Interaction of Oxygen with the Polar HfC(111) Surface: Angle-Resolved Photoemission Study

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Angle-resolved photoemission spectroscopy utilizing synchrotron radiation has been used to study the adsorption state of oxygen on a HfC(111) surface. Oxygen adsorbs dissociatively on the HfC(111) surface at room temperature forming a (1×1) overlayer at the saturation coverage. The two-dimensional band structure of the chemisorption bonding states formed through the hybridization of O $2p$ and Hf $5d$ orbitals (O $2p$ -derived states) is measured for the HfC(111)(1×1)-O surface. It is found that the $2p_z$ -derived band is formed in slightly higher binding energy region relative to the $2p_x$ - and $2p_y$ -derived bands, indicating that the vertical interaction involving the $2p_z$ orbital is slightly more important in the chemisorption bond formation relative to the lateral interaction involving the $2p_x$ and $2p_y$ orbitals. Hf $4f$ spectra are measured for the clean and oxygen-covered HfC(111) surfaces, and it is found that the oxidation of the surface Hf atoms to form a Hf oxide does not proceed at room temperature.

Keywords: Angle resolved photoemission, Chemisorption, Carbides, Low index single crystal surfaces, Oxygen.

I. INTRODUCTION

The group IV and V transition metal carbides (TMCs) have attracted much 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 used as stable field electron emitters, coating materials, catalysts, etc. Because the surface properties play an essential role in all these applications, it has become important to investigate the surface properties of TMCs.

The TMCs have a rocksalt type crystal structure, and previous studies on the physical and chemical properties of the TMC surfaces have concentrated on the two typical low-index surfaces, i.e., the (100) and (111) surfaces [2]. Both the (100) and (111) surfaces give (1×1) LEED patterns, meaning that the surfaces are not reconstructed (an exception has only been found for VC(111) [3]). Such an ideal (100) surface is a neutral surface composed of equal numbers of metal and carbon atoms, while an ideal (111) surface is a polar surface whose first layer should be either a metal layer or a carbon layer. The atomic structure of the (111) surface has been investigated extensively with impact-collision ion scattering spectroscopy (ICISS) for TiC [4], HfC [5], NbC [6] and TaC(111) [7], and it has been established that these surfaces are terminated with (1×1) metal layers. A series of angle-resolved photoemission spectroscopy (ARPES) studies have been made on the electronic structures of TiC [8,9], ZrC [10], HfC [11,12], NbC [13] and TaC(111) [14], and these studies have revealed that metal d -derived surface states are formed around the Fermi level (E_F) on all these surfaces. On the (100) surface, such states are lacking and the density of states around E_F is relatively small [2]. The electronic states around E_F should play an essential role in surface reactions, and it is expected that the TMC(111)

surfaces are much reactive towards gas adsorption relative to the TMC(100) surfaces due to the existence of the surface states around E_F . This has been supported by our previous gas adsorption studies on TMC(100) and (111); for example, H_2 and CO adsorb dissociatively on the ZrC(111) surface with the sticking probability of ~ 1 , while these molecules do not adsorb on the ZrC(100) surface at room temperature [15]. Thus the unreconstructed TMC(111) surface is a very attractive field in surface chemistry, and detailed studies regarding the interaction of gas molecules with the TMC(111) surface are urgently called for.

An oxygen adsorption system can be used as a prototype system for studying the reactivity of a surface towards gas adsorption. In this work, the adsorption state of oxygen on a HfC(111) surface is investigated with ARPES utilizing synchrotron radiation. The adsorption state of oxygen on HfC(111) has been studied by Hayami *et al.* using ICISS [5], and it has been proposed that oxygen adsorbs dissociatively on HfC(111) and that the dissociated O atom adsorbs on the threefold hollow site beneath which the carbon atom in the second layer is absent (fcc site) [5]. It is known that ARPES can give valuable information on the nature of the chemical bond between the surface and adsorbates. In this paper, the electronic structure of the oxygen-covered HfC(111) is investigated with ARPES, and the nature of the chemisorption bond is discussed.

