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Synthesis of Zirconium Oxides on silicon by Radio-Frequency Magnetron Sputtering Deposition

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Abstract

Zirconium oxide films have been synthesized by radio-frequency magnetron sputtering deposition on n-Si(001) substrate with metal zirconium target at variant O_2 partial pressures. The influences of O_2 partial pressures of the morphology, deposition rate, microstructure, and the dielectric constant of ZrO_2 have been discussed. The results show that deposition rate of ZrO_2 films decreases, the roughness, and the thickness of the native SiO_2 interlayer increases with the increase of O_2 partial pressure. ZrO_2 films synthesized at low O_2 partial pressure are amorphous and monoclinic polycrystalline in nanometer scale at low O_2 partial pressure. The relative dielectrics of ZrO_2 films are in the range of 12 to 25.

Keywords : radio-frequency magnetron sputtering deposition, ZrO_2 film, dielectric constant

1. Introduction

Continuous demand for increased circuit complexity and high device performance promotes rapid growth of the semiconductor industry. Due to its excellent properties, including native to Si, high resistivity, excellent dielectric strength, a large band gap, and a high melting point, SiO_2 are in large responsible for enabling the microelectronics revolution. As the physical thickness of SiO_2 gate oxides approaches 2 nm, however, a number of fundamental problems, such as high gate leakage current, impurity penetration through the SiO_2, enhanced scattering of carriers in the channel, and reliability degradation, arise [1-2].

To overcome these fundamental limits for SiO_2-based device scaling, new materials have to be investigated and then integrated with silicon technology. The requirements for the new dielectric include thermal stability with Si and with the gate electrode, compositional uniformity, and the ability to maintain smooth interfaces. To reduce the leakage current, the 'physical' thickness of the dielectric should be kept large while the capacitance still should scale or increase. The dielectric materials with high permittivity are the candidates to replace SiO_2. There are numerous high-k materials under investigation, e.g. ZrO_2 [3-5], HfO_2 [6], TiO_2 [7], Ta_2O_5 [8], Y_2O_3 [9-11], Al_2O_3 [12-14], Gd_2O_3 [15], Hf or Zr silicates [16], La silicates [17] and Gd silicates [18]. The dielectric constants of these materials are in the 10-40 range, a factor of approximately 3-10 higher than that of SiO_2. In other words, the physical thickness of the dielectric of these materials can be extended to 3-10 times.

In this paper, we report the synthesis of ZrO_2 films by radio-frequency (RF) magnetron sputtering deposition with pure zirconium target. The influences of oxygen partial pressure on the morphology, deposition rate, microstructure, and the dielectric constant of ZrO_2 have been discussed.

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2. Experimental methods

The synthesis of ZrO_2 films was carried out in JPG450 UHV magnetron sputtering system. ZrO_2 films were deposited on n-type Si (001) substrates at the substrate temperature of 250℃. The native SiO_2 layer on the silicon wafers were not cleaned by the standard cleaning method. The target in use was metal zirconium with purity of 99.99%. The ZrO_2 films were deposited in the Ar and O_2 mixing atmosphere and the oxygen partial pressure were changed from 7% to 100% while keeping the working pressure at 3.2 Pa. The fluxes of Ar and O_2 flows are listed in Table 1. The base vacuum of the system was lower than 4×10^{-4} Pa. The power of RF magnetron sputtering was 150 W. The distance from target to substrate was 80 mm.

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were used to examine the plane-view morphology and to determine the structure of films. The thickness of ZrO_2 films was determined by using variable angle spectroscopic ellipsometry in the wavelength range of 190 nm to 2200 nm. The angles of incident polarized light were 65° and 75°. The relative dielectric constants and leakage currents of ZrO_2 films were characterized by *C-V* measurement and *I-V* measurement.

3. Results and discussions

The ellipsometry measurement is expressed as psi (Ψ) and delta (Δ) for each wavelength/angle combination. After an ellipsometry measurement, the data are analyzed to determine optical constants, layer thickness, and other properties of interest. In this study, because of the native silicon oxide not removed, the best results were obtained when the sample was modeled as a deposited layer on native silicon oxide ($\leq$10 nm thick) on a silicon substrate. The native silicon oxide optical constants were taken from the literature [19] and not allowed to vary. The index $n(\lambda)$ for all the samples is approximately the same, with the exception of the sample synthesized in pure oxygen atmosphere. The error bars for n n and k were typically between $\pm$ 0.001 and $\pm$0.003 and the error bars for the thicknesses of all layers were approximately 0.2 nm. The thickness change of ZrO_2 films with the O_2 partial pressure is presented in Fig. 1. In the figure, we can see that the thicknesses of ZrO_2 films decrease with the increase of the O_2 partial pressure. This can attribute to the lower sputtering yields of Oxygen in comparison with Ar and the increase of oxide layer on the target. The native SiO_2 layer, however, increases with the increase of the O_2 partial pressure. This implies that the native SiO_2 layer can be influenced by the O_2 partial pressure. In other word, oxygen can penetrate through the native SiO_2 layer during the deposition of ZrO_2 films and enhance the thickness of the native SiO_2 layer. We can also see that the native native SiO_2 layer at O_2 partial pressure lower than 50% is almost the same. At at O_2 partial pressure higher than 50%,

