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Deposition of ZrO_2 and TiO_2 Thin Films Using RF Magnetron Sputtering Method and Study on Their Structural Characteristics

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Abstract

Thin films of ZrO_2 and TiO_2 were deposited on Si(100) substrates using RF magnetron sputtering technique. To study an influence of the sputtering parameters, systematic experiments were carried out in this work. XRD data show that the ZrO_2 films were mainly grown in the [111] orientation at the annealing temperature between 800 and 1000 ℃ while the crystal growth direction was changed to be [012] at above 1000 ℃. FT-IR spectra show that the oxygen stretching peaks become strong due to SiO_2 layer formation between film layers and silicon surface after annealing, and proved that a diffusion caused by either oxygen atoms of ZrO_2 layers or air into the interface during annealing. Different crystal growth directions were observed with the various deposition parameters such as annealing temperature, RF power magnitude, and added O_2 amounts. The growth rate of TiO_2 thin films was increased with RF power magnitude up to 150 watt, and was then decreased due to a sputtering effect. The maximum growth rate observed at 150 watt was 1500 nm/hr. Highly oriented, crack-free, stoichiometric polycrystalline TiO_2<110> thin film with Rutile phase was obtained after annealing at 1000 ℃ for 1 hour.

Keywords : ZrO_2 and TiO_2 thin films, RF magnetron sputtering, Phase transition, Deposition parameter effects

1. INTRODUCTION

Reactive sputtering is widely used to prepare Ti compound thin films such as ZrO_2 and TiO_2. Generally, high flows of the reactive gases such as oxygen are required for formation of Zr and Ti compound films during reactive sputtering of Zr and Ti metals. The deposition rate of the film, however, drops abruptly since compounds are formed on the target surface at high flows of the reactive gases. For the reactive magnetron sputtering, moreover, an influence of deposition parameters on the structural and optical properties has already been studied by several authors[1,2]. The pressures of reactive gases, evaporation rates, and substrate temperatures were the main parameters able to influence the packing density of the films, the film crystallinity, and the optical properties. However, the influence of the substrate nature has not been studied yet in details and only transparent substrates such as glass and silica were used for

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the optical applications.

ZrO_2 films are widely used in the optical and electronics industries. These films usually exhibit properties that differ from the bulk material due to the differences in microstructure and crystal phase. As pure ZrO_2 films, it has been found to exist in monoclinic, tetragonal phase, and cubic phases as well as amorphous structure[3-6]. This depends on the preparation method and the annealing temperature. In case of magnetron sputtering of ZrO_2 film[4,7], it is well known that the crystal structure and the properties of the films prepared by sputtering are strongly affected by the sputtering parameters. Hence, in this study, we carried out the deposition of ZrO_2 films by RF magnetron sputtering method with/without oxygen flux. In addition, the influence of annealing and O_2 flux effect on the characteristics of ZrO_2 films has also been studied.

Titanium dioxide (TiO_2) has many excellent physical properties such as a high dielectric constant, a strong mechanical and chemical stability and good insulating properties. Due to its high refractive index and optical transmittance in the visible range, TiO_2 is especially suitable as material for optical coatings and protective layers for very large-scale integrated circuits[8,9]. The bulk material of TiO_2 is well known to have three main phases namely rutile, anatase and brookite. Rutile is a high temperature stable phase and has a refractive index of about 2.7, while anatase is formed at lower temperature with a refractive index of 2.5[10].

In this study, therefore, we have deposited the ZrO_2 and TiO_2 thin films on Si(100) substrates using RF magnetron sputtering technique. The effect of the deposition parameters on the structural property has also been studied and we then found the crystal growth directions were strongly affected by the various deposition parameters such as annealing temperature, RF power magnitude, and added O_2 amounts.

2. EXPERIMENT

Experiments were carried out using a home-made RF magnetron sputtering system with a magnetron sputter source that has unbalanced magnetrons with total magnetic filed of 300 G. A radio frequency (RF) power supply with 13.56 MHz and maximum 1.5 KW was applied for the plasma ignition. The details of experimental set-up are already reported elsewhere[11].

