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Single domain epitaxial growth of yttria-stabilized zirconia on Si(1 1 1) substrate

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Abstract

Yttria-stabilized zirconia (YSZ) was epitaxially grown on both Si(0 0 1) and Si(1 1 1) substrates using a RF magnetron sputtering method. While YSZ(0 0 1) was grown on Si(0 0 1) with a cubic on cubic relation, YSZ(1 1 1) film on Si(1 1 1) with six-fold symmetry on surface showed two variants; cubic on cubic (type A) and 180° rotation about surface normal along [1 1 1] (type B). X-ray diffraction method confirmed single domain YSZ with type B structure when samples were prepared with the relatively slow deposition rate and low substrate temperature. Interestingly, in a reverse pairing of substrate and film, Si deposited on YSZ(1 1 1) substrates showed single domain with type A structure.

Keywords: A. Films; D. ZrO_2

1. Introduction

Metal oxide film grown on silicon substrate is a key technology for fabrication of integrated devices using well-developed semiconductor technology. Only a few oxide materials can be epitaxially grown on the silicon substrate because of chemical reactions between metal oxide and silicon resulting in formation of silicide, or because of the existence of natural amorphous layer on the surface of silicon resulting in growth of polycrystal structure and because of the inter-diffusion which prevents epitaxial growth of oxide metal [1]. According to Gibbs free energy, many oxides should epitaxially grow on a Si substrate, indicating a stable state on direct contact between oxide and silicon [2], such as MgO [3], SrO [4] and $SrTiO_3$ [5]. Yttria-stabilized zirconia (YSZ) is a promising metal oxide. It is stable on contact with the silicon substrate, and enormous efforts has been focused to epitaxially grow YSZ(0 0 1) on Si(0 0 1) substrate by various methods: pulsed laser deposition [6,7], molecular beam epitaxy and sputtering method. Sputtering method is most suitable for industrial mass production.

While epitaxial growth of YSZ(0 0 1) is achieved on Si(0 0 1) with four-fold rotational symmetry along surface normal direction [0 0 1] [6–11], a YSZ film deposited on a Si(1 1 1) substrate shows six-fold symmetry, which indicates two domains related by 180° rotation about surface normal [1 1 1]. Si(1 1 1) surface with face center cubic structure, which has six-fold symmetry, usually results in epitaxial growth of oxides with twin domain structure [9,12–15], so called *type A* and *type B* structures, which are related by the 180° rotation about surface normal direction [1 1 1]. An interface layer between film and substrate, like SiO_2 for Si substrate, seems to be the key for which variety of structure, type A or type B grows on (1 1 1) substrate [13,16]. Single domain structure is ideal for a buffer layer, otherwise double domain film is resultant from deposition on a double domain buffer layer on a (1 1 1) structure [15].

In order to investigate YSZ growth on various oriented substrates, especially on Si(1 1 1) substrates, the RF magnetron sputtering method was used to deposit YSZ film on Si(1 1 1) substrates, together with Si(0 0 1) and Si(1 1 0) substrates using a zirconia target on which yttria chips were placed. X-ray

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diffraction (XRD) ϕ scan verified single domain YSZ(1 1 1) being epitaxially grown on Si(1 1 1) substrate with the lower deposition rate and lower temperature compared to that of with ordinal epitaxial growth YSZ(0 0 1) film. X-ray reflection (XRR) showed a flat surface of the single domain YSZ, which was verified by atomic force microscopy (AFM).

