanism as explained earlier.



Figure 7.13. Long term chemical induced current generated during the fast and slow reaction regimes.

The temperature kinetics recorded showed a similar behavior to that seen in the earlier Sample 11. The temperature kinetics showed a steep rise in temperature (upto 250°C) when 16 Torr of hydrogen was added to 160 Torr of oxygen and remained constant close to room temperature during the next five steps of hydrogen addition at 5 Torr each step. Once again it can be said that the stable-steady state chemicurrent was generated at room temperature see Figure 7.14. And Figure 7.15 presents the partial pressure kinetics recorded for the corresponding chemicurrent studies.



Figure 7.14. Long term temperature kinetics for Sample 01 during fast and slow reaction modes.



Figure 7.15. Hydrogen partial pressure kinetics for fast and slow reaction modes for Sample 01.

XRD analysis of the grown titanium oxide layer showed higher amounts of rutile phase in comparison to the anatase phase. In comparison to that seen in Figure 7.9 it can be seen that for Sample 01 (Figure 7.16), the peak intensity for rutile peaks is much higher. And also the anatase peak seen at 25° in Figure 7.9 is no longer visible, confirming the higher amounts rutile phase formed on the surface. From this it can be concluded that with increase in the cell potential (anodization current and voltage) the amount of rutile phase increases and also the oxide layer obtained is thicker than in the previous case (Sample 11). The chemicurrents produced also are of the same magnitude to that seen in earlier sample; implying that the oxide layer thickness does not play a major role in the generation of chemicurrents. Figure 7.17 shows the surface morphology of the nanomesh like platinum coated on the porous TiO_2 layer. From the Figure the surface feature size appears to be a little bit finer compared to the previous sample.



Figure 7.16. XRD spectra for sample 01; anodized at 1.69 A and 175 V.



Figure 7.17. Pt coated TiO2 layer for sample 01; Nanomesh support structure.

7.3.3. Sample 10 and Sample 30.

In the following section the electrical and chemicurrent analysis along with the structural characterization for the Samples 10 and 30, anodized at same current 0.85 A and different voltages 150 V and 155 V is discussed. The thickness measurements revealed that the oxide layer thickness was larger for Sample 30 (11 μ m) when compared to Sample 10 (6 μ m). The initial tests carried out to check the electrical diode properties of the two sample systems. For both the sample systems the diode characteristics are tested in the oxyhydrogen mixtures, as mentioned earlier in case of Sample 01; firstly 160 Torr of oxygen is admitted into the chamber in which the sample is suspended, then a 16 Torr of hydrogen is admitted and the later steps included addition of 5 Torr of hydrogen for five steps. The I-V

characteristic curves for the two sample systems (Samples 10 and 30) are shown in Figures 7.18 (a) and 7.18(b) respectively. From these two figures the I-V curves in vacuum showed a linear behavior; for Sample 10 the I-V characteristic curve was linear (straight line) at 0 A over the range of applied current, but Sample 30 deviated from this behavior and showed a linear line with a slope passing through 0 A over the range of applied voltage. And when the reactive mixture is added, Sample 10 displayed non linear I-V dependence (black line, Figure 7.18 (a)) and with addition of the hydrogen gas to the chamber in a step wise manner the I-V dependence displayed more non linearity while shifting the short circuit current Isc to a larger value with increasing hydrogen pressure, which was also seen in case of the earlier Sample 01. This dependence observed is close to that seen in typical n-type Schottky barrier devices. While, Sample 30 also showed a slight non linear dependence in the O_2/H_2 mixtures with increasing H₂ pressure but not as close to a n-type diode structure characteristics that were depicted by Sample 10 and also by Sample 01.



Figure 7.18. Out-of-plane I-V dependence between Ti and one the Pt terminal in vacuum and oxyhydrogen mixture for Sample 10(a) and Sample 30 (b)

