Korean J. Chem. Eng., **15**(2), 217-222 (1998)

EFFECT OF RAPID THERMAL ANNEALING ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF TiO_2 THIN FILMS PREPARED BY PLASMA ENHANCED CVD

Jong-Wha Kim*, Do-Oh Kim* and Yoon-Bong Hahn†

School of Chemical Engineering and Technology,
*Department of Semiconductor Science and Technology, Chonbuk National University,
664-14 Duckjin-Dong 1-Ga, Chonju 561-756, Korea
(*Received 4 December 1997 • accepted 3 February 1998*)

Abstract – Titanium oxide thin films were deposited on p-type Si(100), SiO_2/Si, and Pt/Si substrates by plasma enhanced chemical vapor deposition using high purity Ti(O-i-C_3H_7)$_4$ and oxygen. As-deposited amorphous TiO_2 thin films were treated by rapid thermal annealing (RTA) in oxygen ambient, and the effects of RTA conditions on the structural and electrical properties of TiO_2 films were studied in terms of crystallinity, microstructure, current leakage, and dielectric constant. The dominant crystalline structures after 600 and 800 °C annealing were an anatase phase for the TiO_2 film on SiO_2/Si and a rutile phase for the film on a Pt/Si substrate. The dielectric constant of the as-grown and annealed TiO_2 thin films increased depending on the substrate in the order of Si, SiO_2/Si, and Pt/Si. The SiO_2 thin layer was effective in preventing the formation of titanium silicide at the interface and current leakage of the film. TEM photographs showed an additional growth of SiO_x from oxygen supplied from both SiO_2 and TiO_2 films when the films were annealed at 1000 °C in an oxygen ambient. Intensity analysis of Raman peaks also indicated that optimizing the oxygen concentration and the annealing time is critical for growing a TiO_2 film having high dielectric and low current leakage characteristics.

Key words: TiO_2 Films, Plasma Enhanced CVD, Rapid Thermal Annealing, Structural and Electrical Properties

INTRODUCTION

Titanium oxide has many applications because of 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 such unusual properties as a high dielectric constant and chemical and thermal stability [Ghoshtagore and Noreika, 1970; Fuyuki and Matsunami, 1986; Rausch and Burte, 1993; Choi et al., 1995]. Dynamic random access memory (DRAM) requires a sufficient storage capacity of about 30 fF. As memory size increases, each cell area and the physical dimension of the storage capacitor have to shrink. The conventional SiO_2-based insulators are not adequate because of the physical limit of dielectric strength. Hence, DRAMs need an alternate insulator with a high dielectric constant to store more charges in a unit area. Another critical issue in selecting an insulator for DRAM applications is thermal stability, especially for a trench-type capacitor. TiO_2 is a good candidate as an insulator for a trench-type capacitor because of good thermal stability as well as a high dielectric constant.

Several thin film techniques, including physical and chemical methods, have been reported in fabricating high dielectric thin films. Among these, plasma-enhanced chemical vapor deposition (PECVD) has attracted much attention due to the controllability of film composition, high growth rate, good step coverage, and the possibility of scaling up the process to commercial scale. Williams and Hess in 1984 reported structural properties of TiO_2 films deposited from $TiCl_4$ and O_2 in an RF glow discharge; Frenck et al. in 1991 studied the structural properties of TiO_2 films by plasma-enhanced decomposition of tetraisopropyl-titanate; Lee et al. in 1993 reported the properties of amorphous TiO_2 thin films prepared by plasma enhanced CVD. Lee et al. in 1996 prepared the TiO_2 thin films on p-Si(100) by PECVD, and found that the overall deposition process of TiO_2 films was controlled by surface reaction below 200 °C and by mass transfer of reactive species at temperatures higher than 200 °C.

