Cyclic Chemical-Vapor-Deposited TiO$_2$/Al$_2$O$_3$ Film Using Trimethyl Aluminum, Tetrakis(diethylamino)titanium, and O$_2$

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Titanium aluminum oxide films have been studied as potential alternative gate dielectrics. However, most studies have focused on sputtered films. In this study, we demonstrate that a combination of tetrakis(diethylamino)titanium, trimethyl aluminum, oxygen, and cyclic chemical vapor deposition (CVD) is a promising approach for laminated TiO$_2$/Al$_2$O$_3$ films with low impurities and high thermal stability even at low temperatures. The growth of the films is carried out in a cold-wall CVD chamber at 300°C and 0.7 Torr. Our studies show that the properties of TiO$_2$ improve with the addition of even a few percent of Al$_2$O$_3$. X-ray diffraction analyses indicate that as-deposited TiO$_2$/Al$_2$O$_3$ films have amorphous structure. Upon annealing as-deposited films in Ar at 700°C for 5 min, TiO$_2$/Al$_2$O$_3$ films maintain their amorphous structure, while pure TiO$_2$ films crystallize at these conditions. Atomic force microscopy shows that the surfaces of TiO$_2$/Al$_2$O$_3$ films are smoother than those of TiO$_2$ films deposited at the same conditions. Even though annealing increases the roughness of the TiO$_2$/Al$_2$O$_3$ films, film roughness is still significantly lower than that of as-deposited TiO$_2$ films. Moreover, Rutherford backscattering spectroscopy and X-ray photoelectron spectroscopy show that there is no detectable formation of interfacial silicon oxide and negligible carbon impurity in as-deposited TiO$_2$/Al$_2$O$_3$ films.
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The continuous decrease of transistor feature sizes and related concerns of high tunneling leakage current and low gate capacitance of ultrathin SiO$_2$ have been driving the development of alternative dielectric materials with higher permittivity.[1] Alumina (Al$_2$O$_3$) is a promising gate dielectric material. It is stable on Si and remains amorphous up to high temperatures. Also, it has the largest bandgap (8.8 eV) next to SiO$_2$ and has high band offset with respect to Si (2.8 eV for conduction band offset and 4.9 eV for valence band offset).[1] However, its dielectric constant, k, (in the range of 8–10) makes it a relatively short-term solution for industry needs.[1] TiO$_2$ films have attracted a lot of attention due to their higher dielectric constant, up to 80.[2] However, issues such as several stable oxidation states,[1] low bandgap (3.0–3.5 eV),[3] low crystallization temperature (around 300–400°C),[4] and instability on Si[5] induce high leakage current and impede the application of TiO$_2$ as gate dielectric.

Recently, many studies focus on heterogeneous materials, especially silicates and aluminates,[6] which may modify film properties and overcome the limitations of TiO$_2$ films. Among these composite films, titanium aluminum oxide thin films have emerged as one of the promising alternative high-k materials. It has been reported that alloying titanium oxide and aluminum oxide yields TiAlO materials that retain a high permittivity close to that of TiO$_2$[7,8] and also have excellent thermal stability like that of Al$_2$O$_3$.[8,9] In addition, the high oxygen affinity of Al$_2$O$_3$ decreases the reduction reaction of Ti^{4+} to Ti^{3+} and the formation of oxygen vacancies.[8] The addition of Al$_2$O$_3$ also enhances the adhesion of TiO$_2$ to the substrate and the film does not display an orientation polarization under an electric field.[10] Crystallization retardation due to the alloying of Al$_2$O$_3$ into TiO$_2$ formed by radio-frequency magnetron sputtering[7,10] and oxidation of sputtered TiAl[11] has also been reported.

Even though the studies mentioned above have shown encouraging results, most titanium aluminum oxide films were deposited using sputtering methods. The disadvantage of a sputter process is the directional nature of the process, which does not satisfy conformality requirements. On the contrary, chemical vapor deposition (CVD) or atomic layer deposition (ALD), which provide better step coverage, are promising methods in integration processes of nonplanar topographies. The few studies on the CVD and ALD titanium aluminum oxide films have shown encouraging results in obtaining high-permittivity films. Amorphous low-pressure CVD (LPCVD) TiAlO$_x$ films from a mixture of aluminum tri-sec-butoxide (ATSB),

titanium tetrachloride (TiCl$_4$), and CO$_2$/H$_2$ at 450°C have been reported to have a dielectric constant between 28 and 75.[12] However, the use of halide precursor, i.e., TiCl$_4$, may result in corrosive Cl contamination. ALD Al$_2$O$_3$–TiO$_2$ nanolaminates (11% Al$_2$O$_3$) with a dielectric constant of 45 have been grown using trimethyl aluminum (TMA), tetraisopropyl titanium (TTIP), and water at 250°C.[13] Kim and Yun[13] have reported that the addition of Al$_2$O$_3$ inhibits crystallization of as-deposited ALD TiO$_2$ films without further study on phase transition temperature, which is one of the important characteristics that determines the applicability of the material, because high temperature is used in the integration processes of complementary metal oxide semiconductor (CMOS) devices.

