Characterization of MOCVD grown optical coatings of Sc$_2$O$_3$ and Ta-doped SnO$_2$

S.W. Lee$^a$, A. Daga$^a$, Z.K. Xu$^b$, Haydn Chen$^{a,b, *}$

$^a$Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, USA
$^b$Department of Physics and Materials Science, City University of Hong Kong, 83 Tai Chen Avenue, Kowloon, Hong Kong

Accepted 16 October 2002

Abstract

MOCVD method has been used to grow optical coatings: Sc$_2$O$_3$ is a high index transparent coating while Ta-doped SnO$_2$ is a transparent conductive oxide. Both films show dense packing and excellent properties. The influence of deposition temperature on the microstructure evolution and optical properties of Sc$_2$O$_3$ films was investigated by X-ray diffraction, scanning electron microscopy and spectrophotometry. Nanocrystalline films were obtained with low transmittance but high refractive index and hardness. Ta-doped SnO$_2$ films showed sharp change of conductivity with Ta doping, which is attributed to the increase of electron carrier concentration. Improved crystallinity contributes to the improvement in the mobility among doped samples. Microstructural evaluation and property relationships are discussed.

Keywords: MOCVD; Sc$_2$O$_3$; Ta-doped SnO$_2$

1. Introduction

Optically transparent coatings have seen a wide range of applications. In some cases high conductivity is required such as display panel, solar cell windows, transparent conducting electrode (TCE), etc. In other cases high refraction index is desirable such as for laser optical coatings with high damage threshold. Heitmann [1] reported that Sc$_2$O$_3$ has the suitable refractive index as antireflection (AR) coating on GaAs. Ladany et al. [2] obtained excellent coatings for superluminescent LEDs using Sc$_2$O$_3$. This material has also been used as multiplayer high-reflection (HR) and AR coatings with a refractive index of 2.11 at 248 nm for UV laser applications [3–6].

SnO$_2$ is an n-type wide band gap semiconductor where inherent oxygen vacancies act as an n-type dopant [7–9]. The most notable applications are for sensors and TCE. For sensor applications, porous and fine-grained SnO$_2$ particles are necessary to enable sensitivity. For TCE application, SnO$_2$ is usually doped with a small amount of Sb or F to increase the electrical conductivity. There also exist a variety of other transparent conducting oxides (TCO) such as doped In$_2$O$_3$, ZnO, or CdO. Among these, Sn-doped In$_2$O$_3$ (ITO) is most widely used. However, ITO seems to have reached its maximum capability in high-density applications. Thus, attempts to explore new material systems such as, GaInO$_3$ [10], AgInO$_2$ [11] and ZnO–In$_2$O$_3$–SnO$_2$ [12] have been made, but with limited success in property improvement.

In this article we present our recent progress in the metal organic chemical vapor deposition (MOCVD) growth of two oxide based optical coatings: Sc$_2$O$_3$ as a laser optical coating and Ta-doped SnO$_2$ as a TCE film. Readers may refer to the following publications for more detailed description of results: Sc$_2$O$_3$ films by Xu et al. [12] and Ta-doped SnO$_2$ film by Lee et al. [13].
2. Experimental methods

Novel optical coating applications require deposition of dense, homogeneous and reproducible thin films with high quality optical and mechanical properties. MOCVD offers excellent film uniformity, compositional control, high film densities, high deposition rates, and reproducibility. MOCVD technique was used to produce high quality \( \text{Sc}_2\text{O}_3 \) and Ta-doped \( \text{SnO}_2 \) thin films on Corning 7059 glass substrates. The MOCVD system used belongs a cold-wall, horizontal, low-pressure type. Commercially available tin-tetra-butoxide, \( \text{Sn} \left( \text{OC}_4\text{H}_9 \right) _4 \), tantalum-ethoxide, \( \text{Ta} \left( \text{OC}_2\text{H}_5 \right) _5 \), and scandium tetramethyl heptanedione \( \text{Sc} \left( \text{TMHD} \right) _3 \) were used as the organometallic (OM) precursor sources. Ultra high purity (UHP) \( \text{O}_2 \) was used as the oxidant, with OM precursors transported by UHP \( \text{N}_2 \) as the carrier gas.

Thin films of approximately 200 nm were grown at different temperatures \( (450\text{–}600 \, ^\circ\text{C}) \). The operating vacuum during deposition was about 10 torr. The deposition rate was about \( 3\text{–}4 \, \text{nm min}^{-1} \). All samples were characterized by XRD for phase identification. A field emission SEM was used to examine the surface morphology and grain size. TEM was performed to examine the chemical homogeneity, grain size and crystal structure. Film hardness was measured using a Berkovich nanoindenter. Optical transmittance was measured using a Cary 5G spectrophotometer from 200 to 1800 nm. Film resistivity was determined by a four-point probe method. The Ta concentration in \( \text{SnO}_2 \) was determined by a combination of Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry. The carrier concentration was determined by Hall measurement under 4.5 T with 0.1 mA. The temperature range of the measurements was between 10 and 300 K.

