Structural investigation of the epitaxial yittria-stabilized zirconia films deposited on (0 0 1) silicon by laser ablation

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Abstract

Yittria-stabilized zirconia (YSZ) films doped with 3 and 9 vol% Y2O3, respectively, are epitaxially deposited on (0 0 1) silicon substrates by means of pulsed laser deposition (PLD) technique. Transmission electron microscopy (TEM) and X-ray diffraction are mainly combined to study the film microstructure. It is found that the film structure strongly depends on the amount of Y2O3 dopant. 9% Y2O3-doped films display a near cubic structure; 45°{110} dislocations are the main defects in the film and thermal cracks are formed during cooling. The 3% Y2O3-doped films are dominated by {1 1 0} twin-related tetragonal domains in which monoclinic phase is found. The films are free of thermal cracks even for films thicker than 2 µm. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The structure of pure zirconia displays either monoclinic (P21/c), tetragonal (P42/nmc) or cubic (Fm3 m) symmetry, at low, intermediate and high temperature respectively. The cubic phase has the fluorite structure, while the tetragonal and monoclinic phases are distorted versions of the cubic phase [1]. The transition from tetragonal to monoclinic phases is a martensitic type transformation. The high-temperature cubic phase can readily be stabilized at room temperature by doping with some oxides such as CaO, MgO, Y2O3, etc [2]. Studies reveal that for stabilized zirconia the dopant ions completely fill the active lattice sites and an appropriate number of vacancies emerge on the oxygen anion sites to preserve electrical neutrality of the crystal [3].

In the family of stabilized zirconia, yittria-stabilized zirconia (YSZ) has potential applications in structure ceramics engineering and micro-electronic industry. Used in micro-electronic devices, YSZ can be explored as a dielectric...
layer for capacitors in dynamic random access memories, as a field-effect transistor for oxygen sensors, and as a buffer layer for growing oxide films [4–8]. YSZ has been proved to be an excellent oxide epitaxially deposited on Si [6–8]. However, when the film thickness exceeds 300 nm, thermal cracks may develop in the epitaxial YSZ film mainly due to the larger thermal expansion difference between Si and YSZ [7,8]. This hampers the application of epitaxial YSZ films on Si to some extent.

Pulsed laser deposition is an excellent technique to deposit oxide films because it allows transferring of the target to the substrate with exact composition at high temperature in a reactive gas. Recently, we succeeded in growing YSZ films doped with different Y$_2$O$_3$ content on (0 0 1) Si by means of laser ablation. In this work, we present the microstructural investigation of the YSZ films deposited on (0 0 1) Si.

2. Experimental procedure

The targets used in this experiment are zirconia doped with 3 and 9 vol% Y$_2$O$_3$ respectively. (0 0 1) silicon wafers without the native oxide layer being removed, were put into the chamber of the laser ablation equipment. The substrate was heated at 900°C in vacuum to remove possible surface contamination. The laser was fired and YSZ was transferred to the substrate at about 650°C under an oxygen pressure of 2 × 10$^{-3}$ mbar. More details on the experimental procedure can be found in the Ref. [6]. The 3% Y$_2$O$_3$ films were grown to about 370 nm and 2 μ thick. The 9% Y$_2$O$_3$ film was 330 nm thick.

The films were first observed on a light microscope to check the surface quality. The film orientation was determined by X-ray diffractometry. To study the microstructure, 2.5 × 2.5 mm$^2$ blocks with their edges along ⟨0 0 1⟩ Si were first cut from the wafers. Planar view samples were then prepared for the TEM investigation. These blocks were ground, dimpled and polished from the substrate side until the central area is thinner than 15 μm. Finally, the blocks were ion-thinned to electron perforation on a stage cooled by liquid nitrogen. The TEM microstructure study was carried out with Jeol 2000EX and 4000EX electron microscopes.

