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PREPARATION AND CHARACTERIZATION OF TiO_2 THIN FILMS BY PECVD ON Si SUBSTRATE

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Abstract – Titanium oxide thin films were prepared on p-Si(100) substrate by plasma enhanced chemical vapor deposition using high purity titanium isopropoxide and oxygen. The deposition rate was little affected by oxygen flow rate, but significantly affected by RF power, substrate temperature, carrier gas flow rate, and chamber pressure. Morphology of the film became coarser with increasing deposition time and chamber pressure, and the film showed less uniformity at high deposition rates. It was also found that the overall deposition process is controlled by heterogeneous surface reaction below 200°C, but controlled by mass transfer of reactants at higher temperatures. TiO_2 films deposited at temperatures lower than 400°C was amorphous, but showed the anatase crystalline structure upon 400°C deposition. The dielectric constant was about 47 for the films post-treated by rapid-thermal annealing (RTA) at 800°C. The leakage current was about 2×10^{-5} A/cm^2 for the films deposited at 400°C and RTA-treated at 600°C. However, it was decreased to less than 3×10^{-7} A/cm^2 for the film RTA-treated at 800°C.

Key words: *Titanium Oxide, Thin Films, PECVD, Deposition Rate, RTA, Leakage Current*

INTRODUCTION

Titanium oxide has many applications due to its unusual properties such as high dielectric constant, chemical and thermal stability, high refractive index, and excellent optical transmittance in the visible and near-IR range. In recent years, TiO_2 thin films have been investigated for DRAM applications because of its unusual high dielectric constant and good thermal stability. Dynamic random access memory (DRAM) requires a sufficient storage capacity of about 30fF. As memory size increases, each cell area has to shrink and so does the physical dimension of the storage capacitor. The conventional SiO_2 or Si_3N_4/SiO_2 insulators are not adequate due to a physical limit of dielectric strength. Hence, DRAMs need an alternative insulator with a high dielectric constant to store more charges in a unit area. In recent years, intensive research works have been performed to find and characterize ferroelectric film materials, and to establish an efficient thin film technique.

For DRAM applications, examples are TiO_2, Ta_2O_5, $BaTiO_3$, $PbTiO_3$, PZT, $SrTiO_3$, and BST. Many research results for fabricating TiO_2 thin films have been reported in the literature [Ghoshtagore and Noreika, 1970; Takahashi et al., 1981, 1985; Fuyuki and Matsnami, 1986; Siegering and Griffin, 1990; Won et al., 1993; Rausch and Burte, 1993; Jeon et al., 1994; Choi et al., 1995], but not many studies have been done on plasma enhanced chemical vapor deposition (PECVD) films of TiO_2. Williams and Hess in 1984 reported structural properties of TiO_2 films deposited from $TiCl_4$ and O_2 in an RF glow discharge, and Frenck et al. in 1991 reported the deposition of TiO_2 films by a remote PECVD using $Ti(O\text{-}i\text{-}C_3H_7)_4$. However, these investigations have mainly focused on structural properties of TiO_2 films deposited on several substrate materials. Lee et al. in 1993 also reported preparation of amorphous TiO_2 films by PECVD, and obtained somewhat improvement of electrical properties by post treating as-deposited films by O_2 plasma, but not enough for DRAM applications.

In this work, to study the structural and electrical properties of TiO_2 thin films, TiO_2 films have been deposited by PECVD and characterized by several analysis instruments such as Ellipsometer, α-step, XRD, RBS, SEM, LCR meter, and HP picoam-meter. To enhance the morphology and electrical properties, as-deposited films were treated by rapid thermal annealing (RTA). The RTA treatment shortened the annealing time to a few minutes, and minimized the interaction at the TiO_2-Si interface. The effects of process parameters on film formation also have been discussed.