Si(100) single crystalline wafer was used as substrate, and it was cleaned by either ex situ chemical cleaning method or in situ argon plasma treatment in the temperature range between 100 and 300℃. The general deposition conditions are working pressure of 30~60 mTorr and deposition temperature of RT~150℃. For the thin films deposition, we synthesized a disk-type sputtering targets with 1 inch diameter using a power (99.99% purity) after making pallet and sintering for 8 hours at 1000℃. To see the reactive gas effects, moreover, oxygen was used as reactive gas in the flow range of 0 to 30 sccm and argon was also supplied as working gas. The as-grown thin films were characterized with x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and scanning electron spectroscope (SEM). A effect of the deposition parameters on the structural property has also been studied in this work.

3. RESULTS AND DISCUSSION

3. 1 ZrO_2 thin films

Figure 1(a) shows X-ray diffraction patterns of ZrO_2 thin films grown at room temperature and 120 W without O_2 flux and annealing with different temperatures. Below 600℃, there is no typical diffraction peak, indicating an amorphous structure. Between 800 and 1000℃, the film is mainly grown in the [111] orientation while the crystal growth direction is changed to be [012] in the annealing temperature range of 1000 - 1200℃.

The most good quality film can thus obtain at 1200℃. With oxygen flux, the same tendency of X-ray diffraction pattern as figure 1(a) was observed. But, the relative intensity was decreased a lot, suggesting poor crystallity in these cases. The FT-IR spectra of ZrO_2 films are shown in figure 1(b). There is no strong peak obtained from the ZrO_2 films without annealing. But after annealing at 1200℃ three major peaks seen in figure 1(b) are appeared. The peak seen in the 464.8 cm^{-1} region is attributed to the Zr-O stretching. And the peaks at 794.6 and 1083.9 cm^{-1} are mostly due to Si-O-Si and Si-O stretching of the silicon oxide layers. The reason of arising SiO_2 layers is to inter diffusion caused by the oxygen flux onto ZrO_2 surface or oxygen diffusion into the bulk during annealing. To prove this phenomenon more clearly, the same experiments of ZrO_2 thin film deposition were carried out under different oxygen plasma condition.

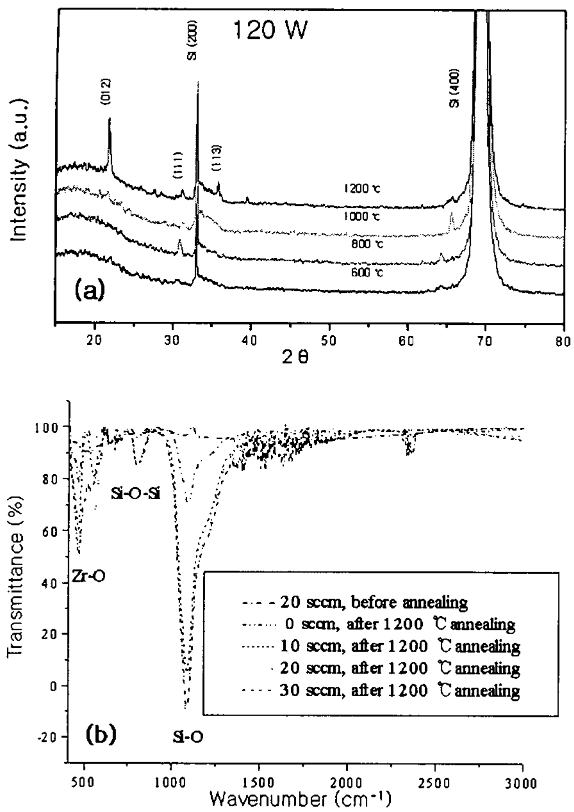

Fig. 1. (a) X-ray diffraction patterns of ZrO_2 thin films obtained with different annealing temperatures. (b) FT-IR spectra of ZrO_2 thin films obtained with different O_2 flux and annealing.

Figure 2(a) shows a SEM image as well as EDX result obtained a ZrO_2 thin film that grown at room temperature and 400 W without oxygen. The surface morphology shows quite smooth surface without a distinct crystal shapes. The EDX data shows a hint of stoichiometric ZrO_2 film formation without SiO_2 layer formation in the interface region, indicating good adhesion between ZrO_2 film layer and Si substrate. With the high resolution XP spectra (shown in Fig. 3) of $Zr3d_{5/2}$ and O1s which obtained the ZrO_2 films grown without oxygen and with 20 sccm O_2 flux, we can also measured the composition ratio between Zr and O to be 1:2. Above 20 sccm, however, excess oxygen species such as non-stoichiometric ZrOx species was also detected.