Once the I-V behavior of the diode structures was evaluated, the samples were used for chemicurrent analysis. Once again, the oxyhydrogen mixtures of the mentioned proportions (160 Torr O_2 + 16 Torr H_2 + 5 x 5 Torr H_2) are used for measuring the chemical induced currents in these samples. After addition of the 16 Torr H₂ the sample was allowed to cool down to room temperature, as the temperature rose to above 200°C for each sample system. After each step of adding 5 Torr H₂ an interval of half hour was given to study the behavior of the chemicurrents produced. While performing the above steps the surface temperature of Pt, chemically induced chemicurrents and the changes in the partial pressure of H_2 was monitored and recorded. The variation in the total pressure while carrying out the analysis by the above mentioned method can be seen in Figure 7.19 (a) and (b) for samples 10 and 30 respectively. From these figures it can be seen that when the hydrogen gas is allowed into the chamber the peak rises sharply and then decreases before come to stable pressure, this decrease in hydrogen pressure also signifies the consumption of the hydrogen gas during the hydrogen oxidation reaction process. The rate of consumption of hydrogen is different for the two reaction regime (fast and slow) as can be seen in the following plots. This particular behavior of hydrogen consumption during the hydrogen oxidation at the catalyst surface is also seen from the mass-spectroscopy plots in Figure 7.20 (a) and Figure 7.20 (b) for the two sample systems (Sample 10 and 30) respectively.



Figure 7.19. Long term Total pressure kinetics for the fast and slow reaction regimes for Sample 10 (a) and Sample 30 (b)



Figure 7.20. Mass spectroscopy for H2 pressure for Sample 10 (a) and Sample 30 (b).

For these two samples the chemicurrent analysis showed well defined fast and slow reaction modes similar to the other two samples discussed earlier. The chemicurrent kinetics for the two samples are shown in Figure 7.21(a) and Figure 7.21(b). These plots reveal large peak currents (in the order of 75 to 115 μ A) during the fast reaction mode, and also steady state chemicurrents during the slow reaction modes of hydrogen oxidation. Even though, Sample 10 showed higher peak current than Sample 30, but the steady state current during the slow reaction mode was smaller than in the latter case. Also, Sample 10 shows a slightly different chemicurrent behavior during the fast reaction process in comparison to the three samples systems studied. The general trend observed showed a sharp peak in the negative polarity with a small peak in the positive polarity and then decrease a negative value before coming close to zero. But in this case the sample shows two sharp peaks with a negative value and no sharp peak in the positive direction. This difference in behavior could be attributed to the damage of the Schottky barrier formed at the thinner TiO₂ oxide layer and the Pt due to the sudden increase in temperature to about 225°C during the fast reaction process. The temperature kinetics associated with this process are shown in Figure 7.22(a) and Figure 7.22(b) for Sample 10 and Sample 30 respectively. This proves to show that the hydrogen oxidation occurs at room temperature on the Pt/TiO2 nanofilm surface.



Figure 7.21. Long term chemically induced current kinetics for both fast and slow reaction regimes for Sample 10 (a) and Sample 30 (b).



Figure 7.22. Temperature kinetics for fast and slow reaction modes for Sample 10 (a) and Sample 30 (b).

XRD spectra of these samples show slightly higher amounts of rutile phase in Sample 30 compared to Sample 10, Sample 10 shows traces of presence of anatase phase in the oxide whereas very minimal amounts of anatase phase are present in Sample 30. From this it could be inferred that the with increase in cell potential at a fixed anodizing current the thickness of the oxide layer increases along with the amounts of rutile phase in the oxide layer. The dependence of the generation of chemicurrents with the oxide layer structure is difficult to conclude from these studies. XRD spectra for the two samples can be seen in Figure 7.23. The SEM analysis of the platinum coated titanium oxide layer for the two samples showed no significant differences in the surface morphology in terms of the pore diameter size or the feature size. It is hard to correlate the current generated during the hydrogen oxidation on the catalyst surface is hard to comprehend at this point. Further detailed study of the surface in the future would help determine the relationship between the chemicurrents generated and also in turn help understand or define the hydrogen spillover mechanism along with other mechanisms that might be involved in the current generation. The SEM images of these two sample surfaces are presented in Figure 7.24.



Figure 7.23. XRD spectra for Sample 10 (a) and Sample 30 (b); Sample 10 showed higher trace amounts of anatase phase compared to Sample 30



Figure 7.24. Pt deposited TiO_2 surface for Sample 10 and Sample 30; Nanomesh support structure.