II. EXPERIMENTAL

The ARPES measurements using synchrotron radiation were conducted on the beam lines (BL) 3B and 11C of the Photon Factory, High Energy Accelerator Research Organization. The valence band spectra were measured at BL-11C where the light was dispersed by a Seya-Namioka monochromator. The Hf $4f$ spectra were measured at BL-3B where the light was dispersed by a grazing incidence monochromator. An electron energy analyzer of

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FIG. 1: Change in the normal-emission spectrum of the HfC(111) surface as a function of O_2 exposure at room temperature. The incidence angle of the light is 60° and $h\nu = 17$ eV.

150° hemispherical-sector type with an acceptance angle of $\pm 1^\circ$ was used for all PES measurements. In this work, the incidence angle of the light (θ_i) and the detection angle of photoelectrons (θ_d) are given relative to the surface normal, and the coordinate system is chosen such that the z -axis is normal to the surface and the x - and y -axes coincide with the crystallographic $\langle 01\bar{1} \rangle$ and $\langle 2\bar{1}\bar{1} \rangle$ directions, respectively. The spectra presented below are normalized by photon flux estimated from the photocurrent of the final stage mirror. The total experimental resolution was estimated at BL-11C to be 0.25 eV at $h\nu = 20.5$ eV [16]. The base pressure in the vacuum system was 8×10^{-11} Torr.

A $HfC_{0.98}$ single-crystal was grown by the floating zone method at the National Institute for Materials Science [17]. The crystal was cut at an orientation of (111) by spark erosion into a disk of 1 mm thickness and subsequently polished mechanically. The (111) clean surface was prepared in a vacuum chamber by flashing to $>1700^\circ\text{C}$ repeatedly. The cleanliness of the surface was checked with Auger electron spectroscopy and PES. The clean surface thus prepared showed a sharp (1×1) LEED pattern. The atomic geometry of the HfC(111) surface has been investigated with ICISS and it has been established that the first layer of the surface is a Hf layer [5].

III. RESULTS AND DISCUSSION

Fig. 1 shows the change in the normal-emission spectrum of the HfC(111) surface as a function of O_2 exposure at room temperature. The incidence plane is parallel to the $\langle 2\bar{1}\bar{1} \rangle$ azimuth and the light is polarized in the incidence plane. The incidence angle of the light is 60° and $h\nu = 17$ eV. The spectrum of the clean surface

