Cubic Zirconia Crystalline Surface Oxide Epitaxial Formation on $\text{ZrB}_2(0001)$ Confirmed by Circularly-Polarized-Light Photoelectron Diffraction

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(Received 10 January 2015; Accepted 20 February 2015; Published 21 March 2015)

Pure cubic zirconia ($c\text{-ZrO}_2$) is unstable at room temperature. We achieved the epitaxial formation of $c\text{-ZrO}_2$ crystalline surface oxide islands on $\text{ZrB}_2(0001)$ by annealing the substrate without sample cleaning at 950°C under ultrahigh-vacuum conditions. The interface structure at the $c\text{-ZrO}_2$ islands and the $\text{ZrB}_2(0001)$ 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 $\text{ZrO}_2(111)$ islands was a twin crystal oriented in $\text{ZrO}_2[1\bar{1}0]//\text{ZrB}_2[2\bar{1}\bar{1}0]$, and was stable up to around 1500°C . The Zr-Zr distance of ZrB_2 bulk and that of $\text{ZrO}_2(111)$ 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; $c\text{-ZrO}_2$; ZrB_2 ; Epitaxial surface oxide

I. INTRODUCTION

Cubic zirconia ($c\text{-ZrO}_2$) is used as a diamond simulant because of its high refractive index. ZrO_2 is a promising candidate for high- k materials and gas sensors [1–3]. However, pure $c\text{-ZrO}_2$ does not exist at room temperature (RT). Pure ZrO_2 has three phases in different ranges of temperature at normal atmospheric pressure: monoclinic phase (space group $P2_1/c$) from RT to 1170°C , tetragonal ($P4_2/nmc$) from 1170 to 2370°C , and cubic fluorite structure ($Fm\bar{3}m$) from 2370 to 2706°C [4, 5]. The addition of solutes such as MgO , CaO , Y_2O_3 , HfO_2 is necessary to stabilize $c\text{-ZrO}_2$ at RT. $c\text{-ZrO}_2$ is the hardest among the three structures. $c\text{-ZrO}_2$ is useful materials as a heat-resistant hard-coating.

ZrB_2 , 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 AlB_2 -type crystal structure consisting of alternative 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 oxidization of ZrB_2 has been studied for a powder ZrB_2 [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 oxidization of ZrB_2 nanoparticle has been reported by G. Zhao, *et al.* in 2014 [13]. However, the oxide surface layer and interface structures on $\text{ZrB}_2(0001)$ have been still unclear. Here we report the fabrication and confirmation of a stable pure $c\text{-ZrO}_2$ epitaxially grown on $\text{ZrB}_2(0001)$ without additive solutes simply by annealing at 950°C under ultrahigh-vacuum (UHV) condition after exposed to the air. This $c\text{-ZrO}_2$ was stable from RT to about 1500°C , which is sufficient for a heat-resistant hard coating.

In this study, we investigated the ZrO_2 atomic struc-

ture and the interface relation between ZrO_2 and $\text{ZrB}_2(0001)$ 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 $\pm 60^\circ$. By scanning the sample azimuth over 360° , 2π -steradian PIAD data were obtained. The $\text{ZrO}_2(111)$ was a twin crystal oriented in $\text{ZrO}_2[1\bar{1}0]//\text{ZrB}_2[2\bar{1}\bar{1}0]$, and was stable up to around 1500°C . The Zr-Zr distance of ZrB_2 bulk and that of $\text{ZrO}_2(111)$ 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 $\text{ZrB}_2(0001)$ 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 $\text{ZrB}_2(0001)$ surface was used as the substrate of $c\text{-ZrO}_2$. The ZrB_2 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

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method. One side of the sample was mirror-polished with diamond and alumina paste [12]. We prepared an atomically clean $\text{ZrB}_2(0001)$ 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 $1400\text{--}1500^\circ\text{C}$ several times by electron bombardment heating. Here we call this sample S1. For a $c\text{-ZrO}_2$ 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 $\text{ZrB}_2(0001)$ 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 $3.97 \pm 0.07 \text{ \AA}^{-1}$ ($3.17 \pm 0.09 \text{ \AA}$) matching with the Zr-Zr atomic distance $3.169 \text{ \AA}$ of the ZrB_2 substrate. For S2, we observed O $1s$, Zr $3d$, and Zr $3p$ peaks from the surface oxide on $\text{ZrB}_2(0001)$ 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 $\text{ZrB}_2(0001)$ 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 $3.45 \pm 0.06 \text{ \AA}^{-1}$ ($3.64 \pm 0.06 \text{ \AA}$) matching with the lattice constant $3.631 \text{ \AA}$ 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 $\text{ZrO}_2(111)$ 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

FIG. 1. RHEED patterns from (a) the $\text{ZrB}_2(0001)$ clean surface and (b) the $\text{ZrB}_2(0001)$ surface after oxidation.