EXPERIMENT

The PECVD system used in this study is schematically shown in Fig. 1. It mainly consists of a source deliverly line with a bubbler of a metal organic, a cold-wall reaction chamber equipped with parallel electrodes, and a vacuum system. The electrodes made of stainless steel are 12.5 cm in diameter with variable spacing. The metal-organic vapor with an oxidant gas is carried into the chamber by 99.999% Ar through a show-

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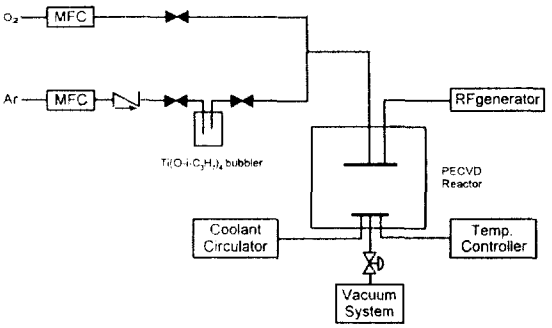

Fig. 1. Schematic illustration of the PECVD system.

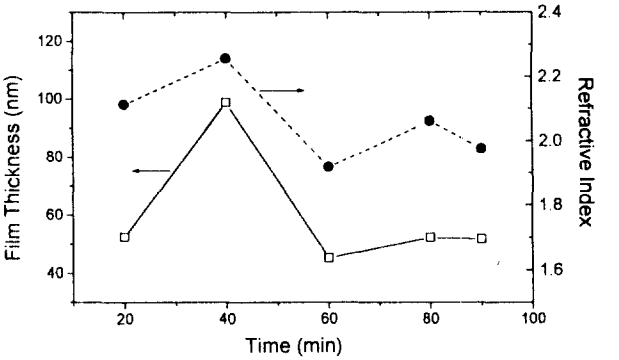

Fig. 2. Film thickness vs. deposition time (T_s=200°C, 60W, 20 sccm Ar, and 30 sccm O_2).

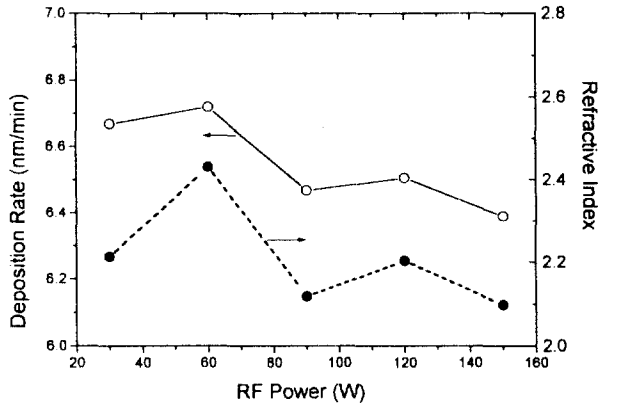

Fig. 3. Effect of RF power on deposition rate (T_s=200°C, 30 sccm Ar, 60 sccm O_2).

er head of the upper electrode. RF power is applied to the upper electrode using matching box operating at 13.56 MHz. The temperature of Si substrate on the susceptor electrode is controlled by a PID controller. The flow rates of gases are regulated with mass flow controllers.

In experiments, boron-doped p-Si(100) wafer was cleaned with piranha solution (H_2O_2/H_2SO_4 mixed solution), dipped in HF solution, rinsed with deionized water, and blown with N_2 gas in sequence. TiO_2 films were deposited on Si substrate using titanium(IV) isopropoxide (99.999%, $Ti[OCH(CH_3)_2]_4$) and high purity oxygen (99.999%). The bubbler temperature was maintained at 35°C, and feed lines at 70°C.

The thickness and refractive index of TiO_2 thin films were measured using an ellipsometer. The morphology of the films was evaluated by scanning electron microscopy (SEM). The crystal structures were analyzed with an X-ray diffractometer (XRD). Compositions of the films were measured with Rutherford Backscattering Spectroscopy (RBS). Electrical properties were measured using Al/TiO_2/Si and Al/TiO_2/Pt/Si structures. The dieletric constant of the film was measured using a LCR meter at 1 MHz.