shows a sharp peak at just below E_F and a broad band peaked at 3.5 eV. The broad band is ascribed to the Hf $5d - C$ $2p$ bulk band emissions, while the sharp peak at just below E_F is attributed to emissions from the surface state mostly composed of $5d$ orbitals of surface Hf atoms [11,12]. The metal d -derived surface states around E_F are commonly observed on all the unreconstructed TMC(111) surfaces [8-14]. The formation of the surface states results in the redistribution of the electronic charge around the surface, which is predicted to stabilize the polar surface through the screening of the long-range electric field inherent to polar surfaces [9-14]. Details of the surface electronic structure of HfC(111) were discussed in our previous papers [11,12]. As the surface is exposed to O_2 at room temperature, a peak develops at 6 eV with increasing exposure. The peak from the surface state is observed to be sensitively attenuated by O_2 exposure, suggesting that the surface state plays an important role in the chemisorption bonding formation. We attribute the peak grown at ~ 6 eV to the chemisorption bonding state formed through the hybridization between the O $2p$ orbitals of dissociatively adsorbed O atoms and the $5d$ orbitals of surface Hf atoms (the state will be called the O $2p$ -derived state, hereafter). The peak at ~ 6 eV grows with increasing exposure up to about 4 L, and no spectral change is observed for further exposure, indicating that the oxygen adsorption is saturated at ~ 4 L exposure. The work function is increased with increasing exposure up to ~ 4 L and is nearly constant with further exposure, also suggesting that the adsorption saturates at ~ 4 L. The work function of the oxygen-saturated surface is found to be higher than that of the clean surface by 1.0 eV. The LEED shows only a (1×1) pattern independently of the exposure. A $(\sqrt{3} \times \sqrt{3})R30^\circ$ pattern observed for the O/ZrC(111) system in the medium coverage region ($\theta \sim 1/3$) [18] is not observed for the O/HfC(111) system. Fig. 1 shows that the O $2p$ -derived state is observed at 6.5 eV at 0.30 L, and shifts to the lower binding energy side with increasing exposure, and the peak is observed at 6.2 eV at the saturation coverage. At the saturation coverage, the adsorbed O atoms form a (1×1) overlayer and the O $2p$ -derived bands show clear dispersions, as will be discussed later. The formation of the band dispersion with increasing coverage should result in the shift of the peak in normal-emission spectra. However, the band which gives a main peak in the ~ 6 eV peak has the highest binding energy at the $\bar{\Gamma}$ point (Fig. 4(a)), and thus the band formation should induce the shift to the higher binding energy side in normal-emission spectra, which is opposite to the observed shift. The shift to the lower binding energy side is expected to arise from the electrostatic interaction between adsorbates. The electrons in an O adsorbate feel negative electrostatic field which originates from the surrounding negatively charged O adsorbates. The negative field is enhanced when the number of the surrounding negatively charged O adsorbates is increased, which should induce the shift of the electronic energy levels to the lower binding energy side as well as the depolarization of the adsorbates. We think that the shift induced by the electrostatic interaction overcomes the shift induced by the band formation in this case. In the case of the O/ZrC(111) system, the O $2p$ -derived peak in normal-emission spectra does not show any shift with increasing

FIG. 2: The normal-emission spectrum of the HfC(111) surface exposed to 4 L of O₂ in the O 2*p*-derived state region. The result of the deconvolution using a Gaussian function is shown as solid lines.

coverage [18], meaning that both shifts are nearly offset. In addition to the peak at ~ 6 eV, the emissions around 2 eV is also enhanced by O₂ exposure (Fig. 1). We measured $h\nu$ -dependence of the spectrum and found that the peak around 2 eV shows a clear dispersion as a function of $h\nu$, indicating that the initial state of the peak should be a bulk band. The 2 eV peak is thus considered to be induced by the adsorbate-induced change of photoionization cross sections of the bulk bands. The adsorption-induced enhancement of bulk band emissions in ARPE spectra has been observed also for H/TMC(111) systems such as H/NbC(111), H/TaC(111) [19] and H/HfC(111) [20].

Fig. 1 shows that the O 2*p*-derived peak at ~ 6 eV has a tail in the lower binding energy side, suggesting the existence of an additional peak. We tried to deconvolute the peak using a Gaussian function, and the best-fitted result for the peak in the spectrum of the 4-L-O₂-exposed-HfC(111) surface is shown in Fig. 2. The background assumed to be an exponential function curve has been subtracted before fitting. The best-fitted result shows that, in addition to the main peak at 6.2 eV, a small peak exists at 5.3 eV in the O 2*p*-derived state region.

Fig. 3 shows off-normal-emission spectra of the HfC(111) surface exposed to 4 L O₂ in the O 2*p*-derived state region taken at various detection angles (θ_d) along the $\langle 2\bar{1}\bar{1} \rangle$ ($\bar{\Gamma}\bar{M}$) and $\langle 01\bar{1} \rangle$ ($\bar{\Gamma}\bar{K}$) directions. The off-normal-emission measurements were made in the incidence plane and the incident light was polarized in the incidence plane for all measurements, thus the O 2*p_x*-, 2*p_z*-derived states and O 2*p_y*-, 2*p_z*-derived states are detected along the $\langle 01\bar{1} \rangle$ and $\langle 2\bar{1}\bar{1} \rangle$ directions, respectively, under the present experimental conditions. The peak positions of the main peak and smaller peak, which are determined from the deconvolution procedure described above, are indicated by red and blue vertical bars, respectively. Assuming that the photoionization cross section of

