Oblique ion texturing of yttria-stabilized zirconia: the {211} <111> structure

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Abstract

Amorphous (Zr,Y)O_x films were synthesized by reactive magnetron sputtering and subsequently crystallized by oblique ion bombardment. Crystalline texture nucleated by the ion beam was replicated by solid-phase epitaxial growth throughout the formerly amorphous YSZ film. The resulting yttria-stabilized zirconia (YSZ) films have (211) orientation normal to the substrate with in-plane directions (111), parallel, and (110), transverse, to the azimuth of the ion beam. We hypothesize that the texture mechanism involves ion-induced film compression and shear. The results, taken together with prior work, show that oblique ion texturing of amorphous films is a general phenomenon that can be used to fabricate substrates with more than one type of crystallographic orientation.

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Ion textured surfaces have great potential as templates for the growth of epitaxial films for many applications, including high-temperature superconducting (HTS) tapes and photovoltaics. Epitaxial film growth on single crystal substrates offers one route to highly textured thin films, but such substrates are often costly and available only in limited size. Thus large-area technical substrates such as metal or glass are desired. Empirical process design can then usually provide films with out-of-plane ("fiber") texture. The out-of-plane crystal texture mechanisms still are not completely understood, but surface energy, anisotropic film stress and surface atom mobility appear to be important.[1] How can in-plane alignment be achieved as well? The leading technique for achieving in-plane alignment is oblique ion beam assisted deposition (IBAD)[2-4]. In this process, the growing film is bombarded by oblique, low-energy ions as it is deposited from a vapor phase. However, the growth of YSZ films by this method, while now rather refined,[5] is a slow competitive growth process requiring the ion-texturing of a layer thousands of unit cells thick before complete crystallographic alignment is achieved.

As an alternative to IBAD growth of YSZ, we are exploring a simpler technique: oblique ion bombardment *after* film deposition is complete. We term this method ITEX, short for Ion TEXturing. In this case, an amorphous film is a natural precursor layer, since it has no pre-existing polycrystalline texture to compete with texture formation initiated by ion bombardment. Amorphous films are inherently metastable, and can be made to crystallize by annealing. For ITEX methods time at temperature is quite important, since elevated temperature can assist with ion-induced crystallization on the one hand and, on the other hand, spontaneous crystallization can create misaligned grains.

Prior literature reveals a few cases in which bombardment of amorphous materials with low-energy (10 to 4000 eV) ions (or atoms) causes the formation of nano-crystallites near the surface.[6-8] Recently, it was demonstrated that the use of an *oblique* ion beam can form crystals that are aligned with respect to the azimuth of the particle beam as well as the free surface:[9,10] An ordered YSZ (001) surface was formed near 800 ^{o}C, and an epitaxial $YBa_2Cu_3O_7$ (YBCO) overlayer had strong c-axis normal ordering, and limited but definite in-plane ordering. In the current letter we demonstrate that by utilizing different ITEX process parameters, we are able to produce a well ordered, readily reproducible, YSZ (211) surface below 200 ^{o}C. Furthermore, the current results show that the ion-induced surface texture can grow down through the precursor film by epitaxial solid phase growth.

Amorphous precursor films were synthesized on smooth Ni-Cr alloy substrates by sputtering of a $Zr_{0.82}Y_{0.18}$ target in the presence of oxygen. Optical reflectance of the films increased at longer wavelengths, showing a metallic character, and Rutherford backscattering analysis indicated that the films contained about half as much oxygen as fully oxygenated YSZ. Bragg-Brentano x-ray diffraction from the precursor films shows only a single broad diffraction peak centered at $2\theta = 34.2^{o}$ with width of 4.0^{o} (FWHM).

Ion bombardment was performed with a 3 cm Kauffman source aligned 55^{o} from the surface normal (Ar^+, 300 eV, 10 mA). In most experiments bombardment proceeded for 30 min. at room temperature and was continued during heating to 500 ^{o}C in 12 min. The chamber atmosphere included 0.4 mTorr O_2 and 0.4 mTorr Ar. Some samples were removed after cooling to room temperature without further processing, while others were capped with epitaxial CeO_2 before cooling (pulsed laser deposition, PLD, 500 ^oC) or with CeO_2 and PLD YBCO. Though some room temperature bombardment was found to be necessary to develop the (211) crystalline texture, later results showed that 30 min was excessive; 2 min was sufficient. It will become clear that the texture has developed already during 3 min of heating to 200 ^oC so lengthy bombardment is not necessary.

