Formation of oxide layer on HfC(100) surface studied by photoemission spectroscopy

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The oxidation process of an HfC(100) surface has been investigated by photoemission spectroscopy utilizing synchrotron radiation. When the HfC(100) surface is exposed to O₂ at room temperature, the C atoms in the surface region are depleted, and the substrate’s Hf atoms are oxidized by stepwise reactions and are finally oxidized to form an HfO₂-like layer at high coverages (> 10 L). When the surface exposed to 10 – 50 L of O₂ is heated, the work function decreases with increasing heating temperature. The work function reaches its minimum value, which is lower than that of the clean surface by 1.2 eV, by heating the surface exposed to 10 L (50 L) of O₂ at 1000 – 1100°C (1100 – 1200°C). The oxidized layer which gives the minimum work function is proposed to be mostly composed of oxycarbides, and a part of the surface is proposed to be covered by an HfO-like layer.

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I. INTRODUCTION

The early transition metal carbides (TMCs) have attracted considerable attention because they have an interesting combination of useful properties such as extreme hardness, a high melting point and metallic conductivity [1]. In practical applications, they have been found to be useful as stable field electron emitters [2]. It is also known that a stable emission current is available from the TMCs particularly when their surfaces are oxidized [3], and thus it is important to elucidate the oxidation process of the TMC surfaces. In addition, the TMCs have recently been shown to form an interesting new group of catalysts [4–9]; for example, they have been found to exhibit high catalytic activities for the reactions involving C-H bond transformation such as dehydrogenation and hydrogenation reactions [6–8]. It has been proposed that the catalytic properties of the TMCs are often improved by slight oxidation of their surfaces [6–9], and thus the oxidation process of the TMC surfaces is of much interest also from a chemical viewpoint.

The oxidation process of TMC has been investigated for the (100) surfaces of TiC, VC and TaC by Souda, et al. using X-ray photoemission spectroscopy (XPS) and low-energy He⁺ ion scattering spectroscopy [10]. They found that the oxidation of TiC(100) proceeds into the bulk even at room temperature while the adsorbed O atoms are bound to surface metal atoms strongly and the oxidation does not proceed into the bulk for the VC(100) and TaC(100) surfaces [10]. These results suggest that there exists systematic difference in the reactivity toward oxidation between the group 4 and group 5 TMC(100) surfaces. The oxidation process of group 4 TMC has been studied in detail for the (100) surfaces of TiC [11] and ZrC [12] using low-energy electron diffraction (LEED), ultraviolet photoemission spectroscopy (UPS) and XPS. These studies revealed that, on both surfaces, the oxidation proceeds via the depletion of substrate’s carbon atoms and the oxidation of substrate’s metal atoms forming a disordered metal oxide layers [TiOₓ (1.5 < x < 2.0) and ZrOₓ (1.0 < x < 2.0) on TiC(100) and ZrC(100), respectively]. In addition, when the surfaces covered with the disordered metal oxide layers are annealed, the oxide layers are reduced and TiO and ZrO suboxide layers are formed on the TiC(100) and ZrC(100) surfaces, respectively, by heating at ∼ 1000°C [11, 12]. When the surfaces are covered with the suboxide layers, it was found that the work functions are decreased by 1.0 [11] and 0.6 eV [12] from those of the clean TiC(100) and ZrC(100) surfaces, respectively, and that the electronic densities of states around the Fermi level (E_F) on the surfaces are increased through the formation of half-filled Ti 3d and Zr 4d states [14] in the TiO and ZrO layers, respectively. Both the decrease of the work function and the increase of the density of states around E_F clearly contribute to the improvement of the field electron emission efficiencies.

HfC is one of the group 4 TMCs, and thus the reactivity of the (100) surface toward oxygen adsorption is predicted to be similar to those of the TiC and ZrC(100) surfaces. On the other hand, the cohesive energy of HfC (10.99 Ry) is much higher than those of TiC (9.48 Ry) and ZrC (10.07 Ry) [1], meaning that the extraction of carbon atoms from the HfC substrate should be difficult relative to the cases of TiC and ZrC. Therefore, it is intriguing to explore whether the oxidation process of HfC(100) is the same as those of TiC(100) and ZrC(100) or not. In this paper, we report the results of a photoemission spectroscopy (PES) study with synchrotron radiation on the...
oxidation process of HfC(100).