3. Experimental results

Figs. 1a and b show the X-ray spectra of YSZ films doped with 3% and 9% Y$_2$O$_3$ respectively. The main film peaks in the spectra correspond to ⟨0 0 2⟩ of YSZ, confirming the ⟨0 0 1⟩ epitaxial growth of YSZ films on silicon. In the 3% Y$_2$O$_3$-doped YSZ film a double ⟨0 0 2⟩ peak is found at around 35°, suggesting a tetragonal structure. The inserted frame shows the enlarged double peak. The lattice parameters of YSZ were derived to be 5.12 and 5.18 Å which corresponds to the a and c parameters respectively of the tetragonal phase. It is also concluded that either the a- or c-axis of tetragonal phase can be along the normal of the film. The peak corresponding to 5.12 Å is twice as high as the 5.18 Å peak, indicating that the a-oriented domains are more prominent than the c-oriented ones. The lower YSZ spectrum corresponding to 9% Y$_2$O$_3$ displays one ⟨0 0 2⟩ peak and two ⟨0 0 4⟩ peaks, which means the film has a near cubic structure. These results agree with

![Fig. 1. X-ray spectra showing epitaxial ⟨0 0 1⟩ orientated YSZ films on (0 0 1) Si. The films are for ZrO$_2$–3% Y$_2$O$_3$ (Fig. 1a) and ZrO$_2$–9% Y$_2$O$_3$ (Fig. 1b), respectively. The inset shows the enlarged double ⟨0 0 2⟩ peak of ZrO$_2$–3% Y$_2$O$_3$.](image)
the Y$_2$O$_3$–ZrO$_2$ phase diagram [9], which states that fully stabilized YSZ can be obtained if the volume of doped Y$_2$O$_3$ exceeds 10%.

Both TEM and optical observations show that thermal cracks develop in the 9% Y$_2$O$_3$-doped YSZ film. Fig. 2a shows the cracks recorded by light microscopy. The cracks at right angles are oriented along both [1 0 0] and [0 1 0] directions of (0 0 1) Si. Vasiliev et al. [8] reported a similar crack configuration in YSZ-buffered superconductor films deposited on Si. Fig. 2b is an electron micrograph of the plan-view film. The arrow marks the crack along $\langle 1 0 0 \rangle$ YSZ. Only dislocations are found in the homogeneous YSZ film. Fig. 2c shows the corresponding HREM image of a single dislocation. The failure of the Burgers circuit results into a vector of $\frac{1}{2}[1 0 0]$ which is the [0 1 0] projected component of the $b = \frac{1}{2}(1 1 0)$, the reported Burgers vector of YSZ [8,10]. The $\frac{1}{2}(1 1 0)$ dislocation is the one with the lowest energy in the fluorite structure. Hence, the observed dislocations are $45^\circ \frac{1}{2}(1 1 0)$ dislocations.

No cracks were found in the YSZ films doped with 3% Y$_2$O$_3$ by optical microscopy. Fig. 3a is a low magnification TEM micrograph of the YSZ film doped with 3% Y$_2$O$_3$. The film thickness is about 370 nm. No cracks are present, agreeing with the result obtained by light microscopy. It is found that the film consists of a patchwork of mostly rectangular domains. Electron diffraction reveals that all the domains are $\langle 0 0 1 \rangle$ oriented. Due to the small tetragonal distortion, it is rather

Fig. 2. Structure of YSZ film doped with 9 vol% Y$_2$O$_3$: (a) optical micrograph showing rectangular thermal cracks in the film; (b) TEM bright image revealing homogenous dislocation-dominated structure. The triangles point a crack; (c) HREM micrograph revealing a $45^\circ \frac{1}{2}(1 1 0)$ dislocation in the film.
It is difficult to distinguish the [001] zone from [010] zones of the tetragonal YSZ by means of electron diffraction. Neglecting the slight tetragonal distortion, all domains keep a cubic-to-cubic relationship with the Si substrate, in agreement with previous reports [6–8]. Some of the larger rectangular domains in Fig. 3a are marked D. The domain walls are inclined in the film and intersect the film surface along \( h_{100} \) YSZ. Tilting experiments revealed that these domain walls lie on \{110\} planes of YSZ. At high magnification one also reveals fine lines along \{110\} YSZ; they are marked by arrows. Tilting experiments show that these defects are in fact domain walls, seen edge-on along \{110\}. These thin domains can either share the edged-on \{110\} walls with each other or share the inclined \{110\} domain walls with the larger D-marked domains. Such an arrangement of the domain walls is quite similar to the microstructure of bulk YSZ reported by Hayakawa et al. [11]. The presence of the domain walls also indirectly proves that the films have the tetragonal structure.