Figure 1 (a) shows the (111) pole figure of an epitaxial CeO_2 layer on a textured YSZ film. The ion beam (300 eV, 5mA) was incident from the right. If the film had the simple fully-textured (001)-normal structure, we would observe four equally spaced (111) poles, 54.7^o from the center. Instead, the pattern is rotated, about a (110) in-plane axis, bringing one of the (111) poles near the center (about 17^o away). Thus the tilt angle appears to be about 38^o. The (002) pole figure, Fig. 1 (b), confirms that the (002) pole is tilted about 37^o from the normal. Figure 1 (c) shows a (002) YSZ pole figure demonstrating that the CeO_2 and YSZ textures are very similar, namely, are epitaxial and aligned.

Essentially the same texture was observed in a number of experiments, but the tilt angle varied slightly, in the range of 32^o to 39^o. We note that at a tilt angle of 35.3^o, a (111) direction lies in the plane of the film (parallel to the azimuth of the ion beam), and the (211) direction is then normal to the film. Within the range of tilt angles just cited, the texture was observed to be stable under minor changes in parameters such as ion energy and angle, and oxygen pressure. In particular, the lattice tilt does not follow the inclination of the ion beam as might be expected if an ion channeling mechanism were operative. In the metallurgical literature the type of texture that we observed is denoted {211} <111> to indicate (211) normal to a metal foil and (111) parallel to the rolling direction, called the copper texture.[11,12]

To clarify the nature of the epitaxial solid phase growth of the transparent oriented crystalline YSZ film from the (~800 nm) amorphous metallic YSZ precursor film, experiments were performed with the standard protocol but interrupted during the temperature ramp at 200 and 300 ^{o}C. At 200 ^{o}C (3 min after start of heating), the resulting transparent, oxygenated YSZ film is found to be 110 nm thick, see Fig. 2 (a). Here, it has been assumed that the YSZ film is fully dense, and has a refractive index of 2.1[13]. That is, the thickness is an optical value determined from the locations of the minima and maxima of the reflectance curve. Processing to 300 ^{o}C (at 5 min., Fig. 2 (b)) yields an optical thickness of 520 nm, and heating to 500 ^{o}C (at 12 min., Fig. 2 (c)) yields a fully oxidized film that is 780 nm thick. Complete oxidation all the way through to the Ni-Cr substrate is indicated by the higher reflectance maxima. It is clear from these data that, as the temperature is elevated, the precursor film is oxidized at a high rate. For comparison, another film was processed to 500 ^{o}C in lower oxygen pressure (roughly 10^{-6} vs. 4×10^{-4} torr). In this case, the thickness of the oxidized layer was only 370 nm and a small size of the reflectance oscillations indicated some optical absorptivity, presumably related to oxygen deficiency. Another comparison film was heated to 500 ^{o}C with the ion beam off. It was also incompletely oxidized, which suggests that ion-beam activation of oxygen assists the oxidation process. It is known, for example, that UV-ozone activation can assist with oxidation of zirconium,[14] and that below about 650 ^{o}C, unassisted oxygen uptake by YSZ can strongly limit the rate of oxygen diffusion.[15]

The optical data demonstrate that for the standard runs the fully oxidized portion of the YSZ film can be modeled as a transparent layer that is gradually consuming the precursor film. The {211} <111> texture is present already in the 110 nm thick film, and x-ray pole figures (not shown) indicate the presence of more textured material (larger peak intensities) in the thicker layers. Clearly, the film oxidation is an epitaxial solid phase growth process that replicates the ion-induced texture created near the surface of the film. The rate of oxygen diffusion from the free surface of the film to the reaction front may be the determining factor in the solid phase growth rate. The high film oxidation rate is a consequence of the fact that YSZ is an excellent oxygen ion conductor.[13] The velocity of the reaction front is higher at higher temperatures, which is consistent with the expectation of faster oxygen diffusion at higher temperatures.

