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Effects of Electrode Materials and Annealing Ambients on the Leakage Current of TiO_2 Films

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In this paper we describe the effects of electrode materials on the leakage current of TiO_2 films, at low and high-temperature processes. The leakage current depends on the electrode materials and varies with annealing temperature. The leakage current is mainly determined by the work function of the electrode before low temperature annealing (450 °C). On the other hand, after 450 °C and 800 °C annealing, the leakage current is affected by the reaction between TiO_2 and the electrode. From the viewpoint of the leakage current, WN is the optimum material for low- and high-temperature processes. The leakage current also depends on the annealing ambients after film deposition. Experiental results indicate that furnace N_2O annealing (RTN_2O) has the lowest leakage current.

I. INTRODUCTION

Titanium dioxide (TiO_2) thin films have been extensively studied for a variety of dielectric applications, because of the material's high refractive index and excellent transmittance in the visible and near-infrared range [1,2]. There has been growing interest with the use of TiO_2 as an insulator with a high dielectric constant for applications to memory cell capacitors or thin gate insulators in VLSI. Previous studies of Ta_2O_5 thin films have found that the electrical characteristics of Ta_2O_5 films depend greatly on the deposition condition, the post-deposition annealing, and the top electrode material [3]. In this study, we investigate the effects of electrode materials and annealing ambients on the leakage current in TiO_2 films.

II. EXPERIMENTAL

18-nm films were deposited on n^+ silicon wafers either by low-pressure CVD using tetra-isopropyl-titanate (TPT = $Ti(i\text{-}O_3H_7)_4$) vapor and oxygen at substrate temperature of 350 °C or by electron-beam evaporation with the base pressure of 1×10^{-6} torr. The deposition rate was about 30 Å/min. For the study of electrode materials, films were first annealed in dry O_2 at 800 °C for 30 min prior to top electrode deposition. The metal (W, and Mo) and metal nitride (WN, TaN and TiN) electrodes were then deposited on top of TiO_2 through reactive sputtering. In order to investigate the effects of backend thermal treatment after the formation of top electrode, these samples were annealed in N_2 for 30 min at 450 and 800 ° C, respectively.

For the annealing ambient experiments, each TiO_2 film after deposition was subjected to one of the following annealing processes: a) Rapid thermal annealing in O_2 (RTO) at 800 °C for 60 sec, b) Furnace O_2

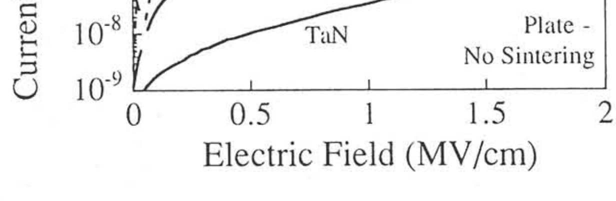

Fig.1 Leakage current of CVD-TiO_2 capacitors before annealing.

annealing (FO) at 800 °C for 30 min, c) Rapid thermal annealing in N_2O (RTN_2O) at 800 °C for 60 sec, and d) Furnace N_2O (FN_2O) at 800 °C for 30 min.

III. RESULTS AND DISCUSSION

Fig. 1 shows the leakage current characteristics of TiO_2 capacitors with several electrode materials before annealing. The negative bias was applied to the electrode. Before annealing, the leakage currents of capacitors with nitride electrodes are lower than those with metal ones. Capacitors with TaN electrode show the smallest leakage current. In order to verify the effects of electrode materials on the leakage current, the work function of the electrode was evaluated. It is found that, in most electrode materials, the leakage current decreases with increasing work function. These results suggest that the barrier height for electrons at the electrode/TiO_2 interface limits the leakage current.

Upon 450 °C annealing the capacitor with WN has the lowest leakage current. After high-temperature (800 °C) annealing, the leakage current of the capacitors with WN is still the smallest as shown in Fig. 2. There is almost no correlation between the work function and the leakage current. It is considered that, after 450 and 800 °C annealing, the leakage current is affected by the reaction between TiO_2 and the electrode. Fig. 3 shows SIMS depth profiles of WN/TiO_2/Si after 800 °C annealing. There is no indication of tungsten diffusion in the TiO_2 film. WN has been known for its thermal stability against Cu diffusion [4]. These results suggest the reason why WN shows a small leakage current is mainly due to the high stability of electrode/TiO_2 interface at high temperatures.