In general, as-deposited films revealed weak crystallinity and poor electrical properties. Resolving these problems requires post-treatment at high temperatures in a conventional tube furnace for a long time. However, such a long-time high temperature annealing causes not only a change in composition and microstructure of the deposited film, but also an interaction between the film and the Si substrate. Hence, the electrical properties of the film are greatly affected by annealing conditions such as annealing time, temperature and environment. To date, no thorough study of these factors has been undertaken, especially for the TiO_2 films prepared by PECVD. In this work, in order to overcome drawbacks of the conventional annealing method, the as-deposited TiO_2 thin films were

†Author for correspondence and also with Department of Semiconductor Science and Technology, Chonbuk National University.
E-mail: ybhahn@che.chonbuk.ac.kr

treated by rapid thermal annealing (RTA) in an oxygen ambient. The RTA method shortens the annealing time to a few minutes and reduces the interaction at the interface [Hahn et al., 1997].

To study the structural and electrical properties of TiO_2 thin films, we deposited films on p-type Si(100), SiO_2/Si, and Pt/Si substrates by PECVD using high purity Ti(O-i-C_3H_7)$_4$ and oxygen. The as-deposited TiO_2 films were treated by RTA in oxygen ambient. The effects of RTA conditions and kinds of substrate on the structural and electrical properties of TiO_2 films were intensively investigated in terms of crystallinity, microstructure, current leakage, and dielectric constant.

EXPERIMENTAL

The PECVD equipment used in this work, which is homemade and schematically shown in Fig. 1, consisted mainly of a source delivery line with a bubbler of metalorganic source, 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 metalorganic precursor vaporized in the bubbler is introduced into the chamber by 99.999 % Ar through a shower head of the upper electrode. Oxygen gas is mixed with Ti(O-i-C_3H_7)$_4$ vapor just before being fed into the reactor. RF power is applied to the upper electrode by using the matching box operating at 13.56 MHz. The temperature of the Si substrate on the susceptor is controlled by a PID controller. The flow rates of the gases are regulated with mass flow controllers. The deposition conditions are summarized in Table 1. The home-made RTA system is heated by halogen lamps and its temperature

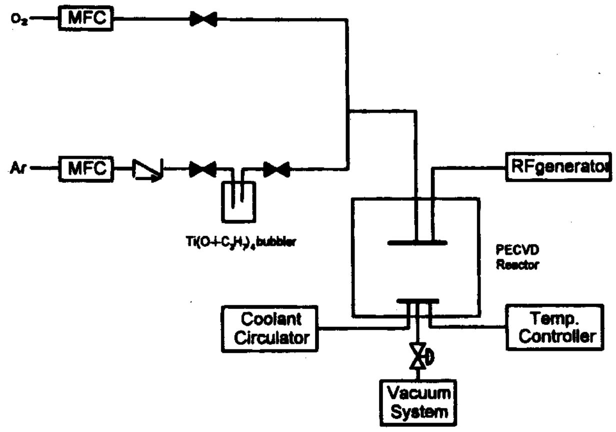

Fig. 1. A Schematic diagram of the plasma enhanced CVD system.

Table 1. Deposition conditions of TiO_2

Substrate	Si(100), SiO_2/Si, Pt/Si
Substrate temperature	200 °C
Source bubbler temperature	35 °C for Ti(O-i-C_3H_7)$_4$
Carrier gas flow rate	30 sccm Ar (99.999 %)
Oxygen flow rate	60 sccm
R. F power	0.54 W/cm^2 (or 60 W)
Base pressure	5×10^{-5} Torr

is controlled by a PID controller connected to a personal computer. Details of the RTA system are available elsewhere [Hahn et al., 1997].

In the experiments, boron-doped p-Si(100) wafer was cleaned with piranha solution, dipped in HF solution, rinsed with deionized water, and blown with N_2 gas in sequence. TiO_2 thin films were deposited on Si, Pt/Si, and SiO_2/Si substrates using Ti(O-i-C_3H_7)$_4$ (99.999 %) and oxygen (99.999 %). The bubbler temperatures were controlled to 35 °C and the feed lines were heated to 70 °C to prevent the condensation of the vaporized reactants. An SiO_2 layer of 4 nm was also grown on a bare silicon wafer to see whether the SiO_2 buffer acts as an effective diffusion barrier against interdiffusion of titanium.

