Preparation of ZrO_2 ultrathin films as gate dielectrics by limited reaction sputtering-On growth delay time at initial growth stage

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Preparation of ZrO_2 ultrathin films as gate dielectrics by limited reaction sputtering

—on growth delay time at initial growth stage

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Abstract

ZrO_2 thin films were produced by limited reaction sputtering process varying the deposition parameters. An interesting growth phenomenon was found in the initial growth stage of amorphous samples, appearing to suppress film growth for the first several minutes. The structure of such ultrathin ZrO_2 films were investigated by HR-Rutherford back scattering and X-ray photoelectron spectroscopy. The results suggest that the existence of interfacial suboxides due to the adsorption-induced surface reaction and diffusion-induced internal reaction, lead to the deteriorated interfacial performance. The mechanism and effects of the growth delay time on the interfacial characteristics are discussed in detail.

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Keywords: ZrO_2; dielectrics; growth delay phenomenon; sputtering.

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1. Introduction

The demand for greater integrated circuit density and performance has forced the thickness of the gate dielectric layer to decrease rapidly. Conventional SiO_2/SiON thin films as gate oxides approach the physical limitation due to the rapid increase in the direct tunneling current that will cause unsustainably large power consumption and worsen device reliability [1~2]. Several metal oxide dielectrics are currently being investigated as potential candidates to replace SiO_2, since they can afford larger capacitance without reliance on film thickness. Among various candidates, zirconia (ZrO_2), possessing good dielectric properties (ε~22) and thermodynamic stability in contact with Si substrate, is considered as one of the most promising materials [3~4]. However, interfacial reactivity of ZrO_2 with Si and SiO_2 has been observed, and the exact nature of this interface (i.e., silicide, silicate, or subsurface oxidation) is still uncertain [5~6].

To improve the interface performance between the gate insulator and Si, we developed a novel sputtering technique named "limited reaction sputtering" [7,8], in which the plasma radiation and the oxygen atom ions with high energy derived from plasma on Si substrate are suppressed, compared to conventional sputtering techniques. By introducing the Ar and O_2 gases into different chambers, respectively, the metal sputtering and oxidation deposition processes are separated. So far, we have successfully prepared the epitaxial yttria-stabilized zirconia thin films with negligible Si surface oxidation through this technique [7,8]. Moreover, thorough understanding of the growth mechanism of the high-k dielectric as well as related physical chemistry

processes will promote the introduction of the high-k dielectric into practical CMOS devices.

Recently, it has been reported that for the ultrathin ZrO_2 films (about several nanometers), the thickness also has strong effects on the structure and properties[9~10]. Generally, the grown thickness is directly proportional to the growth time. However, in the present paper, it is interesting to note that a deposition delay phenomenon appear during the growth of ZrO_2 thin films prepared by the limited reaction sputtering process. From the plots fitting the film thickness of the ZrO_2 films with the sputtering time, it seems that the growth of the film was suppressed in the beginning of the deposition. Moreover, the mechanism of the growth delay phenomenon is discussed in detail.

2. Experiments

The substrates, n-type Si(100) wafers with ρ=0.001~0.02Ωcm, were cleaned through conventional RCA cleaning process, and then dipped in a 1% diluted HF solution for about 30s to leave an H-terminated surface. ZrO_2 thin films were deposited by the limited reaction sputtering system. A pure Zr metal disk with a diameter of 100mm was used as the target, and the detailed process parameters are shown in Table 1.

For the typical thickness measurement by Surface Profilemeter (Dektak^3 ST), the edge region of the Si substrate was covered during the deposition process to make the steps between the Si substrate and the film. Structural analysis was carried out by reflection high-energy electron diffraction (RHEED), X-ray photoelectron

spectroscopy (XPS) and high resolution Rutherford Back Scattering (HR-RBS).

3. Results and discussion

Figure 1 shows the growth characteristics of the Zr and ZrO_2 thin films deposited varying the substrate temperatures from room temperature to 500℃. For ZrO_2 thin films prepared with substrate temperatures below 400℃, a clear offset, namely the growth delay time as large as 9 min is observed. The surface profiles of ZrO_2 prepared at 300°C by the surface profilemeter system are shown in the insert (a) of Fig.1. It can be seen that there is a clear step with about 29nm for the sample prepared for 30min, while large noise without any clear step can be observed for the sample prepared for 10 min, suggesting that the thickness of the film is very small and over the limitation for that method. The results imply that an unusual growth mode governs the first stage of film growth. After that, the growth mode changes to the normal case in which the film thickness is proportional to the growth time. On the contrary, for the sample prepared at 500℃, the growth delay time disappears and a film grows constantly, suggesting that the substrate temperature strongly influences the growth mode. For pure Zr metal films, it can be seen that the plots are fit well on the line which crosses the origin, and no offset is found in the measurement system, which proves that the procedure was carried out successfully.

