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A TiO2 Gate Insulator of a 1-nm Equivalent Oxide Thickness Deposited by Electron-Beam Evaporation

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Introduction

0.07µm-gate CMOS technology needs ultra-thin SiO_2 films less than 2nm. However, 2nm-SiO_2 film shows high leakage current density because of appearance of direct tunneling current. Therefore, high K films, such as Ta_2O_5, Al_2O_3, and TiO_2, have received a lot of interest as substitution for ultra-thin SiO_2 gate insulators. TiO_2 , with the highest dielectric constant in these materials and thermodynamical stability, appears to be a promising dielectric for the application to the future CMOS device technology.

A number of methods for forming TiO_2 films has been reported [1-6]. The most common method is chemical vapor deposition (CVD) techniques. However, in CVD technique, such elements as C or Cl originated from the titanium precursor may cause undesirable influence on the TiO_2 thin film properties. In the preparation of high quality TiO_2 films, we have selected the electron-beam evaporation method in the ambient of ozone plasma for minimizing the effect of oxygen depletion, resulting in pure TiO_2 films.

By optimizing TiO_2 deposition thickness and anneal conditions, we realized TiO_2 films with 1nm equivalent oxide thickness which show low leakage current and interface trap density. This fact develops the application for CMOS device technology.

Experiments

Thin TiO_2 layers were prepared in a high vacuum evaporator system schematically described in Fig. 1. The vacuum chamber was evacuated by turbo-molecular pump and cryo pump resulting in a background pressure of $1x10^{-4}$ Pa. Evaporation of source materials (TiO_2 tablet) was carried out by an electron-beam source. The ozone gas was used for oxidation of growing films. The substrate were maintained at room temperature for preventing the ozone gas from decomposition. A post deposition anneal was carried out in dry oxygen furnaces or in rapid thermal anneal (RTA) apparatus to reduce the leakage current in the final stage.

Au was evaporated on TiO_2 films to prepare the gate electrodes of metal-insulator-semiconductor (MIS) diodes. An ohmic contact was prepared by the evaporation of Al to the backside of the silicon substrate. After the fabrication was complete, a final 450℃ hydrogen anneal was performed.

Determination of the film thickness was made by spectroscopic ellipsometry. X-ray diffraction using Cu $K\alpha$ radiation was utilized to determine the thin film structure. Auger electron spectroscopy was also utilized to verify the stoichiometry of TiO_2 films.

The fabricated MIS diodes were electrically evaluated by current-voltage (I-V) measurement. High- and low- frequency (100kHz and 400Hz) capacitance-voltage (C-V) measurements were performed to get the equivalent oxide thickness (EOT) and interface trap density (Dit).

Results and discussion

Figure 2 (a) shows C-V characteristics of RTA-treated TiO_2 films with 50nm in optical thickness on p-type Si substrate. The characteristics depend on the annealing time. Figure 2 (b) shows the relationship between the relative dielectric constant (K) and annealing time, and Figure 2 (c) shows the relationship between K and annealing temperature. The higher annealing temperature and the longer annealing time, K becomes higher. The film annealing at 900℃ for 240s shows the highest dielectric constant (~150) in our samples.

Figure 3 (a) shows I-V characteristics of various types of TiO_2 films and nitrided oxide (SiO_2) film as a reference. The EOT is extrapolated from the capacitance value at 2V on n-type substrate. The 50-nm thickness film shows the highest dielectric constant as previously stated, but leakage current is larger than reference SiO_2 film. On the other hand, though the 7-nm thickness film has 1.0nm in EOT, the leakage current is smaller than the 50-nm thickness film. The 12-nm thickness film shows the smallest leakage current. The leakage current could be minimized by optimizing deposited thickness and annealing condition. Figure 3 (b) shows the relationship between leakage current density and EOT at any annealing condition. The nitride data is quoted from [7]. The thinner TiO_2 film seems the lower leakage current density.

Dit of TiO_2 films of 50, 25, and 12nm in optical thickness are shown in Fig.5. These samples were annealed in H_2 flow (450℃, 20min.) after RTA treatment (900℃, 240s). The thinner film shows the lower Dit.

Figure 6 shows X-ray diffraction (XRD) pattern of TiO_2 film of 50nm in optical thickness. The XRD pattern shows the complete anatase structure. A 50nm-TiO_2 film was proved high quality crystal. Figure 7 shows the results of Auger electron spectroscopy before and after annealing. Keeping the stoichiometry can be confirmed.