2. Experimental procedure

YSZ films were prepared on Si(1 0 0), Si(1 1 1) and Si(1 1 0) substrates using RF magnetron sputtering method under a mixture of Ar and O_2 gas ambient. Si substrate was prepared by RCA cleaning, and the thickness of the thin SiO_2 on the substrate was estimated to be 0.4 nm by an ellipsometer, assuming the refractive index of 1.46 for SiO_2. The Si substrate was glued on the holder using silver paste, and six yttria chips of 3 mm $\times$ 3 mm were placed on a zirconium metal target near the erosion area. The substrate temperature varied ranging from 550 to 800 °C. YSZ was deposited in an Ar atmosphere without oxygen (*metal mode*), followed by deposition in ambient pressure of 10 mTorr with the oxygen flow ratio, $R_{\rm flow}$ = (O_2 flow rate)/(Ar flow rate), varying between 1 and 10%. As comparison with reverse paring of YSZ and Si, YSZ(1 1 1) substrate was used to deposit Si film by chemical vapor deposition (CVD). The deposition rate and substrate temperature were 1 Å/s and 1000 °C, respectively.

After depositions, XRD was employed to investigate crystal structure (θ–2θ and ϕ scan) and film thickness (XRR). AFM revealed the surface morphology, and compared to the roughness obtained by a simulation from the XRR results. The ratio of XRD peak intensities was used to evaluate crystal orientation of YSZ film deposited on the Si substrate.

3. Results and discussion

Si(1 1 1) substrate with face center cubic structure has six-fold symmetric structure on its surface, resulting in two domain structures of film grown on Si(1 1 1) substrate; *type A* and *type B* structures. Although Si(1 1 1) surface has six-fold symmetry (in plane), XRD ϕ scan, taking Si(1 1 3) peak, for example, shows only three symmetric peaks every 120°. The Si(1 1 3) peak from Si(1 1 1) substrate has three-fold symmetry with neighboring atoms along surface normal (out of plane). Most metal oxides grown on Si(1 1 1) show six-fold symmetry on ϕ scan, meaning the metal oxides consist of two variants: double domain structure. The two variants are related by a 180° rotation around the [1 1 1] direction of surface normal. Out of plane XRD ϕ scan on such two domain structure shows six-fold symmetric peaks with 60° spacing, from the superimposition of each variant which has three-fold symmetry. The type A is a *cubic on cubic* structure related with a (1 1 1) substrate, and type B is related by the 180° rotation with the type A on the (1 1 1) surface normal [12]. Along surface normal of [1 1 1] direction, how the sequence stacks layers determines which of type A or type B grows on the six-fold surface of (1 1 1) plane with face center cubic structure.

YSZ films deposited on Si substrates of (0 0 1), (1 1 0) and (1 1 1) were evaluated by θ–2θ and ϕ scan, indicating epitaxial growth on Si(0 0 1) and Si(1 1 1), and polycrystalline on Si(1 1 0). Fig. 1 is the AFM images of YSZ(0 0 1) deposited on Si(0 0 1), showing the mean square surface roughness (RMS) was 8 Å, while RMS of 6 Å, obtained from the YSZ(1 1 1) deposited on Si(1 1 1), as shown in Fig. 2. Interestingly, YSZ film deposited on Si(1 1 0) showed a flat surface of ~2 Å, in RMS. Although epitaxial growth of YSZ(0 0 1) on Si(0 0 1) was obtained at high substrate temperature of 800 °C, the full width at half maximum (FWHM) of the rocking curve stayed around $\Delta\omega \sim 2°$. The FWHM was strongly dependent on the period of metal mode. Although YSZ was not grown on Si(1 1 1) substrate at $R_{\rm flow}$ = 1%, epitaxial growth of YSZ(1 1 1) on Si(1 1 1) was verified in a wide range of metal modes with high oxygen atmosphere of $R_{\rm flow}$ = 10%, showing good reproductivity compared with growth of YSZ(0 0 1) deposited on Si(0 0 1) substrate.