RESULTS AND DISCUSSION

1. Deposition of TiO_2 Films

1-1. Deposition Time

In order to confirm the relationship between film thickness and deposition time, experiments were carried out varying depositon time at substrate temperature (T_s) of 200°C and RF power of 60W with maintaining the flow rates of carrier gas (Ar) and oxygen to 20 and 30 sccm, respectively. Film thickness and refractive index were measured and plotted in Fig. 2. It is seen that the film thickness showed a maximum value for 40 minutes, but decreased with further increasing deposition time. Similar trend was obtained for the refractive index. This may be explained by the fact that chemical vapor deposition occurs dominantly until 40 minutes, but sputtering may be dominant due to increased density of neutrals after 40 minutes.

1-2. RF Power

The effect of RF power on deposition rate was studied varying RF power from 30 to 60W at 200°C of T_s with 30 sccm Ar and 60 sccm O_2. It is seen from Fig. 3 that the deposition rate and refractive index increase with RF power and reach maximum values at 60W. However, they decrease with increasing RF power higher than 60W. The surface roughness of the TiO_2 film was also increased at higher RF power than 60W. This result indicates that etch or sputtering rate rather than chemical deposition increases with increasing power.

1-3. Effect of Gas Flow Rate

Fig. 4 shows the effect of carrier gas flow rate on deposition rate. Films were deposited at 200°C of T_s and 60W of RF power with flowing 60 sccm O_2. The deposition rate was increased with increasing the flow rate of carrier gas as expected. However, the morphology of the film became coarser with increasing the carrier-gas flow rate. Although not illustrated, the O_2 flow rate showed little effect on the deposition rate and refractive index. This means that as far as the deposition rate is concerned, the O_2 flow rate is not an important variable; but for stoichiometry control of the TiO_2 film it is critical to supply enough oxygen.

1-4. Effect of Substrate Temperature

The substrate temperature has a great effect on the deposition rate. To elucidate the effect of substrate temperature, experiments were carried out with varying the substrate temperature from 150 to 400°C. Film depositions were obtained for 40 minutes at RF power of 60 W for the cases of A (30 sccm Ar, 60 sccm O_2) and B (20 sccm Ar, 30 sccm O_2). The measured results are shown in Fig. 5 in terms of deposition rate and refractive index. It is seen that the deposition rate increases with temperature and reaches a maximum value at 200°C.

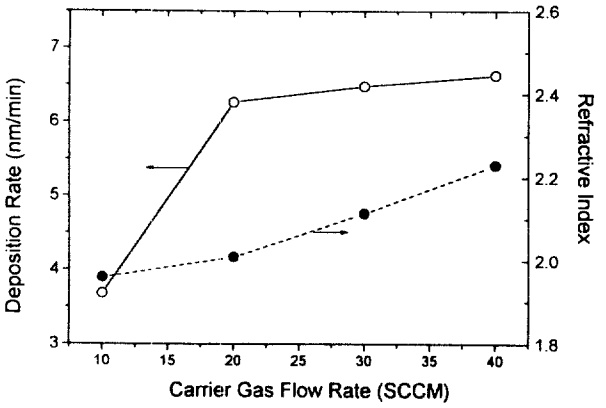

Fig. 4. Effect of carrier gas flow rate on deposition rate (T_s= 200°C, 60W, 60 sccm O_2).

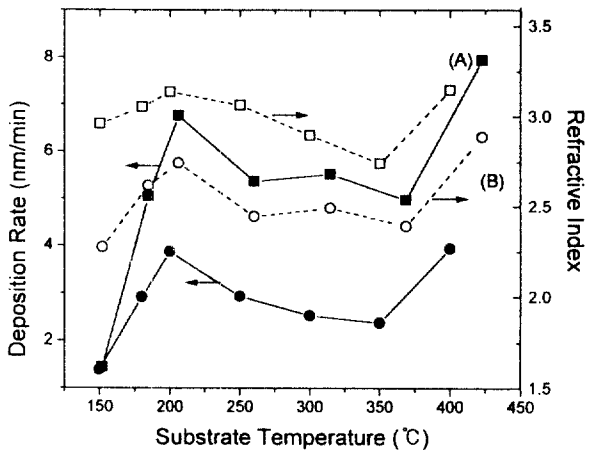

Fig. 5. Effect of substrate temperature on deposition rate: (A) 60W, 30 sccm Ar, 60 sccm O_2; (B) 60W, 20 sccm Ar, 30 sccm O_2.

