Point defects in Sc$_2$O$_3$ thin films by ion beam sputtering


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We show that the concentration of oxygen interstitials trapped in Sc$_2$O$_3$ films by ion beam sputtering from metal targets can be controlled by modifying deposition conditions. We have identified point defects in the form of oxygen interstitials that are present in Sc$_2$O$_3$ films, in significantly high concentrations, i.e., $\sim 10^{18}$ cm$^{-3}$. These results show a correlation between the increase of oxygen interstitials and the increase in stress and optical absorption in the films. Sc$_2$O$_3$ films with the lowest stress and optical absorption loss at 1 $\mu$m wavelength were obtained when using a low oxygen partial pressure and low beam voltage. © 2014 Optical Society of America

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1. Introduction

Sc$_2$O$_3$ is a transparent dielectric with a bandgap of $\sim$6 eV, and a refractive index of $\sim$2 at wavelengths around 1 $\mu$m [1]. For these characteristics, it is sought as the high index component of dielectric coatings operating at wavelengths ranging from the ultraviolet (UV) to the mid-infrared. Sc$_2$O$_3$ has been used in the fabrication of quarter-wave stacks and antireflection coatings in combination with SiO$_2$ and MgF$_2$ for UV applications [2]. Due to its high permittivity, Sc$_2$O$_3$ is also a candidate for replacement of SiO$_2$ as a gate oxide. Wang et al. [3] recently employed atomic layer deposition (ALD) to deposit Sc$_2$O$_3$ on AlGaN/GaN devices to achieve good electrical properties for transistor operation. However, ALD Sc$_2$O$_3$ was found to be sensitive to moisture and an Al$_2$O$_3$ blocking layer was required. Mixed oxides that incorporate Sc$_2$O$_3$ have now been reported. Yakovkina et al. [4] synthesized (HfO$_2$)$_{1-x}$(Sc$_2$O$_3$)$_x$ alloys as a replacement for the SiO$_2$ in metal–insulator–semiconductor devices. The authors found that chemical vapor deposition (CVD) of Hf–Sc–O films within a narrow range of Sc concentrations produced high permittivity and low current leakage, $\sim 10^{-8}$ A/cm$^2$, films. Sc$_2$O$_3$/SiO$_2$ mixed oxide films deposited by ion beam sputtering (IBS) have also been reported [5]. This work used oxide targets to produce amorphous films ranging from pure SiO$_2$ to Sc$_2$O$_3$. Investigations of the laser damage behavior showed that in the nanosecond pulse regime, the laser damage was governed by defect density and showed a large difference between Sc$_2$O$_3$ and SiO$_2$. In contrast, in the short pulse regime, laser damage behavior was found to be independent of composition [5].

In this work we describe a study of the optical and structural properties of amorphous Sc$_2$O$_3$ thin films deposited by IBS. In contrast to a recent report by
Mende et al. [5], we employ a Sc metal target to deposit the Sc$_2$O$_3$ oxide film [6,7]. Among the advantages of using metal targets is the ability to tailor process parameters such as oxygen partial pressure and ion beam energy. A main objective of this work has been to identify modifications in the Sc$_2$O$_3$ structural and optical properties that are linked with the deposition process parameters. The results show that point defects in the form of oxygen interstitials are present in Sc$_2$O$_3$ films in significantly high concentrations, i.e., ~10$^{18}$ cm$^{-3}$. The density of these defects varies with deposition conditions. The results show a correlation between the increase of oxygen interstitials and the increase in stress and absorption in the films. Sc$_2$O$_3$ films with the lowest stress and absorption loss at $\lambda = 1$ $\mu$m were obtained when using a low oxygen partial pressure and low beam voltage. Under these conditions, the density of the oxygen interstitials in the as-deposited Sc$_2$O$_3$ films is minimized.

