Cubic Zirconia Crystalline Surface Oxide Epitaxial Formation on ZrB₂(0001) Confirmed by Circularly-Polarized-Light Photoelectron Diffraction

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Pure cubic zirconia (c-ZrO₂) is unstable at room temperature. We achieved the epitaxial formation of c-ZrO₂ crystalline surface oxide islands on ZrB₂(0001) by annealing the substrate without sample cleaning at 950°C under ultrahigh-vacuum conditions. The interface structure at the c-ZrO₂ islands and the ZrB₂(0001) substrate was investigated using element-specific circularly-polarized-light photoelectron diffraction, angle-resolved X-ray photoelectron spectroscopy, and reflection high-energy electron diffraction (RHEED). The ZrO₂(111) islands was a twin crystal oriented in ZrO₂[110]/ZrB₂[2110], and was stable up to around 1500°C. The Zr-Zr distance of ZrB₂ bulk and that of ZrO₂(111) agree with at the ratio of 8 to 7. [DOI: 10.1380/ejssnt.2015.111]

Keywords: Photoelectron diffraction; Soft X-ray photoelectron spectroscopy; Reflection high-energy electron diffraction (RHEED); Surface structure; c-ZrO₂; ZrB₂; Epitaxial surface oxide

I. INTRODUCTION

Cubic zirconia (c-ZrO₂) is used as a diamond simulant because of its high refractive index. ZrO₂ is a promising candidate for high-k materials and gas sensors [1–3]. However, pure c-ZrO₂ does not exist at room temperature (RT). Pure ZrO₂ has three phases in different ranges of temperature at normal atmospheric pressure: monoclinic phase (space group P2₁/c) from RT to 1170°C, tetragonal (P4₂/nmc) from 1170 to 2370°C, and cubic fluorite structure (Fm3m) from 2370 to 2706°C [4, 5]. The addition of solutes such as MgO, CaO, Y₂O₃, HfO₂ is necessary to stabilize c-ZrO₂ at RT. c-ZrO₂ is the hardest among the three structures. c-ZrO₂ is useful materials as a heat-resistant hard-coating.

ZrB₂, which was used as a substrate crystal in this study, has unique features such as high hardness, high melting point, high corrosion resistance, and metallic conductivity. It has an AlB₂-type crystal structure consisting of alternating stacking of a close-packed Zr layer and a graphene-like B layer. The clean (0001) surface is terminated with a Zr layer [6]. The oxidation of ZrB₂ has been studied for a powder ZrB₂ [7, 8] and a single crystal as a substrate for GaN epitaxial formation [9, 10], as well as for a basic study of surface oxidation [11, 12]. Recently, the oxidation of ZrB₂ nanoparticle has been reported by G. Zhao, et al. in 2014 [13]. However, the oxide surface layer and interface structures on ZrB₂(0001) have been still unclear. Here we report the fabrication and confirmation of a stable pure c-ZrO₂ epitaxially grown on ZrB₂(0001) without additive solutes simply by annealing at 950°C under ultrahigh-vacuum (UHV) condition after exposed to the air. This c-ZrO₂ was stable from RT to about 1500°C, which is sufficient for a heat-resistant hard coating.

In this study, we investigated the ZrO₂ atomic structure and the interface relation between ZrO₂ and ZrB₂(0001) using element-specific two-dimensional photoelectron diffraction (2D-PED) and X-ray photoelectron spectroscopy (XPS) measured by the display-type spherical mirror analyzer (DIANA) [14–16] and reflection high-energy electron diffraction (RHEED). The acceptance angle of DIANA was ±60°. By scanning the sample azimuth over 360°, 2π-steradian PIAD data were obtained. The ZrO₂(111) was a twin crystal oriented in ZrO₂[110]/ZrB₂[2110], and was stable up to around 1500°C. The Zr-Zr distance of ZrB₂ bulk and that of ZrO₂(111) agree with at the ratio of 8 to 7.

2D-PED is a useful element-selective atomic structure analysis method that enables us to observe three-dimensional atomic configurations without surface destruction. A photoelectron from a localized core level is an excellent element selective probe for surface structure analysis. Forward focusing peaks (FFPs) appearing in the photoelectron intensity angular distribution (PIAD) indicate the directions of surrounding atoms seen from the photoelectron emitter atom. When we use circularly-polarized light as an excitation source, the atomic distance between the emitter and the scatterer atoms can be deduced from the circular-dichroism shift of FFP direction [17–20]. In this study, we determined the structure of surface oxides on ZrB₂(0001) as a cubic zirconia by this unique method.