FIG. 3: Off-normal-emission spectra of the HfC(111)(1 $\times$ 1)-O surface in the O 2*p*-derived state region along the $\langle 2\bar{1}\bar{1} \rangle$ and $\langle 01\bar{1} \rangle$ directions. The incidence angle of the light is 60° and $h\nu = 18$ eV.

each state is not changed abruptly as a function of θ_d , it is deduced from Fig. 3 that the bands associated with the main peak and smaller peak disperse generally towards the lower and higher binding energy sides with increasing θ_d , respectively, along both directions. The observation of such clear dispersions of O 2*p*-derived states implies that the adsorbed O atoms form a periodic structure. Since the oxygen-saturated HfC(111) surface gives a clear (1 $\times$ 1) LEED pattern, it is concluded that the adsorbed O atoms form a (1 $\times$ 1) overlayer at the saturation coverage.

The two-dimensional band structure $E(k_{//})$ of the O 2*p*-derived states deduced from off-normal-emission spectra of the 4-L-O₂-exposed-HfC(111) surface (HfC(111) (1 $\times$ 1)-O surface) is shown in Fig. 4(a). In Fig. 4(a), the peak energies of the main peaks and smaller peaks are plotted by red and blue circles, respectively. The bands associated with the main peak and smaller peak seem to cross both in the $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{K}$ directions, however, these states are inhibited to cross because only the bands that are even with respect to the detection plane (the mirror plane) are detected under the present experimental condition. Thus, the crossing should be avoided in reality to form a certain gap in the region of $\theta_d = 10^\circ - 20^\circ$ ($20^\circ - 25^\circ$) along the $\bar{\Gamma}\bar{M}$ ($\bar{\Gamma}\bar{K}$) direction, and thus the peak positions indicated by vertical bars are tentative in this region.

The two-dimensional band structure of the O 2*p*-derived states of the HfC(111)(1 $\times$ 1)-O surface is very similar to that previously observed for the ZrC(111)(1 $\times$ 1)-O surface, where the main peak and smaller peak are observed at 6.0 and 5.2 eV at the $\bar{\Gamma}$ point and the states associated with the main peak and smaller peak shift to the lower and higher binding energy sides, respectively, along both the $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{K}$ directions [18]. The two-dimensional band structure of the O 2*p*-derived states of the ZrC(111)(1 $\times$ 1)-O surface obtained in our pre-

FIG. 4: Measured dispersions $E(k_{\parallel})$ of the O 2p-derived bands for the HfC(111)(1 × 1)-O surface (a) and for the ZrC(111)(1 × 1)-O surface (b).