Experimental results indicate that the leakage current on n-type substrate is less than that on p-type substrate. Fig. 4 shows the effects of substrate boron doping concentration on the current-voltage characteristics. The leakage current of p^+ (~ 1 x10^{18} cm^{-3}) substrate is larger than that of lightly doped p^- (~ 1.6x10^{15} cm^{-3}) substrate. Fig. 5 (a) and (b) show the SIMS depth profiles of TiO_2 films on p^- and p^+ substrates after FO annealing. Clearly the boron segregation into TiO_2 is more serious for p^+ substrate than for p^- substrate. The acceptor-like traps may cause a larger leakage current on the heavily boron doped substrate.

Leakage current characteristics of CVD-TiO_2 capacitors after varios annealing treatments were examined. Capacitor with FN_2O annealing shows the

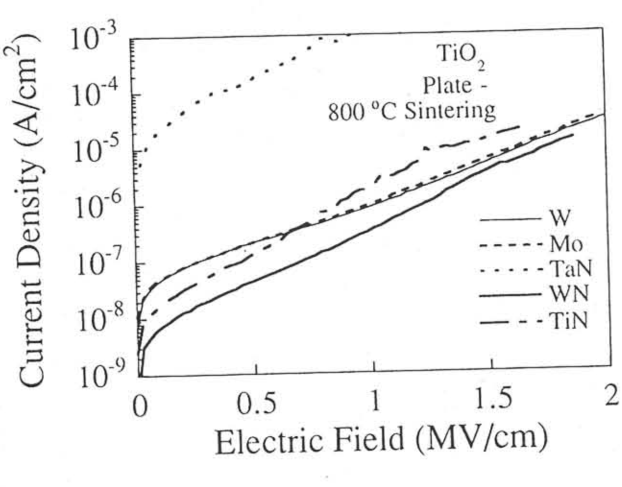

Fig.2 Leakage current of CVD-TiO_2 capacitors after 800 °C annealing.

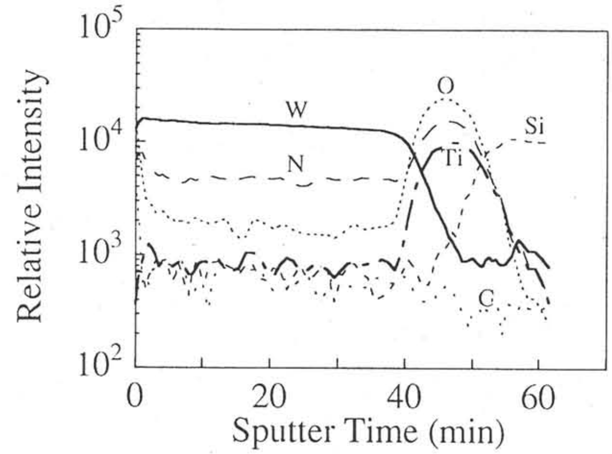

Fig.3 SIMS depth profiles of WN/TiO_2/Si after 800 °C annealing.

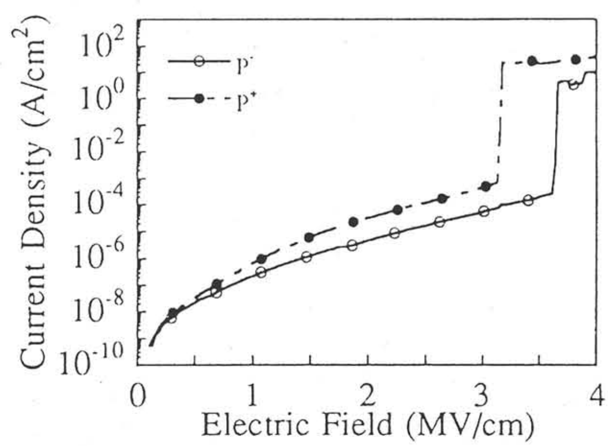

Fig. 4 Effect of substrate doping concentration on the leakage current.

