

Cerium Oxide Film Growth Using Radio-Frequency Sputtering Process

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Abstract

In this study, the radio-frequency (RF) sputtering of cerium oxide was explored to determine the effect of the operating conditions on the film growth of cerium oxide on glass, and silicon substrates. The process variables were sputtering time, input power and R (Ar/O_2) ratio. In order to better understand the influence of process variables on the growth mechanism, the grain size and film thickness of cerium oxides were explored by using SEM, XRD, and *a*-step processes. From the results of SEM photographs, the grains of cerium oxides could be evaluated by using an imaging analysis technique. On the other hand, from the XRD data, with the aid of Scherrer's equation, the crystalline sizes of cerium oxide crystals could be determined. The grain size was higher than the primary size, indicating the agglomeration of cerium oxide crystals. In addition, the effects of parameters on crystal size and film thickness are discussed herein following regression.

Keywords

Sputtering, Cerium Oxide, Scherrer's Equation, Agglomeration

1. Introduction

There are several deposition methods, such as evaporation, chemical vapor deposition (CVD), and sputtering, that are used to deposit thin films [1]-[6]. In the case of the evaporation process, as compared with the sputtering process, some disadvantages are observed, such as a low deposition rate, non-uniformity of film thicknesses, and variation in deposition composition. Nevertheless, the CVD process is broadly used in the semiconductor industry for the growth of thin films because it has some advantages in the depositing process, such as uniform temperature, uniform concentration, uniform deposition rate, and suitability for any shape element. However, as the CVD process was carried out at a relatively high temperature, limitations due to dimensional tolerances became an important consideration [7].

Sputtering has also been classified into physical and chemical sputtering. In this process, deposited films have a composition close to that of the source material. Sputtered films typically have a better adhesion onto the substrate than evaporated films. Therefore, the adhering force for the sputtering method is much higher than the evaporation method. Consequently, higher hardness and higher packing density of thin films were obtained by using the sputtering method. In addition, sputtering can be performed top-down while evaporation must be performed bottom-up. Moreover, advanced processes, such as epitaxial growth, are also possible [8].

As a result, sputtering is extensively used in the semiconductor industry to deposit thin films of various materials in integrated circuit processing [9] [10] [11] [12]. This technique is also used to fabricate thin film sensors, photovoltaic thin films (solar cells), metal cantilevers, and interconnects [13] [14]. Recently, cerium oxide film was also used for water treatment application [15]. A variety of sputtering methods are available for specific applications [14] [16]. The RF (radio-frequency) sputtering technique has a number of advantages, including relatively low cost, good adhesion, and uniform film deposition onto the substrate at a low substrate temperature [17]. In addition, RF sputtering can be done with both conducting and non-conducting materials [18]. Deposition onto a plastic substrate is ideally carried out at very low substrate temperatures, such as room temperature. Therefore, to obtain high quality CeO₂ film by RF sputtering on substrates, such as PC, glass, or silicone plates, it is important to accurately control key parameters, such as RF power, deposition pressure, and gas flux [19] [20] [21]. Lu et al. [17] reported that growth rate increased with the increase in RF power, while grain size of ZnO film decreased with the increase in RF power. The morphology of the ZnO grains was found to be continuous and dense. CeO₂ is a promising material for fast oxygen gas sensing at high temperatures because of its chemical stability and high diffusion coefficient of oxygen vacancies [22]. CeO₂ deposited by sputtering also shows strong oxygen gas sensing properties at high temperatures [10] [12].

Oxygen gas sensors could be used as automotive exhaust gas sensors in gasoline-powered and diesel engines, as well as in two-wheel vehicles [19]. In addition, oxygen gas sensors using concentration cells consisting of oxygen ion conductors are currently being used to measure the oxygen concentration in exhaust gas [20]. However, their structure is complicated, and it is difficult to reduce their size. Oxygen gas sensors for automotive exhaust gas need to be small and capable of fast response time in order to monitor the concentration of oxygen gas, in order to be able to control the air-to-fuel ratio. Therefore, it is important to improve the response of resistive oxygen gas sensors. Research has shown that the predominant ionic defects of resistive oxygen gas sensors based on cerium oxide (ceria) are based on the electrons trapped by the Ce and oxygen vacancy [23] [24].