This indicates that the most stoichiometric ZrO_2 thin film can be obtained under the O_2 flux of below 20 sccm. Figure 2(b) shows the cross-

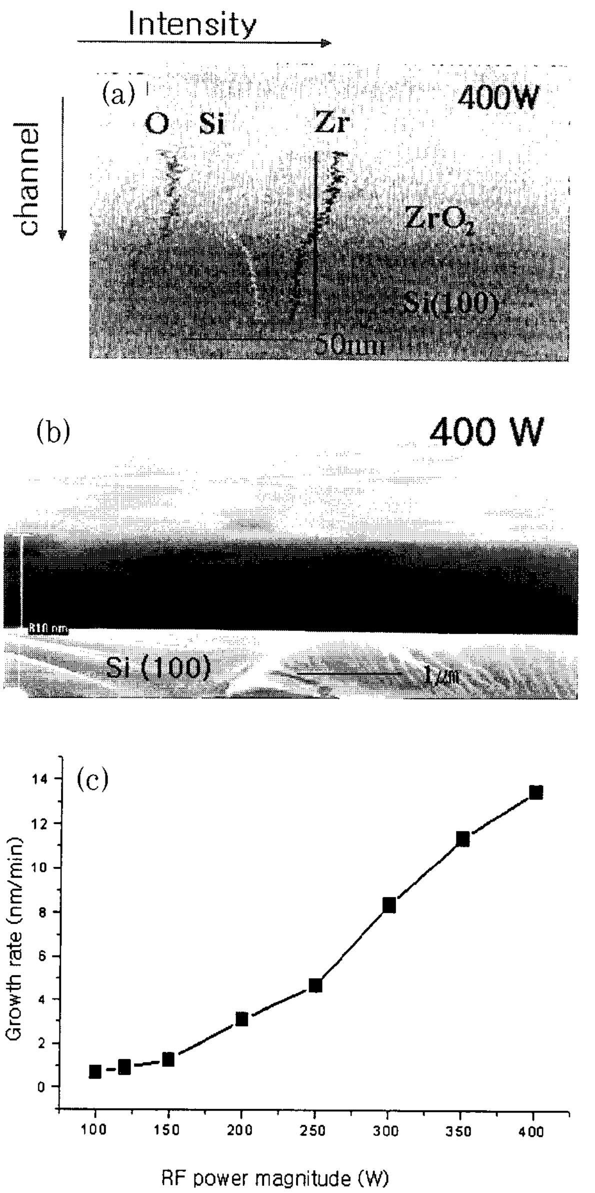

Fig. 2. (a) SEM and EDX image of a ZrO_2 thin film grown at RT and 400 W without oxygen. (b) Cross-sectional SEM image of the same film as figure 2(a). (c) Variation of growth rates of ZrO_2 thin films with RF power magnitude.

sectional SEM image of the same film as figure 2(a). The figure shows a sharp interface without SiO_2 layer formation. With this cross-sectional SEM images, one can calculate the film thickness as well as growth rate. The calculated thickness is 187 nm. Figure 2(c) shows the variation of film growth rate as a function of RF power magnitudes. With increasing RF powers,

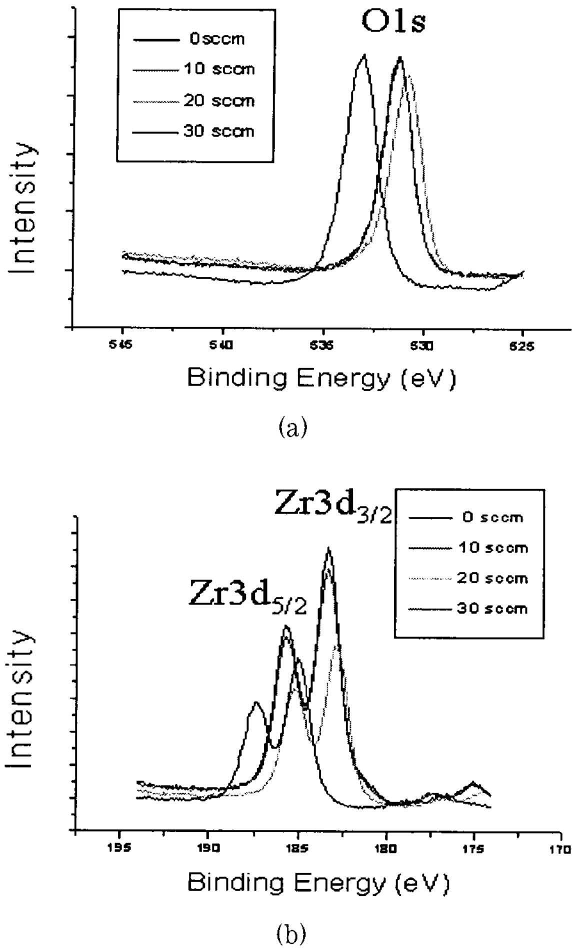

Fig. 3. High-resolution XP spectra of the ZrO_2 films grown without oxygen and with 20 sccm O_2 flux obtained (1) before and (2) after Ar ion sputtering.