vious work [18] is shown in Fig. 4(b), where the peak energies of the main peaks and smaller peaks are plotted by red and blue circles, respectively. In the case of the ZrC(111)(1 × 1)-O surface, the bands associated with the main peaks and smaller peaks were assigned as $2p_x$ - and $2p_z$ - ($2p_y$ - and $2p_z$ -) derived bands in the $\bar{\Gamma}\bar{K}$ ($\bar{\Gamma}\bar{M}$) direction, respectively, by the use of polarization dependent measurements [18]. In this work, we also measured the polarization dependence of the spectra of the HfC(111)(1 × 1)-O surface by measuring the normal-emission spectra at two different incidence angles ($\theta_i = 30^\circ$ and 60°), but the polarization dependence of the intensity ratio of the main peak and the smaller peak is uncertain in this case, due to the very small intensity of the 5.3 eV peak. Thus, the assignment of each band is not determined experimentally in this work. However, since the two-dimensional band dispersion of the O 2p-derived states of HfC(111)(1 × 1)-O surface is very similar to that of the ZrC(111)(1 × 1)-O surface, we conclude that the two-dimensional electronic structures of these systems are essentially identical with each other. This conclusion is reasonable because ZrC and HfC are equielectric compounds and the electronic structures of the (111) surfaces are very similar with each other [10-12]. Thus, we ascribe the bands associated with the main peak and the smaller peak to the O $2p_x$ - and $2p_z$ - (O $2p_y$ - and $2p_z$ -) derived bands, respectively, in the $\bar{\Gamma}\bar{K}$ ($\bar{\Gamma}\bar{M}$) direction, as in the case of the ZrC(111)(1 × 1)-O system. Fig. 4 shows that the $2p_x$ -, $2p_y$ - and $2p_z$ -derived states are formed in roughly the same binding energy region for both the HfC(111)(1 × 1)-O and ZrC(111)(1 × 1)-O systems. These results mean that the $2p_x$, $2p_y$ and $2p_z$ orbitals of O atoms on the ZrC(111) and HfC(111) surfaces have almost an equal contribution to the chemisorption bonding; the bonding states derived from these orbitals are stabilized almost uniformly through the hybridization with the

substrate's orbitals. This chemisorption bonding model is compatible with the previously proposed adsorption structural model that the adsorbed O atoms sit in a fcc site both on ZrC(111) [18] and on HfC(111) [5], because, in this structural model, all the $2p_x$, $2p_y$ and $2p_z$ orbitals of the adsorbed O atom are predicted to be involved in the chemical bond formation with the surrounding surface metal atoms. Fig. 4(a) also shows that, though the $2p_x$ -, $2p_y$ - and $2p_z$ -derived states are formed in roughly the same binding energy region, the $2p_z$ -derived state seems to be slightly more stabilized than other states for the HfC(111)(1 × 1)-O system. This result implies that the vertical interaction involving $2p_z$ orbital is thought to be slightly more important than others in the chemisorption bonding on the HfC(111) surface. The band structures of the O 2p-derived states of the ZrC(111)(1 × 1)-O and HfC(111)(1 × 1)-O systems are rather different from that predicted for an unsupported two-dimensional hexagonal oxygen layer based on a tight-binding model [21], in which the O $2p_x$ - and $2p_y$ -derived bands have the lowest binding energy and the $2p_z$ -derived band has the highest binding energy at the $\bar{\Gamma}$ point. We think that the difference is caused from the fact that the O 2p orbitals are strongly hybridized with the surface metal orbitals and that the contribution of the metal d orbitals to the band structures is important in both the ZrC(111)(1 × 1)-O and HfC(111)(1 × 1)-O systems.

Fig. 5 shows normal-emission spectra of the HfC(111) clean surface and of the HfC(111)(1 × 1)-O surface in the Hf 4f level region. For the clean surface, peaks are observed at 14.2~14.7 eV and 15.9~16.4 eV, which are well ascribed to Hf 4f_{7/2} and 4f_{5/2} levels, respectively [22]. Both the Hf 4f_{7/2} and 4f_{5/2} lines have a doublet line shape. Since the higher binding energy components are shifted to the higher binding energy side by oxygen adsorption (Fig. 5), the lower and higher binding energy components in the doublets are ascribed to the emissions

FIG. 5: Hf 4f spectra of the HfC(111) clean surface and of the HfC(111)(1 × 1)-O surface.

from the bulk and surface Hf atoms, respectively. In the spectrum of the HfC(111)(1 × 1)-O surface, the oxidized $4f_{7/2}$ and $4f_{5/2}$ components are observed at 15.4 and 17.0 eV, respectively. The binding energies of these peaks are higher than those of bulk Hf 4f components by 1.2 eV, however, these are substantially lower than those of the Hf $4f_{7/2}$ and $4f_{5/2}$ levels observed for a Hf oxide (HfO₂) (18 and 20 eV, respectively) [22], or those observed for a HfO₂ layer formed on Si(100) (17.4 and 19.1 eV, respectively) [23]. This result implies that the oxidation of the HfC(111) surface to form a Hf oxide does not proceed at room temperature at least up to ~10 L. This result suggests that the adsorbed O atoms stay above the surface plane independently of the exposure, and the penetration of O atoms to form a Hf oxide does not proceed at room temperature on the HfC(111) surface.