II. EXPERIMENT

The experiments were performed at the circularly polarized soft-X-ray beamline BL25SU at SPring-8, Japan [21]. 2D-PED and RHEED experiments were performed in an UHV system at RT. A single crystalline ZrB₂(0001) surface was used as the substrate of c-ZrO₂. The ZrB₂ single crystal was grown using the rf (radio frequency) heated floating-zone method [22]. A 1-mm-thick sample of 7–8 mm diameter was cut from the crystal rod after orientating to a (0001) plane using the X-ray Laue
method. One side of the sample was mirror-polished with diamond and alumina paste [12]. We prepared an atomically clean ZrB$_2$(0001) surface with the method reported in ref. [6]. The sample was at first heated up to 1000°C for degassing. After waiting for the vacuum to recover, the sample was flash heated at 1400-1500°C several times by electron bombardment heating. Here we call this sample S1. For a c-ZrO$_2$ formation, the ZrB$_2$ substrate was once exposed to atmosphere. We annealed the sample at 950°C for 10 min without cleaning by direct current injection after transferring into an ultra-high vacuum below 3×10$^{-8}$ Pa. We call this sample S2. We measured angle-resolved constant-final-state (CFS) mode XPS spectra, RHEED patterns, and PIADs for S1 and S2.

III. RESULTS AND DISCUSSION

The XPS spectra of S1 showed no contaminants of C and O. The surface structure was characterized by RHEED. We confirmed a sharp (1×1) pattern coming from the clean surface. Figure 1(a) shows the RHEED pattern from the ZrB$_2$(0001) clean surface after flash-heating to 1400°C. The incident kinetic energy was 15 keV. The intervals of 1×1 fundamental diffraction spots appeared were 3.97 ± 0.07 Å$^{-1}$ (3.17 ± 0.09 Å$^{-1}$) matching with the Zr-Zr atomic distance 3.169 Å of the ZrB$_2$ substrate. For S2, we observed O 1s, Zr 3d, and Zr 3p peaks from the surface oxide on ZrB$_2$(0001) in the XPS spectra. RHEED patterns from ZrB$_2$ surface with and without oxygen were compared. Figure 1(b) shows the RHEED pattern from the ZrB$_2$(0001) surface after oxidation. The transmission diffraction pattern was observed, which is similar to the observation by Armitage et al. [9]. The intervals of diffraction spots were 3.45 ± 0.06 Å$^{-1}$ (3.64 ± 0.06 Å) matching with the lattice constant 3.631 Å of the ZrO$_2$ substrate. Note that seven times the length of Zr-Zr in-plane distance in ZrO$_2$ lattice matches with eight times the length of Zr-Zr distance of ZrB$_2$ substrate lattice. We clarified that the ratio of Zr-Zr distance parallel to the surface between ZrB$_2$ bulk and that of ZrO$_2$(111) was 8 to 7.

The RHEED result in Fig. 1(b) shows that the surface oxide forms small islands. The size of the islands was about 1 nm. This size was much smaller than the size of the excitation light spot of about 0.3 mm. We considered that the CFS-mode XPS was effective to estimate the average thickness of the oxide islands. We measured CFS-mode photoelectron spectra for the estimation of the oxide islands thickness of S2. Figure 2 shows the angle resolved CFS mode photoelectron spectra of Zr 3d at a kinetic energy of 600 eV. We measured the emission angle dependence of CFS-XPS from 0° to 90° relative to the surface normal. Mean free path of photoelectron was kept constant. The peaks at photon energy of 786.5 and 789.0 eV shown in Fig. 2 correspond to Zr atoms bonded to B atoms (Zr-B) and O atoms (Zr-O), respectively. The Zr-O peak intensity increases with the increasing emission polar angle. The estimated chemical shift of Zr-O relative to Zr-B was 3.6 eV. This value was larger than that of O atom adsorbed on the ZrB$_2$ surface forming (2×2) superstructure but smaller than that of fully oxidized state Zr oxides [12]. We estimated the average thickness of the oxide islands using the following formula.

\[
d = \lambda_O \cos\theta \ln \left( \frac{N_S \lambda_S I_O}{N_O \lambda_O I_S} + 1 \right) \quad (1)
\]

\[
\approx \lambda_O \cos\theta \ln \left( \frac{N_S I_O}{N_O I_S} + 1 \right) \quad (2)
\]

$I_O$ and $I_S$ are the photoelectron intensities from the oxide island and the substrate, respectively. $N_O$ and $N_S$ are the atom densities of the surface oxide and substrate, respectively. $\lambda_O$ and $\lambda_S$ are the attenuation lengths in the surface oxide and the substrate. We used the common value of 17 Å deduced by simulation code SESSA [23, 24] as the attenuation lengths for $\lambda_O$ and $\lambda_S$. The thickness of the oxide islands was determined to be 11.0 ± 0.7 Å, which corresponds to the thickness of four Zr layers in c-ZrO$_2$(111).