In this study, cyclic CVD TiO$_2$/Al$_2$O$_3$ films were deposited on Si(100) using tetrakis(diethylamino)titanium (TDEAT), TMA, and oxygen at 300°C. TMA is a promising Al-containing precursor and has been extensively studied for CVD or ALD Al$_2$O$_3$ films. Amide-based titanium precursors, i.e., TDEAT, have been used mainly for titanium nitride deposition. Amide-based metal precursors are promising for low-temperature film deposition due to their high reactivity, which induces lower impurity incorporation even at low deposition temperatures.[14-17] We have demonstrated that TDEAT is a promising precursor for TiO$_2$ film deposition.[18] Here, we further explore it for TiO$_2$/Al$_2$O$_3$ film deposition. Moreover, cyclic CVD is utilized in this study; this not only allows easy control of the Ti/Al ratio in the films but also lowers impurity incorporation by reducing possible gas-phase reactions when compared to that in traditional CVD processes. The focus of this study is to obtain high-k TiO$_2$/Al$_2$O$_3$ films at low deposition temperatures with high crystallization temperatures, low impurity levels, and negligible interfacial reactions, which can lead to low leakage current.

Experimental

TDEAT and TMA precursors were introduced into the reactor by bubbling Ar carrier gas at 20 and 15 sccm, respectively. Due to the low vapor pressure of TDEAT, its bubbler was maintained at 40°C and 80–320 Torr, depending on the desired flow rate of TDEAT. The TMA bubbler was kept at 760 Torr and 25°C. In order to prevent the condensation of the precursors, the temperatures of TMA and TDEAT lines were maintained at 50 and 90°C, respectively. The flow rates of oxygen and Ar purge gas were maintained constant at 10 and 30 sccm, respectively. The experiments were carried out in a custom-designed cold-wall CVD chamber.[19] The base pressure was 0.03 Torr. The substrate holder was heated resistively and controlled with a proportional-integral-differential controller. The substrate temperature was 300°C and the chamber pressure was 0.7 Torr.

One-side polished Si(100) wafers were treated with H_2SO_4/H_2O_2 (4:1) for 15 min to remove organic contamination and with 49% HF for 10 s to remove the native oxide. This was followed by deionized (DI)-water rinse and N_2 purge dry. Then the sample was immediately loaded into the reactor and continuously purged with Ar for 1 h at 0.7 Torr. Next, the sample temperature was ramped to 300°C within 2 min. This was followed by alternating exposures of the sample to TMA (30 s), O_2 (30 s), TDEAT (30 s), and O_2 (30 s), with Ar purging (1 min) in between reactant exposures at the operating pressure of interest. This process is similar to the ALD process which minimizes undesired reactions and particle formation in the gas phase. First, Al_2O_3 was deposited to increase the stability of the deposited films to Si. In order to study phase transitions and interfacial reactions, films were rapid thermal annealed in Ar for 5 min at a temperature between 500 and 900°C at 1 atm in a preheated quartz horizontal furnace (Lindberg Blue STF). The furnace was kept in Ar ambient during wafer loading. The temperature in the furnace can be maintained within ±2°C.

The thickness of TiO_2/Al_2O_3 film was measured using spectroscopic ellipsometry (J. A. Woollam Co. M-44). The surface roughness of both as-deposited and annealed films was analyzed using atomic force microscopy (AFM, Digital Instruments Dimension 3100) using the tapping mode. The bonding states and atomic composition of the samples were investigated using X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA and Kratos AXIS-165). The data was calibrated with respect to the C 1s peak at 285 eV. Peak fitting was accomplished using Gaussian–Lorentzian functions and Shirley background subtraction. X-ray diffraction (XRD, Philips X'pert) was utilized to identify the phase and structure of the film. The analysis was characterized using Cu Kα radiation (wavelength r_{X-ray} = 0.1542 nm) at a glancing incident angle of 1°. The X-ray generator was operated at 45 kV and 40 mA. Rutherford backscattering (RBS) spectroscopy with a General Ionex Tandetron accelerator employing 2 MeV He^+ particles was used to study the bulk composition of the films. The simulation was done using RUMP software.