On the other hand, it indicates that oxidation process plays a major role in the delay time growth. Fig. 2 shows the RHEED images of the ZrO_2 films prepared at 300℃ and 500℃ for 5 min, respectively. No spots or streaks can be found in Fig.2 (a), indicating the amorphous state of the sample prepared at 300℃, while increasing the

temperature to 500°C, the sample exhibits relatively sharp spots pattern, indicating the crystalline structure and smooth surface morphology as shown in Fig.2 (b).

The gradient of the plots shows the film growth rate as shown in the inset (b) of Fig.1. The difference in the growth rate of Zr and ZrO_2 by varying the substrate temperature is derived from the variation in the structures. Considering crystalline structures and corresponding lattice constants of ZrO_2 (5.21Å in CaF_2 structure) and Zr (3.61Å in bcc structure), we carried out a simple calculation on the density of the films by assuming the amount of Zr arriving at the substrates are the same. This indicates that the growth rate of the crystallized ZrO_2 film is about 1.5 times larger than that of pure Zr, which matches our experimental results, which show that the growth rate of Zr and crystalline ZrO_2 films prepared at 500℃ are about 0.8nm/min, 1.2nm/min, respectively. Furthermore, the insert (b) of Fig.1 indicates that the substrate temperature influences the growth rate of the ZrO_2 films, while crystalline ZrO_2 shows a smaller growth rate than that of the amorphous structure, because the crystalline structure is expected to have a larger density than that of the amorphous structure.

In general, the growth delay phenomenon could be explained by the desorption of ZrO_2 from the Si surface due to re-sputtering process, and the diffusion process into the substrate. In order to investigate the physics behind the growth delay phenomenon, HR-RBS and XPS analysis were performed.

Figure 3 shows the elemental composition depth profile measured by HR-RBS analysis on the samples prepared by the limited reaction sputtering at 300℃ for 15sec

and 5min, respectively, both of which belong to the period of the growth delay time. It can be seen from Fig. 3(a) that Zr and O are gradually increased and Si is decreased towards the surface, thus a Zr-Si-O mixing layer is formed within 2nm of the surface for the sample prepared for 15sec. A clear layer structure of ZrO_2 prepared for 5min is observed in Fig. 3(b). The composition of the layer shows approximately for the ratio Zr:O= 1:2 over 4nm. Also a mixing region of approximately 3nm is observed between ZrO_2 and Si substrate. Similar phenomenon are reported which shows that the $ZrSi_xO_y$ interfacial layer extends approximately over 2.5nm in ALD grown ZrO_2 on Si [11,12], and the growth of interfacial region is believed to be very sensitive to the oxygen condition in the deposition process. The GIXR and HR-RBS results from the ultrathin ZrO_2 film indicate the growth rate in that stage is about 1nm/min. Diffusion depth for the growth delay time would be simply estimated by extrapolating the plots to 0 point of growth time in Fig.1. As a result, a large value of around 14nm is obtained. Since the total diffusion depth is about 7nm for growth in 5min according to the RBS depth profile in Fig.2, the depth would be just 14nm in terms of 10min. Thus it can be said that it is in good agreement with the fitting results as shown in Fig.1.

These results indicate that the formation of ZrO_2 and Zr-O-Si mixing layers by surface and internal reactions dominates the initial growth stage. Since the amount of Zr flux is almost constant, the lagged growth of the thin film implies that there is a film loss caused by the desorption of ZrO species, and an initial adsorption of oxygen control the main process at low temperature. The oxidation process occurring in the interfacial layer is examined by XPS.

Figure 4 depicts the XPS Zr3d and Si2p spectra of the samples prepared at 300℃ for 5sec and 15sec. In Fig.4 (a), there is a doublet corresponding to Zr3d3/2 and Zr3d5/2 peaks that are centered at 185.2eV and 182.7eV for the sample prepared in 5sec, which represent the Zr^{4+} oxidation states, that corresponds to the bonding energy of Zr-O in ZrO_2 structure. Increasing the time to 15sec, the Zr3d peaks show enhanced intensity due to the increased thickness of the layer, and a slight blueshift centered at 185.5eV and 183.0eV, respectively. The increase in Zr3d binding energy is associated with the increased oxidization in Zr states [13] caused by prolonging the deposition time. This means that the oxidation process of the grown film is visibly dependent on the deposition time, suggesting the thermodynamically unstable status of the interface and sufficient energy of the oxygen diffusion.