II. EXPERIMENTAL

An HfC0.98 single crystal was grown by the floating zone method at the National Institute for Materials Science [15]. The crystal was cut at an orientation of (100) by spark erosion into a disk with an approximate thickness of 1 mm. Subsequently, the surface was polished mechanically to a mirror surface. The (100) clean surface was prepared in a vacuum chamber by repeatedly heating it to above 1700°C. The temperature of the surface was monitored with an optical pyrometer. The clean surface thus prepared showed a clear (1 x 1) LEED pattern.

The PES measurements using synchrotron radiation were performed on the Beam-line 11D of the Photon Factory, High Energy Accelerator Research Organization (KEK). A Scienta SES-200 electron energy analyzer was used for all PES measurements. The total experimental (KEK). A Scienta SES-200 electron energy analyzer was used for all PES measurements. The total experimental setup was described elsewhere [11]. A Rear View LEED optics (VG Model 8011) was used for the PES measurements. The base pressure in this vacuum system was 1 x 10−10 Torr.

The LEED measurements were performed in a separate chamber equipped with LEED, UPS and XPS apparatuses. Details of this chamber were described elsewhere [11]. A Rear View LEED optics (VG Model 8011) was used for the LEED measurements. The base pressure in this vacuum system was 1 x 10−10 Torr.

III. RESULTS AND DISCUSSION

A. Oxidation of HfC(100) at room temperature

Figure 1(a) shows a LEED pattern of the HfC(100) clean surface. A clear (1 x 1) pattern is observed. The surface structure of HfC(100) was studied by Grzazliski, et al. using LEED I-V analysis, and it has been shown that the HfC(100) surface is almost bulk-oriented, though the surface Hf and C atoms are slightly displaced inward and outward, respectively [16]. As the HfC(100) surface is exposed to O2 at room temperature, the pattern becomes diffuse and only a diffuse background is observed at more than 10 L exposure, suggesting that a disordered overlayer is formed on the HfC(100) surface as a result of oxygen adsorption. Figure 1(b) shows the LEED pattern of the HfC(100) surface exposed to 50 L of O2.

The area intensities of the O 1s, C 1s and Hf 4f peaks in PES spectra are plotted as a function of O2 exposure at room temperature in Fig. 2. The O 1s and C 1s spectra are measured at hv = 600 eV, and the Hf 4f spectra are measured at hv = 65 eV. The background drawn by the Shirley procedure [17] has been subtracted from each raw spectrum prior to the estimation of the peak intensity. As shown in Fig. 2, both the C 1s and Hf 4f peaks are decreased in intensity with increasing oxygen coverage. The C 1s and Hf 4f peak intensities are decreased by 18% and 40% from those in the spectra for the clean surface, respectively. These results are thought to be partly due to the formation of oxygen overlayer on the surface. However, the escape depth of the C 1s photoelectrons (~320 eV) is estimated to be roughly twice as large as that of the Hf 4f photoelectrons (~50 eV) [18], meaning that the Hf 4f peak intensity should be more decreased than that of the C 1s peak if the surface Hf and C atoms are equally covered by oxygen adatoms. Therefore, we interpret the large decrease of C 1s peak intensity as originating from the depletion of substrate’s C atoms during O2 exposure, probably due to their desorption as CO or CO2 molecules. The decrease of the C 1s intensity by 40% corresponds to the removal of the C atoms within roughly two layers below the surface (~2 Å), which is estimated using the mean free path of the C 1s photoelectrons (9.4 Å at 320 eV) [18].