Results and Discussion

The growth rate of laminated TiO_2/Al_2O_3 films was studied at various TDEAT feed flow rates. One layer of Al_2O_3 and one layer of TiO_2 typically constitute one deposition cycle. The Ti/Al ratio in TiO_2/Al_2O_3 film was controlled by varying the thickness of the TiO_2 layer while keeping the thickness of the Al_2O_3 layer constant. This was accomplished by altering the TDEAT bubbler pressure while maintaining all other conditions constant. Because the flow rate of the carrier gas, Ar, is constant and TDEAT vapor pressure is constant at constant temperature, lowering the TDEAT bubbler pressure increases the ratio of TDEAT partial pressure to total bubbler pressure, which results in higher TDEAT flow rate and, in turn, in higher TiO_2 deposition rate. Figure 1 illustrates the deposition rate of TiO_2/Al_2O_3 films as a function of number of deposition cycles at various TDEAT bubbler pressures. The linear increase of the growth rate with increasing deposition cycle number indicates that, at a given TDEAT bubbler pressure, the thickness increase resulting from each cycle is constant.

Because the deposition rate of Al_2O_3 is held constant at 0.54 nm/cycle (Fig. 2a), the thickness ratio of TiO_2/Al_2O_3 at each cycle as a function of TDEAT bubbler pressure can be derived and it is as shown in Fig. 2b. Thus, by altering the TDEAT bubbler pressure, laminated TiO_2/Al_2O_3 films with controllable Ti/Al ratio can be deposited.

The surface roughness of both as-deposited and annealed films is important because it affects shifts in electronic energy levels and degrades electrical characteristics.[20] Figure 3 shows AFM images of surface roughness of as-deposited TiO_2, laminated TiO_2/Al_2O_3, and Al_2O_3 films on Si substrates. The images shown are from 2 $\times$ 2 μm scan areas. The Al_2O_3 film is flat and its root-mean-square (rms) roughness is only 0.11 nm, which is comparable to that of the
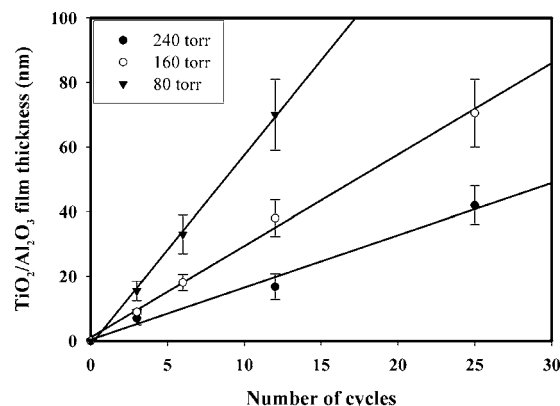

Figure 1. Thickness of TiO_2/Al_2O_3 films as a function of cycle number [sequential expose of TMA (30 s), oxygen (30 s), TDEAT (30 s), and oxygen (30 s), with Ar purging (1 min) in between each reactant feed]; TDEAT bubbler pressure is 80 (triangles), 160 (hollow circles), and 240 Torr (solid circles). The films were deposited at a substrate temperature of 300°C and chamber pressure of 0.7 Torr.

Si substrate; the TiO_2 film is rougher and its rms is about 0.99 nm. Typically, TiO_2 films are rough. It has been reported that TiO_2 films deposited using TTIP have rms of more than 4 nm.[21,22] The probable difficulty with TTIP is that its activation energy is very high and such a TiO_2 film is usually deposited at temperatures above 300°C.[5] It was reported that LPCVD TiO_2 films using TTIP as precursor are crystallized at deposition temperatures as low as 320°C.[5,23] Generally, when TiO_2 is deposited using TTIP, the columnar growth structure is known as a prime factor which causes the roughness of the film.[8,9,24] In our study, LPCVD TiO_2 deposited using TDEAT maintains amorphous structure up to 500°C, as evidenced by XRD (data not shown here). It is likely that the amorphous structure of TiO_2 deposited using TDEAT results in a relatively flat surface, which may make TDEAT an effective precursor for TiO_2 deposition.