Sample 10 was further evaluated to understand the load dependence on the effective functioning of the system. For this analysis the resistance of the nanofilm is varied at a fixed interval by changing the resistance from 0.001 K Ω to 10 M Ω in 20 steps. By this method we

could determine the maximal power output at which the device would work efficiently. Figure 7.25 presents the changes in chemicurrent generated with changing load resistance on the nanofilm surface. From the figure it can be seen that under the regular testing regime (fast and slow reaction regimes) the stable chemicurrent observed is in the order of 20 μ A after the fast reaction and the 3 steps of adding 5 Torr of hydrogen. And when the resistance is varied the chemicurrent grew till the last step and when the load being applied was removed the chemicurrent reduced and stabilized at the steady state chemicurrent value observed before the additional load was applied to the nanofilm. This shows the robustness and steadfastness of the device. Figure 7.26 shows the dependence of the chemicurrent generated, the voltage and the electric power output with respect to load resistance. From this figure, an asymptotic open circuit voltage of a magnitude of 240-250 mV is apparent, and an internal resistance of 2.3 k Ω is obtained where the efficiency is maximal. From the procedure explained earlier in section 7.3.1. the efficiency value is calculated to be about 0.5% at the maximum power output. These values of efficiency and open circuit voltage are incompatible with the thermal mechanism at room temperature. This process confirms the involvement of a non-thermal origin of the chemicurrents besides the reverse current direction. The dependence of hydrogen consumption on the power output would point out the involvement of spillover mechanism, where the protons are replaced with neutral H-atoms at higher R due to the buildup of charge in the structure, without affecting the overall reaction flow.



Figure 7. 25. Chemicurrent kinetics for sample 10; with varying load resistance regime.



Figure 7. 26. Variance of the chemicurrent, voltage and electrical power output (inset) with load resistance.

7.3.4. Effect of Hydrogen Pressure on Schottky Barrier Height and Ideality Factor Measurements.

Hydrogen-sensitive Schottky diodes demonstrate a decrease in Schottky barrier height with increasing the hydrogen pressure in the atmosphere. This effect is due to the penetration of the hydrogen gas between the Pt catalyst film and the semiconducting layer that forms the Schottky barrier and forms a polarized layer which causes a negative shift in the work function of the metal layer. This results in the lowering of the barrier height. The three samples analyzed, for the electrical diode properties mentioned earlier were further studied to see the effect of the hydrogen gas on the Schottky barrier height.

The Schottky barrier height for the three samples analyzed at six different hydrogen pressures in the chamber is shown in Figure 7.27. Sample 10 and 30 showed a slow decrease in Schottky barrier height, but Sample 01 showed an exponential decrease suggesting higher sensitivity to hydrogen, this observation is also in agreement with the I-V curve characteristics for this sample.

Figure 7.28 shows the dependence of hydrogen pressure on ideality factor is not well established so far, but it has been understood that with the increase in hydrogen pressure the ideality factor decreases as well. This is also explained in relation to the decrease in Schottky barrier height with increase in hydrogen pressure. It is believed that due to the decreasing effect of Schottky barrier height the thermionic emission over the barrier become dominant even at lower forward biases. This leads to a decrease in the ideality factor. From the Figure 7.28, Sample 10 shows a higher amount of decrease in comparison to the other two samples.



Figure 7.27. Schottky barrier height dependence on Hydrogen gas pressure.



Figure 7.28. Dependence of ideality factor on the hydrogen pressure for the three samples.

7.3.5. Effect of Anodization Parameters on the Oxide Layer Structure and Surface Morphology.

As mentioned earlier, the surface morphology and the oxide layer structure changed with changing the anodization parameters. The changes in the sample systems due to these parameters are expected to play an important role in the outcome of the chemicurrent density generated. The XRD studies on each of the nine samples fabricated showed a change in the titanium oxide structure with change in anodization potential. These studies showed an increase in rutile phase fraction with ultimate anodizing voltage and also leading to an increase in the oxide film thickness with increase in the rutile phase at a constant supplied current. Also, with increase in the total anodizing cell potential at different current outputs, an increase in rutile phase fraction is observed. Figures 7.29, Figure 7.30 and Figure 7.31 show the XRD spectrum for the samples fabricated at three different voltages and 0.85 A, 1.20 A and 1.69 A of current respectively. The chemicurrent analysis of these nine fabricated samples showed no significant difference in the magnitude of the chemicurrent produced per sample, but it was observed that thicker oxide layer structures worked efficiently. That is samples having rutile phase showed steady state currents for longer duration of time in contradiction to the expected theory that anatase phase would produce higher currents due to its photcatalytic properties.

The SEM analyses on these samples showed a strong dependence on the final voltage and a weaker dependence on current density. The imaging in the area covered with platinum and those masked during the PVD showed no difference in the surface morphology. To understand the changes caused by the anodizing parameters a detailed and high resolution technique must be used in the future. From these SEM images obtained, it can be seen that with increase in the voltage the porosity and the irregularity of the surface increases significantly. At lower voltages it can be seen that the surface features are finer and the surface is much smoother in comparison to that seen in case of sample fabricated at higher voltages. It is hard to comment on the dependence of the chemicurrents generated to the sample surface topography. In the future a detailed study on the Pt nanomesh structure, feature size (pore sizes) and the pore depth and shape will help identify the possible spillover and overall reaction mechanism. Figure 7.32 presents the comparison of these changes observed in the surface morphology for the sample fabricated at different anodizing parameters.