By electron diffraction the relationship between the different \{101\}-related domains could be studied. Although some domains such as T1, T2 in Fig. 3b are too fine to produce the selective diffraction pattern from the isolated domain, it is straightforward to derive their relationships from the composite diffraction pattern. Fig. 4a is the EDP taken over two thin domains, T1 and T2 in Fig. 3b along \( h_{001} \), i.e., film normal. The \{202\}* row of reflections is unsplit. But all other reflections parallel to \( (20-2)* \) are split. The spot splitting increases with the distance from the origin, as demonstrated by the top inset which is the enlargement of the rectangular frame. This splitting shows that domains T1 and T2 have a different orientation related by a \( (101) \) mirror operation. It is also inferred that the c-axes of T1 and T2 are not aligned. Fig. 4b is a diffraction pattern obtained from three connecting domains T1, T2, and T3. It is also taken along the normal of the film i.e., \( \{001\} \) zones. The domain walls between T3 and the domains T1 and T2 are...
inclined in the film with respect to the film normal. Triple splitting of the spots is visible, as shown by the enlargement of the rectangular frame. It is, therefore, concluded that the arrangement of the $c$ axes in the domains $T_1$, $T_2$ and $T_3$ is different. In other words, $T_1$, $T_2$ and $T_3$ are mutually perpendicular tetragonal variants. The microstructure of YSZ films with 3% $Y_2O_3$ is in fact a herringbone structure described by Hayakawa et al. [11]. Such a structure consists of alternating differently oriented tetragonal domains sharing $\{101\}$ planes of YSZ. This structure is often observed in the YSZ alloys doped with 3% $Y_2O_3$ [11,12]. Such an arrangement of the tetragonal domains results from the cubic to tetragonal structure transition, and can be found in the microstructure of many compounds (e.g. $BaTiO_3$) experiencing a cubic-to-tetragonal phase transition [13,14].

Fig. 5 is a HREM image of the edge-on domain wall between $T_1$ and $T_2$. Clearly, the domain wall is not very sharp and is spread out over several cells. The $\{110\}$ planes of the two joining tetragonal domains are not exactly aligned, as indicated by the lines in Fig. 5. The angle between the $\{110\}$ planes of the neighboring domains is about $1.5^\circ$, in agreement with the lattice parameters of the tetragonal phase. This further agrees with the ED information of Figs. 3 and 4. HREM studies of $90^\circ$ domain walls of $BaTiO_3$ reveals a similar result. Floquet et al. [14] reported that the domain walls of $BaTiO_3$ are, in fact, a thin intermediate area of several cells thick, instead of a sharp and fixed plane. Such a wall is compatible with the wall movement that can adjust the width of domains.

Occasionally, fine monoclinic lamellae can also be found in the film. Fig. 6a is an image of a 2 $\mu$m thick YSZ film. No cracks are found in this film. Its microstructure is similar to that presented in Fig. 4a. The triangles mark the presence of some monoclinic lamellae. Fig. 6b is the corresponding HREM image of the tetragonal–monoclinic interface. The tetragonal and monoclinic phases keep the orientation relationship of $b_M||b_T$, $c_M||c_T$, and $c_M||c_T$.

Fig. 5. HREM image showing that domain wall of several cells in thickness. The open arrows mark the domain wall.

Fig. 6. (a) Plan view image revealing the monoclinic lamella embedded in the tetragonal phases. (b) HREM image showing the interface between tetragonal matrix and monoclinic lamella. M and T, respectively, denote monoclinic and tetragonal phases.
(100)M || (100)T. The interface between the monoclinic lamella and tetragonal phase is about 14° away from the (100)M plane; in agreement with the extensive study of the microstructure of tetragonal and monoclinic YSZ [15].