the growth rate is linearly increased within our /experimental condition. The maximum growth rate obtained in this study is 12 nm/min.

3. 2 TiO_2 thin films

Fig. 4(a) shows the typical XRD patterns of the as-grown TiO_2 films sputtered on Si(100) substrates at room temperature and RF power of 150 W with different annealing temperatures without reactive gas. In Figure 4(a), amorphous - like TiO_2 films with anatase phase were obtained at below 500℃. With increasing the annealing temperature, however, the film structure was changed to be rutile phase and the film

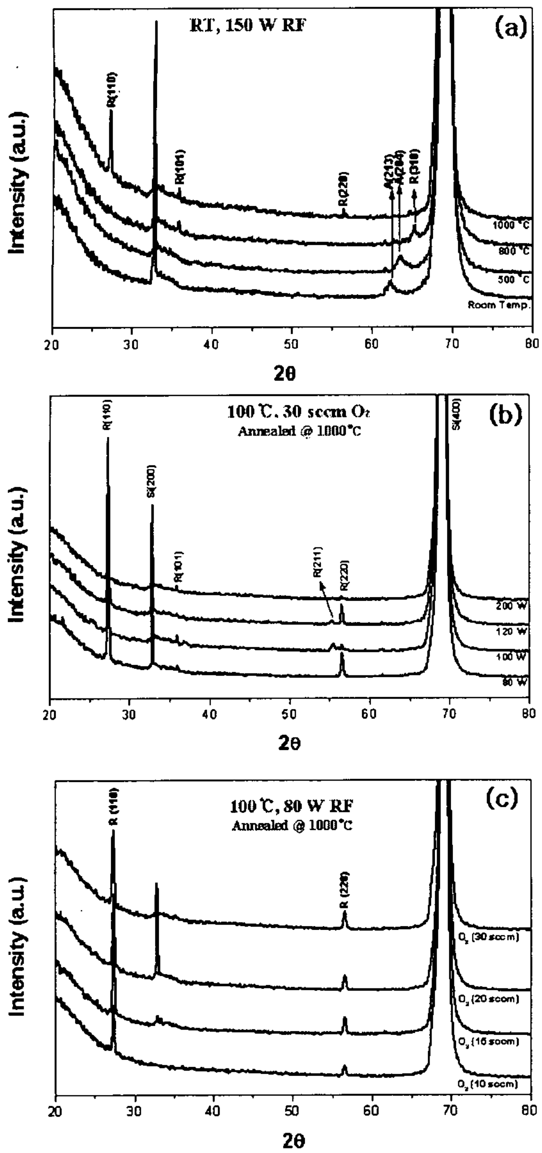

Fig. 4. (a) XRD patterns of the as-grown TiO_2 films sputtered on Si(100) substrates at room temperature and RF power of 150 W with different annealing temperatures without reactive gas. Figures 4(b) and 4(c) show the XRD patterns obtained from the as-grown TiO_2 films that deposited on Si(100) at 100℃ and different RF power (b) and oxygen flow (c).

crystallinity was also enhanced to polycrystalline with highly oriented TiO_2<110> crystals, indicating the annealing temperature can be affected to the film quality. Figures 4(b) and 4(c) also show the XRD patterns obtained from the as-grown TiO_2 films that deposited on Si (100) at 100℃ and different RF power (b) and oxygen flow (c) and took after annealing at 1000℃ for 1 hr. From the Figures 4(b) and 4(c), we realized two things. One is that the TiO_2 films were mainly grown in the [110] direction and have the rutile structure. The other one is that more highly oriented film can be deposited at relatively low RF power and high oxygen flow rate rather than that of high RF power and low oxygen flow rate. However, when the glass substrates were adapted and oxygen flow is over 30 sccm, the film quality was more poor than that grown on Si(100) at lower oxygen flow, suggesting that the substrate nature and oxygen flow rate can be one of important factors to influence the film quality as well as crystal growth direction.