Figure 7.29. XRD spectra showing increase in the rutile phase fraction in TiO_2 for a greater final anodizing voltage or film thickness at a constant supplied current of 0.85 A (increasing voltage from top to bottom).



Figure 7.30. XRD spectra showing increase in the rutile phase fraction in TiO₂ for a greater final anodizing voltage or film thickness at a constant supplied current of 1.20 A (increasing voltage from top to bottom). 156



Figure 7.31. XRD spectra showing increase in the rutile phase fraction in TiO_2 for a greater final anodizing voltage or film thickness at a constant supplied current of 1.69 A (increasing voltage from top to bottom).



Figure 7.12. SEM imaging of the samples fabricated at different anodizing parameters. Finer features observed at lower voltages at all three current densities.

7.4. Conclusions

New metal-oxide systems developed showed reaction induced chemicurrents flowing through the inter-phase boundaries as a direct depiction of the fundamental charge transfer process, giving more information about the fundamentals in heterogeneous catalysis processes.

Chemicurrent based techniques of the in-situ analysis can be applied to both rarefied and high pressure studies, unlike the traditional vacuum based methods for surface analysis.

The Pt/TiO2 system developed showed excellent n-type Schottky diode properties. These systems showed a steady stable chemicurrent generation without the need an external heat source to initiate the hydrogenation process. Room temperature hydrogen oxidation on the platinum and titanium oxide catalyst surfaces has been presented to work efficiently for longer durations. A new mechanism explaining the proton spill over from platinum to titanium oxide which in turn help make the process efficient has been proposed and explained. This mechanism is different than the well known nonadiabatic chemicurrent mechanisms and the usual galvanic fuel cell functionalities.

Stable chemicurrents were observed for structures with thicker oxide layers for longer durations of 10 hours. Implying thicker oxide structures are required to fabricate a robust energy conversion device of this type (Pt/TiO₂/Ti).

The hydrogen spillover mechanism can be inferred to be a promising functional technique for electrolyte free energy conversion devices. These Pt/TiO2 nanostructured

devices with further in depth understanding of the spillover mechanism can be used as solid state energy storage devices utilizing the theory of hydrogen spillover.

The developed systems lead the path to more ecologically friendly, sustainable energy and electrolyte free solid state energy conversion devices.

8. CONCLUSIONS

The objective of this work was to take advantage of the nonthermal component of the diabatic chemicurrents over the Schottky barriers in catalytic Schottky nanostructures to explore the low temperature chemicurrent generation during hydrogen to water oxidation on metal-semiconductor planar nanostructures, and to realize novel analytical techniques and alternative chemicurrent mechanisms in metal-oxide microporous nanostructures. The important observations from these results obtained for the two systems can be concluded as;

- A new noninvasive thermometry technique using platinum nanofilm on semiconductor supports was developed, based on the dependence of the changes in nanofilm resistance.
- Larger chemicurrent magnitudes observed in presence of pure hydrogen when compared to that observed in the mixtures of nitrogen and hydrogen gas mixtures at atmospheric pressures.
- New technique to accurately separate the non-adiabatic component of current from the total generated was devised, based on the method of resistively heating the nanofilm cathode.
- In-situ heating lead to lower heat losses with the surrounding environment and helped in maintaining a stable temperature dependence for the in-plane resistance of the nanofilm cathode.
- Metal-oxide system (Pt/TiO₂) developed, lead to discovery of involvement of newer mechanisms like hydrogen spillover. This device system helped understanding the insitu analysis at higher pressure studies.

- The metal-oxide system showed steady stable chemicurrents at room temperature. That is no external heat was required source was required to initiate the hydrogen oxidation process.
- Metal-oxide system showed long term room temperature hydrogen oxidation on platinum surface to work efficiently with up to 0.62 electron yield and 0.5% energy conversion efficiency for impedance unaffected loads.
- The stability of the system was dependent on the thickness of the oxide layer. That is samples with thicker oxide layers showed stable chemicurrents for indefinitely long durations.
- Observed weak dependence of chemicurrent magnitude on oxide-metal structure morphology implies presence of specific limiting stages of hydrogen surface oxidation for all the samples, possibly the product H₂O desorption process.

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