2. Experimental

Thin films of Sc$_2$O$_3$ were grown by IBS using a Veeco Spector. In one set of runs the beam voltage of the main Ar sputtering source was set equal to 1250 V, the current was 600 mA, and the variable was the oxygen partial pressure. The O$_2$ partial pressure was varied from 2 to 40 $\mu$Torr. In a second set, the oxygen partial pressure was constant at 3 $\mu$Torr and the energy of the Ar sputtering ions was varied between 600 and 1250 eV. The target was Sc metal with 99.9% purity and Ta impurity of <0.05%. Sc$_2$O$_3$ single layers were grown on fused silica substrates with a surface roughness of 0.6 nm. The surface roughness was measured to be ~0.6 nm from scans obtained using a NovaScan ESPM 3D atomic force microscope (AFM) operated in tapping mode with a 5 $\mu$m x 5 $\mu$m scan area.

Glancing angle x-ray diffraction (GAXRD) and x-ray photoelectron spectroscopy (XPS) measurements were carried out to determine the degree of crystallinity and the composition of these films, respectively. The thicknesses and optical constants of the transparent films were determined using a combination of transmission and ellipsometric data. Deposited films had nearly constant thicknesses, (205 ± 7) nm, and were transparent. The refractive indices of all films at $\lambda = 1$ $\mu$m, extracted from ellipsometric measurements, were equal to 2. The magnitude and sign of the stress in the Sc$_2$O$_3$ films, grown on 1 mm thick fused silica substrates, were determined using a Twyman–Green interferometer. Fits of five phase-shifted interference patterns to Zernike polynomials were used to determine the radius of curvature of the film-substrate structure. Stress was calculated from the inverse of the radius of curvature [3]. The optical absorption of the films was measured at two different wavelengths, $\lambda = 1.064$ $\mu$m and $\lambda = 0.514$ $\mu$m, using the photothermal common-path interferometry (PCI) technique [9]. A pump beam at $\lambda = 1.064$ $\mu$m and $\lambda = 0.514$ $\mu$m was used to excite a thermal response in the coating, respectively, while common-path interference of a HeNe probe beam at $\lambda = 0.633$ $\mu$m allowed for detection of the absorption of the film at each pump wavelength.

Electron paramagnetic resonance (EPR) studies were carried out at room temperature using a Bruker EMX EPR spectrometer with 100 kHz field modulation. Films were deposited on thin fused silica slides and placed in a quartz sample tube. EPR spectra for each deposition condition were taken for nearly equivalent film volumes, in the same cavity, on the same day and with the microwave propagation normal to the film surface. The microwave frequency used to probe the spin populations was 9.6 GHz for the measurements taken. Background spectra confirmed that the bare substrates and quartz sample tube signals were insignificant compared to the signals measured from the Sc$_2$O$_3$ films. This small background signal was subtracted from the scans of the Sc$_2$O$_3$ films. The relative spin concentrations were determined from the relative areas of the absorption signals. The EasySpin MATLAB library was used to fit the spectra to extract a g-tensor [10,11]. (All the analytical tools employed in this report have been detailed elsewhere [10]).

3. Results and Discussion

Figure 1 shows x-ray diffraction (XRD) spectra from the set of films deposited at different oxygen partial pressures in the range of 2–38 $\mu$Torr. The most prominent feature in the XRD spectra is the (222) diffraction peak of the cubic Sc$_2$O$_3$. The films are considered amorphous, as the crystallite size was determined to be ~10 nm based on the full width at half-maximum (FWHM) of the (222) peak compared with the crystalline quartz standard. An increase of the oxygen partial pressure affects the spectra in two ways: the position of the (222) peak shifts toward smaller $\theta$, and the FWHM of the (222) peak increases by approximately 50%. Increases in the FWHM could be due to reduction in the crystallite size, increased stress, or a combination of both. The shift of the diffraction peak toward smaller diffraction angles with increasing oxygen partial pressure indicates a change in the lattice constant that is correlated with increased compressive stress in the films. Analysis of the XRD spectra in the Sc$_2$O$_3$ samples deposited using different beam voltages showed the (222) peak shifted by ~0.1% and broadened by ~10% between 600 and 1000 V. Results from independent stress measurements are shown in Fig. 2. The stress varied from 0.55 to 0.75 GPa when the beam voltage was varied from 600 to 1250 V. The stress in the Sc$_2$O$_3$ films deposited using different oxygen partial pressures varied from 0.77 to 1.3 GPa. Thus, the combination of low oxygen partial pressure and low beam voltage results in Sc$_2$O$_3$ films with the lowest stress.