The Hf 4f spectra of the HfC(100) surface exposed to various amounts of O2 are shown in Fig. 3(a). For the clean surface, Hf 4f7/2 and 4f5/2 levels are observed at 14.5 and 16.1 eV, respectively. As the surface is exposed to O2, the peaks at 14.5 and 16.1 eV are attenuated and the 4f components of the oxidized Hf atoms are grown in the higher binding energy side. Figure 3(b) shows the differences between the spectra for the HfC(100) exposed to various amounts of O2 and that of the clean surface. To subtract the unoxidized Hf 4f component, the spectral intensity of the clean surface is adjusted so that the intensity of the unoxidized 4f7/2 peak (14.5 eV) becomes coincident with those of O/HfC(100) before obtaining the difference. A series of difference spectra show that there exist at least three types of oxidized components, whose Hf 4f7/2 components are located at 15.3, 15.8 and 16.9 eV. In this paper, the oxidized states corresponding to the Hf 4f7/2 levels at 15.3, 15.8 and 16.9 eV are labeled as α, β and γ states, respectively, hereafter. In the initial stage of oxidation (up to 2 L), the oxidized Hf atoms are predominantly in the α state. The oxidized components of β and γ states grow with increasing exposure, and the oxidized Hf atoms are predominantly in the γ state at high coverages (>10 L). These results suggest that the oxidation of HfC(100) proceeds via a stepwise oxidation process. The Hf 4f7/2 and 4f5/2 levels of the γ state are observed at 16.9 and 18.5 eV, respectively. The Hf 4f7/2 and 4f5/2 levels of HfO2 thin films formed on Si(100) were observed at 16.4 – 16.8 and 17.9 – 18.2 eV, respectively [19], which are comparable to those of the γ state. Therefore, we attribute the γ state to an HfO2-like (Hf4+2) state. The α and β states should be attributed to the partially oxidized states, and we tentatively assign the states to Hf2+ and Hf4+ states, respectively.

The valence band spectra of the HfC(100) surface exposed to various amounts of O2 are shown in Fig. 4. For the clean surface, a valence band composed of hybridized Hf 5d - C 2p states is observed in the energy region of EF − 5 eV. A similar result has been obtained in the PES study for the Hf(111) surface, in which the Hf 5d - C 2p bulk band is observed at EF − 6 eV [20]. A small projection centered at 10.4 eV is assigned to the C 2s band. A small peak at 6.5 eV may be due to the remnant O contaminant. As the surface is exposed to O2, two peaks at
FIG. 1: LEED patterns of (a) the HfC(100) clean surface, (b) the HfC(100) surface exposed to 50 L O$_2$, and (c) the 50-L-O$_2$-exposed HfC(100) surface after heating at 1200°C, measured with a primary electron energy of 146 eV.

4.8 and 6.4 eV grow with increasing coverage. The peak at 6.4 eV is dominant in the initial stage (≤ 2 L) while the peak at 4.8 eV becomes dominant at high coverages (> 8 L). These results suggest that the O-induced state at 6.4 eV corresponds to the α state and the state at 4.8 eV corresponds to the β and γ states. In addition, at low coverages (2 – 6 L), additional peaks, that are better resolved in the difference spectrum obtained between the spectrum for 2 L and that for the clean surface, are observed at 8.5 and 11 eV (Fig. 4, upper portion). The 8.5 and 11 eV peaks are assigned as 5σ + 1π and 4σ levels of CO adsorbates, respectively [21, 22]. Since the CO induced peaks disappear at high coverages (> 8 L), it is unlikely that the CO adsorbates arise from the adsorption of CO in the residual gas. We consider that the CO adsorbates arise from the reaction between the substrate’s C atoms and the adsorbed oxygen. At low-coverages, it is considered that the adsorbed O atoms preferentially react with C atoms to form CO molecules and a part of them are remained on the surface. The depletion of CO adsorbates at high coverages is considered to proceed via the thermally induced desorption caused by the local heating due to the progress of the exothermal oxidation of the Hf atoms, or via the Hf-C bond breaking by the insertion of oxygen forming CO$_2$ molecules. At high coverages, the C atoms in the surface region have been depleted and thus the formation of CO molecules should be terminated. As the surface is exposed to O$_2$, the emission from the C 2s band is observed to be enhanced. This observation is hard to explain because the C 1s peak is substantially decreased in intensity by O$_2$ exposure (Fig. 2). The origin of this enhancement is unknown at present, and one of the possible explanations is that the matching of the wave functions of the C 2s photoelectron in the bulk and of the free electron in the vacuum at the surface is modified to enhance the transmission of photoelectrons through the surface by oxygen adsorption.

FIG. 2: Changes in the C 1s and Hf 4f peak intensity normalized by that observed for the clean surface respectively and change in the O 1s peak intensity normalized by that observed for the O$_2$ 50 L exposed surface as a function of O$_2$ exposure.