As stated previously, leakage current density and interface trap density in thin TiO_2 films are lower than in thick films. Here, we consider this reason by using a model for the oxide growth in the TiO_2/Si interface which is described by a similar Deal and Grove method [8]. As seen in Fig. 5, SiO_2 growth rate is proportional to the oxidizing species concentration in the oxide adjacent to the TiO_2/Si interface (C_i) under the reaction-controlled condition. The flux of the oxidizing species (F) is described as $F = k\,C_i$, where k is a constant. (The notations α, β, γ, δ stated later are all constants.) On the other hand, the flux is also described as the diffusion equation in the TiO_2 film. Therefore, the next relations are satisfied.

$$F = k\,C_i = D\,\frac{C_o - C_i}{t_{TiO2}} \qquad (1),$$

where D is the diffusion constant, C_o is the equilibrium concentration in the oxide at the outer space. Combining (1) and the relation ($t_{SiO2}=\alpha\,C_i$) leads the next equation.

$$t_{SiO2} = \frac{\gamma}{1 + \beta\,t_{TiO2}} \qquad (2).$$

From $\beta t_{TiO2} >> 1$ because of $t_{TiO2} >> t_{SiO2}$, the rough relation ($t_{SiO2}= \delta / t_{TiO2}$) can be obtained. It reveals the inverse proportion relation between t_{TiO2} and t_{SiO2}.

t_{SiO2} can be estimated by the measured data from the following relation;

$$\frac{1}{C_m} = \frac{t_{TiO2}}{\varepsilon_{TiO2}} + \frac{t_{SiO2}}{\varepsilon_{SiO2}} \qquad (3),$$

under the assumption K~30 with thin TiO_2 films. Figure 8 shows that anneal of TiO_2 film thinner than 25nm in O_2 ambient results in appearance of SiO_2 film thinner than 1nm. This is why thin TiO_2 film can reduce the leakage current and Dit, which suggests that enough annealing in O_2 ambient is needed to use TiO_2 thin films as gate insulators of CMOS devices.

Conclusion

The electric properties of TiO_2 gate insulators deposited by electron-beam evaporation have been studied. 1nm-equivalent oxide thickness can be achieved, and its leakage current density is comparable to 3.3nm nitrided oxide. X-ray diffraction pattern of the TiO_2 film shows pure anatase structure. After the H_2 annealing, interface trap density was found to be $3x10^{11}$(/eV/cm^2). Low leakage current and interface trap density is assumed to be caused by SiO_2 growing in the TiO_2/Si interface. We found the combination between a TiO_2 film thickness deposited by electron-beam evaporation and an annealing condition in O_2 ambient is important to fabricate high quality TiO_2 gate insulators of CMOS devices.

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References

[1] He *et al.*, IEEE Tech. Dig. of IEDM 1998, p.1038
[2] H. S. Kim *et al*, Appl. Phys. Lett. 69 (1996), p.3860
[3] J. V. Grahn *et al.*, J. Vac. Sci. Technol. A 16 (1998), p.2495
[4] T. Fuyuki *et al.*, Jpn. J. Appl. Phys. 25 (1986),p1288
[5] N. Rausch *et al*, J. Electrochem.., vol. 140 (1993), p. 145
[6] S. A. Campbell *et al.*, IEEE Trans. Electron Dev., vol. 44 (1997), p104
[7] T. P. Ma, IEEE Trans. Electron Dev., vol. 45 (1998), p680
[8] S. M. Sze , "VLSI Tecnology", *MacGRAW-HILL INTERNATIONAL EDITIONS*

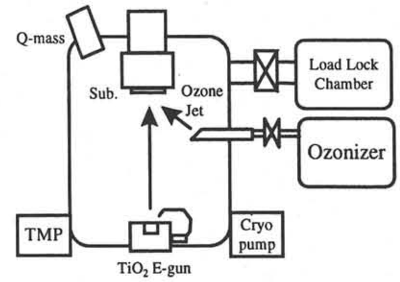
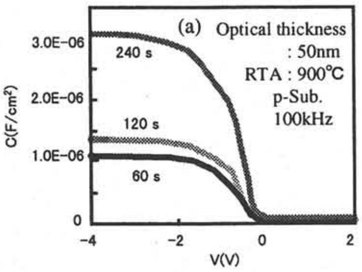
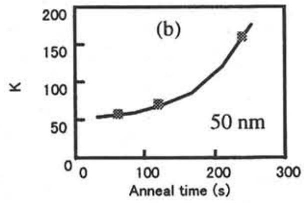


Fig.1 Schematic illustration of electron-beam evaporation system. TiO_2 thin film growth was carried out in the room temperature in the ambient of the ozone gas.





