Morphology and Microstructure of (111) Crystalline CeO₂ Films Grown on Amorphous SiO₂ Substrates by Pulsed-Laser Ablation


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Morphology and Microstructure of (111) Crystalline CeO₂ Films Grown on Amorphous SiO₂ Substrates by Pulsed-Laser Ablation


Abstract

The surface morphology and microstructure of (111)-oriented CeO₂ thin films, grown on amorphous fused silica (SiO₂) substrates by low-energy-ion-beam assisted pulsed laser ablation, have been studied by atomic force microscopy (AFM) and x-ray diffraction (XRD). These CeO₂ films are aligned with respect to a single in-plane axis despite being deposited on an amorphous substrate. There is a honeycomb-like growth morphology to the films and island-growth can be observed in thicker films. These islands, inside of which are high density of honeycomb-like clusters, are separated by a void network with ~700 nm width. However, on the surface of the thinnest film (~3 nm), only very small clusters (diameter <60 nm) appear, and the boundaries of the void network are undefined, which implies that the film is just beginning to coalesce into clusters (grains). The combined AFM images and XRD pattern suggest these clusters probably are the initial seeds for the subsequent island growth. Based on these results, the growth mechanism of oriented CeO₂ films on amorphous fused silica substrates is discussed.

Introduction

It is well known that normal-incidence ion bombardment during thin film growth can be used to modify film structure and properties, such as increasing film density, reducing porosity, enhancing electricity properties, and changing film stress, microstructure, and orientation [1]. Weissmantel was the first to demonstrate this technique in film growth [2]. Since then ion-beam assisted deposition (IBAD) has been widely used and reviewed [11]. Recently, though a new technique of off-axis IBAD has been used to grow oriented thin-film buffer layers on polycrystalline and amorphous substrates [3–6]. These aligned buffer layers have a single crystalline orientation, such as (100) yttria-stabilized-zirconia (YSZ), or (100) and (111) CeO₂, which can be used as a transition buffer layer from a polycrystalline or amorphous substrate to an epitaxial overlayer. Using scanning tunneling microscopy (STM), Chatterjee et al recently, observed a planarlike surface morphology for 9 nm thick YBa₂Cu₃O₇₋ₓ films on an oriented YSZ buffer layer grown by modified biased sputtering [7]. The well textured YSZ film had the same surface structure as a single crystalline substrate. Both YSZ and CeO₂ have potential as a transition layer for growing superconducting thin films. However, since the quality of a thin-film buffer layer directly affects the properties of desired upper-layer films, it is important to study the crystallinity, microstructure, and morphology of IBAD thin films.

The structure zone model (SZM) has been used to classify the surface morphology of thin films deposited by various growth techniques, and many experimental and theoretical studies have been used this model [8–10]. Using vapor-deposition or electrodeposition with ion bombardment, Thornton extended the SZM to bombardment-induced mobility effects on film growth [9]. Messier et. al. found columnar growth features with five distinct levels of surface physical structure after examining the surface morphology of ion-bombarded amorphous Si films [10]. Although the microstructure and morphology have been investigated for both ion-
bombarded and non-bombarded films of various materials deposited by different techniques, the microstructure and surface morphology of a crystalline film grown on amorphous substrate by ion-beam assisted pulsed-laser deposition (IBAPLD) are reported here for the first time.

**EXPERIMENTAL CONDITIONS**

The details of CeO₂ thin film growth on amorphous SiO₂ substrates by IBAPLD were described in a previous paper [5]. A KrF (248 nm, ~46 ns FWHM) pulsed laser was used to ablate a commercial CeO₂ target [11]. at an energy density ~1.5 - 2 J/cm². According to the previous studies, [5] (111)-oriented crystalline CeO₂ films were found to grow on an amorphous substrate at high temperature and low oxygen pressure. Therefore, films for this study were deposited at 750°C heater temperature and 5 × 10⁻⁵ Torr oxygen pressure. Ar⁺ ions generated by a secondary rf ion source [12], incident at ~55° away from substrate normal, simultaneously bombarded the film during the growth. The ion beam energy and beam current were 200 eV and 10 mA, respectively. The film thickness was varied from 3 nm to 1 µm.

After film growth, all samples were stored in a desiccator before measurements. X-ray diffraction (XRD) patterns were measured by a SCINTAG automated diffractometer using Cu Kα radiation and a Ge detector. The XRD patterns showed (111)-normal orientation for all of the ion-bombarded films. Atomic force microscopy (AFM) images were obtained using a Tapping Mode AFM operating in air. The surface roughness of films was determined from the AFM line-scan profiles.

