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High Dielectric Constant of RF-Sputtered HfO_2 Thin Films

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Hafnium dioxide (HfO_2) thin films are deposited on indium-tin-oxide (ITO)-coated glass substrates by the radio-frequency (RF) sputtering method using a HfO_2 sintered target. The deposition conditions, dielectric loss and dielectric constant of HfO_2 films before and after heat treatment are studied. The best deposition conditions for HfO_2 films are RF power 200 W, substrate temperature 100°C and sputtering gas pure Ar. The maximum dielectric constants are about 150 and 45 with 1 kHz signal excitation before and after annealing, respectively. They are higher than any ever reported.

KEYWORDS: sputtering, electroluminescent, dielectric constant, storage charge density, signal excitation

§1. Introduction

To scale down LSI's, it is necessary to reduce the device size. In the case of dynamic random access memory (DRAM), shrinking the storage capacitor area is inevitable. This reduction in capacitor area has made it difficult to maintain the storage charge, so high dielectric constant films are of interest because they use a storage capacitor dielectric in matal-oxide-semiconductor (MOS) dynamic memories.[1] However, conventional films, such as Si_3N_4/SiO_2 film on polycystalline silicon, have reached their physical limits in terms of thickness.[2] In recent years, tantalum pentoxide (Ta_2O_5) films have been intensively studied among the various high dielectric materials, but Ta_2O_5 films on Si exhibit very high leakage current. In this experiment, high-dielectric-constant HfO_2 films were studied.

Thin-film electroluminescent (EL) devices have been actively investigated because they have a number of attractive properties such as high brightnees, high resolution and the potential for use in large area, completely solid-state,multicolor flat-panel displays. The stability and reliability of the display devices are direct functions of the quality of the dielectric used. Display device efficiency and breakdown voltage are both related to the dissipation and breakdown strength of the dielectric. The most common figure of merit of a dielectric is the charge density or the electric displacement at breakdown ($Q_{bd}=\varepsilon\times E_{bd}$) where ε, Q_{bd} and E_{bd} are dielectric constant, storage charge density and electric field strength at breakdown, respectively. Its value should be at least three times that of the active layer. Therefore, high-dielectric-constant and low-loss thin films have attracted much attention as the insulating layers of EL devices.[3-7]

In particular, by employing electron-beam-evaporated HfO_2 dielectric thin-film layers, high dielectric constant and low leakage current for the metal-insulator-metal (MIM) structure were achieved.[8] However, the dielectric constant of electron-beam-evaporated HfO_2 thin films, about 25, is less than the result of this experiment. In this paper, the dielectric properties of RF-sputtered HfO_2 thin films are expected to be superior to the electron-beam-evaporated film.

A capacitor structure, glass/ITO/HfO_2/Al, was studied. The ITO transparent electrode and electrode Al were used for the consideration of EL device fabrication. The relationships between the dielectric properties of HfO_2 films and deposition conditions were also discussed.

§2. Experimental Procedure

Hafnium dioxide (HfO_2) thin films of 0.5 μm thickness were deposited on glass substrates coated with indium-tin-oxide (ITO) films of 0.2 μm thickness. Sheet resistance and transmittance of the ITO films were approximately 100 $\Omega/\square$ and larger than 80%, respectively. The surfaces of glass substrates were carefully cleaned with $H_2O+H_2O_2+NH_4OH=5:1:1$ before deposition.

The purity of the HfO_2 sintered target was higher than 99.99%. Deposition of HfO_2 thin films was performed using a RF-sputtering apparatus (TOKUDA MODEL CFS-4ES). A uniform thickness, within 5% over the entire substrate, was obtained. The target-to-substrate distance was fixed at 80 mm. With the use of mass flow controllers, sputtering Ar gas of precisely 12 sccm was introduced into the chamber at a growth pressure of about 5×10^{-3} Torr.

In this paper, the various properties of HfO_2 thin films versus substrate temperature, RF power, and oxygen content were investigated. The substrate temperature was changed from room temperature to 200°C, the RF power was changed from 130 W to 230 W and the oxygen content was changed from 0% to 40%.

After deposition, some of the HfO_2 thin films were heat treated at 400°C for 45 min. This heat treatment corresponds to that used for EL devices to improve emission properties. The upper Al electrodes were deposited on the HfO_2 films by the resistance heating evaporation method. The capacitance, and dielectric loss of these samples were measured with a low-frequency impedance analyzer (HP4192A). The dielectric constant, ε_r, can be calculated from a simple formula.