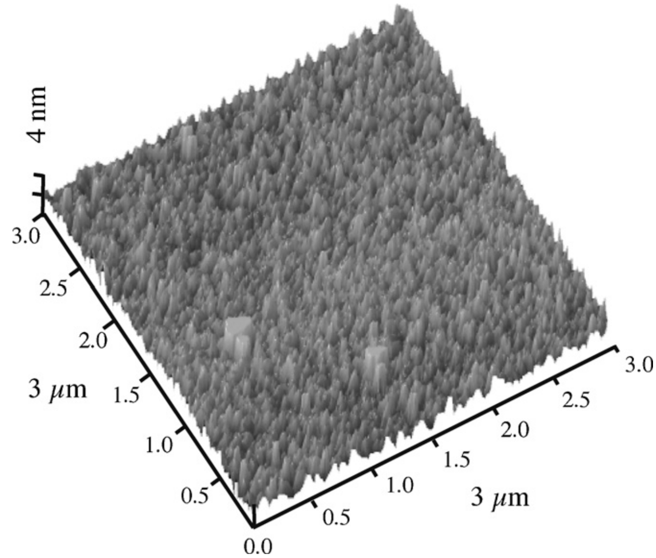

Fig. 1. AFM image of YSZ(0 0 1) deposited on Si(0 0 1) substrate, showing the roughness (RMS) to be 8 Å.

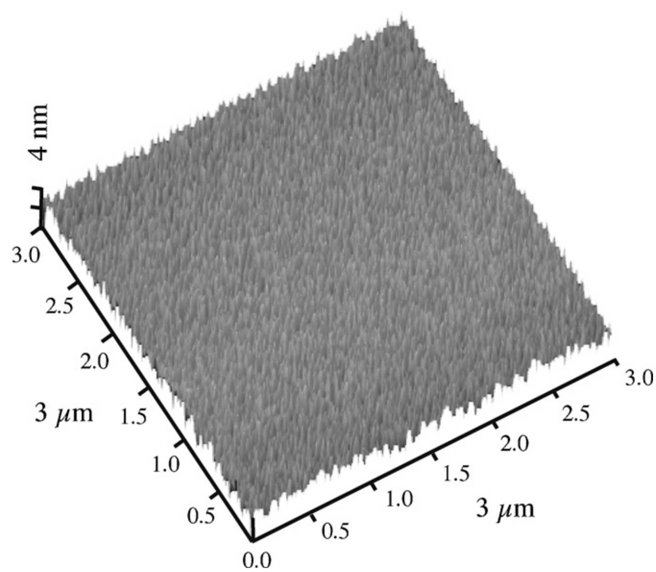

Fig. 2. AFM image of single domain YSZ(1 1 1) with type B. The surface was flat on the single domain growth.

Crystallinity was dependent on the period of metal mode. Especially deposition onto Si(0 0 1), the optimal period lies within the range of a few seconds, otherwise crystal structure turned into amorphous structure. Deposition onto Si(1 1 1) seemed to allow a wider range of metal mode periods, ranging from a few seconds to 10 s. Optimizing the metal mode resulted in increasing the intensity of YSZ(1 1 1) peak. The details of optimizing conditions will be found elsewhere [17]. Epitaxial growth of YSZ(1 1 1) was verified by XRD θ–2θ and ϕ scan. Fig. 3(a) shows a typical ϕ scan of YSZ film deposited at 750 °C in 10 mTorr of pressure with R_{flow} of 1%. The dotted line shows the direction of Si[1 1 3] in ϕ angle, which crosses the Si surface with three-fold symmetry. The ϕ scan shows six-fold peak of YSZ(1 1 3), indicating the epitaxial YSZ(1 1 1) grew with two domains of both type A and type B.

Single domain YSZ(1 1 1) was grown at the relatively low substrate temperature of 700 °C with $R_{flow} = 10\%$, and the FWHM of ϕ scan was $\sim 7^\circ$ instead of the broad FWHM of 20° on the double domain structure YSZ. As shown in Fig. 3(b), three peaks from YSZ(1 1 3) were placed between the Si[1 1 3] direction, indicating single domain structure of type B grown on the Si(1 1 1) substrate. As shown in Fig. 2, the single domain crystal shows a flat surface, and the roughness was comparable with the results obtained by the XRR measurement (Fig. 4). The film thickness and roughness estimated from XRR were 486 and 5 Å, respectively.