By incorporating Al_2O_3 into TiO_2, the roughness of the film is improved dramatically as shown in Fig. 3. Addition of Al_2O_3 into TiO_2 (7:3 Ti/Al atomic ratio) decreases the RMS of the film from 0.99 to 0.16 nm, which is close to that of Al_2O_3 film. The appear-
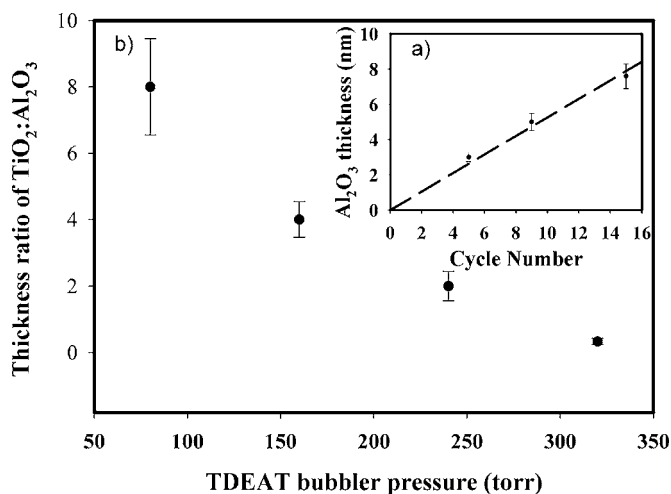

Figure 2. (a) Al_2O_3 growth rate as a function of cycle number and (b) calculated thickness ratio of TiO_2/Al_2O_3 as a function of TDEAT bubbler pressure (other conditions are constant). The growth rate of A_2O_3 is constant at 0.54 nm in each cycle. The films were deposited at a substrate temperature of 300°C and chamber pressure of 0.7 Torr.
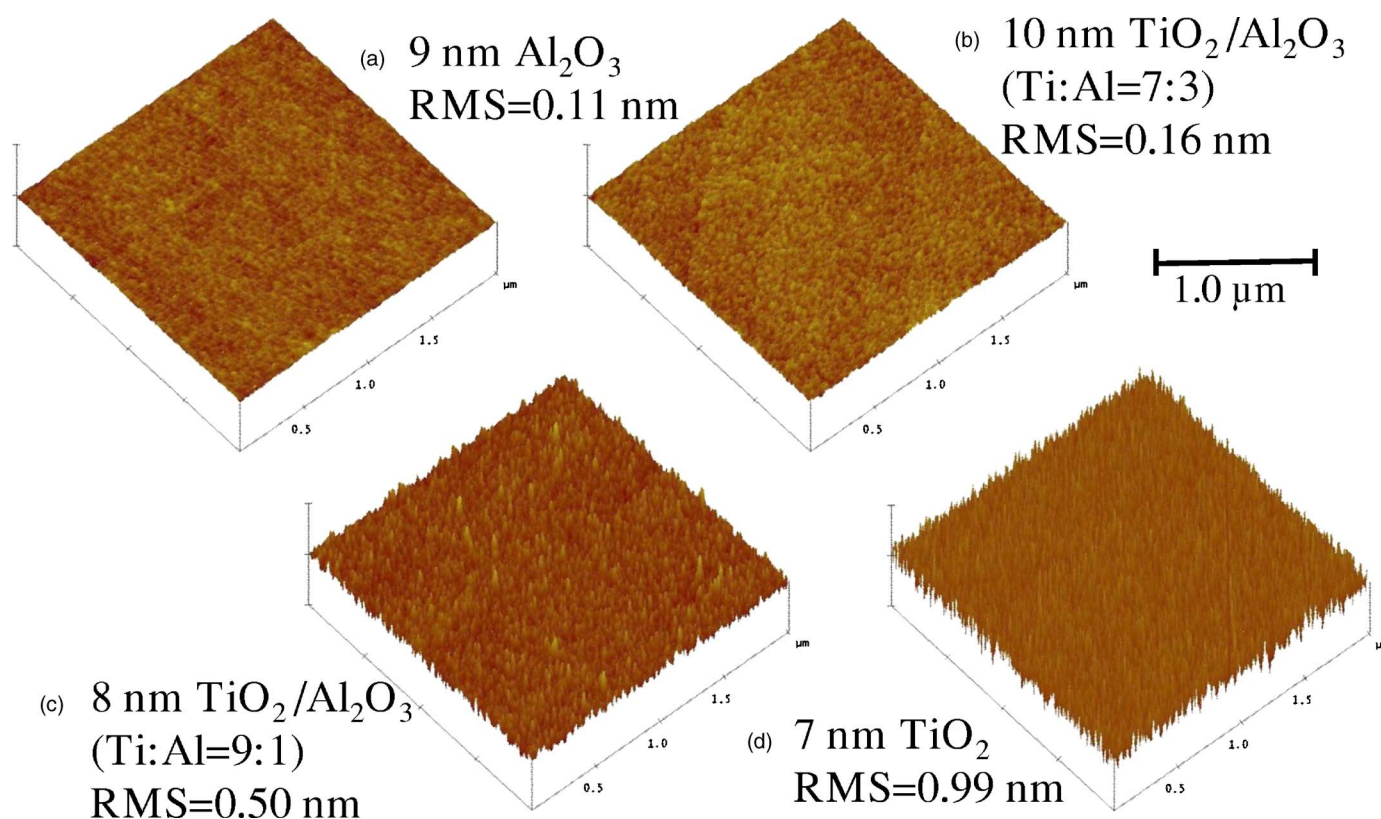
Figure 3. (Color online) AFM surface roughness of as-deposited (a) 9 nm thick Al_2O_3 film (rms roughness is 0.11 nm), (b) 10 nm thick TiO_2/Al_2O_3 film (7:3 Ti/Al atomic ratio, rms roughness is 0.16 nm), (c) 8 nm thick TiO_2/Al_2O_3 film (9:1 Ti/Al atomic ratio, rms roughness is 0.50 nm), and (d) 7 nm thick TiO_2 (rms roughness is 0.99 nm) on Si substrate at 300°C and 0.7 Torr.