![Fig. 1. XRD patterns of CeO₂ films grown at 750°C (a) 1 µm film grown without IBAD; (b) 3 nm film grown with IBAD.](image)

**RESULTS**

A comparison of XRD patterns for both ion-bombarded and non-bombarded CeO₂ thin films grown on amorphous fused silica substrates is shown in Fig. 1. The 1 µm film grown without ion bombardment, Fig. 1(a), is polycrystalline with the strongest grain orientations decreasing in the order (311), (111), and (200). However the texture of CeO₂ thin films can be changed by ion bombardment during film growth and this change occurs at the initial stage of film growth. For example, Figure 1(b) shows a XRD pattern taken from a nominally 3 nm-thick CeO₂ film. The only grain orientation in this film is (111)-normal, although the XRD peak is broad.
Figure 2 shows a θ-2θ scan of a thick CeO$_2$ film (~300 nm) bombarded by Ar$^+$ ions during film growth. This film has strong (111)-normal orientation but the in-plane mosaic spread is large. The full width half maximum (FWHM) of rocking curve is ~4°. The inset in Fig. 2 is a phi-scan pattern of this film. The three-fold symmetry of the XRD pattern indicates that the film is well aligned with respect to a single in-plane direction but the FWHM of phi-scan peaks (in-plane mosaic spread) is ~28°.

The evolution of three films of different thicknesses is shown in Fig. 3(a) and 3(c). The AFM image of a 3 nm-thick film, Fig. 3(a), reveals a smooth and flat surface except for a few particles which sometimes appeared on the surface of PLD films while using low ambient pressure. The mean roughness of this film is ~0.3 nm. Since the film is ultrathin, several dark parts and lines that appeared on the surface may be due to the surface structure of the substrate. The grain boundaries are not distinct, but some fine clusters with diameter ~20–30 nm can be observed within these grains.

In Fig. 3(b), a 30 nm-thick film reveals a different microstructure. Many well-defined clusters are present on the film surface, resulting in a honeycomb-like surface structure. The size of these clusters is ~70 nm. The film is growing three-dimensionally and the clusters apparently, terminate at different layers. The size of clusters on the upper layer is larger than the lower-layer clusters, which implies that the clusters grew with a “corn” structure which may have started at the initial stage of film growth. It also is observed that there is a distribution of cluster density in this image, with the high-density-cluster parts located toward the upper-left and bottom-right corners with a high-density-void line is between these regions.

When the film thickness increases to 300 nm, as shown in Fig. 3(c), the film surface contains many large and small clusters with diameter ~30–70 nm and again shows the honeycomb-like structure, but the density of cluster is much higher than for the 30 nm-thick film. The 300 nm-thick film also is much smoother, with surface roughness ~1.5 nm, than the 30 nm-thick film.

A large-scale surface morphology of the 30 nm-thick film is shown in Fig. 3(d). This image reveals two features: (1) there is island growth and the islands have nearly round (grain) boundaries separated by a void network; and, (2) within each island there are many small clusters producing a honeycomb-like surface. From a side view picture (not shown), the peaks of the clusters and islands are directed toward to the film-normal direction, away from the ion-beam-incident direction. This cluster growth direction also was displayed by a computer simulation [8]. The diameter of these islands is less than 2 µm and the valley (high density voids) network has a ~700 nm width. The mean roughness of this film is ~3.5 nm obtained from the image statistics.
Fig. 3. AFM images of CeO$_2$ films with thickness (a) 3 nm, (b) 30 nm, (c) 300 nm, and (d) 30 nm.
DISCUSSION AND CONCLUSION

The favored (111) crystalline orientation obtained in ion-bombarded CeO₂ films probably develops as a result of several effects including (1) Ar⁺ ion channeling and sputtering during film nucleation and growth; (2) laser-ablated adatoms gain energy by collisions with bombarding ions to suppress unfavored grain orientations and to reduce film stress; and, (3) low concentrations of Ar may be incorporated within the films causing an expansion normal to the substrate. Based on the influences of channeling and sputtering, Bradley suggested that a preferred crystalline orientation can be selected by using ion bombardment during film growth [13]. At the initial stage of deposition, only a small fraction of the film will be oriented in the (111)-normal direction, as indicated in Fig. 1(a). Under low-energy ion bombardment, this layer is not removed completely and these adatoms form small clusters which may be well oriented, Fig. 3(a). A fraction of the film is left in an amorphous or polycrystalline state, which makes a flat film surface with unclear grain boundaries. When new adatoms arrive on the film surface, a new layer is formed with a larger fraction of preferred crystalline orientation, due to epitaxial growth on the preceding layer that is partially oriented at the preferred direction. The Ar⁺ ions bombard not only the present layer but the preceding layers, and the adatoms sputtered by Ar⁺ ions are redeposited on the film surface. This redeposited material has more possibility to attach to the well-oriented clusters, as was observed for a Cu surface bombarded by low-energy Ar⁺ ions [14].