Crystal growth of (1 1 1) structure seems to be related to the interface layer between film and substrate. Either type A or type B can be selected by the thickness of interface layer on CaF_2 growth, and type A growth is verified on Sc_2O_3 film with abrupt interface free [13]. With the existence of an interface layer (1 1 1) structure tends to be type B structure. Transmission electron microscope (TEM) images often show an amorphous layer at the interface between YSZ film and Si substrate [18]. Praseodymium (Pr_2O_3), known as an ionic material like YSZ, forms type B of

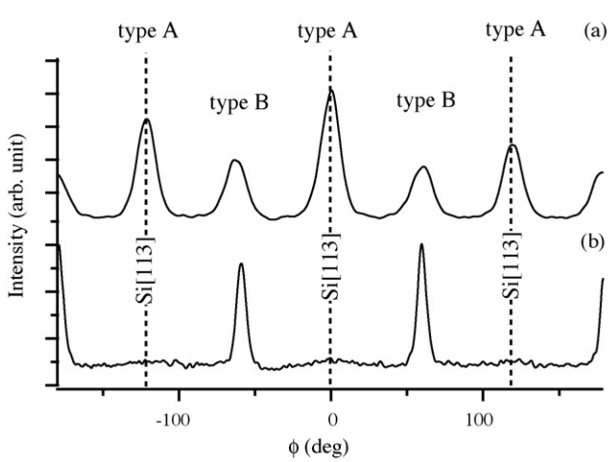

Fig. 3. (a) XRD ϕ scan of YSZ deposited on Si(1 1 1) at substrate temperature of 750 °C with $R_{flow} = 1\%$. Six-fold peak of YSZ(1 1 3) clearly shows the epitaxial growth of YSZ(1 1 1), which consists of a two domain structure type A and type B. (b) Three-fold peaks were observed from YSZ film deposited at the relatively low substrate temperature of 700 °C. Compared with the doted line showing the three-fold Si[1 1 0] direction, YSZ grew as single domain structure of type B.

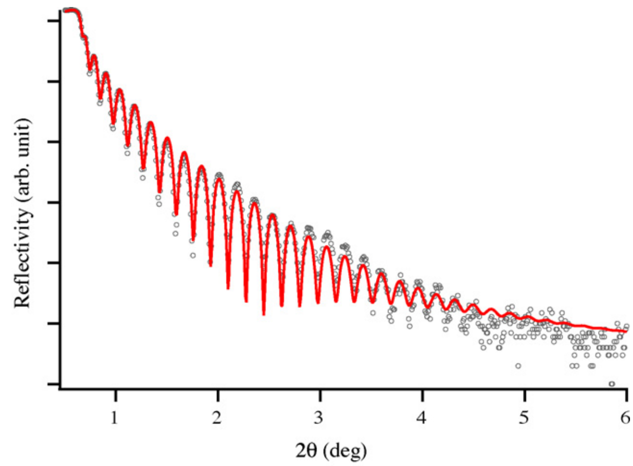

Fig. 4. X-ray reflectivity (XRR) measurement on single domain YSZ film, shows film thickness of 486 Å, and roughness of 5 Å, which was comparable with surface roughness estimated from AFM images.

Pr_2O_3 (1 1 1) structure, with the existence of an oxide interface layer formed by post-oxygen annealing, because of the high mobility of oxygen in Pr_2O_3 films [19]. In this study, the high R_{flow} of 10% affected the interface, and an interface layer may have formed during the deposition. For growth of the type B structure on a Si(1 1 1) substrate, the following conditions were preferred: (1) low substrate temperature, (2) low deposition rate, and (3) existence of interface layer (high oxygen atmosphere). The first layer both of type A and B uniquely lie with six symmetry on six-fold Si(1 1 1) surface. Which type of structure grows is dependent on how the sequence stacks layers along the [1 1 1] direction. Lower substrate temperature emphasizes the energy difference between type A and type B. High oxygen gas atmosphere might form an interface layer the same as praseodymium, where the high mobility of oxygen affects the formation of an interface layer.

