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Structure and Properties of Silicon Titanium Oxide Films Prepared by Plasma CVD Method

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We have developed a novel material of silicon titanium oxide with high dielectric constant and low leakage current. The silicon titanium oxide films were prepared by plasma enhanced chemical vapor deposition (plasma CVD) with the gas mixture of $TiCl_4$-SiH_4-N_2O. It was found that these films have intermediate properties of silicon dioxide and titanium dioxide by varying the ratio of $SiH_4/(SiH_4+TiCl_4)$. The properties of silicon titanium oxide corresponded to those of Ta_2O_5 when the gas mixture ratio was 0.075, with a dielectric constant of 18 and a leakage current density of 2.5×10^{-8} A/cm^2 at 1 MV/cm.

1. Introduction

With the advance of VLSI's integration, the reduction of the device size is needed. It is necessary to develop the materials with high dielectric constant for use as storage capacitors in dRAMs in order to maintain those capacity. Tantalum oxide (Ta_2O_5)[1-3], lead-zirconium-titanium oxide (PZT)[4,5], strontium titanium oxide ($SrTiO_3$)[6] and so on have been studied for capacitor dielectric films. However, these are novel materials for present Si-based VLSI devices.

We have proposed a novel material of silicon titanium oxide as a high dielectric. The oxide is a silicon based material and is considered to have intermediate properties of silicon dioxide and titanium dioxide. Silicon dioxide has a low dielectric constant, but shows a very small leakage current and large dielectric breakdown endurance. On the other hand, though titanium dioxide shows a large leakage current, it has a large dielectric constant. Therefore, this intermediate material, such as silicon titanium oxide, is expected to show a low leakage current with a high dielectric constant.

In this paper, we describe the results on the structural and electrical properties of silicon titanium oxide films prepared by plasma CVD method.

2. Experimental

Silicon titanium oxide films were deposited on phosphorous-doped polycrystalline silicon film over n-type silicon substrates by plasma CVD method using $TiCl_4$, SiH_4 and N_2O mixed gases. Figure 1 shows a schematic diagram of the plasma CVD apparatus used in this work. The liquid source of $TiCl_4$ was vaporized at 70 °C and was introduced into the plasma reactor through the mass flow controller. SiH_4 and N_2O gases were mixed with $TiCl_4$ gas just before being introduced into the plasma reactor. The deposition conditions of silicon titanium oxide films are summarized in Table 1. The ratio of $SiH_4/(SiH_4+TiCl_4)$ was varied, keeping the total flow rate constant (40 sccm) except for the case of silicon oxide deposition. Prior to the deposition, H_2 plasma cleaning was carried out under the RF power condition of 132 mW/cm^2 for 5 minutes. After the deposition, silicon titanium oxide films were subjected to post-annealing in a dry oxygen atmosphere at 400 °C.

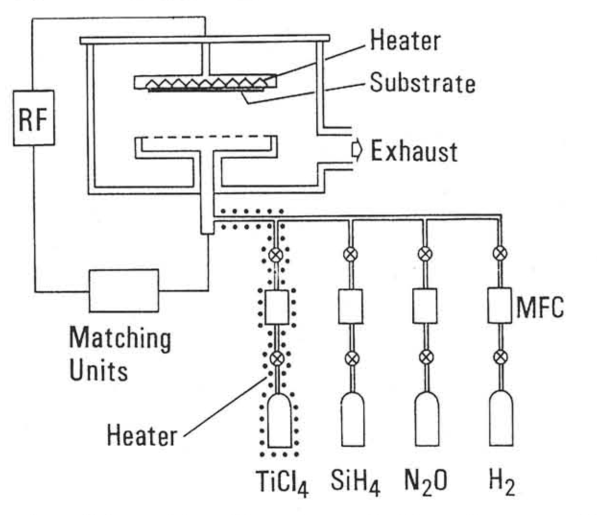

Fig. 1. Schematic diagram of the plasma CVD apparatus for silicon titanium oxide film deposition.

The structural properties of the films were analyzed by infrared (IR) absorption measurements. For the IR absorption measurements, a crystalline silicon wafer was used for the substrate. The leakage current was evaluated by the dc current-voltage measurement. The capacitance of the films was measured by an impedance analyzer at a frequency of 1 MHz. Al/ silicon-titanium oxide/ n-poly Si/ Si MIS capacitor structure was used for the electrical measurements.