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. λ_O and λ_S are the attenuation lengths in the surface oxide and the substrate. We used the common value of $17 \text{ \AA}$ deduced by simulation code SESSA [23, 24] as the attenuation lengths for λ_O and λ_S . The thickness of the oxide islands was determined to be $11.0 \pm 0.7 \text{ \AA}$, which corresponds to the thickness of four Zr layers in $c\text{-ZrO}_2(111)$.

Then 2π -steradian Zr $3d$ and O $1s$ PIADs from the clean $\text{ZrB}_2(0001)$ surface and the oxide islands on $\text{ZrB}_2(0001)$ 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 $\text{ZrB}_2(0001)$ 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

FIG. 2. (a) Angle-resolved constant-final-state mode XPS spectra for Zr 3d core level and (b) enlargement at the vicinity of peak top region.

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 ZrB₂ 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 ZrB₂(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 atom as indicated by arrows (1) and A in Fig. 4(c). From this comparison of FFP arrangement, we concluded that the arrangements of Zr atoms were the same in the substrate and the oxide islands forming triangular lattice in the two-dimensional horizontal plane. Aizawa *et al.* reported that ZrB₂(0001) surface has a metallic character with high reactivity to gas adsorption and oxygen is adsorbed dissociatively onto the three-fold hollow site at RT [11]. According to their work, we propose that the ZrB₂(0001) substrate for *c*-ZrO₂(111) formation was terminated with O atoms at the hollow sites.

Figure 3(c) is O 1s PIADs from the ZrB₂ with oxide after annealing at 950°C. The open circles labeled as B and B' at the polar angle of 71.5° in Fig. 3(c) correspond to the FFP directions of the first nearest Zr atoms seen

FIG. 3. (a) Photoelectron intensity angular distribution (PIAD) pattern for Zr 3d core level from the ZrB₂ clean surface (S1). (b) Same as (a) but for the ZrB₂ surface with oxide layer (S2). (c) O 1s PIAD pattern from the ZrB₂ surface with oxide layer (S2). (d) Circular dichroism pattern of (c).

from 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 58.5°. These patterns indicate that the epitaxial crystalline *c*-ZrO₂(111) was formed on the ZrB₂(0001) surface. The corresponding crystal structure of ZrO₂ 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 ZrO₂ on ZrB₂(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 ZrO₂. Among the three structures of ZrO₂; monoclinic, tetragonal, and cubic fluorite structure, only the cubic structure has this configuration. From these peaks, we easily and directly concluded that the *c*-ZrO₂ formed on ZrB₂(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 σ^+ and σ^- 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

FIG. 4. Structure models for a ZrB_2 substrate and a $c\text{-ZrO}_2$ thin film. (a) and (b) Top views of the ZrB_2 substrate and ZrO_2 film, respectively. (c) Side view. The smaller Zrs are located in the back.

$\Delta\phi$ which is well described by the Daimon's formula:

$$R = \tan^{-1} \frac{m_f^*(\theta_{\text{out}})}{k\Delta\phi \sin^2 \theta_{\text{out}}} \quad (3)$$

where $m_f^*(\theta_{\text{out}})$ and k are the angular momentum and the wave number of photoelectron, respectively [16]. θ_{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 $2.7 \pm 0.7 \text{ \AA}$ and $4.9 \pm 1.7 \text{ \AA}$, respectively, which are in good agreements with the value of $c\text{-ZrO}_2$ crystal; $2.22 \text{ \AA}$ and $4.25 \text{ \AA}$. Note that there are six FFPs for the first and second nearest Zr atoms due to the twin crystal structure of ZrO_2 islands [9].

IV. CONCLUSIONS

In conclusion, we achieved the epitaxial formation of $c\text{-ZrO}_2$ crystalline oxide islands on $\text{ZrB}_2(0001)$ by annealing the substrate without sample cleaning at 950°C under ultrahigh-vacuum conditions. We investigated the surface oxide and interface structure of ZrO_2 on the $\text{ZrB}_2(0001)$ substrate by 2D-PES and RHEED. We found that the 11-nm pure $c\text{-ZrO}_2(111)$ grew epitaxially on the $\text{ZrB}_2(0001)$ substrate with a commensurate condition. The Zr-Zr distance of ZrB_2 bulk and that of $\text{ZrO}_2(111)$ agree with at the ratio of 8 to 7 and $\text{ZrO}_2 [\pm 1 \mp 10] // \text{ZrB}_2 [2\bar{1}\bar{1}0]$.

ACKNOWLEDGMENTS

We appreciate the grateful support by Dr. Tetsuya Nakamura and Dr. Takayuki Muro. This research was performed at the Japan Synchrotron Radiation Research Institute (Proposal Nos. 2011A1471 and 2011B1583). This work was partly supported by JSPS Grant-in-Aid for Scientific Research on Innovative Areas: Grant Number 26105001.

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