Figures 5(a) and 5(b) show the selected plan-view and cross-sectional SEM images obtained after annealing the TiO_2 films that grown on Si (100) substrates at 100℃ and oxygen flow of 30 sccm with RF power of (a) 120 W and (b) 150 W. Generally speaking, the TiO_2 thin films grown with different RF powers under the same oxygen flow rate and substrate temperature showed quite smooth surfaces with no cracks and sharp interfaces between film layers, signifying good adhesion and uniformity in depth. However, the film adhesion and the surface morphologies were drastically changed to be weak and rough with increasing RF power under the same annealing temperatures, indicating less hard film formation. Figure 5(c) shows the variation of growth rate obtained from the cross-sectional SEM images with different FR powers. Up to 150 W of RF power, the TiO_2 film growth rate is gradually increased with RF power magnitude and then decreased rapidly

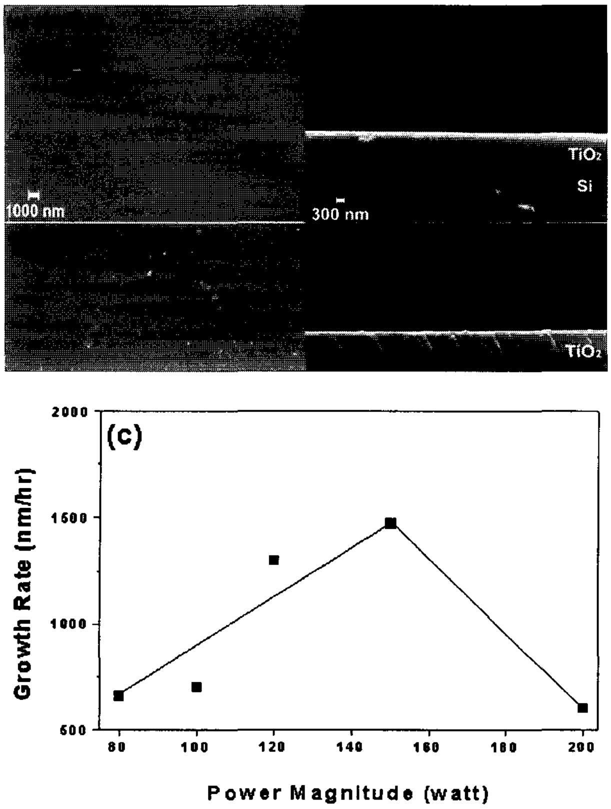

Fig. 5. Selected plan-view and cross-sectional SEM images obtained after annealing the TiO_2 films that grown on Si(100) substrates at 100℃ and oxygen flow of 30 sccm with RF power of (a) 120 W and (b) 150 W. Figure 2(c) shows dependence of growth rate with different FR powers.

above 150 W due to a sputtering effect. In this study, the maximum growth rate observed at 150 W of RF power was thus reached to be 1500 nm/hr.

Figure 6 shows the Ti2p and O1s high-resolution XP spectra obtained (1) before and (2) after Ar ion sputtering of a TiO_2 thin film that deposited at 100℃, 80 watt of RF power, 1000℃ of annealing temperature, 1 hour of deposition time, and 30 sccm of O_2. In the figure 6, two oxide states attributed O^{2-} and OH^- species were observed from the as-deposited film without Ar ion bombardment.

However, the OH^- shoulder peak disappeared after ion bombardment and the main O1s peak