The thickness and refractive index of TiO_2 films were measured with an ellipsometer. A Rutherford backscattering spectrometer (RBS) was used to determine the stoichiometric composition of the deposited films. The crystal structure of annealed TiO_2 films was investigated by an X-ray diffraction (XRD) system and transmission electron microscope (TEM). To measure the electrical properties of the TiO_2 films, an aluminum film of 350 nm thick was deposited on the TiO_2 film by evaporation and patterned by standard photolithography processes to form a top electrode. The aluminum top electrode was a circular dot having 0.8 mm diameter. The current density vs electric field (I-V) characteristics were measured with an HP4145 picoam-meter. The dielectric constant was calculated by using the film thickness and the capacitance measured with an LCR meter at 1 MHz.

RESULTS AND DISCUSSION

TiO_2 thin films were deposited on Si, SiO_2/Si and Pt/Si substrates at 200 °C and post-treated by RTA varying temperatures. Rutherford backscattering spectrometry (RBS) was used to determine the stoichiometry of the TiO_2 film. The RBS measurements were taken with a 2.135 MeV $^4He^+$ incident beam directed normal to the surface. Details of the deposition and characterization of the TiO_2 films on Si are described in a previous work [Lee et al., 1996], in which deposition variables are intensively examined.

Fig. 2 shows a typical RBS spectrum of TiO_2 films deposited on Si(100) substrate at 200 °C. The RBS analysis shows that the atomic ratio of Ti to O is 1 : 2. Similar results were obtained for the films deposited on SiO_2/Si and Pt/Si substrates. These results indicate that stoichiometric TiO_2 films can be prepared under an oxygen enriched environment.

The effects of annealing time and oxygen partial pressure were investigated by Raman scattering (see Figs. 3 and 4). Fig. 3 shows Raman spectra of the TiO_2 films on SiO_2/Si after 800 °C annealing with varying annealing time under oxygen pressure of 1 Torr. Fig. 4 shows Raman peak intensities of the TiO_2 films with varying annealing time under various oxygen partial pressures. A higher intensity of a Raman peak indicates better crystallinity. It is seen that Raman peak intensity is substantially dependent on oxygen pressure and annealing time. The decrease in Raman peak intensity with higher oxygen pressure and longer annealing time may be explained by the fact that an increased oxygen concentration togeth-

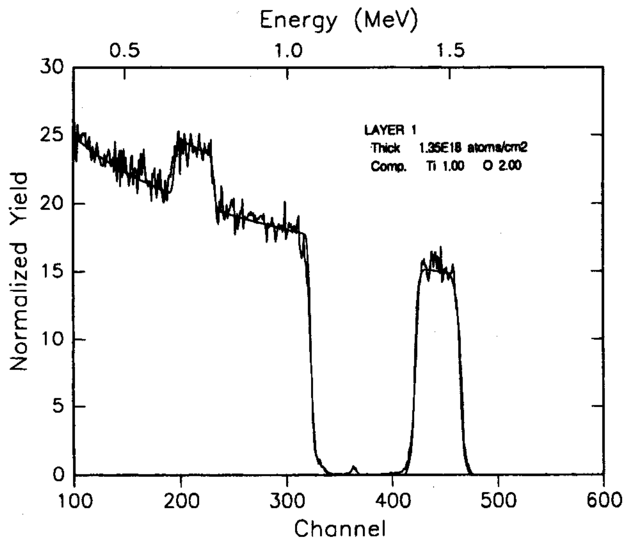

Fig. 2. Rutherford backscattering spectrum for a TiO_2 film on p-Si(100) deposited with $Ti(O\text{-}i\text{-}C_3H_7)_4$ at 200 °C.