Then 2π-steradian Zr 3d and O 1s PIADs from the clean ZrB$_2$(0001) surface and the oxide islands on ZrB$_2$(0001) were measured using DIANA installed at BL25SU. A set of 2π-steradian PIADs excited by $\sigma^+$ and $\sigma^-$ helicity lights was measured by switching the path of storage ring electrons in twin helical undulators at 0.1 Hz [21].

As shown in Fig. 3(a), Zr 3d PIAD from the clean ZrB$_2$(0001) surface was six-fold symmetric. The photoelectron kinetic energy was 900 eV and the excitation photon energy was 1089 eV. FFPs appearing at the directions to the first, second, and third nearest Zr atoms seen from Zr emitter atom are indicated by encircled numbers. The corresponding crystal structure of ZrB$_2$ is depicted...
as the top and side views in Fig. 4(a) and (c). These FFPs were also observed in the Zr 3d PIADs from the oxidized surface as shown in Fig. 3(b) indicating that the substrate structure was also observed. FFP of B close to Zr could not be detected because of its small scattering cross-section. Figure 3(b) is a PIAD pattern for the ZrB 2 surface with oxide islands. Figure 3(b) does not have strong effect of oxide islands. We consider that the oxide forms small islands and does not form uniform layer, and the substrate ZrB 2(0001) appears on the surface in some extent, which is inferred from the transmission pattern of RHEED in Fig. 1(b). The arrangement of the peak (1) in Fig. 3(b) and the peak A in Fig. 3(c) were seen in the same azimuthal directions. These peaks correspond to the arrangement of Zr atoms in a Zr layer just above the emitter O atoms at the polar angle of 70.5°. The open circles labeled as A at the polar angle of 55.0° correspond to the FFP directions of the second nearest Zr atoms seen from emitter O atoms at the polar angle of 55.0° from Fig. 3(b). The corresponding crystal structure of ZrO 2 is depicted as the top and side views in Fig. 4(b) and (c). In Fig. 3(c), the FFP from O scatterer atoms were too weak for detection because the scattering cross-section of O atom is much smaller than that of Zr. The open circles labeled B and B’ indicate the FFP of three-fold symmetry of the first nearest Zr seen from O as shown in Fig. 4(b). In a single domain, we could see only B or B’ peaks. The fact that both B and B’ peaks are seen in Fig. 3(c) leads us to conclude that there were twin domains of ZrO 2 on ZrB 2(0001). As shown in Fig. 3(c), the directions of B and B’ peaks of the first nearest Zr from O atoms were three-fold symmetric and their polar angles were 71.5° corresponding to the atomic structure of ZrO 2. Among the three structures of ZrO 2: monoclinic, tetragonal, and cubic fluorite structure, only the cubic structure has this configuration. From these peaks, we easily and directly concluded that the c-ZrO 2 formed on ZrB 2(0001).

Furthermore, the distances between O atom and Zr atoms were determined from the analysis of O 1s FFP shifts in a circularly-polarized-light PIAD. Figure 3(d) is the circular dichroism pattern, i.e., the difference of two PIADs excited by \( \sigma^+ \) and \( \sigma^- \) circularly polarized light. A pair of black and white contrast pattern indicates where rotational circular dichroism shift is apparent. The interatomic distance \( R \) was deduced from FFP rotational shift...
The angle between the incident photon axis and the wave number of photoelectron, respectively [16].

\[ R = \tan^{-1} \frac{m^*_f(\theta_{\text{out}})}{k \Delta \phi \sin^2 \theta_{\text{out}}} \]  

where \( m^*_f(\theta_{\text{out}}) \) and \( k \) are the angular momentum and the wave number of photoelectron, respectively [16]. \( \theta_{\text{out}} \) is the angle between the incident photon axis and the outgoing direction of the emitted photoelectrons. The shift is inversely proportional to the interatomic distance \( R \) between the photoelectron emitter and the scatterer atoms. The interatomic distance from each O atom to the first and second nearest Zr atoms were determined to be 2.7 ± 0.7 Å and 4.9 ± 1.7 Å, respectively, which are in good agreements with the value of c-ZrO₂ crystal; 2.22 Å and 4.25 Å. Note that there are six FFPs for the first and second nearest Zr atoms due to the twin crystal structure of ZrO₂ islands [9].

IV. CONCLUSIONS

In conclusion, we achieved the epitaxial formation of c-ZrO₂ crystalline oxide islands on ZrB₂(0001) by annealing the substrate without sample cleaning at 950°C under ultrahigh-vacuum conditions. We investigated the surface oxide and interface structure of ZrO₂ on the ZrB₂(0001) substrate by 2D-PES and RHEED. We found that the 11-nm pure c-ZrO₂(111) grew epitaxially on the ZrB₂(0001) substrate with a commensurate condition. The Zr-Zr distance of ZrB₂ bulk and that of ZrO₂(111) agree with at the ratio of 8 to 7 and ZrO₂ [±1±10]///ZrB₂[2110].

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