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§3. Experimental Results and Discussion

3.1 *Sputtering rate*

The relationships between the deposition rate of the HfO_2 films and (a) the substrate temperature, (b) the RF power, and (c) the oxygen content are shown in Fig. 1. In Fig. 1(a) the sputtering gas was Ar, and the pressure and RF power were kept at 5×10^{-3} Torr and 150 W, respectively. In Fig. 1(b) the sputtering gas was Ar, and the pressure and substrate temperature were kept at 5×10^{-3} Torr and 100°C, respectively. In Fig. 1(c) the substrate temperature was 100°C, and the pressure and RF power were kept at 5×10^{-3} Torr and 200 W, respectively.

Figure 1(a) indicates that the deposition rate decreases as the substrate temperature increases. This is due to a lower sticking coefficient with increasing substrate temperature. Figure 1(b) shows that the deposition rate increases with the RF power. This can be well explained as the increased energy of the incident ion, Ar^+, to the target. The effect of oxygen content on the deposition rate is shown in Fig. 1(c). The deposition rate is suddenly decreased when the oxygen content is equal to 10%. Then, the deposition rate shows almost no change when the oxygen content changes from 10% to 40%. Lower sputtering yield due to oxygen in the chamber explains this phenomenon.

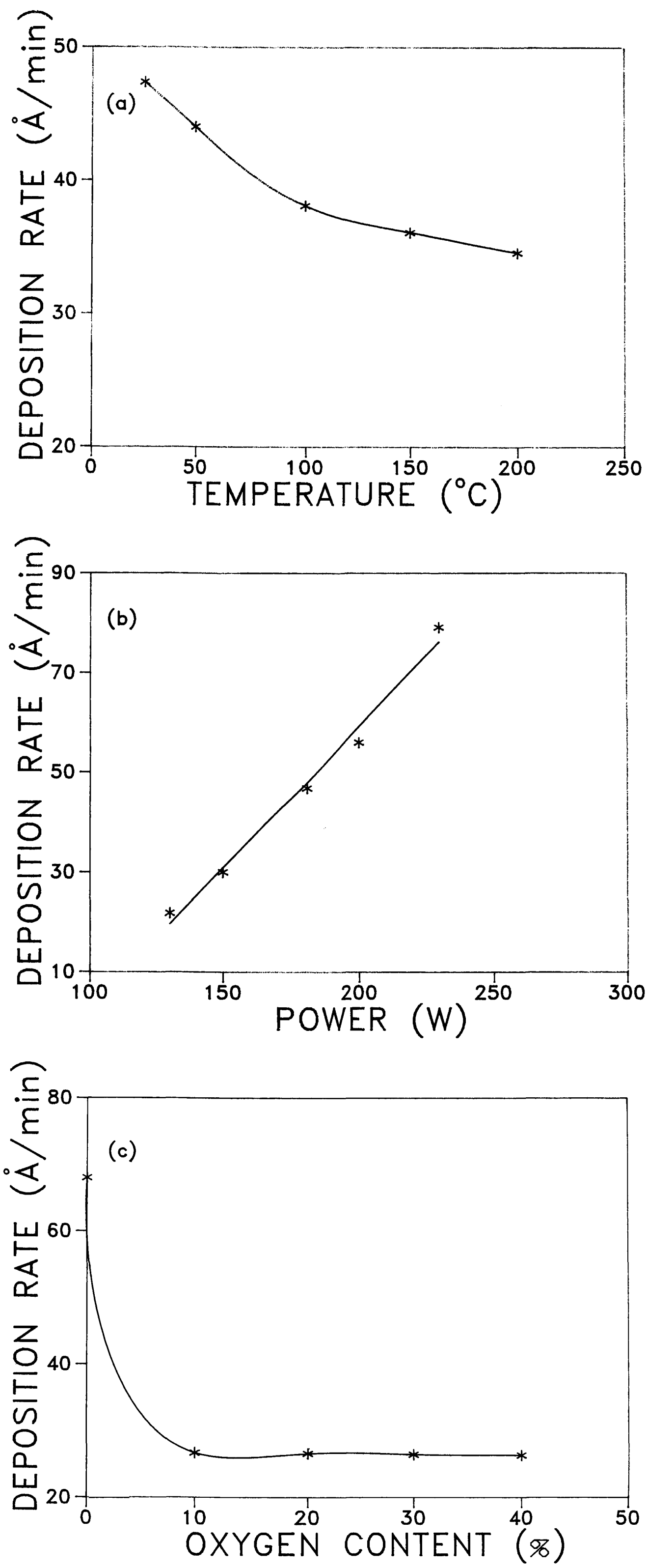

Fig. 1. The relationships between the deposition rate of the HfO_2 films and (a) the substrate temperature, (b) the RF power, and (c) the oxygen content.

