Microstructure and optical properties of scandium oxide thin films prepared by metalorganic chemical-vapor deposition

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(Received 27 August 2001; accepted for publication 11 October 2001)

Dense, high-index, and reproducible scandium oxide (Sc$_2$O$_3$) thin films with high mechanical strength were grown on glass substrates by metalorganic chemical-vapor deposition. The influence of deposition temperature on the microstructure evolution and optical properties of Sc$_2$O$_3$ thin films was investigated by x-ray diffraction, scanning electron microscopy, atomic-force microscopy, transmission electron microscopy, and spectrophotometry. A close relationship between microstructure and optical properties was found for Sc$_2$O$_3$ thin films prepared at different deposition temperatures. © 2001 American Institute of Physics. [DOI: 10.1063/1.1424072]

Scandium oxide (Sc$_2$O$_3$), among the high-index materials in the ultraviolet (UV) spectral range is a promising material for laser optical coatings, due to its relatively high damage threshold.1–6 It was first reported by Heitmann that Sc$_2$O$_3$ has a suitable refractive index for antireflection (AR) coating on GaAs.1 Excellent coatings for superluminescent light-emitting diodes were obtained by Ladany et al. using Sc$_2$O$_3$.2 This material has also been used as multilayer high-reflection and AR coatings with a refractive index of 2.11 at 248 nm for UV laser applications.3–6 In early studies, Sc$_2$O$_3$ coatings were vacuum deposited with an electron-beam gun at a substrate temperature of 150–250 °C. Films prepared by this process in different laboratories had different optical behaviors.7 More recently, Sc$_2$O$_3$ porous xerogel optical coatings were produced on fused silica substrates by sol-gel chemistry. As shown by UV transmission experiments, these films exhibited a good transparency to UV radiation and a refractive index of 1.84 (at 330 nm) when calcined at 500 °C.8 This refractive index is lower than that of bulk Sc$_2$O$_3$ (2.0 at 350 nm).9

Optical coating applications require deposition of dense, homogeneous, and reproducible thin films with high-quality optical and mechanical properties. Metalorganic chemical-vapor deposition (MOCVD) offers excellent film uniformity, compositional control, high film densities, high deposition rates, and reproducibility. However, MOCVD has not been applied to Sc$_2$O$_3$ coatings. The primary purpose of this study is to use the MOCVD technique to produce high-quality and reproducible Sc$_2$O$_3$ thin films on Corning 7059 glass. While the optical behavior of Sc$_2$O$_3$ thin films is well known, less attention has been paid to the relationship between microstructure and optical properties. In this study, the effect of microstructure on the optical properties of Sc$_2$O$_3$ thin films was investigated as a function of deposition temperature. It is expected that this study might lead to a better understanding of the processing–structure–property relationships of Sc$_2$O$_3$ thin films for optical coating applications.

The deposition of the films was carried out using a cold-wall, horizontal, low-pressure MOCVD system equipped with a resistive substrate heater.10 Commercially available scandium tetra-methyl heptanediol Sc(TMHD)$_3$ (Strem Chemicals, Newportbury, MA) was used as the scandium precursor. Sc$_2$O$_3$ thin films were grown on Corning 7059 glass at different temperatures (450–600 °C) for 90 min.11 All samples were characterized by using x-ray diffraction (XRD) (Rigaku D-Max) for phase identification. A Hitachi S-4700 field-emission scanning electron microscope (SEM) was used to examine the surface morphology and grain size. A Dimension 3000 atomic-force microscope (AFM) was used for imaging of the surface topology and measurement of surface roughness. Transmission electron microscopy (TEM) was performed using a Phillips CM-12 to examine the chemical homogeneity, grain size, and crystal structure. Film hardness was measured using a Berkovich nanindenter. Optical transmittance was measured using a Cary 5G spectrophotometer from 200 to 1800 nm.

Figure 1 shows XRD patterns of Sc$_2$O$_3$ thin films as a function of deposition temperature. The films grown at 450 °C or below are still amorphous. Sc$_2$O$_3$ started to crystallize at 500 °C and was fully developed at 600 °C. No other second phases were detected and the 2θ positions of each reflection match those of cubic Sc$_2$O$_3$ (a=9.845 Å) from JCPDS file 5-629. Figure 2 illustrates the evolution of the

FIG. 1. XRD patterns of Sc$_2$O$_3$ thin films grown at different temperatures.
microstructure, as observed from the surfaces of films deposited at different temperatures, in the SEM. The film grown at 450 °C was dense, smooth, and almost featureless [Fig. 2(a)]. As the growth temperature increased, the films crystallized into a nanocrystalline Sc$_2$O$_3$. The average grain size increased from ~20 nm at 500 °C to ~50 nm at 600 °C. In addition, the film grown at 500 °C shows uniform round grain morphology, while the film grown at 600 °C became irregular and more faceted. SEM examination of a cross section of Sc$_2$O$_3$ thin films indicated that all films have a similar thickness of ~2000 Å and a dense fine grain nanostructure through thickness. The surface topography of the films was further examined by AFM. The surface of film deposited at 450 °C is featureless [similar to Fig. 2(a)] and smooth with a rms surface roughness value of 1.054 nm. As the deposition temperature increased, the surface roughness increased as the films crystallized and the grains grew larger. Films grown at 500, 550, and 600 °C have rms surface roughness values of 2.649, 7.208, and 16.40 nm, respectively.