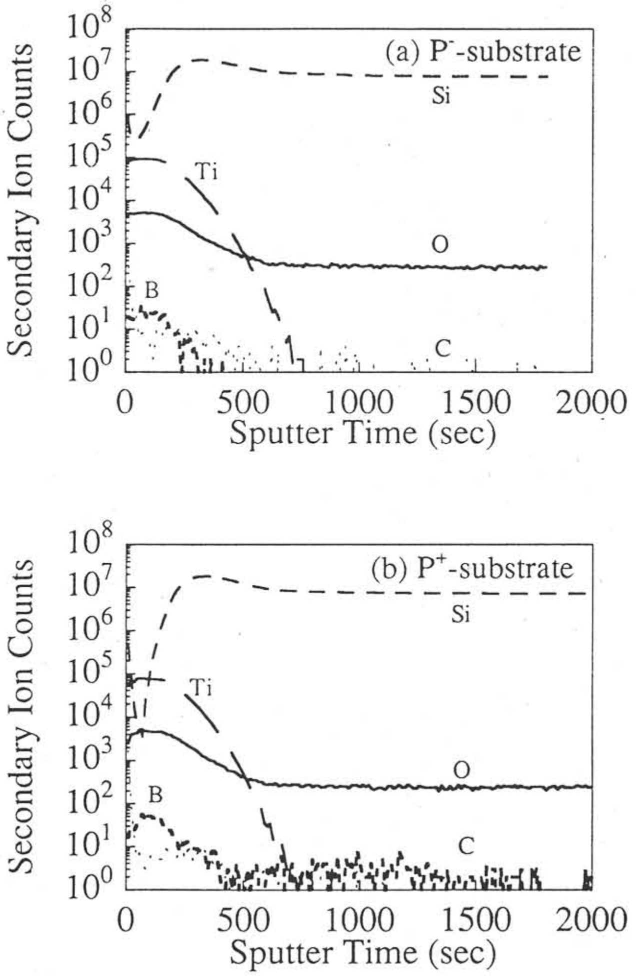

Fig. 5 SIMS depth profiles of boron concentration in the TiO_2 film for (a) p- substrate and (b) p+ substrate.

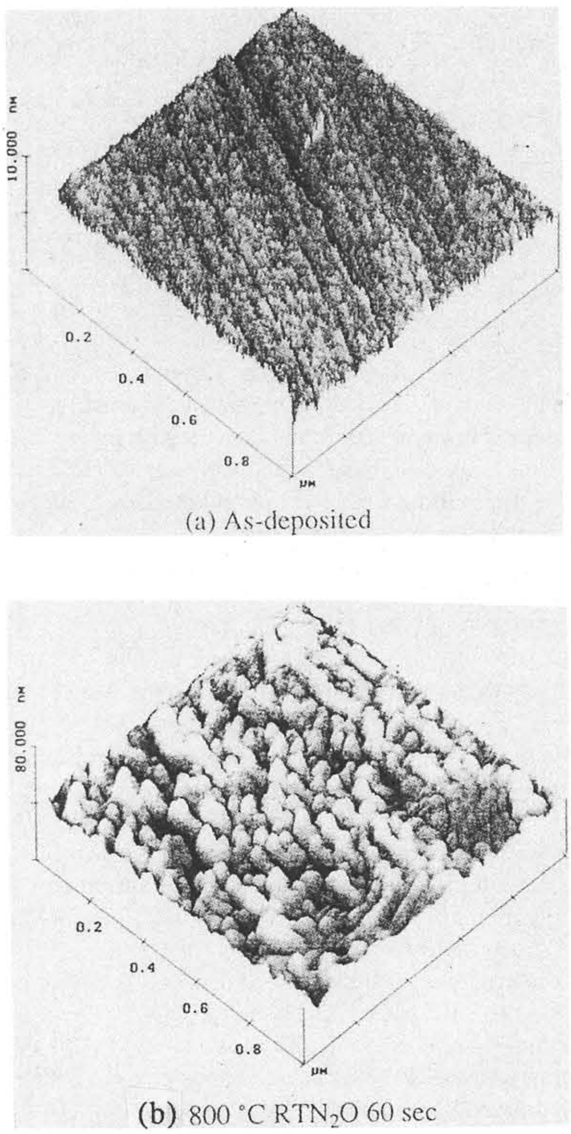

Fig. 6 AFM micrographs of (a) as-deposited and (b) RTN$_2$O-annealed TiO_2 films.

lowest leakage current. The effective dielectric constant is also the lowest among the four post-deposition thermal treatments. It indicates that there is a correlation between the leakage current and the effective dielectric constant due to the growth of interfacial oxide between TiO_2 and the n^+ substrate.

Fig. 6 shows thw surface morphology of e-gun evaporated TiO_2 films. The r.m.s. values of the surface roughness for the as-deposited and RTN$_2$O-annealed films are 0.38 and 3.12 nm, respectively.

IV. CONCLUSION

This paper shows that WN is the optimal electrode for high-temperature process due to its thermal stability. Capacitor with furnace N_2O annealing was found to have the lowest leakage current.

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REFERENCES

[1] K.H. Guenther, Appl. Opt. **23** (1984) 3612
[2] W. Bron and W. Grannenmann, Solid State Electron. **21** (1978) 837
[3] H. Matsuhashi and S. Nishikawa, Jpn. J. Appl. Phys., **33** (1994) 1293
[4] Y.T. Kim, et al., Jpn. J. Appl. Phys., **32** (1993) 6126