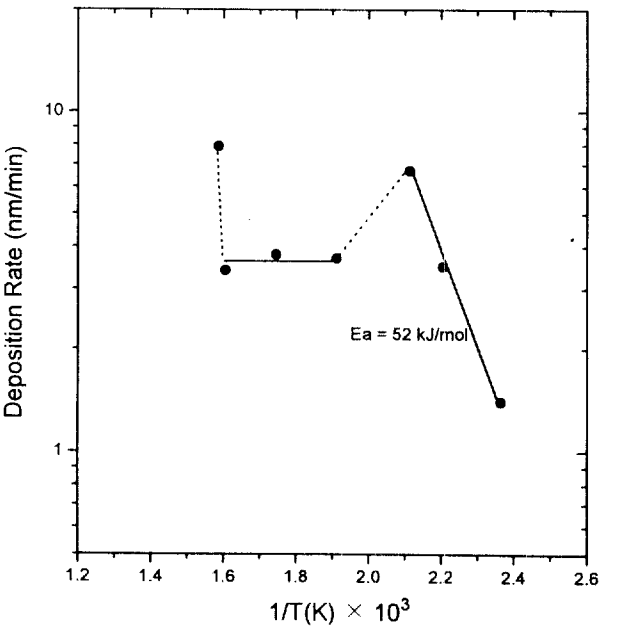

Fig. 6. Arrhenius plot of deposition rate of TiO_2 thin film.

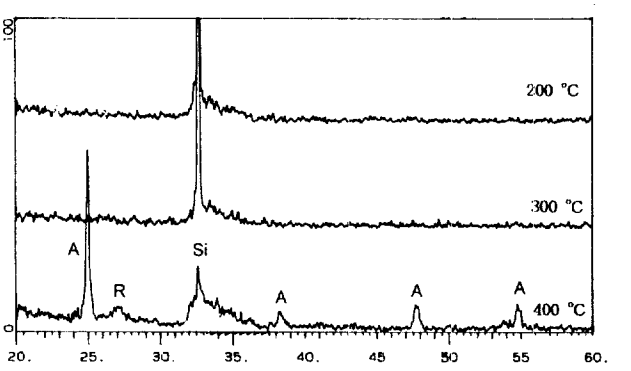

Fig. 7. XRD patterns of as-deposited TiO_2 films at various substrate temperatures.

However, it decreases at temperatures higher than 200°C; increases again at 400°C. Same trends were obtained for both cases of A and B. These results may be explained by viewing the control steps and crystal structure of the film.

The overall process of TiO_2 film deposition may be controlled by heterogeneous surface reaction kinetics below 200°C, and thus the deposition rate increases with temperature. Arrhenius plots of measured deposition rates are shown in Fig. 6. The figure shows that the deposition rate exponentially increases with temperature when $T_s \leq 200$°C. In general, deposition is controlled by surface reaction kinetics when activation energy is greater than 41.8 kJ/mol. The apparent activation energy obtained from Fig. 6 was 52 kJ/mol. Fig. 6 also revealed that the deposition rate is almost independent on temperatures between 200 and 400°C, indicating that the deposition rate is mainly controlled by mass transfer of reactant gases. However, this is a contrast to the general aspect of PECVD or LPCVD in which mass transfer coefficient is very large compared to the chemical reaction rate. Lee et al. in 1993 also reported low deposition rate of TiO_2 in PECVD at temperatures higher than 250°C. Such a result may be due to the increase of homogeneous reaction and the lack of reactants participating in the film deposition at high temperatures compared to the case of low temperature deposition. As the susceptor temperature increases, the upper electrode temperature becomes high due to the convection heat transfer from the hot susceptor. This in turn leads to decomposition of metal organic Ti precursors before the glow discharge region, resulting in the lack of reactants on the substrate surface. High temperatures also induce the desorption of reactants adsorbed on the substrate surface.