ance of the TiO_2 surface is also different from that of the films with Al_2O_3. The surface of pure TiO_2 is a dense narrow spike in shape, while the TiO_2 alloyed with Al_2O_3 is more mountainlike.

The roughness of TiO_2/Al_2O_3 films (9:1 Ti/Al atomic ratio) as a function of annealing temperature is shown in Fig. 4. The as-deposited and annealed samples originated from the same 55 nm TiO_2/Al_2O_3 film. The AFM scan area was 1×1 µm. The samples annealed at temperatures of 500 and 700°C have a smooth surface similar to that of the as-deposited sample with a rms value below 1 nm, which suggests that the film is stable up to 700°C. However, when the annealing temperature is increased to 900°C, the film shows apparent nucleation with larger grain size and its roughness increases to more than 2 times that of as-deposited films. This sharp roughness change indicates phase transformation.

Even though there are studies on the crystallization inhibition of TiO_2 films by Al_2O_3 incorporation,[7,10,11] very few focus on CVD or ALD films. Kim and Yun have studied laminated ALD TiAlO films but did not report annealing studies.[13] In this study, XRD was utilized to study the morphology of both as-deposited and annealed films. All as-deposited TiO_2/Al_2O_3 and TiO_2 films are amorphous. Upon annealing in Ar at 700°C for 5 min, the XRD patterns shown in Fig. 5 reveal that the 64 nm thick TiO_2 film is crystallized. The peaks are well interpreted to be a mixture of anatase and little rutile phase.[7,25] However, at the same annealing conditions, the 50 nm thick TiO_2/Al_2O_3 film (9:1 Ti/Al atomic ratio) remains amorphous. This film crystallizes when the annealing temperature is increased to 900°C and only anatase phase reflections appear in the XRD spectrum. These results corroborate AFM results that suggest TiO_2/Al_2O_3 films maintain amorphous structure at temperatures up to 700°C, which is comparable with some LPCVD Al_2O_3 films reported in the literature.[13]

High deposition rate in a low-temperature CVD process likely introduces impurities in films, especially carbon, when a metallor-

ganic precursor is used. Carbon impurity could increase the film crystallization temperature, but it degrades the electrical characteristics of the gate dielectric layer by increasing the interfacial and bulk trap densities. In this study, RBS and XPS were utilized for studies on impurities. Figure 6 shows RBS spectra of as-deposited TiO_2, Al_2O_3, and TiO_2/Al_2O_3 films. The RBS spectra reveal that all films have no detectable amount of carbon or nitrogen. XPS analyses of these films (Fig. 7), after sputtering to remove the surface contamination, corroborate the RBS results. Less than 1.5% carbon and nitrogen were detected, which is close to the XPS detection limit. This suggests that the deposited films have negligible carbon contamination and the high crystallization temperature of the LPCVD TiO_2/Al_2O_3 films is not attributed to the incorporation of carbon impurities.

The two important factors which may contribute to the high crystallization temperature and the low impurity incorporation in the films are the choice of the precursors and the deposition method. TiO_2 films have been deposited via hydrolysis. It has been found that TiO_2 formed using titanium tetra-n-butoxide $[Ti(OBu)_4]$ is more likely to crystallize than that formed using other precursors (e.g., TDEAT). It was reported that Et_2NH formed and incorporated in the film during the hydrolysis of TDEAT inhibits the crystallization of TiO_2.[25] However, that is not likely the case in our study, because negligible amounts of nitrogen impurity were found. It seems that the precursor itself plays an important role in the film structure. Because amide-based metal precursors have been reported to be promising due to their high reactivity and lower impurity incorporation,[16,17] TDEAT, as an amino Ti-containing precursor, should result in a lower level of impurity incorporation than that obtained using an alkoxide-based precursor, i.e., TTIP, even at low process temperatures. Also, it has been reported that CH_4, which may be a major product in the TMA–H_2O reaction and may participate actively in the carbon incorporation mechanism, can be re-