3.2 *Dielectric loss and dielectric constant*

The dielectric loss and dielectric constant versus substrate temperature of HfO_2 films before and after annealing are shown in Figs. 2(a) and 2(b), respectively. The deposition conditions of the samples are the same as that of the samples of Fig. 1(a). The loss exhibits a

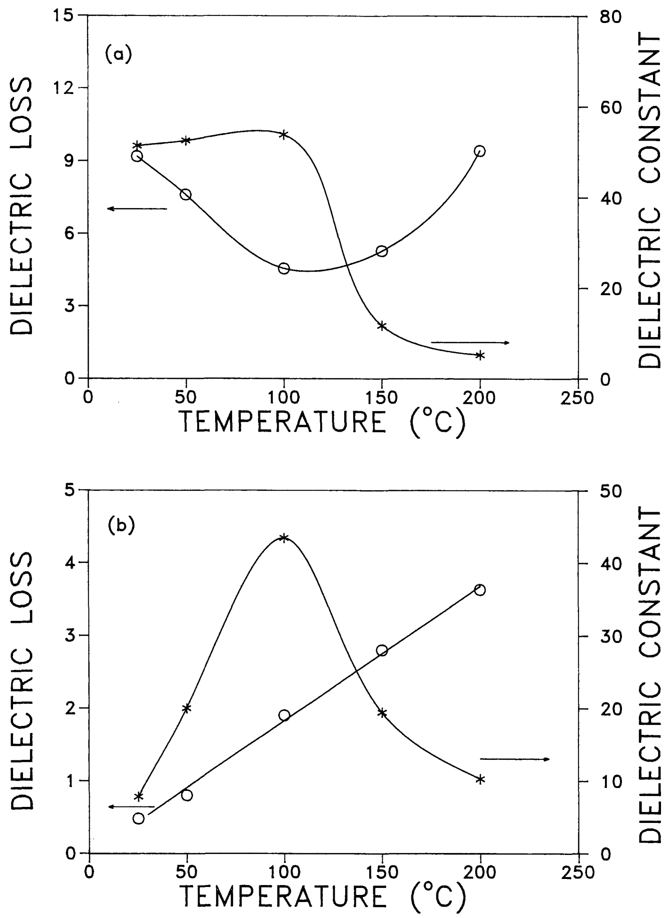

Fig. 2. The dielectric loss and dielectric constant versus substrate temperature (T_s) characteristics of HfO_2 films (a) before annealing and (b) after annealing.

minimum and the dielectric constant a maximum around 100°C, as shown in Fig. 2(a). After annealing, the dielectric constant shows a maximum around 100°C, which is higher than the values at other substrate temperatures, as shown in Fig. 2(b). The loss increases with substrate temperature, but the changes are very small. Therefore the optimal substrate temperature is about 100°C. Figures 3(a) and 3(b) show the dielectric loss and dielectric constant versus RF power of HfO_2 films before and after annealing, respectively. The deposition conditions of samples are the same as those of Fig. 1(b). From Figs. 3(a) and 3(b), when the power is around 200 W, the maximum dielectric constant can be obtained. The loss suddenly decreases when the power is about 180 W, while the changes are very small from 180 W to 230 W. Thus the optimal RF power is 200 W.

The dielectric loss and dielectric constant versus oxygen content charactericstics of HfO_2 films before and after annealing are shown in Figs. 4(a) and 4(b), respectively. The deposition conditions of the samples are the same as those of Fig. 1(c). In this experimental process, when the sputtering gas is not pure Ar, the RF power and sputtering pressure cannot be kept constant. This is due to an unstable plasma. It is the reason why the dielectric loss and dielectric constant versus oxygen content characteristics are irregular. Also for this reason, pure Ar is selected as the optimal sputtering gas.