3. Results and Discussion

Figure 2 shows the transmittance spectra of the films in the IR absorption measurements as a function of $SiH_4/(SiH_4+TiCl_4)$ ratio. The spectra of the films at the ratios of 0 and 1 correspond to those of titanium oxide film and silicon oxide film, respectively. The spectrum of the titanium oxide film has a broad absorption at 400 - 700 cm^{-1} probably relating to Ti-O bond. For the silicon oxide film, there existed absorptions due to Si-O bonds at 450 cm^{-1}, 805 cm^{-1} and 1070 cm^{-1}. The broad absorption due to Ti-O bond decreases and those due to Si-O bonds increase as the gas mixture ratio increases. At the ratios of 0.175 and 0.25, there appeared a peculiar absorption mode at 950 cm^{-1}. This absorption is considered to be originated from Si-O-Ti bond.

From the results mentioned above, it is likely that the structures of the films vary from the structure of titanium oxide to that of silicon oxide continuously, as the ratio increases.

The leakage properties of these films annealed at 400 °C with the thickness of about 200 nm are shown in Fig. 3. As shown in this figure, the leakage current through the film decreases and the dielectric breakdown endurance becomes larger as the ratio of $SiH_4/(SiH_4+TiCl_4)$ increases. In order to show the variation of these properties understandably, the characteristic of the leakage current density at the electric field of 1 MV/cm as a function of SiH_4 and $TiCl_4$ gas flow rates is shown in Fig. 4.

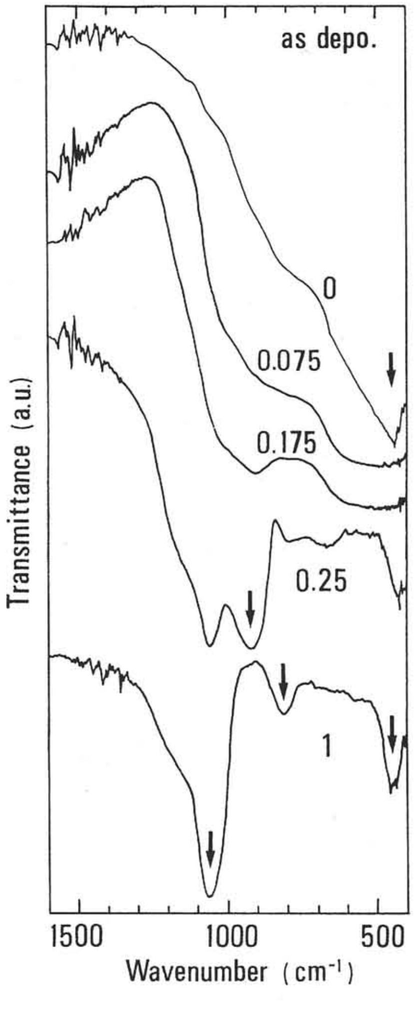

Fig. 2. IR absorption spectra of the films as a function of $SiH_4/(SiH_4+TiCl_4)$ ratio.

Table I Typical deposition conditions of silicon titanium oxide films.

source gas flow rate:	SiH_4	1 - 20 sccm
	$TiCl_4$	20 - 40 sccm
	N_2O	100 sccm
gas pressure		0.4 Torr
rf frequency		13.56 MHz
rf power density		132 mW/cm^2
substrate temperature		300 °C

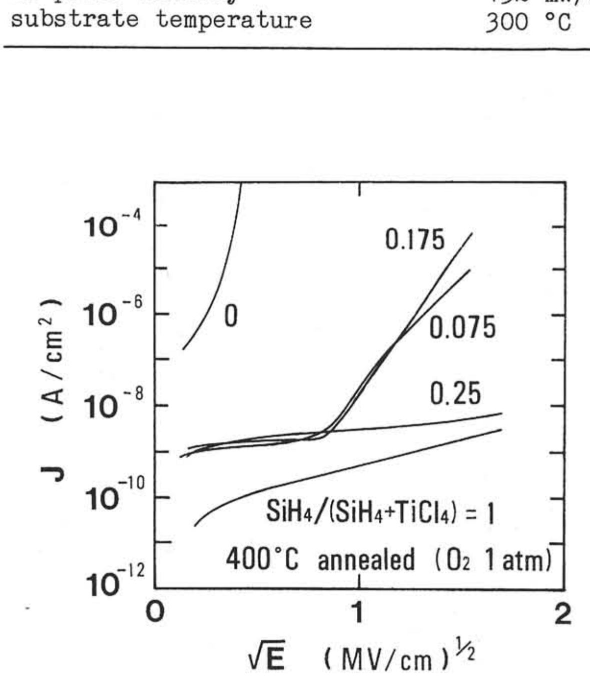

Fig. 3. Leakage characteristics of the films being annealed at 400 °C with the thickness of about 200 nm.

Figure 5 shows the $SiH_4/(SiH_4+TiCl_4)$ ratio dependence of the dielectric constant of the films. As the ratio increases, the dielectric constant becomes lower, as can be seen from this figure.