The distribution of chemical states for the SiO_x films is analyzed by peak fitting (standard Guassian fitting) of Si2p spectra as shown in Fig.4 (b). The spectra of both samples show the same peak positions and full width at half maximum (FWHM), which indicates the chemical state of Si on the surface changed negatively with increasing the deposition time from 5sec to 15sec. It is interesting to note that the spectrum is composed of metallic Si (Si^0, substrate), three suboxide species (Si^{1+}-Si^{3+}) and fully oxidized SiO_2 (Si^{4+}) at the Si2p3/2 binding energies of 99.59, 100.23, 101.34, 102.37, and 103.15eV, respectively. Although there are errors in measuring and calculating the exact amount of the suboxides, it can be inferred that the concentration of suboxides is even larger than fully oxides. It was reported [14,15] that for the growth of the Si suboxides on the interface between the oxide and Si, the

temperature and oxygen concentration have strong influence on the bonding structure resulting in the shift of the XPS peak position and intensity. Low temperature or low oxygen partial pressure during the deposition process would increase the amount of suboxides. It is considered that the reaction energy of oxygen gas is degraded due to the low plasma density in the deposition chamber by the limited reaction sputtering system, resulting in the suppression of the direct initial oxidation of the surface Si atoms. Moreover, the oxygen deficiency in the ZrO_2 layer drives the activity of oxygen atom and suppresses the further oxidation of the SiO_x interlayer.

Generally, once the ZrO species or oxygen atoms are chemically absorbed on the Si surface, they can neither diffuse further nor make ZrO desorption. The absorbed oxygen atoms would diffuse into the internal sites of the film, and the ZrO species would be ejected to vacuum. On the other hand, it causes the formation of suboxides, which are identified by the elementary depth concentration and relevant chemical state analysis, suggesting that there is an adsorption-induced surface reaction and a diffusion-induced internal reaction in the initial growth stage. Moreover, it is observed that there is no clear signal assigned for the Zr–Si bonds in the XPS spectra as shown in Fig.4(a), which indicates that the amount of silicate is limited because of the weak reaction and diffusion between the Zr-O species and Si substrate.

Generally a crystalline structure with low oxygen deficiency defects can be obtained at higher temperature, resulting in the constant growth of crystalline ZrO_2 prepared at 500℃. Thus, crystalline structure is preferable to avoid the growth delay phenomenon, and there is still a challenge in which it needs sufficient oxidation of

high-k oxide without oxidized the Si substrate.

4. Conclusion

ZrO_2 thin films were prepared by limited reaction sputtering process. A "growth delay time" phenomenon was discovered. The structure properties of ultrathin films were carried out by XPS and RBS, suggesting that the growth of the amorphous samples underwent two quite different steps, one being the formation and growth of the interface in which ZrO_2 is thermodynamically unstable and an adsorption-induced surface reaction and a diffusion-induced internal reaction in the initial growth stage are identified; the other being the stoichiometric growth of the thin films, which has a linear relationship with the deposition time. The delay time phenomenon may severely degrade the interface performance and result in poor electrical properties and stability problems. Thus, these results could help to understand oxygen diffusivities, oxygen activities and the growth of interfacial phases during the deposition process.

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Figures and Tables

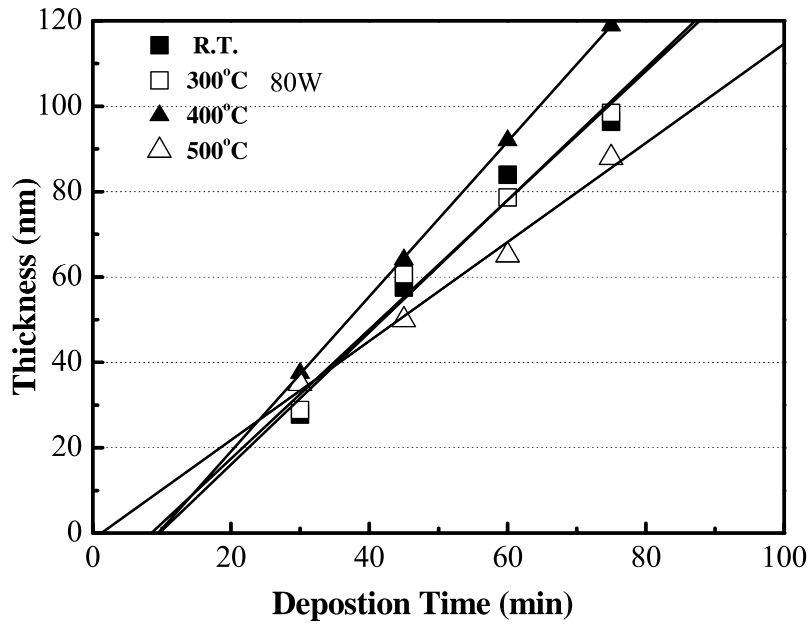
Figure 1 The deposition rate of ZrO_2 and Zr thin films prepared at different substrate temperature. The insert (a) is the raw data from the surface profilemeter measurement on the ZrO_2 film prepared at 300℃ for 10 and 30 min, the insert (b) shows the growth rates.