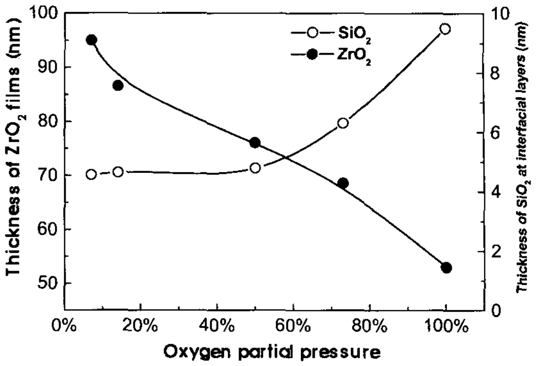
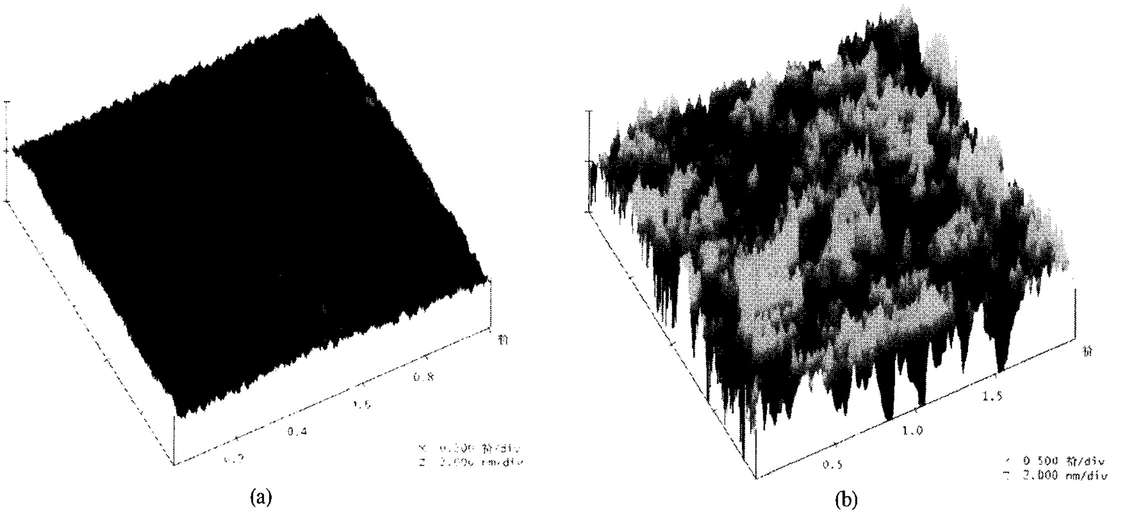


Fig. 1. Thicknesses of ZrO_2 films at variant O_2 partial pressures.

Table 1 The flow fluxes of Ar and O_2

O_2(sccm)	5	10	20	30	40	50
Ar(sccm)	67	60	45	30	15	0
O_2 partial pressure	7%	14%	31%	50%	73%	100%



(a) (b)

Fig. 2 Morphologies of ZrO_2 films at the O_2 partial pressures of (a) 14% and (b) 100%.

however, increases considerably. We suppose the increase of the native native SiO_2 layer is related with oxygen ions, which can be accelerated to very high speed under electric field and penetrate through the native native SiO_2 layer.

Figure 2 is the surface morphologies of the ZrO_2 films synthesized at the O_2 partial pressure of 14% and 100%, respectively. As can be seen, the film synthesized at the O_2 partial pressure of 14% is much smoother than that at the atmosphere of pure oxygen. To determine quantitatively surface morphology, Fig. 3 presents the change of surface roughness of the ZrO_2 films with the increase of the O_2 partial pressure. We can see that both Rms (mean square root roughness) and Ra (area roughness) increase linearly with the increase of the O_2 partial pressure. The minimum roughness of at the O_2 partial pressure of 14% is lower than 0.2 nm. This means the films synthesized at low O_2 partial pressure is as smooth as in atomic level (1-2 atomic layers). Uniform film is very important in the application of dielectric gate.