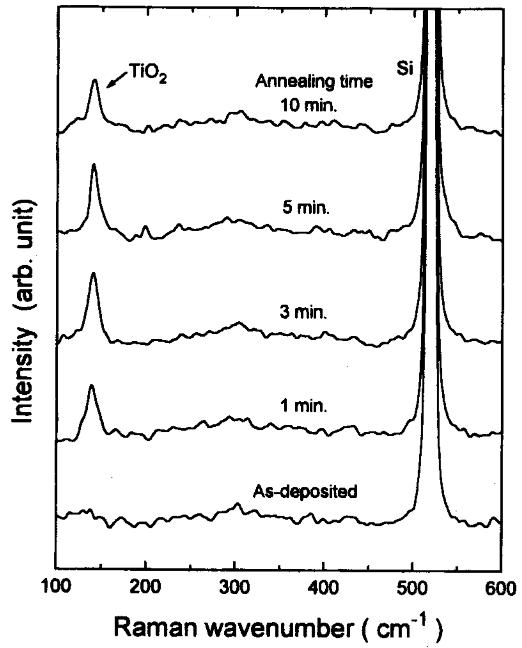

Fig. 3. Raman spectra of the TiO_2 films on SiO_2/Si substrate annealed at 800 °C varying annealing times under oxygen pressure 1 Torr.

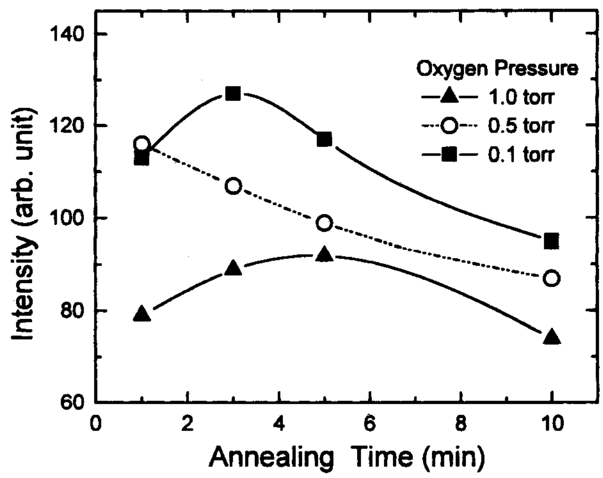

Fig. 4. Raman peak intensities of TiO_2 films on SiO_2/Si substrate annealed at 800 °C with varying oxygen partial pressure and annealing time.

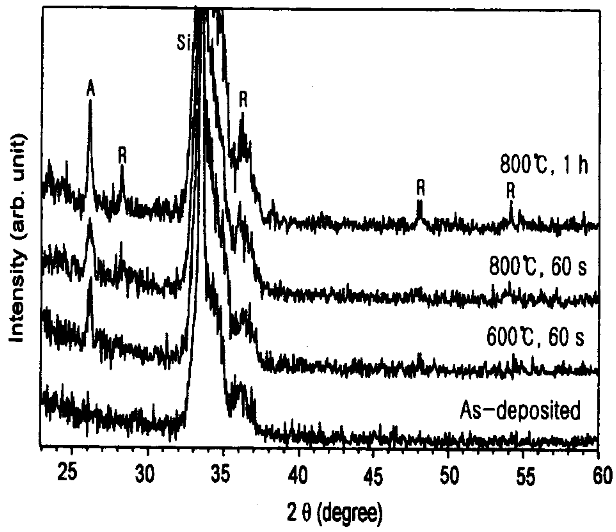

Fig. 5. XRD patterns of the TiO_2 thin films on SiO_2/Si substrate annealed varying temperatures.

er with a long annealing time enhances the thermal diffusion of O^- ions throughout the TiO_2 film, which results in the formation of titanium low oxides such as TiO and Ti_2O_3, and further growth of the SiO_2 layer rather than TiO_2 film. This Raman peak analysis indicates that an important variable for better crystallinity of TiO_2 films in RTA treatment is the oxygen concentration as well as the annealing time.