We have made a series of oxygen adsorption studies on the group IV TMC surfaces. The oxygen adsorption process on HfC(111) is found to be very similar to those on TiC(111) [24] and ZrC(111) [18]; oxygen adsorbs dissociatively forming a (1 × 1) overlayer. On the TiC, ZrC and HfC(111) surfaces, the sticking probability of O₂ on the clean surface is nearly unity, but the adsorption saturates when the (1 × 1) overlayer is completed and the oxidation of the substrate does not proceed at room temperature. On the other hand, in the case of the O/TiC(100) [25] and O/ZrC(100) [26] systems, though the sticking probability is rather low, the oxidation of the substrate proceeds gradually even at room temperature. When the TiC and ZrC(100) surfaces are exposed to O₂, it has been found that the substrate's C atoms are depleted probably due to their desorption as CO or CO₂ and the substrate's metal atoms react with oxygen to form metal oxides [25,26]. The marked difference in oxygen adsorption processes on the (100) and (111) surfaces can be explained from the differ-

ence in atomic and electronic structures of the surfaces. The (100) surface is composed of equal numbers of metal and carbon atoms, and the electronic structure can be viewed as a cross section of the bulk electronic structure [2]. The highest occupied level of the group IV TMC has been proved to be composed of C 2p orbitals [27]. Thus, on the (100) surface, oxygen should attack preferentially the surface C atoms, which should result in the desorption of C atoms as CO or CO₂. The residual metal atoms should be easily oxidized after depletion of C atoms, and thus the desorption of C atoms is considered to be a key process in the oxidation of TMCs. On the other hand, the (111) surface is covered with a hexagonal metal layer. In addition, the surface metal atoms are activated due to the existence of the metal d-derived surface states around E_F [8-12], and thus the oxygen should interact preferentially with the surface metal atoms in the case of the (111) surface. The access of O atoms to the substrate C atoms is thus hindered both sterically and electronically, which is thought to be the reason why the oxidation does not proceed on the (111) surface.

IV. SUMMARY

The adsorption state of oxygen on the HfC(111) surface was investigated with angle-resolved photoemission spectroscopy. It was found that adsorbed oxygen atoms form a (1 × 1) overlayer on the HfC(111) surface at the saturation coverage. The two-dimensional band structure of the (1 × 1)-O overlayer was measured in the $\overline{\Gamma M}$ and $\overline{\Gamma K}$ directions. It was found that the $2p_x$ -, $2p_y$ - and $2p_z$ -derived bands are formed roughly the same binding energy region, however, the $2p_z$ -derived state is formed in slightly higher binding energy region relative to the $2p_x$ - and $2p_y$ -derived states. These results indicate that, though all the O $2p_x$, $2p_y$ and $2p_z$ orbitals contribute to the chemisorption bond formation, the vertical interaction involving the $2p_z$ orbital is slightly more important in the chemisorption bonding on the HfC(111) surface. Hf 4f core-level spectra were measured for the clean and oxygen-covered HfC(111) surfaces. The surface-shifted 4f peaks are observed in the higher binding energy side of the bulk 4f components. The 4f levels of the surface Hf atoms are shifted to the higher binding energy side by oxygen adsorption, however, the binding energies of the shifted $4f_{7/2}$, $4f_{5/2}$ levels (15.4 and 17.0 eV) are substantially lower than those of Hf atoms in HfO₂, indicating that the oxidation of the HfC(111) surface to form HfO₂ does not proceed under the present experimental condition.

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