Figure 5(a) shows the C 1s spectra of the HfC(100) surface exposed to various amounts of O$_2$. The C 1s peak is monotonically decreased in intensity with increasing coverage, however, the peak is observed at 281.5 eV independent of the exposure. At low coverages (≤ 5 L), an O-induced feature is observed as a tail in the higher binding energy side of the main peak. We tried to fit the peak using Gaussian functions, and the best fit results show that the tail is due to the existence of a peak at 283 eV, which is in good agreement with the result obtained in the present study. A series of spectra in Fig. 5(a) show that any oxidized C 1s components are not observed except for that assigned as the C 1s level of the
CO adsorbate. This result suggests that the C atoms in the substrate are not directly bound to the adsorbed O atoms in the oxidized layer.

On the basis of the above-mentioned results, the oxidation process of HfC(100) at room temperature is summarized as follows: As the HfC(100) surface is exposed to O₂ at room temperature, the substrate’s C atoms are depleted probably due to their desorption as CO or CO₂ molecules, and the Hf atoms are oxidized through a step-wise process. Figure 2 shows that the O 1s peak intensity gradually increases even at > 20 L while the decrease of the C 1s peak intensity nearly saturates at > 20 L, sug-
suggesting that the adsorbed O atoms are exclusively consumed for the oxidation of Hf atoms to form an HfO$_2$-like layer at $> 20$ L. We have studied the oxidation process of the other group 4 TMC(100) surfaces (TiC(100) [11] and ZrC(100) [12]), and have proposed that the oxidation of these surfaces proceeds via the process including the depletion of the substrate’s C atoms and oxidation of the metal atoms. Thus, it is concluded that the oxidation process proposed in this study is essentially common to all the group 4 TMC(100) surfaces. Our previous study on the oxidation of the HfC(111) surface has revealed that the HfC(111) surface is very reactive to O$_2$ adsorption; O$_2$ adsorbs dissociatively with the sticking probability of approximately 1 [24]. However, on the (111) surface, the adsorption saturates when the (1 $\times$ 1) overlayer is completed (2 L), and the oxidation of the substrate below the surface does not occur [24]. It is considered to be due to the fact that the HfC(111) surface is covered with an Hf layer. In this case, the surface Hf layer should function as a passivation layer for the reaction of the substrate’s C and adsorbed O atoms, and, as a result, prevent the depletion of C atoms from the substrate. Therefore, the depletion of C atoms as a result of the reaction with the adsorbed O atoms is considered to be a key process in the oxidation of TMC.

**B. Oxidation of HfC(100) at high temperatures**

Next, we discuss the change in the oxidation state of the oxide layer on the HfC(100) surface induced by heat treatment. The data presented below were obtained by heating the sample at each temperature for 5 min, and all the data were measured after the sample was cooled to nearly room temperature.

The results of the work function measurements for the HfC(100) surface oxidized by several procedures are summarized in Fig. 6. The left-hand panel of Fig. 6 shows the change in the work function as a function of O$_2$ exposure at room temperature. The work function increases monotonically with increasing coverage, and the increase nearly saturates at $> 20$ L. The work function is increased by $\sim 1$ eV at $> 20$ L. The right-hand panel shows the change in the work function of the HfC(100) surface exposed to 10 L (open squares) and 50 L of O$_2$ (filled circles) as a function of heating temperature. As the surface exposed to 10 L (50 L) of O$_2$ is heated, the work function is decreased with increasing heating temperature up to 1000$^\circ$C (1100$^\circ$C), reaches its minimum value at 1000 – 1100$^\circ$C (1100 – 1200$^\circ$C), and finally returns to the initial value of the clean surface upon heating above 1100$^\circ$C (1200$^\circ$C). The work functions in their minimum regions are lower than that of the clean surface by $\sim 1.2$ eV. The HfC(100) surface exposed to 50 L of O$_2$ gives a diffuse LEED pattern with no observable spots (Fig. 1(b)). When the surface is heated, weak (1 $\times$ 1) spots recover at $\sim 900^\circ$C, and the (1 $\times$ 1) pattern becomes sharper as the heating temperature is increased. Fig. 1(c) shows the LEED pattern of the 50-L-O$_2$-exposed HfC(100) surface after heating at 1200$^\circ$C. The clear (1 $\times$ 1) pattern is observed, however, the spots are slightly diffuse as compared to those in the pattern of the clean surface (Fig. 1(a)).