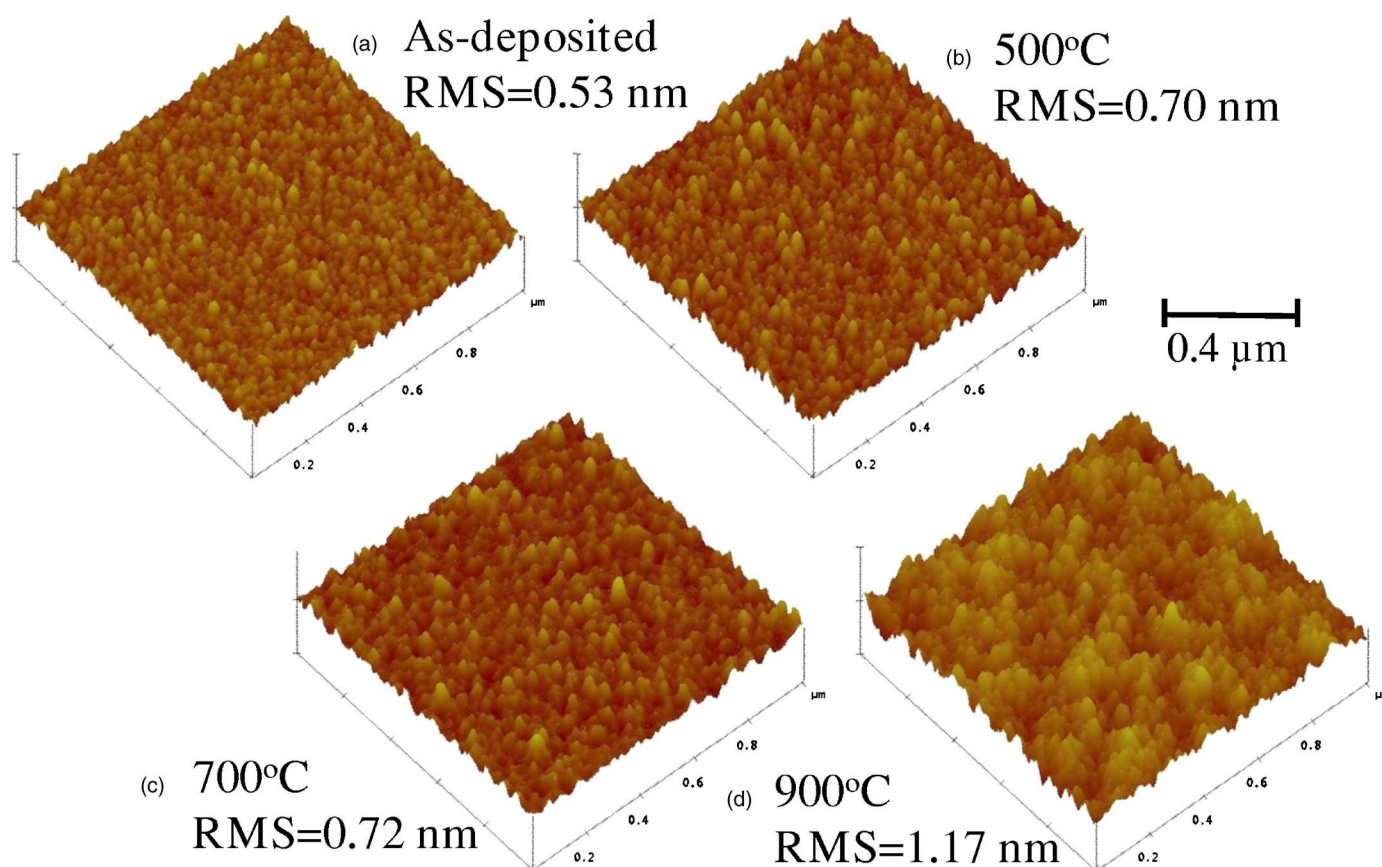**Figure 4.** (Color online) AFM surface roughness of 55 nm thick TiO_2/Al_2O_3 film with 9:1 Ti/Al atomic ratio: (a) as-deposited film at 300°C and 0.7 Torr has rms roughness of 0.53 nm and (b–d) Ar-annealed at 500, 700, and 900°C for 5 min with rms roughness of 0.70, 0.72, and 1.17 nm, respectively.

moved as CO_2 when oxygen is used as oxidizer.[26] Furthermore, the low impurity level can also be due to the ALD-like cyclic deposition method used. In our earlier studies on LPCVD TiO_2 films using TDEAT, about 3 atom % carbon and 2 atom % nitrogen impurities were found in the films.[27] In this study, we use the cyclic deposition

Figure 5. XRD diffraction patterns of Ar-annealed 64 nm thick TiO_2 film and 50 nm thick TiO_2/Al_2O_3 film (9:1 Ti/Al atomic ratio). Annealing time was 5 min. The analysis by XRD was carried out using Cu Kα radiation (wavelength r_{X-ray} = 0.1542 nm) at a glancing angle of 1°.

method, in which excess reactants in the gas phase are purged out and the reaction takes place only on the substrate surface. Consequently, lower impurity levels are obtained.