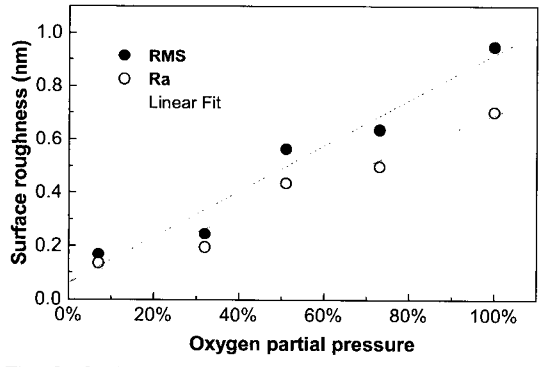
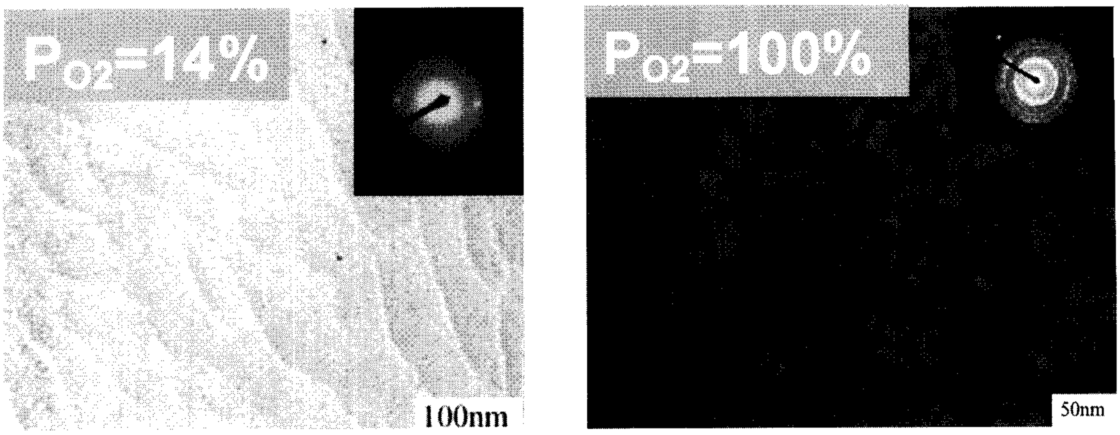


Fig. 3. Surface roughnesses of ZrO_2 films at variant O_2 partial pressures.

Figure 4 shows the TEM observation of morphologies and electron diffraction patterns of ZrO_2 films synthesized at the O_2 partial pressure of 14% and 100%, respectively. In the and electron diffraction patterns, we can determine the film synthesized at the O_2 partial pressure of 14% is amorphous and the film synthesized at the atmosphere of pure oxygen is monoclinic polycrystalline in the gain size of 15-40 nm. This implies that the increase of the oxygen pressure promotes the nucleation of monoclinic ZrO_2 and the nucleation of monoclinic ZrO_2 will induce the growth of the films in 3-dimensional islands. This may be the reason why the roughness increases linearly with the increase of O_2 partial pressure. In the application of dielectric gate, dielectric layer should be uniform in the texture. Grain boundaries and defects will be able to reduce the dielectric capacitance and insulating properties.



(a) (b)

Fig. 4. The morphologies and electron diffraction patterns of ZrO_2 films at O_2 partial pressure of (a) 14% and (b) 100%.

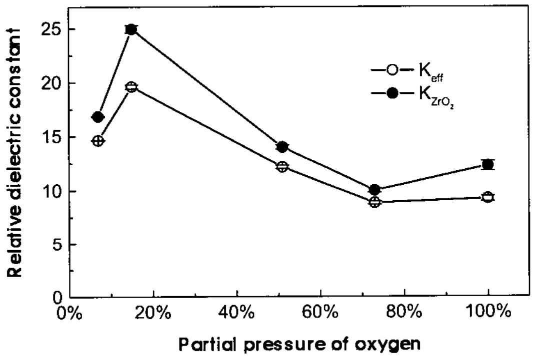


Fig. 5. Relative dielectric constants of ZrO_2 films at variant O_2 partial pressures.

To determine the relative dielectric constant, C-V measurement was carried out. Figure 5 is the relative dielectric constants of ZrO_2 films synthesized at variant O_2 partial pressures. Because the native SiO_2 layers were not removed, two kinds of the relative dielectric constants of the films are showed in the figure, the effect (real) relative dielectric constant keff and the relative dielectric constant of ZrO_2 layer $kZrO_2$. As can be seen in the figure, both effect relative dielectric constant and the relative dielectric constant of ZrO_2 layer of the films synthesized at low O_2 partial pressure are higher than that at high O_2 partial pressure. The relative dielectric constant of ZrO_2 layer synthesized at the O_2 partial pressure of 14% is as high as 25. The decrease of relative dielectric constant of ZrO_2 layer synthesized at high O_2 partial pressure may be caused by the appearance of monoclinic polycrystalline of ZrO_2.

4. Conclusions

1) With the increase of O_2 partial pressure, deposition rate of ZrO_2 films decreases and the thickness of the native SiO_2 interlayer increases; The roughness of ZrO_2 films increases linearly with the increase of O_2 partial pressure.
2) ZrO_2 films synthesized at low O_2 partial pressure are amorphous. With the increase of O_2 partial pressure, ZrO_2 films change to monoclinic polycrystalline in nanometer scale.
3) The relative dielectrics of ZrO_2 films are in the range of 12 to 25. At the O_2 partial pressure of 14%, the relative dielectric of ZrO_2 film is as high as 25.

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