Cerium oxide is one of the materials used for resistive oxygen gas sensors since it has a large diffusion coefficient and good corrosion resistance [23] [25] [26]. Izu *et al.* [23] found that the response time of sensors using films with a particle size of 200 nm was approximately one order of magnitude smaller than that for corresponding sensors using films with a particle size of 2000 nm. They found that the response time was shortened if the particle size decreased. Furthermore, CeO₂ has been shown to enhance the dissociation of carbon monoxide on ceramics. The focus of new sensor development concerns research into novel materials which could provide increased sensitivity, selectivity, and stability [10] [12]. The excellent properties of CeO₂ make it a useful material for catalysts, stable capacitor devices and fuel cells [13] [16] [27]. From an examination of the relevant literature, we found that the important parameters for sputtering are argon pressure, sputter voltage, substrate temperature, substrate to target distance, and deposition time. Therefore, determining how to control the particle size of CeO_2 and the film thickness for sputtering is essential in the application of oxygen gas sensors. In addition, adding a magnetic field in the sputtering process will hugely increase the ionization density of argon gas and the possibility of collision. Therefore, the deposition rate can be increased [7]. In a word, cerium oxide can function as a catalyst, fuel cell, hydrogen production, oxygen sensor, and anticorrosion. The texture of these thin films can affect the mechanical, electronic, and corrosion properties.

In this work, we deposited CeO_2 films by RF magnetron sputtering onto two substrates at room temperature in order to investigate the effects of the process variables on the structural, optical, and particle size properties of the deposited films. The process variables were Ar/O_2 ratio, sputter voltage, and deposition time. In order to characterize the properties of CeO_2 film on the substrates, the films were examined by FESEM, XRD, and *a*-step machines.

2. Experimental Details

 CeO_2 films were deposited on Si (100) and glass at room temperature using an RF sputtering system, as shown in Figure 1; it was divided into two parts: a vacuum system and a sputtering system. Ce, with a diameter of 4 inches, was used as the target. First, the vacuum chamber was evacuated to 10^{-2} Torr, and the total pressure was continuous down to 10^{-6} Torr. Subsequently, the desired ratios of Ar/O₂ were adjusted through mass-flow controllers which let the gases flow into the chamber. Two sputtering powers: 100 and 120 W, were used in this work, and the deposition times were 1 - 3 h. A total of six series of experiments were carried out in this work: three series for the silicon substrate as S1 - S3 and three series for the glass substrate as G1 - G3. Series S/G1 (100 W-2:1-time) investigated the effect of deposition time on the formation of thin film; Series S/G2 (100 W-1:2-time) was used to study the effect of the sputtering power. The Ce target was pre-sputtered in an argon atmosphere for 30 min to eliminate surface pollution. After deposition, the thickness of the CeO₂ film was measured



Figure 1. RF sputtering system for the deposition of cerium oxide film.

using an *a*-Step Microfigure measuring instrument (Surfcorder; ET-4000A, Kosata). The structural properties of the CeO₂ films were investigated using X-ray diffraction (XRD; D/MAX 2200, JEOL) with Cu Ka radiation ($\lambda = 0.1542$ nm) and Field Emission Scanning Electronic Microscopy (FESEM; JSM-6500F, JEOL) in the contact mode.

3. Results and Discussion

3.1. Experimental Data

Table 1 showed the data at various conditions for S-series, including full width at half maximum (FWHM), 2θ , crystal size (d_p) , grain size (d_G) , film thickness (H) and growth rate (R_d) . In here, FWHM of the CeO₂ (111) diffraction peaks and corresponding Bragg diffraction angles (2θ) for silicon substrates under different sputtering conditions can be used to evaluate the crystal size (d_p) of the films based on the XRD results, we used Scherrer's equation:

$$d_p = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where λ , *B*, and θ are the X-ray wavelength (1.54056°A), FWHM of the CeO₂ (111) diffraction peak, and Bragg diffraction angle, respectively. The grain sizes can be determined by using imaging analysis, while the film thickness was obtained using *a*-step analysis. In addition, the growth rate was evaluated as the grown thickness divided by the deposition time. The crystal sizes ranged from