The thermal stability of TiO_2/Al_2O_3 film on Si was investigated through postthermal annealing at temperatures of 500 and 700°C in Ar for 5 min. The interface chemistry was analyzed using XPS. Figure 8 shows the XPS spectra of Si 2p obtained from 6 nm thick as-deposited and annealed films. The bonding energy at 99.1 eV is attributed to Si 2p from the substrate.[28,29] There is no signal from Si^{n+} ($n > 0$) in the as-deposited film; such a signal starts appearing in the annealed film. The atomic composition calculated from XPS analyses suggests that the as-deposited TiO_2/Al_2O_3 film has about 10% excess oxygen. After annealing in inert environment at temperatures of 500 and 700°C, the film appears almost stoichiometric, with less than 2% oxygen vacancies. This change in oxygen content, from oxygen-rich in the as-deposited film to almost stoichiometric in the annealed film, suggests that excess oxygen may facilitate the interfacial reactions and induce SiO_x formation at increased annealing temperatures.

Conclusions

Laminated TiO_2/Al_2O_3 films with a controllable Ti/Al ratio have been successfully deposited with TDEAT, TMA, and oxygen using cyclic LPCVD at low temperatures. AFM analyses revealed that the roughness of TiO_2 film decreases dramatically with the addition of even a few percent of Al_2O_3. As-deposited films are found to have negligible amounts of carbon and nitrogen impurities as probed using both XPS and RBS. XRD shows that