The Sc$_2$O$_3$ thin films were also characterized by XPS to assess the stoichiometry and bonding
environment. These results showed that the Sc in the IBS Sc$_2$O$_3$ films is in a single binding environment, while analysis of the O1s peak showed the oxygen had more than one signature for all the measured samples, indicating oxygen trapped in the films. The stoichiometry in the films varied from 1.72 to 1.84 for beam voltages of 600–1000 V, respectively. Instead, in the Sc$_2$O$_3$ films deposited using different oxygen partial pressures, the stoichiometry varied from 1.84 to 2.05, showing excess O$_2$ in the films [6]. Figure 3 illustrates the characteristics of the EPR spectra from samples deposited using different oxygen partial pressures. The signal was fitted using the EasySpin EPR MATLAB tool to extract the g-tensor component values, which for the dominant defect are ($g_{xx} = 2.017$, $g_{yy} = 2.017$, $g_{zz} = 2.055$). This g-tensor corresponds to an oxygen interstitial defect [12]. EPR measurements on the samples deposited using beam voltages ranging from 600 to 1250 V produced the same results in terms of the defect characteristics. The density of oxygen interstitials obtained from the spectra in Fig. 3 for the two sets of samples is presented in Table 1. These oxygen interstitial defect densities are 2–5 times lower in the samples deposited at different beam voltages than found in the sample set deposited at different oxygen partial pressures.

Figure 4 plots the absorptivity or absorption coefficient (m$^{-1}$) at $\lambda = 1.064$ μm of the set of samples

![Figure 1](image1.png)

**Fig. 1.** (a) X-ray diffraction spectra of amorphous Sc$_2$O$_3$ for films deposited as a function of oxygen partial pressure. The film obtained at 2 μTorr shows diffraction features of crystalline scandium, and was opaque. All other films instead showed diffraction peaks that are identified with the (222) and (440) peaks of cubic Sc$_2$O$_3$. (b) The FWHM of the (222) peak increases and the peak position decreases to smaller angles with oxygen partial pressure, indicating an increase in the lattice parameter due to increased strain.

![Figure 2](image2.png)

**Fig. 2.** Stress in Sc$_2$O$_3$ films with (a) variation in the beam voltage and (b) variation in the oxygen partial pressure.

![Figure 3](image3.png)

**Fig. 3.** EPR spectra for Sc$_2$O$_3$ films deposited at different oxygen partial pressures. A line shape analysis of the spectra is used to identify the defects and determine their density. An increase in the signal intensity correlates with a larger density of defects.

![Figure 4](image4.png)

**Fig. 4.** Plots the absorptivity or absorption coefficient (m$^{-1}$) at $\lambda = 1.064$ μm of the set of samples
deposited by varying the oxygen partial pressure and beam voltage, respectively. The absorption coefficient increased with oxygen partial pressure by about a factor of $4 \times$, while it only increased by $2 \times$ with an increase in beam voltage. The variation of the absorption coefficient with process parameters correlates well with the variations in the density of oxygen interstitials. The data in Fig. 4 also show the absorptivity of the Sc$_2$O$_3$ films deposited using different oxygen partial pressure with the use of the argon assist source during deposition. We attribute the decrease in absorptivity with the use of the assist source to preferential sputtering of oxygen and associated reduction in the density of oxygen point defects.