Fig. 5 shows the XRD spectra for the TiO_2 films deposited on SiO_2/Si substrate at 200 °C and annealed at 600 and 800 °C in an oxygen ambient. It is seen that the as-deposited TiO_2 film has an amorphous structure, but the films annealed at 600 and 800 °C for 60 s show only the anatase phase. To examine the effect of the conventional annealing method on TiO_2 crystallinity, the as-deposited film was also annealed at 800 °C for one hour. As a result, the rutile phase appeared together with increased peak intensity of the anatase phase. This result implies that the RTA treatment of the TiO_2 film on SiO_2/Si substrate has little effect, especially in terms of the rutile phase.

The TiO_2 films deposited on Pt/Si substrate were also annealed at 600 and 800 °C in an oxygen ambient for 60 s, and the XRD patterns of the films were shown in Fig. 6. It is seen that the anatase and rutile phases coexist when annealed at 600 °C, but only the rutile phase appears after 800 °C annealing. This result shows that Pt plays an important role in the transformation of TiO_2 films to rutile structure; thus Pt may be a good diffusion barrier as well as a good bottom electrode material.

Table 2 summarizes the measured dielectric constants (ε) of the as-deposited and annealed TiO_2 films on Si, SiO_2/Si, and

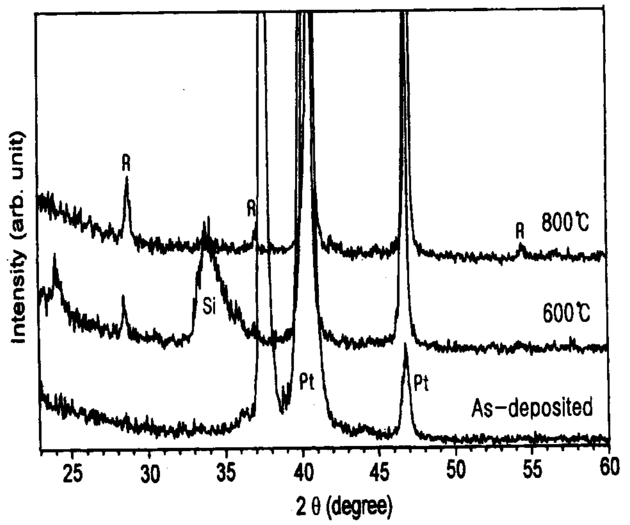

Fig. 6. XRD patterns of the TiO_2 thin films on Pt/Si substrate annealed varying temperatures.

Table 2. Dielectric constants of TiO_2 thin films

Films	As-deposited	RTA (600 °C, 60 s)	RTA (800 °C, 60 s)
TiO_2/Si	3.0	3.9	5.1
$TiO_2/SiO_2/Si$	3.5	4.9	6.8 (12.1)*
$TiO_2/Pt/Si$	11.2	13.9	21.2

*Dielectric constant after 800 °C annealing for 1 h.

Pt/Si substrates. It is seen that ε values of the TiO_2 films increased depending on substrates in order of Si, SiO_2/Si and Pt/Si. Compared to the film deposited on bare Si substrate, TiO_2 film on SiO_2/Si resulted in a somewhat higher dielectric constant, but lower than that on a Pt/Si substrate. The dielectric constant of the $TiO_2/SiO_2/Si$ capacitor increased to 12.1 after 800 °C annealing for one hour. The measured ε of a $TiO_2/Pt/Si$ capacitor was 21.2 mainly due to the presence of a rutile phase formed after 800 °C annealing as shown in Fig. 6. These results confirm that the rutile phase is essential to ensuring a high dieletric TiO_2 thin film.