Ion bombardment effects on crystalline texture are often interpreted in terms of ion channeling, [16] selective sputtering, [17] or selective ion damage [18]. It appears to us that some sort of ion "damage" mechanism is operative here. Ion channeling is an improbable process for 300 eV Ar ions, as the penetration range is only roughly 1–2 nm. The pole figure data show that the ion beam does not align with a high symmetry direction in the ITEX YSZ, as would be expected with a channeling or selective sputtering process. What is clear is that during the room temperature bombardment the surface zone of the amorphous precursor film is strongly perturbed by ion impacts; and that, as the temperature is raised, a crystalline layer grows down into the amorphous film from the perturbed surface zone.

The number of ion impacts per second at 5 mA is about 2.5×10^{15} cm^{-2} sec^{-1}. Thus during bombardment each surface atom is struck about once per second. The relaxation processes after impact occur on a much faster time scale. Thus each ion impact is independent of the next except for the changes it imposes on the film nanostructure. Since we are using ion bombardment times of minutes, each surface atomic position is impacted 100's of times, and the surface must gradually recede due to sputtering.

From a mesoscopic point of view, the effect of the ion bombardment is to cause an increase in the local film density due to knock-on atoms and some "plastic" shear flow of the surface region. There will be a compressive stress in the plane of the film that can assist the formation of crystal nuclei. The effect of film compression alone however is insufficient to account for the in-plane orientation of film crystallites. The oblique nature of the ion bombardment, however, will cause the knock-on atoms near the surface to flow preferentially along with the ion beam, thus establishing a preferred in-plane direction for crystallite formation. Since the surface zone experiences a shearing motion due to the ion impacts, the alignment process may have some similarities to the alignment due to shear in metallurgical processing.

Shearing of an amorphous metal can cause the formation of oriented crystallites in the shear bands that occur.[19-21] Further, it is known that the copper type texture that we observe in YSZ occurs in certain fcc metals after cold deformation. It is thought that this texture is at least partly due to slipping of crystal planes and crystallite rotation during deformation. YSZ has oxygen vacancies and mobile oxygen ions, rather like a fluid, and the cation Zr(Y) lattice is of the fcc type. Thus, texture formation by deformation processing in metals may have features in common with oblique ion texturing.

Additionally, similar texture has been observed in MgO films synthesized by inclined substrate deposition using e-beam evaporation.[22] For an inclination angle of 55^o, the MgO (001) direction is tilted by about 32^o from the surface normal, producing an approximate {211}<111> texture.

While our YSZ ITEX-211 process has yet to be optimized, we nevertheless deposited YBCO on a CeO_2/ITEX-211 structure. High critical current values have not yet been obtained but it is interesting to observe the nature of the YBCO epitaxy in our first ITEX samples. The YBCO lattice fits the CeO_2 lattice along the CeO_2 (110) YBCO (100) direction, but does not fit along the CeO_2 in-plane (111) direction due to the 35^o tilt. The YBCO crystallites have a reduced average tilt of only 14^o from the c-axis normal configuration as shown by the YBCO (103) pole figure (Fig. 3) and analysis of AFM images. Other researchers have managed to deposit high-current YBCO films on tilted (single crystal) YSZ texture,[23] and we plan to accomplish this goal as well.

In summary, we produced fully textured YSZ {211} <111> films by oblique ion bombardment of an amorphous oxygen-deficient precursor film. Texture created near the surface by the ion beam was replicated throughout the film by solid phase epitaxial oxidation.

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Figure captions

1. X-ray pole figures documenting the {211}<111> texture in a CeO_2 overlayer and the crystallized YSZ film. **a**, CeO_2 (111) pole figure, **b**, CeO_2 (200) pole figure, **c**, YSZ (200) pole figure. The azimuth of the ion beam is indicated with a dash.

2. Optical reflectance data documenting the growth of the transparent YSZ film down into the metallic precursor film. Film growth was interrupted at **a**, 200 ^{o}C, **b**, 300 ^{o}C, **c**, 500 ^{o}C.

3. X-ray pole figure of YBCO film, (103) pole, showing a tilt of about 14^{o} from the c-axis normal position.