Although films can grow in a preferred orientation for various ion incident angles [15], the in-plane alignment in CeO₂ films is affected strongly when the film is bombarded at a channeling direction. CeO₂ has the fluorite-structure for which the strong channeling directions are <100> and <110> located at 54.7° and 35.7° from <111>, respectively [5]. Energetic ion bombardment also increases the surface mobility of adatoms by collisions. Combined with thermal excitation and preferential sputtering of misoriented grains, these adatoms with long range mobility will suppress the unfavored grains by migrating to the clusters that have preferred orientation. It is noted in Fig. 3(b) and 3(c) that the clusters seem to have a critical size ~70 nm. Beyond this size, these clusters coalesce to form islands in which there is a high density of clusters, as shown in Fig. 3(d). Some small clusters also are present among the large clusters on the surface of the 300 nm film, Fig. 3(c), but they cannot be observed in the 30 nm film. This may imply that new cluster seeds start to form when the large clusters are sufficiently dense to yield a dense and smooth surface structure. This type of structure also was observed in ion-bombarded thick a-Si films and was considered to signify a transformation from one zone to another. This transformation was explained by saying that the physical structure develops faster than the crystal structure [10]. Due to the channeling effect, the IBAPLD CeO₂ films have a single preferred crystal orientation although the surface morphology of CeO₂ films grown by IBAD is similar to the a-Si films. The energetic Ar⁺ ions incident on the surface of the growing film transfer energy and momentum to the adatoms. The knock-on adatoms at the surface are driven not only along the surface to have long range mobility but into the lower layers to fill voids as well.

The nominally 3 nm-thick film, Fig. 3(a), is flat and smooth, and at this stage grows laterally. Yet, the nominally 30 nm-thick film shows island growth with many clusters, indicating a growth transformation occurs before the thickness reaches 30 nm. This morphologic feature may result from three influences during IBAPLD film growth: (1) the sputtering yield varies with ion beam incidence angle; (2) enhanced adatom surface mobility; and, (3) defects generated by Ar⁺ ion-bombardment. For low-energy Ar⁺ ion-bombardment, the sputtering yield typically increases with the angle of incident ions from 0° (incidence from film-normal) to ~60° at which a maximum yield is reached [16]. Beyond 60°, the sputtering yield drops drastically. Based on the relationship of sputtering yield vs incident angle, Kester and Messier explained that the etch pits (voids) appearing on the surface of BaTiO₃ thick films grown by rf-sputtering have an angular distribution. The surface defects provide the initial angular distribution [17]. For IBAPLD CeO₂ films a similar surface structure is observed. At the earliest growth stage the film surface is flat and the ion beam uniformly bombards the film surface at ~55°.
The side of clusters will be ion-bombarded at angles less than 55°, which will result in a smaller sputtering yield than for the flat film regions and the tops of clusters. Since the Ar⁺ ions bombard both the new top layer and lower layers, the flat surface regions around clusters have the highest sputtering yield. Consequently, large clusters and islands are formed and the surface becomes rough with the large clusters and deep void-network, Fig. 3(b). With the addition of new adatoms from redeposition and target ablation, a balance of sputtering and deposition is achieved and the clusters reach an equilibrium size and shape. The new adatoms cover the voids to provide a dense film and flat surface with small clusters, resulting in a less rough surface with both large and small clusters, as seen in Fig. 3(c).

In summary, the microstructure and surface morphology have been invested for (1 1 1)-oriented crystalline CeO₂ thin films grown on amorphous fused silica substrates by IBAPLD. The (1 11) CeO₂ films are in-plane aligned with respect to a single axis and this orientation is present from an early stage of growth. The Ar⁺ ion-bombardment greatly improves the crystallinity of CeO₂ films by combined the influences of channeling, sputtering, and enhanced surface mobility. However, the complex evolution of these thin films is grown by a combination of effects, including angular-dependent sputtering yields, surface defects, and ion-enhanced-atom surface mobility, that result in the honeycomb-like and island growth features seen in CeO₂ films.

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