TiO_2/Al_2O_3 film with 9:1 Ti/Al atomic ratio maintains an amorphous structure up to 700°C, while TiO_2 film crystallizes at the same conditions. There was no interfacial SiO_x detected in the as-deposited films, but it was formed
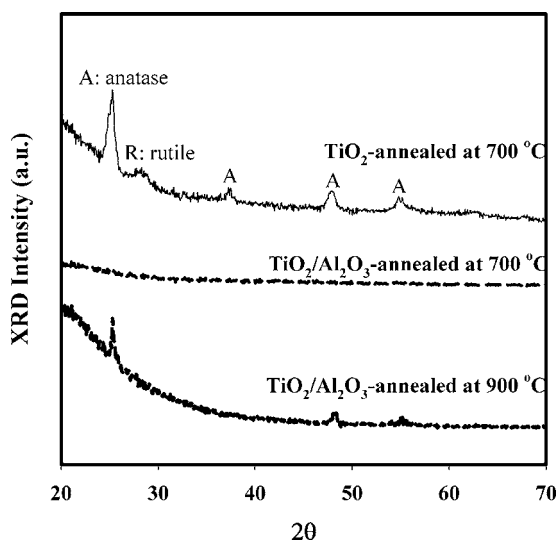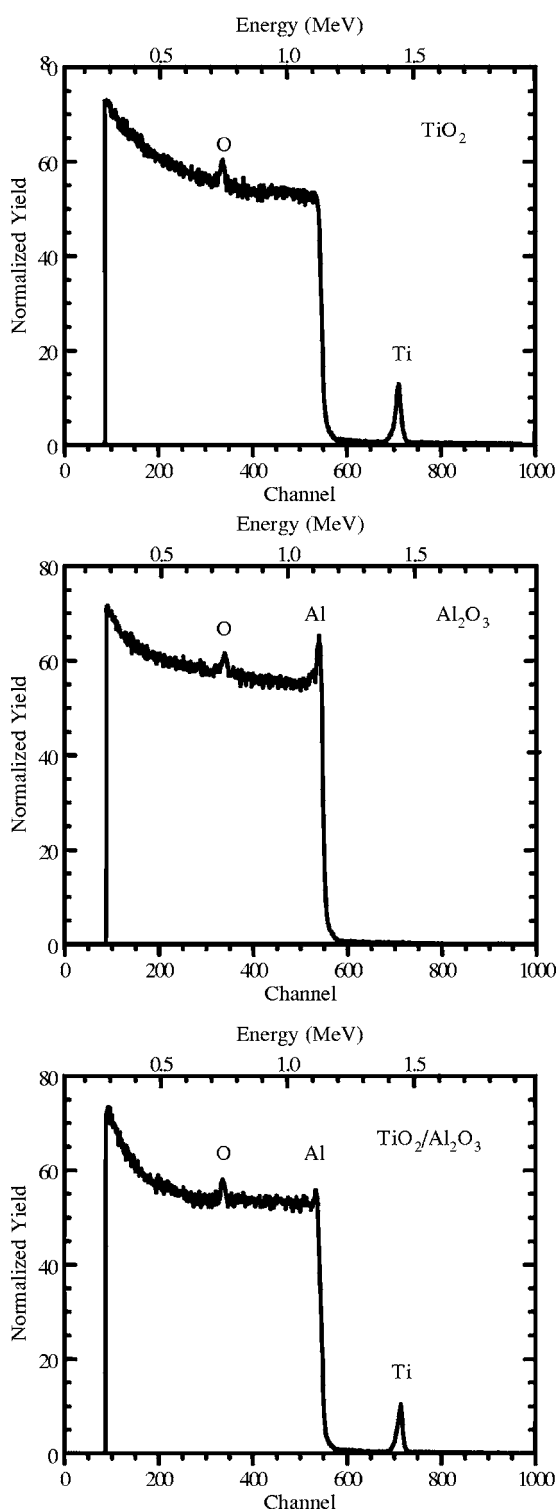
Figure 7. C 1s and N 1s XP spectra of TiO_2/Al_2O_3 film at 90° take-off angle collected before Ar^+ sputtering and 5 min after Ar^+ sputtering, indicating less than 1.5% carbon and nitrogen incorporation in the film.
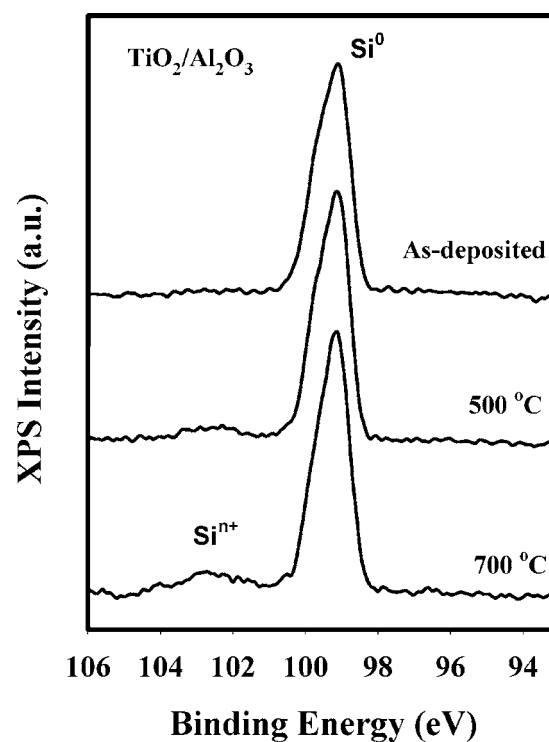
Figure 8. XP spectra of Si 2p collected at 90°C take-off angle for a 6 nm thick TiO_2/Al_2O_3 (9:1 Ti/Al atomic ratio) film deposited at 300°C and 0.7 Torr: as-deposited film and after annealing in Ar for 5 min at 500°C and 700°C.

Figure 6. RBS spectra of as-deposited TiO_2, Al_2O_3, and TiO_2/Al_2O_3 (3:7 Ti/Al atomic ratio) films at 300°C and 0.7 Torr. 2.0 MeV He^+ particle was used for the analysis. RBS revealed that there is no detectable carbon and nitrogen incorporation in the film.

upon annealing in Ar at high temperatures. The laminated cyclic CVD TiO_2/Al_2O_3 films using TDEAT, TMA, and O_2 at low temperatures can be promising high-*k* structures for gate dielectric applications. Electrical characterization of such structures remains to be done so that their full potential can be investigated.
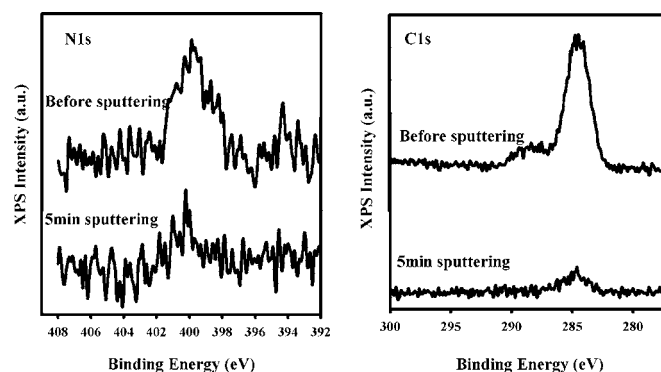
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