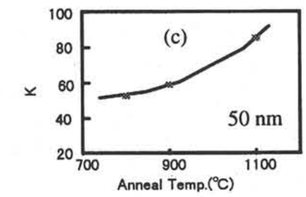
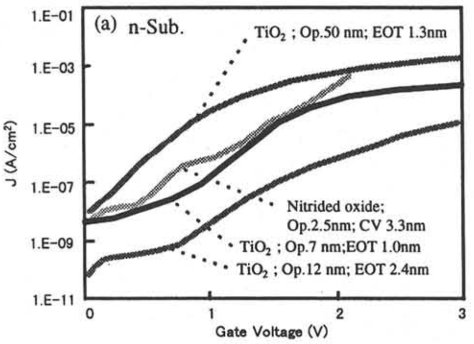


Fig.2 (a) C-V characteristics of TiO_2 films with 50 nm in optical thickness. These films were treated by RTA at 900°C for 60, 120, 240 seconds, respectively. (b) The relation of K with annealing time. (c) The relation of K with annealing temperature.



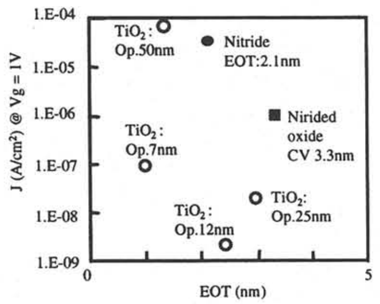


Fig.3 (a) The relationships between leakeage current density and gate voltage on various thicknesses of TiO_2 films and nitrided oxide (SiO_2) film. The optical thickness has been measured with ellipsometry. EOT means the equivalent oxide thickness. The 50,12,and 7-nm thickness films show the highest dielectric constant (~150), the lowest leakage current density, and the smallest EOT in our samples, respectively. (b) The relationships between leakage current density and EOT at any annealing condition of TiO_2 films. The nitride data is quoted from [7].

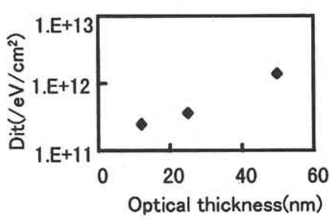


Fig.4 Interface trap density of TiO_2 film of 50, 25, 12nm in optical thickness. These samples were annealed in H_2 flow (450°C, 20min.) after RTA treatment (900°C,240s). This result may show SiO_2 growth in the TiO_2/Si interface by that treatment.

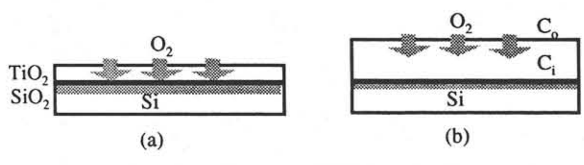


Fig.5 Schematic illustration of the model for oxygen though titanium dioxide. in case of thinner film (a) or thicker film (b). C_o is the equillibrium concentration in the oxide at the outer space. C_i is the oxidizing species concentration in the oxide adjacent to the oxide-silicon interface. t_{SiO2} is assumed to be proportion to C_i. Therefor, the thinner TiO_2 film makes easy to grow a SiO_2 thin film. The thicker TiO_2 film makes difficult to grow even a SiO_2 thin film.

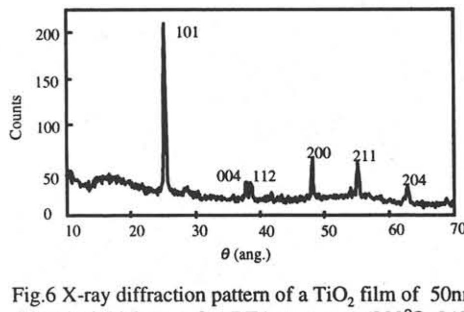


Fig.6 X-ray diffraction pattern of a TiO_2 film of 50nm in optical thickness after RTA treatment (900°C, 240s). This pattern shows the complete anatase structure.

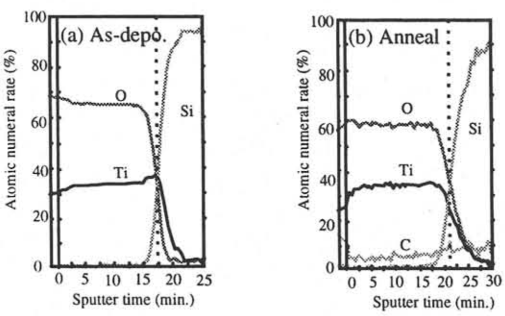


Fig.7 Auger Electron Spestroscopies of (a) as-depo sample and (b) annealed sample.

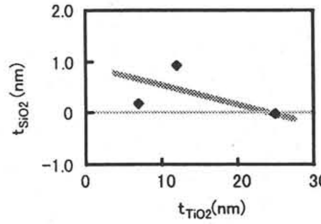


Fig.8 Estimation of SiO_2 thin film at the TiO_2/Si interface in the assumption of K~30 with thin TiO_2 films.