Figure 2 The RHEED patterns of the ZrO_2 thin films prepared at (a) 300℃, (b) 500℃.

Figure 3 Elemental depth profiles derived from the RBS data for the ZrO_2 thin films deposited at 300°C with different deposition time, (a) 15 second (d) 5 minutes.

Figure 4 XPS spectra of Zr3d (a) and Si2p (b) of the ZrO_2 thin films prepared at 300°C for different deposition time.

Table 1 Process parameters of the limited reactive sputtering.



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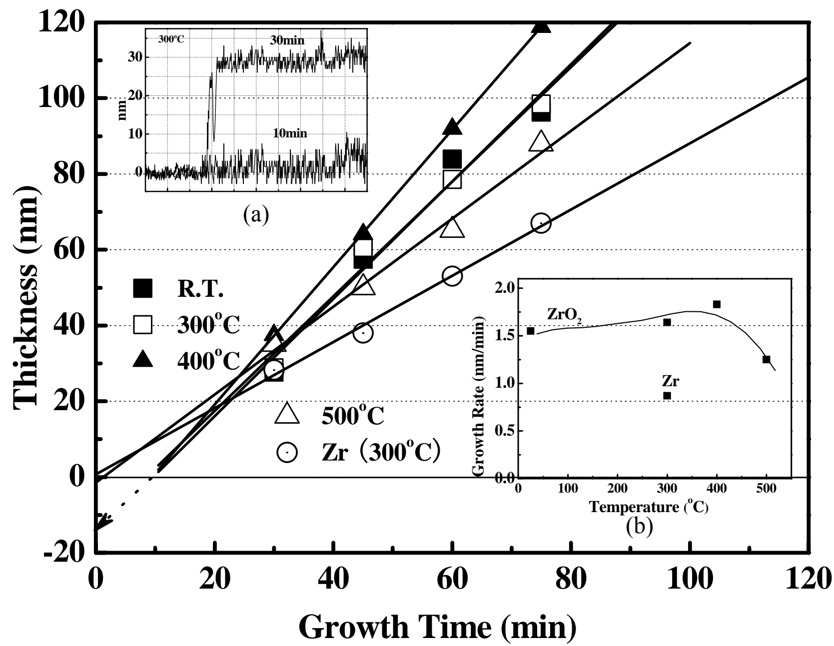
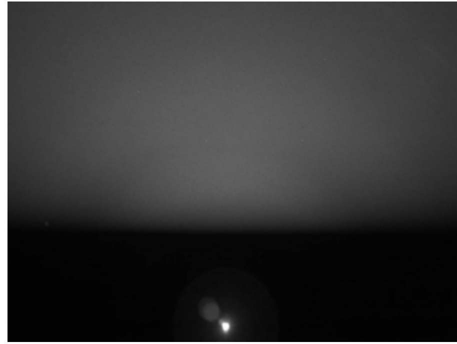
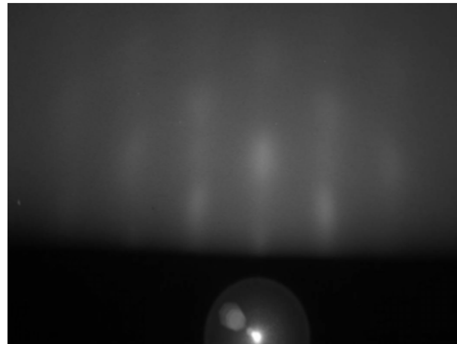




(a)



(b)