3. Results and discussion

Optical properties in terms of the transmittance versus wavelength for the \( \text{Sc}_2\text{O}_3 \) and Ta-doped \( \text{SnO}_2 \) films are shown in Fig. 1(a and b), respectively. Transmittance of \( \text{Sc}_2\text{O}_3 \) films decreases slightly with increasing deposition temperature, with films grown at 450 \( ^\circ\text{C} \) exhibiting the highest transmittance values of about 90\% in the visible spectrum. For Ta-doped \( \text{SnO}_2 \) films, transmittance shows some variation with Ta content with an average transmittance in the visible spectrum being around 85\%.

Both types of films achieve excellent transparency comparable, if not superior, to reported data in other transparent oxide coatings of similar thickness.

As a TCO, low resistivity is required besides high optical transparency. For Ta-doped \( \text{SnO}_2 \), resistivity shows a strong dependence on the Ta content (Fig. 2) with an apparent minimum appearing near \( C_{\text{Ta}} = 3.6 \) (\( C_{\text{Ta}} \) is defined as a ratio of \( X_{\text{Ta}} \) to \( \left( X_{\text{Ta}} + X_{\text{Sn}} \right) \), where \( X_i \) is the atomic fraction of the \( i \)-th species.). The lowest measured resistivity is about \( 2 \times 10^{-4} \ \Omega\cdot\text{cm} \). It is perceived that an even lower resistivity, down to about \( 1 \times 10^{-4} \ \Omega\cdot\text{cm} \), could be reached at \( C_{\text{Ta}} \sim 2 \). The resistivity behavior shown in Fig. 2 can be understood because intrinsic \( \text{SnO}_2 \) is an n-type semiconductor due...
to the presence of oxygen vacancies. Addition of smaller amount of Ta, which is of group VB, increases electron carrier density as clearly shown in Fig. 2, so that conductivity is raised. However, further increase in Ta doping would eventually cause electron scattering effect from Ta substitutional atoms to a level that would impede electron mobility as shown in Fig. 2, so that conductivity begins to decrease.

Ta-doped SnO\textsubscript{2} films as prepared by MOCVD have shown good optical and electrical quality to become a promising alternative TCO to the exiting variations. Development of these films was based upon two criteria from which Ta was chosen as dopant. The first criterion concerns primarily with the electrical property, for which n-type doing is needed because of the intrinsic n-type semiconductor properties of SnO\textsubscript{2}. This led us to consider elements in group V, VI and VII because Sn exists as Sn\textsuperscript{4+} in SnO\textsubscript{2}. The second criterion applies to the crystallinity and grain sizes. To maintain a homogeneous substitution of dopant for Sn, it would be desirable to have the ionic radius of the substitutional atom close to that of Sn\textsuperscript{4+}. Ta\textsuperscript{5+} is about 0.68 nm as compared with 0.71 nm for Sn\textsuperscript{4+}.

The Sc\textsubscript{2}O\textsubscript{3} films grown at 450 °C have the highest transmittance values. XRD results indicate that those films are amorphous (Fig. 3) with smooth surfaces as revealed by both SEM and AFM. Therefore, light scattering from amorphous film with a smooth surface is small, which leads to high transmittance. On the other hand, crystallization of amorphous layers leads to an increased surface roughness, which in turn gave rise to a decreased light transmittance. Moreover, with increasing deposition temperature, films showed increased surface roughness as revealed by AFM results, thereby leading to a reduction of optical transmittance.

Fig. 4 shows the index of refraction of Sc\textsubscript{2}O\textsubscript{3} thin films grown at different temperatures as a function of 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. 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. Moreover, a slight increase of refractive index with increasing grain size is also noted.

Not only the Sc\textsubscript{2}O\textsubscript{3} thin films grown by MOCVD in this work have high refractive indices, they also display some good mechanical property also. Hardness measurements of Sc\textsubscript{2}O\textsubscript{3} thin films revealed that the hardness increases as deposition temperature increases (Fig. 5). The Sc\textsubscript{2}O\textsubscript{3} films grown at 450 °C have a hardness value of 8.3 GPa and the 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).

---

**Fig. 3.** Room temperature X-ray diffraction pattern taken for Sc\textsubscript{2}O\textsubscript{3} films after heat treatment at various temperatures for 30 min.

**Fig. 4.** Refraction index vs. wavelength for Sc\textsubscript{2}O\textsubscript{3} films undergone heat treatment at various temperatures.

**Fig. 5.** Hardness values vs. heat treatment temperature for Sc\textsubscript{2}O\textsubscript{3} films of approximately 200 nm thicknesses.
4. Summary

It is demonstrated that high quality optical coatings can be obtained using MOCVD techniques. Dense packing and smooth surfaces are important to the good optical quality of the coatings, as well as the grain size and degree of crystallinity. Sc$_2$O$_3$ films show a light transmittance greater than 85% in the visible spectrum, whereas an as high as 90% transmittance was achieved for Ta-doped SnO$_2$. Sc$_2$O$_3$ films are hard and exhibiting high refraction index. Ta-doped SnO$_2$ can also reach a resistivity level as low as in the range of $1 \times 10^{-4}$ Ω-cm.

Acknowledgements

This work was primarily supported by the US Department of Energy Grant No. DEFG02-96ER45439 through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign. Additional support was provided by the City University of Hong Kong (No. 9380015) for Xu and Chen to complete the analysis and the manuscript.

References