4. Discussion

Films doped with different amounts of Y₂O₃ display a different microstructure. The film doped with 9% Y₂O₃ displays a near cubic structure containing 45° 1/2(001) dislocations. Thermal cracks develop in the film. The films doped with 3% Y₂O₃ are mainly composed of {110} twin-related tetragonal domains in which embedded monoclinic lamellae are occasionally found. Depending on the orientation of connecting domains, the domain wall can be edge on or be inclined with respect to the film normal. No thermal cracks are observed in films as thick as 2 μm.

An extensive study of the microstructure of bulk YSZ shows that at room temperature YSZ can have the monoclinic, tetragonal or stabilized cubic structures by increasing the doping level with Y₂O₃. In other words, the tetragonal to monoclinic transformation temperature drops with increasing Y₂O₃ doping. At room temperature, only the monoclinic phase is observed in pure ZrO₂. The tetragonal phase is observed in films doped with 3% Y₂O₃. Occasionally the monoclinic phase is found together with the tetragonal phase (Fig 6a). The microstructure of the tetragonal phase at this composition normally adopts a herringbone structure [11,12]. When the Y₂O₃ doping exceeds 10%, the transition of tetragonal to monoclinic phase is depressed and a fully stabilized cubic phase results. The observed structure of the YSZ films in this study completely agrees with the reported structure of bulk YSZ of the same composition [12]. Therefore, our YSZ films should almost have the exact composition as the target, suggesting that laser ablation is a good procedure to deposit YSZ films with a reliable composition.

As previously reported, thermal cracks inevitably develop in a YSZ film doped with 9% Y₂O₃, For YSZ deposited on (001) Si, studies show that the epitaxial strain can be released by misfit dislocations when the film thickness is more than 6 nm [7]. The remarkably different thermal expansion coefficients between Si and YSZ (aₜ = 2.5 × 10⁻⁶ K⁻¹ and a₉YSZ = 11.4 × 10⁻⁶ K⁻¹) suggest that thermal tensile stress will develop in the films during cooling. Moreover, the thermal stress increases with the thickness of the films. It is, therefore, expected that the thickest film (the 2 μ one in this work) should exhibit thermal cracks. However, it was found that thermal cracks, only develop in the thinnest film that is doped with 9% Y₂O₃. The presence of cracks thus depends on the doping level of the YSZ films. Several mechanisms may contribute to the thermal stress-relaxation in the 3% Y₂O₃-doped tetragonal film. On the one hand, the analysis shows that the well-developed herringbone structure is a self-accommodation structure, i.e., the final arrangement of {110} plane-shared tetragonal domains, is compatible with the applied strains during the transformation [11]. The total internal stress in the final structure is zero. Hence by adopting such a self-accommodation structure the thermal stress in the films can be relaxed to some extent. This point is also reflected by the fact that the 3% Y₂O₃ doped YSZ displays the best mechanical properties [12]. Moreover, the herringbone structure will improve the roughness of YSZ and stop the crack propagation [12]. On the other hand, thermal stress in the tetragonal film can induce the tetragonal to monoclinic phase transformation, i.e., stress-induced martensite transformation [16,17]. By such a transformation, stress can be further relaxed. Stress-induced phase transformations in the zirconia alloy had extensively been studied and is one of the important ways to improve the toughness of engineering ceramics [17]. For the 9% Y₂O₃ doped YSZ, the doped Y₂O₃ stabilizes the near cubic phase at room temperature. It is impossible for the film to relax stress by adopting a self-accommodating structure or by stress inducing phase transformation. A dislocation movement is, therefore, the only way to relax thermal stress. Consequently, thermal stress in the film generated during cooling cannot be easily relaxed and thermal cracks are formed in the film.
5. Conclusion

Epitaxial YSZ films with different dopant volumes are deposited on Si by means of a PLD technique. The 9% Y$_2$O$_3$-doped film has a near cubic structure and shows an abundance of $\frac{1}{2}(110)$ dislocations. Cracks along the $\langle 100 \rangle$ directions develop in the film due to thermal stress during cooling. The films doped with 3% Y$_2$O$_3$ are free of thermal cracks and develop a herringbone microstructure with $\{110\}$ twined tetragonal domains. Such an arrangement of tetragonal domains is compatible with the thermal stress and can relax the stress. This stress can relax further by inducing the tetragonal-to-monoclinic phase transformation.

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References