The reason why the deposition rate is increased at 400°C may be explained by the crystallization of the film. As-deposited TiO_2 films at temperatures below 400°C were amorphous, but they were converted to the anatase phase at 400°C. This temperature agrees well with the crystallization temperature of 366.2°C determined from DSC analysis of TiO_2 film. An increase in film thickness is also expected due to the fact that volume expansion is about 1.95 times for anatase. This explanation can be verified by X-ray diffraction spectra of TiO_2 films deposited at various substrate temperatures. It is seen from Fig. 7 that as-deposited films below 400°C are amorphous, but the anatase phase dominates over the rutile phase in the

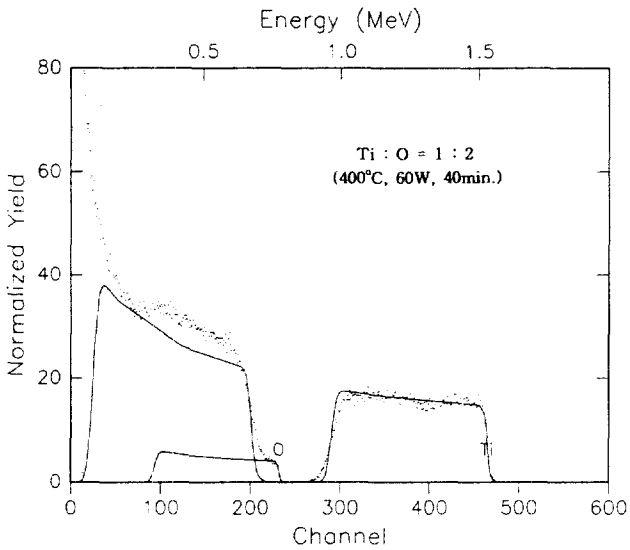

Fig. 8. RBS analysis of as-deposited films (T_s=400°C, 60W, 30 sccm Ar, 60 sccm O_2).

film deposited at 400°C.

1-5. Film Composition and Uniformity

The stoichiometric composition of TiO_2 films was analyzed by Rutherford Backscattering Spectroscopy analysis as shown in Fig. 8. It is seen that the atomic ratio of Ti to O is exactly 1 : 2 for the film deposited at 400°C.

In general, the deposition rate is also affected by chamber pressure. Typical experimental results are shown in Fig. 9 in terms of scanning electron micrographs. It is seen that the TiO_2 film deposited at 0.14 Torr is dense and uniform, but coarse and nonuniform at 2 Torr. This result may be explained by the fact that as the chamber pressure increases the residence time of gaseous species becomes long, and thus homogeneous gas-phase reactions are favored. This then leads to a decrease in the amount of reactive species required for the heterogeneous surface reaction. In addition, the particles produced by homogeneous gas-phase reactions sit on the surface to increase roughness and decrease uniformity.

2. Electrical Properties of TiO_2 Films

Electrical properties of TiO_2 films were measured using a metal-oxide-semiconductor structure with aluminium electrode. As-deposited films were post-treated by rapid thermal annealing (RTA) in oxygen atmosphere for 1 minute varying annealing temperature. It was observed that the anatase phase dominated over the rutile phase below 600°C, but it completely transformed to the rutile phase upon annealing at 800°C. The dielectric constant was 2.1 for the film deposited below 400°C, and 11.5 for 400°C deposition film. However, it was increased to 47.4 for RTA treated film at 800°C. High dielectric constant of the post-treated film at 800°C is probably attributed to the crystalline structure of rutile phase.

Fig. 10 presents typical current-voltage characteristics for the same films described above. The leakage current was substantially large for the as-deposited film at 400°C and RTA-treated film at 600°C, more than 10^{-5} A/cm^2. However, it was less than 3×10^{-7} A/cm^2 for the film RTA-treated at 800°C.