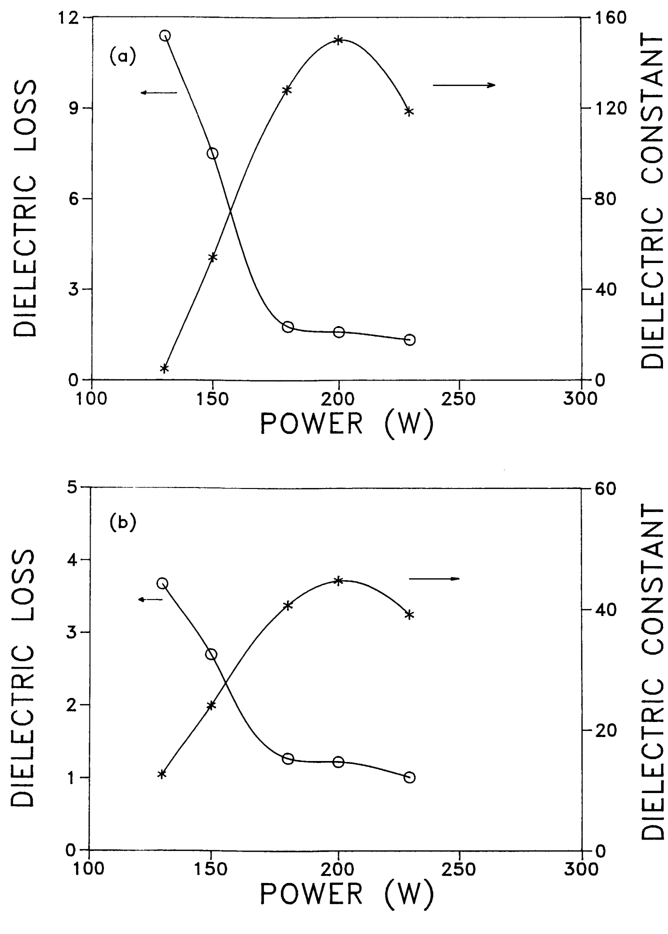

Fig. 3. The dielectric loss and dielectric constant versus RF power characteristics of HfO_2 films (a) before annealing and (b) after annealing.

Figures 2 to 4 clearly indicate that not only the dielectric constant, but also the dielectric loss, depend on annealing. The annealed samples have lower dielectric constant and loss, so the stability of these samples have better properties after annealing.

From the results above, the optimum deposition conditions for HfO_2 films are substrate temperature 100°C, RF power 200 W and sputtering gas pure Ar. The HfO_2 thin films have high dielectirc constant and low loss. Table I compares dielectric constants of HfO_2 films obtained here and of other dielectric materials previously published.[6] The dielectric constant of HfO_2 is much higher than those of other dielectric materials.

The dielectric loss in HfO_2 films decreases after annealing. This mean that HfO_2 films are of very high quality. On the other hand, the HfO_2 films have a low concentra-

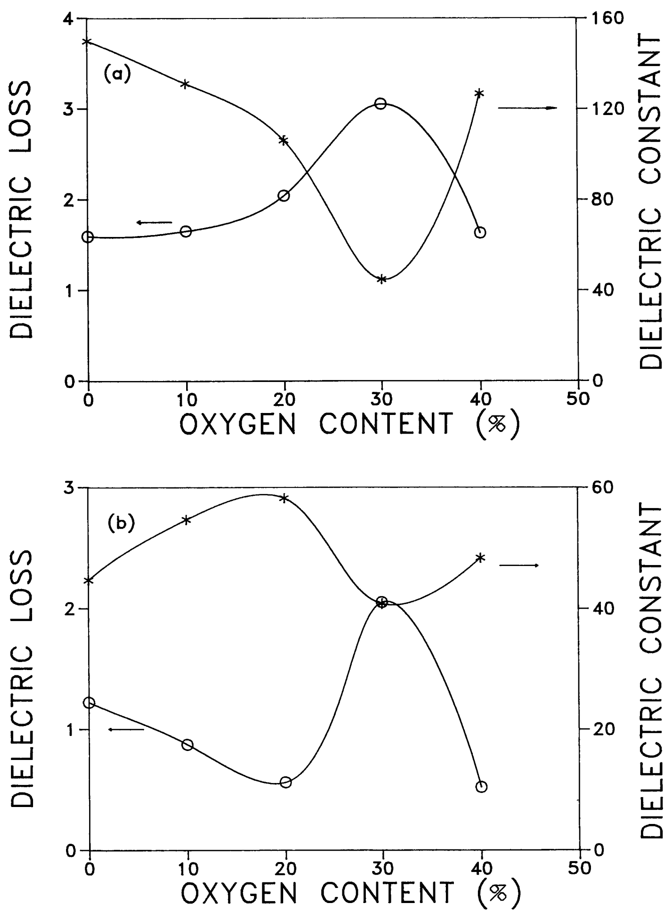

Fig. 4. The dielectric loss and dielectric constant versus oxygen content characteristics of HfO_2 films (a) before annealing and (b) after annealing.

Table I. The dielectric constant of various dielectric materials.

Material	Dielectric constant
Y_2O_3	12–14
Al_2O_3	10–11
Si_3N_4	7
Ta_2O_5	25
SiAlON	8
HfO_2	45

tion of oxygen vacancies.[8,9)]

HfO_2 is of polar structure, therefore the polarizability includes electronic polarzability (a_e), atomic polarizability (a_a) and dipole polarizability (a_d). The dielectric constant is proportional to the polarization vector and the polarization vector is proportional to polarizability. A polar material has greater polarizability than a nonpolar material, so HfO_2 has large polarizability. This means that the HfO_2 films have high dielectric constants.

§4. Conclusions

The deposition rate and the dielectric properties of HfO_2 films deposited by RF-sputtering before and after annealing are studied. The optimal deposition conditions are substrate temperature 100°C, RF power 200 W and sputtering gas pure Ar. High dielectric constants and low loss for HfO_2 films have been obtained. The dielectric constant is about 45 after annealing of 400°C for 45 min at 1 kHz signal excitation.

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