In Fig. 7, the intensities of the O 1$s$ and C 1$s$ peaks in PES spectra of the 10-L-O$_2$-exposed HfC(100) surface are plotted as a function of heating temperature. Figure 7 shows that the O 1$s$ peak is decreased in intensity with increasing heating temperature, however, most of the adsorbed O atoms remain up to 1000$^\circ$C. The O 1$s$ peak intensity decreases rapidly at 1000 – 1300$^\circ$C, however, more than half of the adsorbed O atoms remain on the surface.
in the work function minimum region (1000 − 1100°C), indicating that a certain oxidized layer is responsible for the low work function. The decrease of the O 1s peak intensity is thought to be due to the desorption of O atoms, however, the diffusion of some of the O atoms into the bulk may also contribute to the decrease of the O 1s peak intensity at ≤ 1000 − 1100°C, as will be discussed later. The C 1s peak is increased in intensity with increasing heating temperature, probably due to the segregation of C atoms from the bulk. The C 1s peak intensity is increased gradually up to 1100°C and rapidly at 1100−1300°C, and almost returns to that for the clean surface at > 1300°C.

Figure 8(a) shows the valence band spectra of the 10-L-O₂-exposed HfC(100) surface after heating at various temperatures. The O 2p-induced bands are totally shifted to the higher binding energy side upon heating at ≤ 810°C. The O 2p-induced bands are observed at 5.3 and 6.6 eV at 810°C, and the former band is decreased in intensity more rapidly with increasing heating temperature. The band at 6.6 eV becomes dominant in the work function minimum region (1000 − 1100°C). The spectra of the oxidized surface heated at elevated temperatures are different from those of the surface exposed to O₂ at room temperature (Fig. 4), in which the O 2p-induced bands are observed at 4.8 and 6.4 eV, indicating that the oxide layer on the surface is changed into a different phase upon heating. Fig. 8(b) shows the magnified spectra around E_F. A slight Fermi edge is observed in the spectrum of the clean surface, and the intensity at the Fermi edge is nearly unchanged by 10 L of O₂ exposure. However, the intensity around E_F is increased by heating the 10-L-O₂-exposed HfC(100) at more than 965°C. The intensity around E_F is higher than that of the clean surface upon heating the 10-L-O₂-exposed HfC(100) surface at 965 − 1185°C, and the intensity around E_F returns to that for the clean surface upon heating at ≥ 1220°C. These results suggest that the oxidized HfC(100) surface with the lowered work function has a high density of states (DOS) around E_F.

Figure 9 shows the Hf 4f spectra of the 10-L-O₂-exposed HfC(100) surface after heating at various temperatures. A series of spectra show that the oxidized layer formed on the HfC(100) surface is gradually reduced with increasing heating temperature, and the reduction process is rather complicated. When the HfC(100) surface is exposed to O₂ at room temperature, the Hf atoms are oxidized through a stepwise process (+2 → +3 → +4). However, when the HfC(100) surface exposed to O₂ is heated, some Hf 4f peaks associated with the oxidized Hf atoms seem to be shifted continuously towards the lower binding energy side with increasing heating temperature, indicating each reduction state includes fractionally oxidized Hf atoms. Thus, it is considered that a complex oxycarbide layers in which the Hf atoms are bound to both O and C atoms are formed by heating the O₂-exposed surface. This is supported by the observation of the gradual increase of the C 1s peak intensity with increasing heating temperature (Fig. 7), which implies that the C atoms segregate from the bulk. When the HfC(100) surface is exposed to O₂ at room temperature, the oxidized Hf 4f components are grown, however, the Hf 4f_{7/2} and 4f_{5/2}
Peaks of the HIC substrate are observed at 14.5 and 16.1 eV, respectively, independent of the coverage up to 50 L. However, the Hf 4f peaks of the HfC substrate shift to the higher binding energy side when the O₂-exposed surface is heated. The shift reaches its maximum in the work function minimum region, where the shift is observed to be 0.3 eV. This result suggests that the diffusion of some of the adsorbed O atoms into the bulk occurs by heating and the electrons in the Hf atoms in the HfC substrate in the surface region with the thickness larger than the escape depth of the Hf 4f photoelectrons are partially transferred to the O atom.