The current leakage density vs electric field characteristics of the annealed TiO_2 films on SiO_2/Si and Pt/Si substrates are shown in Figs. 7 and 8, respectively. It is seen from Fig. 7 that the current leakage of the as-grown TiO_2 film on Si wafer is substantially larger than that of the TiO_2 film on SiO_2/Si substrate. The latter was further decreased with annealing at high temperatures. It is known that Ti reacts with Si even at a low temperature before oxygen reaches a Ti/Si boundary and forms titanium silicide ($TiSi_x$) at the interface, resulting in large current leakage. The improved current leakage densities of the TiO_2 films on SiO_2/Si with annealing at 600 and 800 °C indicate that the SiO_2 buffer layer may play an important role in preventing the formation of titanium silicide at the interface. It is also worth noting that, although not illustrated, the current leakage of TiO_2 film on SiO_2/Si annealed at 800 °C for 1 h was substantially high, even higher than that of as-grown TiO_2 on Si, indicating that conventional long-time annealing is not an effective method compared to the RTA. Fig. 8 shows the current leakage density vs electric field characteristics of

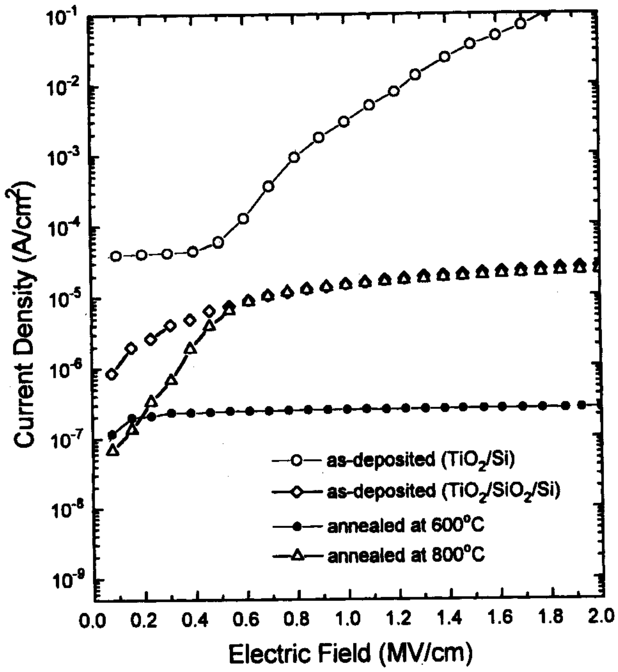

Fig. 7. Current density vs electric field curves for TiO_2 films on Si and SiO_2/Si substrates annealed at various temperatures for 60 s.

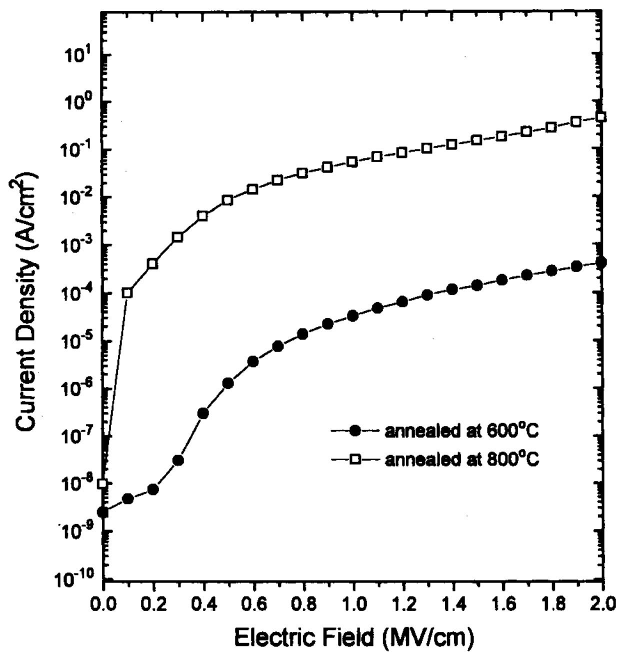

Fig. 8. Current density vs electric field curves for TiO_2 films on Pt/Si substrate annealed at 600 and 800 °C for 60 s.

the annealed TiO_2 films on Pt/Si substrate. The film annealed at 600 °C showed lower current leakage than that at 800 °C. High current leakage after 800 °C annealing was mainly due to peeling-off of platinum on the substrate.