From these results, it is found that the electrical properties of the films also vary with the gas mixture ratio from the properties of titanium oxide to those of silicon oxide in succession. The properties of silicon titanium oxide correspond to those of Ta_2O_5 when the $SiH_4/(SiH_4+TiCl_4)$ ratio is 0.075, with a dielectric constant of 18 and a leakage current density of $2.5x10^{-8}$ A/cm^2 at 1 MV/cm.

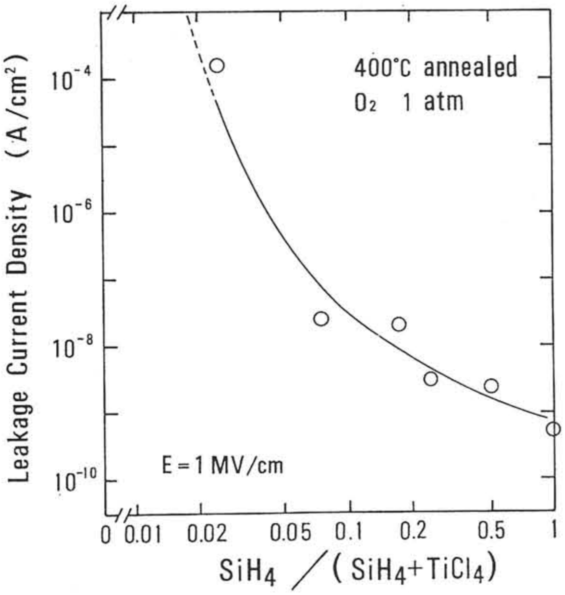

Fig. 4. Characteristic of the leakage current density at the electric field of 1 MV/cm as a function of SiH_4 and $TiCl_4$ gas flow rates.

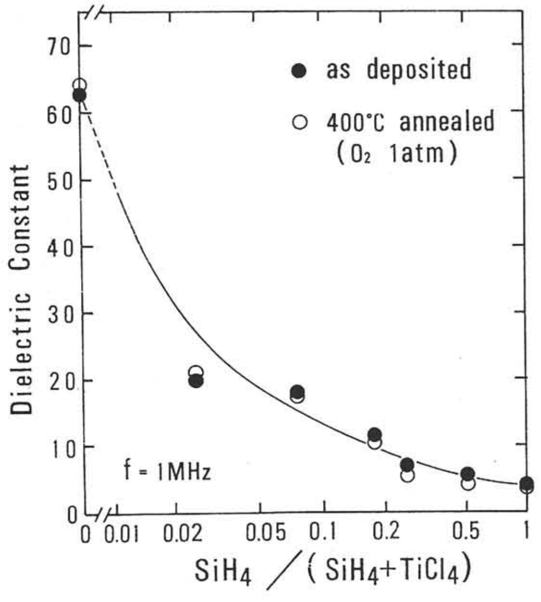

Fig. 5. $SiH_4/(SiH_4+TiCl_4)$ ratio dependence of the dielectric constant of the films.

4. Conclusion

We have developed a novel material of silicon titanium oxide with a high dielectric constant and a low leakage current. The silicon titanium oxide films were prepared by plasma CVD method with the gas mixture of $TiCl_4$- SiH_4-N_2O. It was found that these films have structural and electrical properties between silicon dioxide and titanium dioxide by varying the ratio of $SiH_4/(SiH_4+TiCl_4)$. The properties of silicon titanium oxide correspond to those of Ta_2O_5 when the gas mixture ratio of 0.075, with a dielectric constant of 18 and a leakage current density of $2.5x10^{-8}$ A/cm^2 at 1 MV/cm.

In this oxide, the electrical properties can be controlled at will by varying the gas mixture ratio. The formation technology of this dielectric will easily be introduced to present Si-based VLSI devices.

References

1)M.Matsui, S.Oka, K.Yamagishi, K.Kuroiwa and Y.Tarui, Jpn. J. Appl. Phys. 27 (1988) 506.

2)Y.Numasawa, S.Kamiyama, M.Zenke and M.Saka-moto, IEEE IEDM Tech. Dig. (1989) 43.

3)H.Shinriki and M.Nakata, IEEE Trans. Electron Devices, ED-38 (1991) 455.

4)B.M.Melnick, C.A.Araujo, L.D.McMillan, D.A. Carver and J.F.Scott, Proc. 2nd Sympo. Integrated Ferroelectrics (1990) 79.

5)R.Moazzami, C.Hu and W.H.Shepherd, 28th Annual Proc. Reliability Physics (1990) 231.

6)S.Yamamichi, T.Sakuma, S.Matsubara, H.Yama-guchi and Y.Miyasaka, Jpn. Soc. Appl. Phys., 38th Spring Meet. (1991) 28p-P-4.