Our previous studies showed that, when the O₂-exposed TiC(100) and ZrC(100) surfaces are heated, the work functions are decreased and reach their minimum values by heating at ~1000°C [11, 12]. The work functions are decreased by 1.0 [11] and 0.6 eV [12] from those of the clean TiC(100) and ZrC(100) surfaces, respectively. Therefore, the formation of the oxidized surface with the low work function by heating the O₂-exposed surface at ~1000°C is concluded to be common to group 4 TMC(100) surfaces. When the O₂-exposed TiC(100) and ZrC(100) surfaces are heated at ~1000°C, the surfaces are covered with ordered TiO(100) [11] and ZrO(100) [12] layers, respectively, and as a result, the DOS around E_F are substantially increased due to the formation of Ti 3d and Zr 4d states [12] in the TiO(100) and ZrO(100) layers, respectively. In the case of HfC(100), the DOS around E_F is also increased by heating the 10-L-O₂-exposed HfC(100) surface at 965 – 1185°C (Fig. 8(b)), suggesting that an ordered HfO-like layer is also formed. Figure 9 shows that the peaks attributed to the Hf^{2+} state are surely observed in the spectra for the 10-L-O₂-exposed HfC(100) surface heated at 965 – 1185°C. In other words, the increase of the DOS around E_F is observed only when the Hf 4f peaks of the Hf^{2+} state are observed, indicating that the Hf^{2+} state should be responsible for the high DOS around E_F. However, the peaks of the Hf^{2+} state are not dominant in the Hf 4f spectra even in the work function minimum region, and thus, it is considered that the surface is covered with the HfO-like layer only partly upon heating at 965 – 1185°C. The DOS around E_F in the HfO-like layer is thought to be increased due to the formation of the partially filled Hf 5d state. Figure 9 shows that, even in the work function minimum region (1000 – 1100°C), the surface seems to be partially covered with the HfO-like layer but the most part is covered with oxycarbide layers. Therefore, not only the formation of the HfO-like layer but the formation of the oxycarbide layer should contribute to the lowering of the work function. When the HfC(100) surface is exposed to O₂ at room temperature, the Hf atoms in the surface region are oxidized to form the α state at low coverages (≤2 L), in which the Hf atoms are in the Hf^{2+} state as in the case for the HfO-like layer. However, the electronic structure of the HfO-like layer is thought to be different from that of the α state, because the emissions around E_F in the valence band spectra are not enhanced for the α state. Since the LEED pattern becomes diffuse when the surface is exposed to O₂ at room temperature, we think that the α state is a disordered state. On the other hand, the (1×1) pattern recovers when the surface exposed to 10 – 50 L of O₂ is heated at ≥900°C, and thus we think that the HfO-like layer is a sort of an ordered layer with a (1×1) periodicity.

IV. CONCLUSIONS

The oxidation process of HfC(100) was investigated by PES utilizing synchrotron radiation. It is found that, when the HfC(100) surface is exposed to O₂ at room temperature, the C atoms in the substrate are depleted and the Hf atoms in the substrate react with oxygen to form disordered Hf oxide layers. The oxidation of the Hf atoms is found to proceed via a stepwise reactions (Hf^{4+} → Hf^{3+} → Hf^{2+} → Hf^{2+}), and finally an HfO₂-like layer is formed at high coverages (>10 L). When the O₂-exposed surface is heated, the work function decreases with increasing heating temperature. The work function reaches its minimum value, which is lower than that of the clean surface by 1.2 eV, by heating the HfC(100) surface exposed to 10 L (50 L) of O₂ at 1000 – 1100°C (1100 – 1200°C). As the O₂-exposed surface is heated, the HfO₂-like layer is gradually reduced. Each reduced layer includes the fractionally oxidized Hf atoms, suggesting the formation of Hf oxycarbides. It is found that the DOS of the surface around E_F is increased by heating the 10-L-O₂-exposed surface at about 1000 – 1200°C, which is proposed to be due to the formation of HfO-like layers which partially cover the surface.

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