The cross-sectional TEM photographs of the annealed TiO_2 films are shown in Fig. 9: (a) the film on Si after 800 °C annealing for 60 s, (b) the film on SiO_2/Si after 800 °C annealing for 60 s, and (c) the film on SiO_2/Si after 1,000 °C anneal-

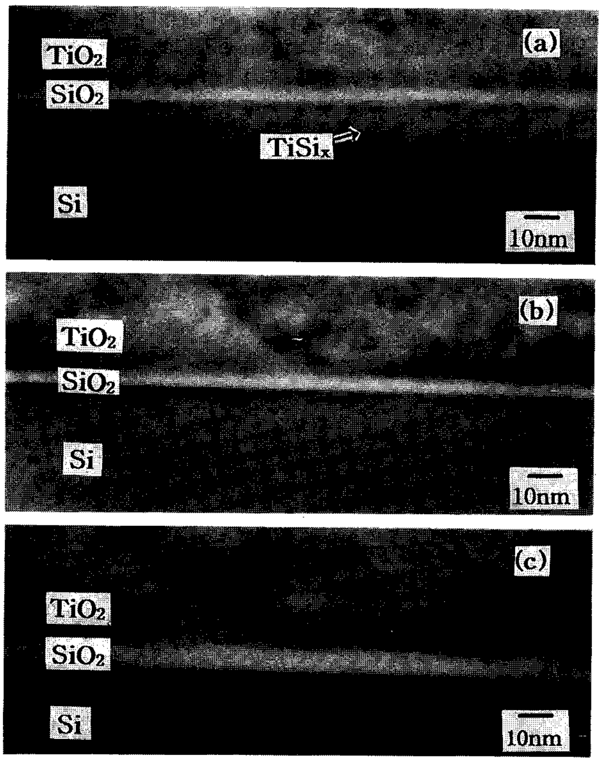

Fig. 9. TEM photographs of the TiO_2 films annealed: (a) TiO_2 on Si annealed at 800 °C for 60 s; (b) TiO_2 on SiO_2/Si annealed at 800 °C for 60 s; (c) TiO_2 on SiO_2/Si annealed at 1,000 °C for 1 h.

ing for 1 h. It is seen from Fig. 9(a) that the boundary of the SiO_2 layer was not as clear as in Figs. 9(b) and 9(c), and titanium silicide ($TiSi_x$) was formed at the interface, implying that Ti reacts with Si at the Ti/Si boundary. On the other hand, Fig. 9(b) shows the 4-nm-thick SiO_2 layer clearly distinguished from the TiO_2 film and Si substrate, indicating no formation of titanium silicide at the interface. It is interesting to see from Fig. 9(c) that the thickness of the SiO_2 layer increased from 4 nm to 7 nm after 1,000 °C annealing for 1 h. The additional growth of SiO_x is believed to be mainly due to the oxygen supplied from both the SiO_2 and TiO_2 films because the as-grown films were annealed at 1,000 °C in an oxygen-enriched ambient for a long time. However, this increased silicon oxide layer can contribute to the increase in current leakage of the TiO_2 films. Combined with the aforementioned effect of oxygen concentration, it may be deduced that although the oxygen ambient may be a more logical choice for preventing oxygen deficiency in TiO_2 films, annealing in enriched oxygen can also induce further growth of the SiO_x layer and formation of titanium low oxides, resulting in a low dielectric constant and high current leakage. Hence, it is very important to optimize annealing conditions for growing high dielectric and low current leakage TiO_2 films.