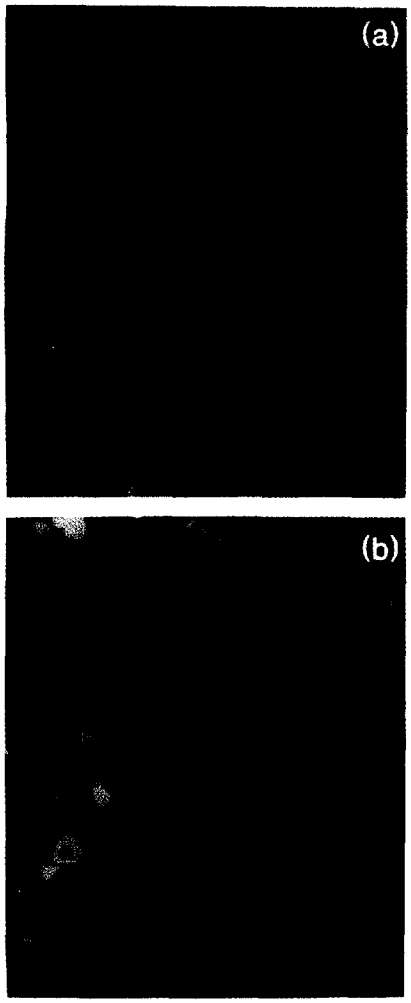

Fig. 9. Scanning electron micrographs of TiO_2 films deposited at different chamber pressure (T_s=400°C, 60W): (a) 0.14 Torr; (b) 2 Torr.

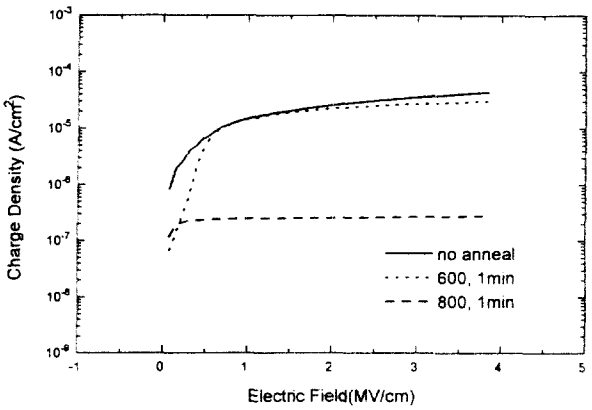

Fig. 10. Variation of leakage current density of as-deposited and RTA-treated TiO_2 films.

This result clearly indicates that RTA improves a leakage problem of TiO_2 films. This improvement is mainly attributed to the RTA treatment which inhibits silicide formation at the interface

and decreases in defects density of the film. However, the leakage current is still higher than 10^{-9} A/cm^2 that is a limit value for DRAM application.

CONCLUSION

TiO_2 films were successfully prepared on p-Si(100) substrate by plasma enhanced chemical vapor deposition using high purity titanium isopropoxide and oxygen. The deposition rate was little affected by oxygen flow rate, but significantly affected by RF power, substrate temperature, carrier gas flow rate, and chamber pressure. Morphology of the film became coarser with increasing deposition time and chamber pressure; the film showed less uniformity at high deposition rates. It was also found that the overall deposition process is controlled by heterogeneous surface reaction below 200°C, but controlled by mass transfer of reactants from the bulk gas to the surface above 200°C. TiO_2 films deposited at temperatures lower than 400°C was amorphous, but showed the anatase crystalline structure after 400°C deposition. The anatase phase dominated over the rutile phase by RTA below 600°C, but it completely transformed to the rutile phase upon annealing at 800°C. The dielectric constant was increased to about 47.4 by RTA at 800°C mainly due to the crystalline structure of rutile phase. The leakage current was substantially large for the as-deposited film at 400°C and RTA-treated film at 600°C, more than 10^{-5} A/cm^2. However, it was less than 3×10^{-7} A/cm^2 for the film post-treated by RTA at 800°C.

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