Run No.	FWHM	2θ	$d_p(nm)$	$d_G(nm)$	H(nm)	R_d (nm/h)
S1-1/100W-2:1-1hr	0.515	28.451	16.64	88.93	117.5	117.5
S1-2/100W-2:1-2hr	0.691	28.404	12.40	51.03	230.2	115.1
\$1-3/100W-2:1-3hr	0.635	28.397	13.49	41.18	329.7	109.9
S2-1/100W-1:2-1hr	0.555	28.545	15.44	51.03	130.2	130.2
S2-2/100W-1:2-2hr	0.536	28.402	15.98	47.70	221.9	111.0
S2-3/100W-1:2-3hr	0.634	28.549	13.52	40.98	293.4	97.8
S3-1/120W-2:1-1hr	0.485	28.496	17.66	50.36	128.1	128.1
S3-2/120W-2:1-2hr	0.549	28.496	15.61	35.50	327.8	164.8
\$3-3/120W-2:1-3hr	0.661	28.548	12.96	47.86	424.2	141.4

Table 1. Data obtained for the deposition of CeO₂ onto the silicone substrate.

12.4 to 17.66 nm; the grain sizes obtained were in range of 40.98 - 88.93 nm; the film thicknesses were in the range of 117.5 - 329.7 nm; the growth rate ranged from 97.8 - 164.8 nm/h; depending on the operating conditions. The crystal sizes were much smaller than the 100 nm fabricated by the screen-printing method on an alumina substrate [19] [23]. In order to understand the effects of process variables on the experimental data, it requires to be discussed later.

3.2. XRD Patterns for Materials Deposited onto Substrates

Figure 2 shows the XRD patterns obtained for CeO₂ films deposited on silicon substrates for different deposition times, Ar/O₂ ratios, and sputtering powers. It was found that the 2θ Bragg diffraction angles for the major peaks were (111), (220), (311), (222), and (400), respectively, indicating that the deposition material was cerium oxide compared with standard peaks. The peaks obtained here were similar to those reported in the literature for the growth of ceria thin films [23] and nanopowders [28] [29]. In addition, the intensity for series S1 increased with an increased deposition time, and the strength at (111) was enhanced with the increase in deposition time. However, the intensity at (111) was more strength when the Ar/O₂ ratio was changed in series S2. The similar effect was more significant for series S3. However, this phenomenon was reversed when the Ar/O₂ ratio was changed in Series S2. The reverse effect was more significant for Series S3. These results indicated that deposition time, Ar/O_2 ratio, and sputtering power had obvious effects on the crystalline structure of cerium oxide. For comparison, an XRD examination of Series G1 (glass substrates) was conducted, as shown in Figure 3. The absorption strengths for Series G1 were found to be higher than those of Series S1, indicating that the deposition of CeO₂ onto a glass substrate (series G1) resulted in a better microcrystalline structure than that obtained from Series S1. This result also showed the effect of the substrate on the crystallinity of CeO₂. In here, it can be found that regardless of the operating conditions, the deposited CeO_2 films showed a preferred orientation in (111) and (400) faces, which was due to that increasing deposition time at various conditions, the CeO_2 (111) and (400) reflections increase in intensity growing films with preferred (111) and (400) orientations.



Figure 2. XRD diffraction patterns for series S at different operating conditions.



Figure 3. XRD patterns for series G1 at different deposition times.

The microstructure and texture of thin films were explored in a transverse analysis of deposited samples, by the use of FESEM photographs. The SEM pictures for Si-substrate are shown in **Figure 4**. The results show that the film thickness resulting from 1 h of sputtering lacks smoothness; the structure became smooth and thicker after 2 and 3 h of sputtering, indicating that the structure was affected by the operating time. This indicates that why the peak intensity increases with increasing operating time. For purposes of comparison, the deposited films observed for Series S1 as examples were measured according to the SEM pictures, as shown in **Figures 4(a)-(c)**. The thicknesses of the three samples, S1-1, S1-2, and S1-3, were about 100 nm, 210 nm, and 320 nm, respectively. The values were close to those determined by using the *a*-step method (117.5 nm, 230.2 nm, 329.7 nm). It was found that the film growth of cerium oxide could be adjusted by the sputtering time, Ar/O_2 ratio, and input power.