A Si film on a YSZ(1 1 1) substrate, as a reverse pairing, was investigated to better understand how layers stack in sequence. Si was deposited on YSZ(1 1 1) substrate using CVD in contrasting conditions: (1) high substrate temperature (1000 °C), (2) high deposition rate (1 Å/s), and (3) low oxygen atmosphere (deoxidization atmosphere), preferable for type A growth. XRD ϕ scan revealed the epitaxial growth of Si(1 1 1) on YSZ(1 1 1) substrate with the relation of Si[1 1 0] parallel to YSZ[1 1 0], type A structure, as expected. Fig. 5 shows the dependence on the film thickness of the rocking curve FWHM and real space distance (d value) of Si(1 1 1) deposited on YSZ(1 1 1) substrate, which was estimated by the cross-section image observed using scanning electron microscopy (SEM) images. With increasing film thickness, the FWHM of Si(1 1 1) decreased to 0.2° and the real space distance of Si(1 1 1), the d value, settled at 3.147 Å, instead of 3.136 Å, as for the bulk silicon. The inset is an XRD ϕ scan using Si(1 1 3) and YSZ(1 1 3) peaks, showing epitaxial growth with type A structure (cubic on cubic), as mentioned above.

Epitaxial growth of single domain YSZ indicated how the sequence stacks layers, being affected by neighboring atoms, not only from the six-fold surface on Si(1 1 1). The difference

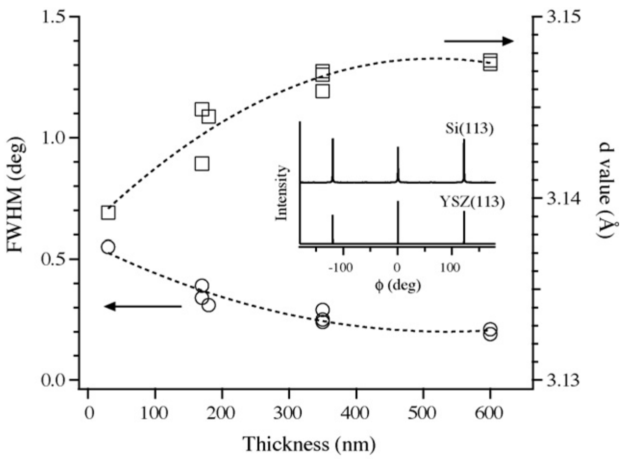

Fig. 5. The FWHM and d value of Si(1 1 1) deposited on YSZ(1 1 1) substrate correlated with film thickness. The inset is XRD ϕ scan using Si(1 1 3) and YSZ(1 1 3) peaks, showing epitaxial growth with type A structure (cubic on cubic).

of the interface energy between type A and type B must be emphasized at lower substrate temperatures, and the requirement of a low temperature to grow type B was indicative of the energetic stability of type B rather than type A. A high oxygen flow rate was another factor affecting crystal growth. Oxygen mobility in praseodymium forms an interface layer even after post-annealing, and the crystal structure turns into type B together with the interface layer. Such an interface layer is not formed when annealing takes place in a high vacuum atmosphere [19]. In this study, the growth of type B single domain required a high R_{flow} (high oxygen flow). During deposition in such a high oxygen atmosphere, an interface layer should form, the same as during oxygen annealing on praseodymium, resulting in the growth of type B structure of YSZ(1 1 1), a known electrolyte.

4. Conclusions

In this study, XRD ϕ scans verified epitaxial YSZ(1 1 1) grown on Si(1 1 1) substrate using the sputtering method. Six-fold peaks from ϕ scan indicated YSZ(1 1 1) film to consist of two variants, type A and type B which were related by 180° rotation around surface normal of Si(1 1 1). Higher oxygen flow rate and lower substrate temperature resulted in single domain YSZ(1 1 1) growth with three-fold peaks on ϕ scan. The position of ϕ scan peaks, compared with Si substrate peaks, revealed the single domain YSZ with type B structure.

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