The absorptivity of the Sc$_2$O$_3$ films was also measured at $\lambda = 0.514 \, \mu\text{m}$. These results showed the absorptivity to be significantly larger, $\sim 10 \times$, than at $\lambda = 1.064 \, \mu\text{m}$ (Fig. 5). Absorption in the large bandgap Sc$_2$O$_3$ films is due to the presence of trap states. These results suggest the presence of trap states at energies of 1.165 and at 2.412 eV near the band edges. We do not have sufficient information to discern whether these trap states are discrete energy states in k-space or a broad band as the absorption measurements were carried out at discrete wavelengths. Further studies are needed to identify the origin of the defect bands. This behavior is not unique to Sc$_2$O$_3$. We have shown that similar trap levels exist in IBS Ta$_2$O$_5$ and that the population and depopulation of these traps by electrons impacts the absorption of the films [13].

The parameter space in IBS is very broad as there are many degrees of freedom to realize thin films with similar optical and structural properties. In these studies we choose to vary the oxygen partial pressure because this is a critical parameter for reactive sputtering of metal oxides. We choose to vary the beam voltage because it has a direct impact on the energy distribution of the sputtered Sc target neutrals, and on the energy of reflected Ar neutrals [14]. The sputtering rate is also reduced when reducing the beam voltage. An increase of the oxygen partial pressure results in an increase of the oxide-to-metal target coverage and in the oxygen trapped within the growing film [10,15,16]. In both cases we have identified oxygen interstitials as being present. The concentration of oxygen interstitials was found

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<th>Beam Voltage (V)</th>
<th>Defect Density (cm$^{-3}$)</th>
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<tr>
<td>600</td>
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<tr>
<td>800</td>
<td>$2.8 \times 10^{18}$</td>
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<td>1000</td>
<td>$3.8 \times 10^{18}$</td>
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<tr>
<td>1250</td>
<td>$3.4 \times 10^{18}$</td>
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<tr>
<th>Oxygen Partial Pressure (µTorr)</th>
<th>Defect Density (cm$^{-3}$)</th>
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<tr>
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<td>$1.3 \times 10^{18}$</td>
</tr>
<tr>
<td>7</td>
<td>$3.9 \times 10^{18}$</td>
</tr>
<tr>
<td>38</td>
<td>$1.04 \times 10^{19}$</td>
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<tr>
<th>Absorption Coefficient (m$^{-1}$)</th>
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Fig. 4. Absorptivity of amorphous Sc$_2$O$_3$ films deposited using (a) different oxygen partial pressures and (b) different beam voltages. The triangle symbols identify a set of samples grown without use of the assist source. Both sets of data show an increase in absorptivity with oxygen partial pressure. The increase in absorptivity correlates with the increase in the density of oxygen defects.

Fig. 5. Normalized absorptivity for Sc$_2$O$_3$ films at $\lambda = 1064 \, \text{nm}$ and $\lambda = 514 \, \text{nm}$. The data were normalized to the value of the absorptivity at $\lambda = 1064 \, \text{nm}$ for the film deposited at a beam voltage of 1250 V.
to be an order of magnitude lower in the set of Sc$_2$O$_3$ samples deposited using different beam voltages compared with the set of samples deposited using different oxygen partial pressure. The scaling of the absorption and stress in the films with increased oxygen partial pressure suggests that these defects play a role in affecting the optical and mechanical properties of the Sc$_2$O$_3$ thin films.

4. Conclusions
Isolating the role of defects in IBS metal oxide thin films in the optical and mechanical properties of amorphous metal oxides is quite challenging. In this work, we have identified oxygen interstitials. Signatures of these defects were also found in IBS HfO$_2$ and Ta$_2$O$_5$ and were observed to scale with the thickness of the film [13,17]. However, it is possible that other types of defects, such as oxygen vacancies, could be affecting absorption, and stress in the amorphous Sc$_2$O$_3$. In crystalline HfO$_2$, model predictions show there exists a distribution of deep and shallow defect states within the bandgap [18]. Different experiments are required to identify other types of bulk defects. Moreover, the effect of surface and interface defects in the absorption and stress in Sc$_2$O$_3$ amorphous thin films should not be discounted.

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