The TEM images in Fig. 3 reveal details of the fine grain nanostructure of a Sc$_2$O$_3$ thin film grown at 550 °C. Figure 3(a) is a bright-field image, which shows that the average grain size was ~30 nm and the film was dense. Similar TEM images were obtained from films grown at higher temperature except that the grain size was found to increase with increasing deposition temperature. The diffraction rings in a typical selected-area electron diffraction pattern of Sc$_2$O$_3$ films [Fig. 3(b)] can be indexed in terms of cubic Sc$_2$O$_3$ with $a=9.845$ Å and the four rings are due to (222), (400), (440), and (622) diffractions, respectively. The TEM results are consistent with the XRD and SEM results. No chemical inhomogeneities were detected in the films by energy-dispersive x-ray spectroscopy, indicating the uniform chemical composition of the Sc$_2$O$_3$ thin films prepared by MOCVD in this work.

Optical transmission spectra of Sc$_2$O$_3$ thin films grown at different temperatures are shown in Fig. 4. All films had a similar thickness of ~2000 Å measured by SEM. Transmittance of films decreases slightly with increasing deposition temperature. The Sc$_2$O$_3$ films grown at 450 °C have the highest transmittance values and the transmittance of these films in the visible spectrum is about 90%. Previous XRD results indicated that the films grown at 450 °C are amorphous. In addition, both SEM and AFM images showed that the surface of amorphous films was very smooth. Therefore, light scattering from amorphous materials with a smooth surface is small, which leads to high transmittance. On the other hand, crystallization of amorphous layers leads to increased surface roughness, which increased with increasing deposition temperature, as revealed by the AFM results. Increased scatter loss due to the rougher surface leads to reduction of the transmittance of films as the deposition temperature increases.

Modeling work was done to obtain the index of refraction of the Sc$_2$O$_3$ thin films [using the WVASE 32 software by J.A. Woollam Co, Inc. (1997)]. The data in Fig. 4 were fit to Cauchy's dispersion equation and the results are given in Fig. 5, which shows the index of refraction of the Sc$_2$O$_3$ thin films grown at different temperatures as a function of the wavelength of light. The refraction index was found to increase slightly with increasing deposition temperature and
ranges from 1.9 at 1200 nm to 2.15 at 300 nm, which are similar to those reported by Arndt et al.\textsuperscript{7} The films grown at 600 °C have the highest index while the films grown at 450 °C have the lowest index. This might be related to the increase of film density with increasing deposition temperature and the refractive index of films increases as the film density increases.\textsuperscript{13} Other systems such as TiO\textsubscript{2} and CeO\textsubscript{2} also showed a similar trend between refractive indexes and deposition temperature.\textsuperscript{14,15} In addition, a slight increase of refractive index with increasing grain size was reported in ion-assisted HfO\textsubscript{2} thin films.\textsuperscript{16} The grain sizes of Sc\textsubscript{2}O\textsubscript{3} thin films in this study increased from \(20\) to \(50\) nm as the deposition temperature increased from 500 to 600 °C. Not only do the Sc\textsubscript{2}O\textsubscript{3} thin films grown by MOCVD in this work have high refractive indices, but these films also display good mechanical properties. Hardness measurements of Sc\textsubscript{2}O\textsubscript{3} thin films revealed that the hardness of the films increases as the deposition temperature increases. Sc\textsubscript{2}O\textsubscript{3} films grown at 450 °C have a hardness value of 8.3 GPa and films grown at 600 °C have a hardness value of 11.4 GPa. The latter value is higher than that of transparent bulk Sc\textsubscript{2}O\textsubscript{3} (8.92 GPa),\textsuperscript{17} indicating that the Sc\textsubscript{2}O\textsubscript{3} films have high mechanical strength.

In summary, dense, high refractive index, and reproducible Sc\textsubscript{2}O\textsubscript{3} thin films with high mechanical strength were grown on Corning 7059 glass by MOCVD. The microstructure and properties of the films were strongly dependent on deposition temperature. Films grown below 450 °C are amorphous with a very smooth surface and higher transmittance, but have lower refractive index and hardness. Nanocrystalline films were grown at \(T>500\) °C. Crystallinity, grain size, and surface roughness were found to increase with increasing deposition temperature. Nanocrystalline films have lower transmittance, but higher refractive index and hardness.

This work was supported by the U.S. Department of Energy through Grant No. DEFG02-96ER45439. Two of the authors (Z. X. and H. C.) would like to acknowledge a grant (No. 9380015) from the City University of Hong Kong for completing the analysis and the manuscript.

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