3.3. Effects of Process Parameter Crystal Sizes of Cerium Oxide Crystals

Figure 5 shows a plot of crystal size versus deposition time for the S series and the G series experiments, showing the different growth sizes depending on the Ar/O_2 ratio and sputtering power. In this study, we found that the size decreased with the increase in deposition time, revealing that the CeO_2 film was formed layer by layer during continuous sputtering. For this reason, the supersaturated vapor in the sputtering chamber became higher as the deposition time increased further; therefore, more nuclei were formed and grew continuously, resulting in the formation of smaller sizes, as explained by the Gibbs-Thomson theory [30]. A similar viewpoint was expressed by Lu *et al.* [17] who stated that more nuclei existing on the substrate implied more sites for grain growth, which meant that a large number of small grains could grow simultaneously and finally result in a small grain structure. In addition, a comparison of the different substrates according to crystal size was explored in this study. The results showed that the sizes for Series G1 of 22.86, 16.51, and 15.87 nm were coarser than the sizes of 16.64, 12.40, and 13.49 nm for Series S1.

In order to better understand the effects of parameters on the crystalline size of S-series, a regression of parameter to size can be shown below:

$$d_{p} = 2.6280 P^{0.3963} R^{-0.03563} t^{-0.1875}$$
⁽²⁾

The regression error is 2.58% with $R^2 = 0.6876$. The result showed that d_p increased with *P*, while it decreased with *R* and *t*. In addition, the parameter importance showed that P(1.075) > R(0.9518) > t(0.8138). Alternatively, the regression result for G series was found to be:

$$d_{p} = 3.1879 P^{0.4148} R^{-0.03826} t^{-0.2411}$$
(3)

The regression error is 1.43% with $R^2 = 0.8674$. The trend was similar to that S series. The reliable confidence for both systems was shown in **Figure 6**, a plot of calculated value versus measured value for both series.



Figure 4. SEM pictures of deposited films showing the transverse structure and texture for the sputtering of Si-substrate.



Figure 5. A plot of crystal size versus time at various series.



Figure 6. A plot of calculated value versus measured value for particle size.

3.4. SEM Photographs for Cerium Oxide Particles

Figure 7 shows the SEM photographs of the CeO₂ films for the S series experiments: the morphology of the films is uniform and dense; however, the grain sizes are approximated several tens to several hundreds of nanometers, and thus, are larger than the sizes evaluated from Equation (1), indicating the agglomeration of cerium oxide crystals during crystallization. Using an imaging analysis technique (ASTM, E112 standard), the average grain sizes were found to be in the range of 35.50 to 88.93 nm; the results are also listed in Table 1 for comparison. A similar result regarding underestimation of the sizes was reported by Kim and Kim [16] regarding the growth of ZnO on Si substrates; however, they surmised that the underestimation was not due solely to the instrumental broadening of FWHM, but also to stress-induced broadening and mosaic structure-induced broadening. For Series S1, the SEM imaging analysis shows that the grain size decreased with an increase in deposition time, and that the distribution of the grain was denser. These results also reflected the Gibbs-Thomson theory mentioned in Section 3.2. For Series S2, the trend was similar to that in Series S1; the grain size was smaller compared with Series S1, thus showing the effect of the Ar/O_2 ratio on grain size. For Series S3, the grain size was smaller than in Series S1, thus showing the effect of sputtering power because increasing the sputtering power led to an increase in the deposition rate and in the average kinetic energy of the sputtered species [8], which can be found in Table 1. In addition, it can be reasoned that higher RF power means more argon ions in the plasma, with the bombardment on the target increased accordingly [17]. The SEM images for Series G1 are shown in Figure 8. It was found that the grain sizes obtained by using imaging analysis were 38.84, 44.29, and 57.38 nm, for 1 h, 2 h, and 3 h sputtering, respectively. The effect of deposition time on the grain size differs from that obtained in a silicon substrate, indicating the effect of the substrate.

