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Deposition and x-ray photoelectron spectroscopy studies on sputtered cerium dioxide thin films

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Cerium dioxide is a rare earth oxide material that can be useful in various optical and electronic applications because of its high refractive index and its dielectric constant. The purpose of this study was to conduct an x-ray photoelectron spectroscopy analysis of sputtered cerium dioxide thin films. The thin films were deposited onto glass substrates using rf magnetron sputtering. A cerium dioxide target was used and various oxygen–argon gas flow ratios under different sputtering power levels were used for deposition. The results presented here characterize the properties of the rf sputtered cerium dioxide thin films under different deposition conditions. © 1997 American Vacuum Society. [S0734-2101(97)02001-0]

I. INTRODUCTION

Rare earth oxides are potentially useful materials for various optical and electronic applications such as optical waveguides, optical filters, and capacitors. One such material is cerium dioxide (CeO_2) and cerium dioxide thin films have been investigated by many researchers. Thin films of CeO_2 have been used in single layer and multilayer optical coatings and are also used for energy related applications.^{1–3} CeO_2 was used as a gate insulator for enhancement type n -channel metal–oxide–semiconductor transistors.⁴ Having a large dielectric constant (~ 26), CeO_2 has the potential for application to stable capacitors with small dimension, as for example, the storage capacitor in the dynamic random access memory devices.⁵ CeO_2 films can be prepared by a variety of techniques. Netterfield *et al.* deposited CeO_2 by an oxygen ion assisted process and investigated its optical properties.² Misiano and Simonetti studied CeO_2 – SiO_2 mixed films using CeO_2 – SiO_2 as source materials in a cosputtering process.¹ The purpose of the cosputtering was to investigate the variation of indices of refraction as widely as possible with the aim of obtaining both homogeneous films with any intermediate index of refraction and inhomogeneous films with predetermined profiles. The sputtering atmosphere was pure argon for all depositions. Greene *et al.* prepared and characterized CeO_2 films through a bias sputtering process using a doped CeO_2 target with 5 mol % Y_2O_3 .⁶ For these also all films were deposited in Ar at a pressure of 20 mTorr. Al-Dhhan *et al.* studied the optical absorption edge in thin amorphous mixed systems of $\text{CeO}_2/\text{SnO}_2$ and $\text{CeO}_2/\text{GeO}_2$.⁷ The mixed oxide films were deposited by the coevaporation process using CeO_2 , SnO_2 , and GeO_2 powder from molybdenum boats. In earlier work, Sundaram *et al.* studied the optimum conditions for CeO_2 films deposited by rf magnetron sputtering in terms of their optical

properties.⁸ The deposition conditions for an oxide film can be optimized in a rf sputtering process by changing the partial pressure of argon and oxygen. The partial pressure of oxygen has a significant impact on the deposition rate as well as on the composition of the film. Hence in the present work, the emphasis was to analyze the composition of the CeO_2 films as a function of oxygen content in the sputtering gas. The CeO_2 was prepared by a rf magnetron sputtering process using a CeO_2 target. The films were deposited at various input sputtering power levels and various oxygen–argon gas flow ratios. The film compositions were analyzed by x-ray photoelectron spectroscopy in terms of deposition parameters.

FIG. 1. Deposition rate of CeO_2 films vs oxygen/argon flow ratios for various input power levels.

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FIG. 2. Typical XPS spectrum of CeO_2 film on glass.

II. EXPERIMENT

The cerium dioxide (CeO_2) films were deposited in a cryopumped vacuum system containing a water-cooled rf magnetron sputtering gun (US Gun II), operating at 13.56 MHz. A 5-cm-diam pressed cerium dioxide target (99.99% purity, Cerac Inc.) was used for deposition. The target to substrate distance was 3.2 cm and was kept fixed at this distance for all depositions. The system also had a manually operated shutter between the target and the substrate holder. Before each deposition the target was presputtered using the shutter for 15 min to remove any contamination on the surface of the target. The system was initially pumped to 1×10^{-6} Torr. The pressure during sputtering was maintained at 3×10^{-2} Torr by adjusting the argon and oxygen flows in the system. The flow rates of argon and oxygen were measured using gas flow meters. The depositions were carried out for various argon-oxygen flow ratios. Even though the films were deposited without any substrate heating, substrate temperatures in the range of 80–140 °C were attained for various input power levels and sputtering durations. In order to keep the temperature as stable as possible, a metal block was placed on the back of the substrate to act as a heat sink. The temperature was measured with a *J*-type (iron-Constantan) thermocouple paced between the substrate and the metal block. The films were deposited onto cleaned glass substrates 2.5 cm $\times$ 7.5 cm (Corning 2947) at three input power levels, namely, 100, 150, and 200 W, with the reflected power adjusted to zero at all times by tuning. The typical durations for sputtering ranged from 45 to 90 min.

The thicknesses of the deposited films were measured using the standard optical interferometer technique (Bausch & Lomb, interferometer model 31-1871). Occasionally, the thickness measured by the interferometer technique was also checked for accuracy with measurements using a Tencor Alpha Step 200. The average deposition rate was calculated by dividing the measured thickness by the sputtering time. The chemical surface analysis of the films was done using an

x-ray photoelectron spectrometer (XPS) (Kratos XSAM 800). Mg *K α* x rays of 12 kV and 15 mA were used for analysis. The films were sputter etched for periods ranging from 2 to 5 min to a depth of nearly 5 nm and surface analysis was performed. The samples were etched using an argon ion beam. The argon pressure was 5×10^{-5} Torr inside a differentially pumped ion gun. The following ion gun parameters were used during etching: ion beam energy 3 keV, electron energy 150 eV, emission current 15 mA, and filament current 2.1 A.