CONCLUSIONS

Titanium oxide thin films were deposited on p-type Si(100), SiO_2/Si, and Pt/Si substrates by plasma enhanced chemical vapor deposition using high purity $Ti(O\text{-}i\text{-}C_3H_7)_4$ and oxygen. As-deposited amorphous TiO_2 thin films were treated by rapid thermal annealing in oxygen ambient, and the effects of RTA conditions such as temperature, annealing time and oxygen partial pressure on the structural and electrical properties of TiO_2 films were studied in terms of crystallinity, microstructure, current leakage, and dielectric constant. The dominant crystalline structures after 600 and 800 °C annealing were an anatase phase for the TiO_2 film on SiO_2/Si and a rutile phase for the film on Pt/Si substrate. The dielectric constant of the as-grown and annealed TiO_2 thin films increased depending on substrates in order of Si, SiO_2/Si, and Pt/Si. The SiO_2 layer was effective in preventing the formation of titanium silicide at the interface and current leakage of the film. TEM photographs showed additional growth of an SiO_x layer from oxygen supplied from both SiO_2 and TiO_2 films when the films were annealed at 1,000 °C in an oxygen ambient. Experimental results showed that although an oxygen ambient may be a more logical choice to prevent oxygen deficiency in TiO_2 films, annealing in O_2 could introduce further growth of the SiO_x layer, resulting in a lower dielectric constant. Intensity analysis of Raman peaks also indicated that optimizing the oxygen concentration and annealing time is critical for growing a TiO_2 film having high dielectric and low current leakage.

ACKNOWLEDGMENTS

This work was supported by the Korea Science and Engineering Foundation (KOSEF) under Grant No. 961-1104-024-2.

REFERENCES

Choi, S. J., Lee, Y. E., Cho, H. S. and Kim, H. J., "Characterization of Structure and Electrical Properties of TiO_2 Thin Films Deposited by MOCVD", *Korean J. Materials Research,* **5**, 3 (1995).

Frenck, H. J., Kulisch, W., Kuhr, M. and Kassing, R., "Deposition of TiO_2 Thin Films by Plasma-Enhanced Decomposition of Tetraisopropyltitanate", *Thin Solid Films,* **201**, 327 (1991).

Fuyuki, T. and Matsunami, H., "Electronic Properties of the Interface between Si and TiO_2 Deposited at Very Low Temperatures", *Japan J. Appl. Phys.,* **25**, 1288 (1986).

Ghoshtagore, R. N. and Noreika, A. J., "Growth Characteristics of Rutile Film by CVD", *J. Electrochem. Soc.,* **117**, 1310 (1970).

Hahn, Y.-B., Kim, J.-W., Youn, C.-J. and Lee, I.-S., "Preparation of $PbTiO_3$ Thin Films by Plasma Enhanced MOCVD and the Effect of Rapid Thermal Annealing", *J. Electronic Materials,* **26**, 1394 (1997).

Lee, I.-S., Kim, J.-W., Youn, C.-J., Park, S.-K. and Hahn, Y.-B., "Preparation and Characterization of TiO_2 Thin Films by PECVD on Si Substrate", *Korean J. Chem. Eng.,* **13**, 473 (1996).

Lee, W. G., Woo, S. I., Kim, J. C., Choi, S. H. and Oh, K. H., "Preparation and Properties of Amorphous TiO_2 Thin Films by Plasma Enhanced Chemical Vapor Deposition", *Thin Solid Films,* **215**, 1 (1993).

Rausch, N. and Burte, E. P., "Thin TiO_2 Films Prepared by Low Pressure Chemical Vapor Deposition", *J. Electrochem. Soc.,* **140**, 145 (1993).

Williams, L. M. and Hess, D. W., "Structural Properties of Titanium Dioxide Films Deposited in an RF Glow Discharge", *Thin Solid Films,* **115**, 13 (1984).