3.5. Effects of Process Parameters on Film Thickness

Figure 9 shows the thickness of the deposited CeO_2 film on silicon substrate as a function of deposition time at different sputtering powers and Ar/O_2 ratios. The film thickness increased almost linearly with the increase in deposition time. The thickness for Series S1 was greater than that of Series S2, but smaller than that of Series S3. The results showed that sputtering power had a more significant effect on the film thickness of CeO_2 than resulted from a glass substrate (see **Figure 10**). The explanation was that higher supersaturated vapors were generated at stronger sputtering powers, resulting in the formation of thicker CeO_2 film. It is speculated that with a high RF power, the cerium atoms had more opportunity to reach the substrate implies more sites for grain growth [15]. Another reason for the increased film thickness could be the possible thermal damage of the CeO_2 film arising from the difference in the coefficient of thermal expansion between CeO_2 and the substrate. A similar explanation was presented concerning the growth of ZnO film [8] [16]. A plot for the glass substrate is shown in

Figure 10. The results show that deposition time and sputtering power have a marginal effect on the deposited thickness of CeO_2 . Film thickness increasing with an increase in sputtering power was also reported by Sohn *et al.* [31] in the growth of ZrO_2 film. In here, the effects of parameters on the film thickness can be discussed after regression. The results for both systems were shown below:

 $H = 0.3324 P^{1.2744} R^{0.01211} t^{-0.06511}$

and

$$H = 30.6153P^{0.2725}R^{0.06914}t^{1.07906}$$
(5)

(4)

The regression error for Equation (4) (S-series) was 1.77% with $R^2 = 0.6165$, while the error for Equation (5) (G-series) was found to be 0.926% with $R^2 = 0.9787$. For both substrates, the thickness increased with an increase in *P* and *R*, while the effect of *t* on *H* of silicone substrate was weak but the effect was stronger for glass substrate. The data deviations for both systems were shown in **Figure 11**, a plot of calculated value versus measured value for both series. It can be found that the power law models were reliable for both. In addition, the parameter importance for S-series substrate was P(1.2615) > R(1.0170) > t(0.9309), while the parameter importance for G-series became P(1.0509) < R(1.1005) < t(3.2722). The reverse effect can be said that power was more important for silicone substrate and operating time was more significant for glass substrate.



Figure 7. SEM photographs for the deposition of cerium oxide onto Si substrates showing the effect of process parameters.



Figure 8. SEM photographs for the deposition of cerium oxide onto glass substrates showing the effect of deposition time.



Figure 9. Film thickness of CeO_2 onto Si substrates increase with time.



Figure 10. Film thickness of CeO₂ onto glass substrates increase with time.



Figure 11. A plot of calculated value versus measured value for H, showing the confidence for both.

4. Conclusion

CeO₂ films were deposited onto silicon and glass substrates at room temperature by RF sputtering under various operating conditions. The CeO₂ films deposited on both glass and silicon substrates were physically stable and showed excellent adhesion. Regardless of substrate type, deposition time, Ar/O₂ ratio, or sputtering power, the deposited CeO_2 films showed a preferred orientation in (111) and (400) faces. Adopting the Scherrer formula with XRD data revealed that the crystal size obtained was tens of nanometers. The grain sizes estimated by the SEM imaging analysis technique compared with the crystal size obtained from XRD data revealed the agglomeration phenomena of CeO₂ nanocrystals. The SEM images indicate that the grain size became smaller with increased film thickness, as explained by the Gibbs-Thomson theory. The regression analysis found that crystal size increases with sputtering power and decreases with deposition time and Ar/O₂ ratio. The sputtering power is a more significant parameter. In addition, deposition time and Ar/O₂ ratio both have a litter effect on the thickness of S-series but the thickness is strongly affected by the sputtering power. On the other hand, the deposition time has a significant effect on the film thickness of G-series.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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