III. RESULTS AND DISCUSSION

A. Deposition rates

The deposition was uniform within a circular area of 4 cm in diameter on the substrate. All the thickness measurements were carried out in this uniform area. Figure 1 shows the deposition rates (*d*) of CeO_2 films as a function of O_2/Ar flow ratios for various sputtering power levels. All the depo-

TABLE I. Typical binding energies for CeO_2 films.

Peak	Binding energy (eV)
Ce $3d_{5/2}$ principal	881.2
Satellite 1	883.8
Ce $3d_{3/2}$ principal	899.5
Satellite 1	897.5
Satellite 2	902.5
Satellite 3	915.8
O 1s	529.2
C 1s	284.7
Ce 4p	219.2
Ce 4d	112.0

FIG. 3. Typical C 1s spectra for as-deposited film compared with a 10 min argon etched film.

FIG. 4. XPS high resolution of the O 1s peak of the CeO_2 film.

FIG. 5. O 1s spectra for an as-deposited film compared to an 8 min sputter etched film.

FIG. 6. XPS high resolution spectrum of the Ce 3d peak of the CeO₂ film.

sition rates peaked at a near O₂/Ar ratio of 0.8. Beyond this ratio, d decreased. Generally, for higher power levels and an increase in O₂/Ar ratio, there is a decrease in d . This may be due to the following reasons. At higher power levels a considerable number of negative ions is formed at the target during the sputtering process. These negative ions achieve energy levels similar to those of Ar ions after being accelerated through the cathode dark space. The high energy negative ions rapidly lose the extra electron upon entering the plasma and bombard the substrate film as energetic neutral particles. Oxygen provides an abundant species causing ion bombardment with the negative ion yield being a function of oxygen partial pressure in the sputtering chamber. Further, oxygen has a lower sputtering yield of Ce in the CeO₂ target than the (Ar) plasma species. The deposition rate for the films ranged from 2 to 8 nm/min depending on the deposition conditions.

B. XPS studies

Figure 2 shows the surface spectrum of a typical CeO₂ film on glass as deposited. Peaks due to Ce 3d, Ce 4p, Ce 4d, O 1s, and C 1s were observed. The principal binding energies of the peaks observed are listed in Table I. The carbon peak at 284.7 eV is probably due to air exposure. Figure 3 shows high resolution XPS spectra of the carbon peak before etching and after a 10 min argon etch. The intensity of carbon peak decreased considerably after argon etching. The carbon peak consisted of two components. The peak at 284.7 corresponds to graphite or ambient hydrocarbon deposits. A second smaller peak at 290 eV corresponds to ambient deposited CO.

A typical high resolution XPS spectrum of the O 1s region is shown in Fig. 4. The principal binding energies of the peaks observed are listed in Table I. The peak position of the

FIG. 7. Ce 3d spectra for an as-deposited film compared to an 8 min sputter etched film.

O 1s around 529.2 eV is characteristic of metallic oxides. A slight shoulder was observed (Fig. 4) on the high energy side for the O 1s peak for all the samples and this appears to be due to chemisorbed oxygen.⁹ This shoulder due to chemisorbed surface oxides is very dominant as seen in the high resolution spectra of O 1s for an as-deposited film compared to a film sputter etched for 8 min shown in Fig. 5. The O 1s peak positions ranged from 528.6 to 529.2 eV. Cerium forms two oxides, namely, CeO₂ and Ce₂O₃, with O 1s peaks at 529.2 eV for CeO₂ and at 530.3 eV for Ce₂O₃, respectively.¹⁰ The films deposited at 100 W input sputtering power and below a 0.4 O₂/Ar ratio showed the O 1s peak between 528.9 and 529.2 eV, which suggests the presence of CeO₂.

Figure 6 shows the Ce 3d_{5/2,3/2} spectrum of the film exhibiting two prominent peaks at 881.2 and 899.5 eV. These lines represent the 3d_{5/2} and 3d_{3/2} lines, respectively, with a spin-orbit splitting of 18.3 eV. These values are close to one given for CeO₂.¹¹ The three satellite lines at 883.8, 897.5, and 902.5 eV can be assigned as "shake-down" satellites, while the line at 915.8 eV is due to a small cerium (IV) impurity in the sample.^{11,12} All the films except the one deposited with zero O₂/Ar ratio showed Ce 3d_{5/2} peaks between 881.0 and 881.7 eV that corresponded to CeO₂.⁹ The Ce 3d_{5/2} peaks for films deposited at zero O₂/Ar ratio showed between 882.3 and 883.4 eV indicating that they were oxygen deficient films since pure Ce has a 3d_{5/2} peak at around 883.9.¹³ Once again the surface analysis done after etching the films did not show any significant shift for Ce 3d peaks as can be seen in Fig. 7 where the spectra of an as-deposited film are compared to a sample sputter etched for 8 min.

IV. CONCLUSION

CeO₂ films were deposited by a rf sputtering process using a cerium dioxide target and were characterized using

XPS for different deposition conditions. An optimum oxygen/argon gas flow ratio of 0.8 was found to give the highest deposition rate for the films at various sputtering power levels. The XPS analysis indicated that the films deposited without oxygen yielded mixed oxides of cerium. Cerium and cerium oxides are very complex systems due to having several satellite peaks. It was seen that the binding energy for the Ce element peak (884 eV) is the same as the Ce 3d satellite of CeO₂.

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