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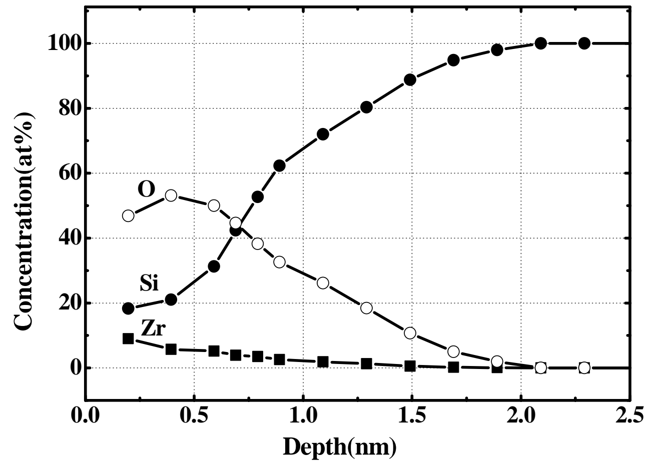

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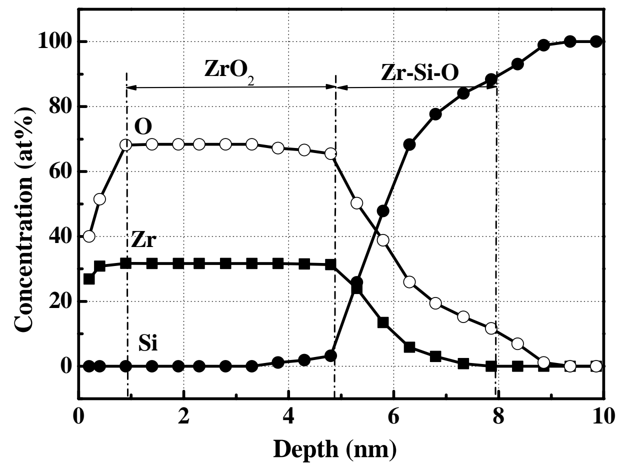

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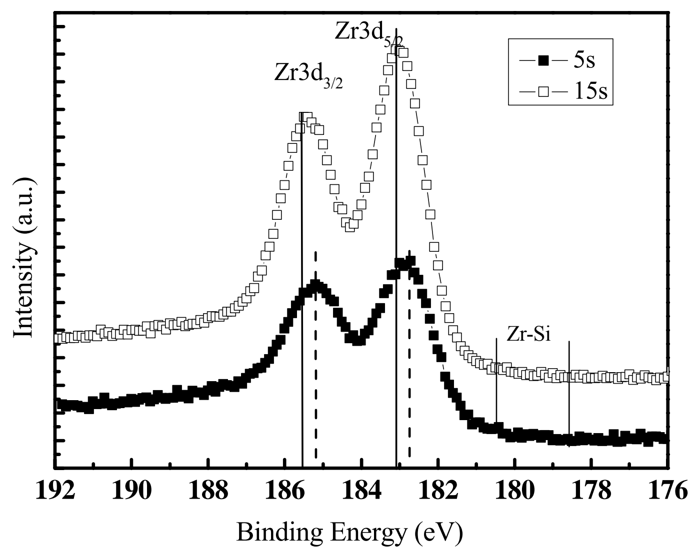
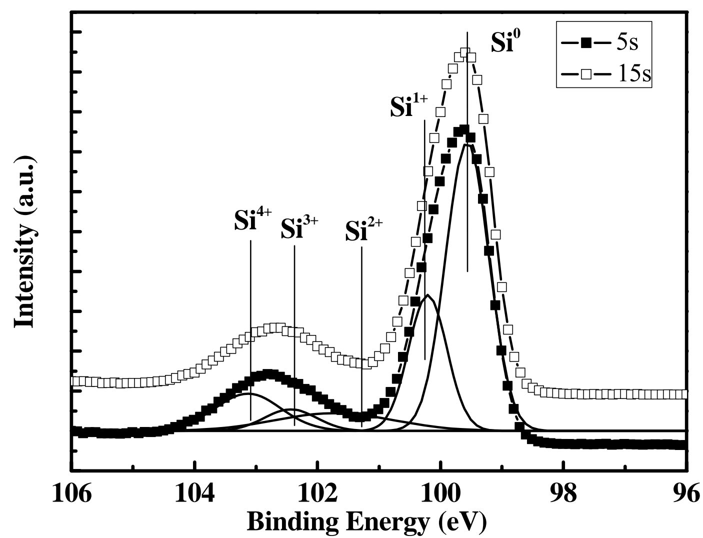


(a)



(b)

Figure 4 By Y. Zhou *et.al.*

O_2 concentration	0, 4%
Sputtering power	80W
Substrate temperature	R.T.~500℃
Working pressure	10mTorr
Substrate-target distance	128mm

Table 1 By Y. Zhou *et.al.*