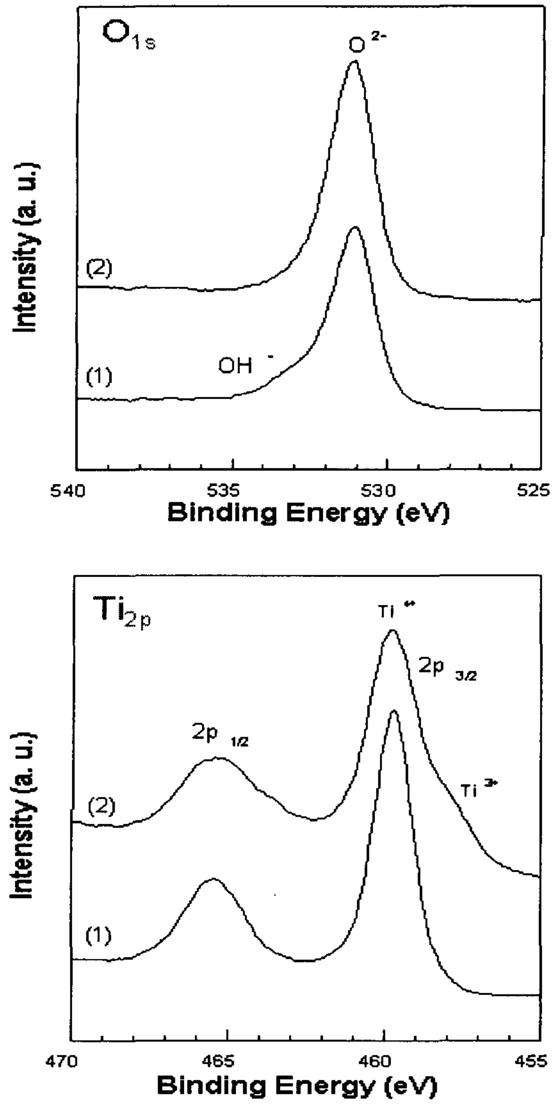

Fig. 6. High-resolution XP spectra of a TiO_2 thin film that deposited at 100℃, 80 watt of RF power, 30 sccm of O_2, and 1000℃ of annealing temperature obtained (1) before and (2) after Ar ion sputtering.

(531.0 eV) shifted its binding energy to the reference value of O^{2-} peak[12]. This indicates that the OH^- peak is just a surface contamination peak probably due to water adsorption in the air. On the other hand, the $Ti2p_{3/2}$peak showed a single peak at binding energy of 459.7 eV before Ar ion bombardment, which was attributed to Ti^{+4}[12]. After Ar ion sputtering, the $Ti2p_{3/2}$ peak showed a shoulder on the low binding energy side, which was evidenced by the presence of Ti^{3+} [13], explaining that O atoms in TiO_2 thin film could be removed from the film surface by preferential sputtering. The atomic composition of Ti and O of the TiO_2 thin film obtained from the figure 6 was nearly 1:2. However, more oxygen-deficient films were obtained under the growth conditions of higher RF power and lower oxygen flow rate. The annealing temperature is also affected to the film composition ratio, for example, more stoichiometric TiO_2 film can be deposited at high annealing temperature over 800℃. In conclusion, the most stoichiometric TiO_2 film was obtained at 80 watt of RF power, 1000℃ of annealing temperature, 1 hour of deposition time, and 30 sccm of O_2.

4. CONCUSIONS

We have been deposited ZrO_2 thin films by RF magnetron sputtering in order to study an influence of deposition parameters (such as annealing temperature and reactive gas) on the film structure and optical and electrical properties. XRD showed that a highly oriented cubic ZrO_2 thin film in the [111] direction was obtained after annealing at 800℃. On the other hand, tetragonal ZrO_2 thin film was grown on Si (100) substrate and the main film growth direction was also changed to be [012] direction at above 800℃ of annealing temperature. FT-IR data showed a strong vibrational peak at 464.8 cm^{-1} due to Zr-O vibration. With annealing temperature at 1200℃, however, additional vibrational peaks were also appeared at 904.6 and 1083.9 cm^{-1}. This means that at higher annealing temperature, the surface oxygen will be diffused into the bulk, resulting in a SiO_2 layer formation in the interface region. I-V data show that the film grown without oxygen gives the smallest leakage current density. With increasing O_2 flux in leakage current is also increased due to the defect sites of ZrO_2 films. The refractive index of ZrO_2 thin films are increased by annealing and O_2 flux. Among them, the O_2 flux is mainly affected to enhance the optical properties of ZrO_2 films. A highly oriented, crack-free, stoichiometric polycrystalline TiO_2 thin film with rutile phase was also deposited on Si (100) substrates under the deposition condition of 100℃ of film growth temperature, 80 W of RF power, and 30 sccm of O_2 and after annealing the film at 1000℃ for 1 hour. To study a effect of the deposition parameters on the structural property, we mainly measured the surface characteristics of the as-grown films as a function of annealing temperature, RF power magnitude, and reactive gas flow. We then found that the crystal growth directions were strongly affected by the various deposition parameters such as RF power, added O_2 amount as well as annealing temperature. The film growth rate was also increased with RF power magnitude up to 150 watt, and was then decreased due to a sputtering effect. The maximum growth rate observed in this study was 1500 nm/hr.

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