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Synchrotron radiation photoemission study of Ba adsorption on the vicinal SiC(111)-8° surface

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Abstract. The electronic structure of the Ba/SiC(111)-8° interface has been studied in detail in situ in an ultrahigh vacuum using synchrotron radiation photoelectron spectroscopy. The SiC(111)-8° samples were grown by an original method of epitaxy of low-defect unstressed nanoscaled silicon carbide films on silicon substrates. The Si 2*p*, C 1*s* core level spectra have been investigated as a function of Ba submonolayer coverage with photon energies in the range of 100–450 eV. Upon Ba adsorption, a drastic change in the C 1*s* spectrum was revealed. It was found that Ba adsorption leads to the formation of a new, previously unknown carbon-based structure of C nanoclusters on the surface. Experimental data show that the nanoclusters can be created exclusively on the vicinal SiC(111)-8° surfaces in the presence of stabilizing adsorbed metal atoms, specifically, Ba atoms. It is shown that the surface nanoclusters are formed due to the local interaction between silicon vacancies, carbon atoms and Ba adatoms. It is established that the carbon clusters are composed of carbon rings and their chemical bonds are similar in nature to the bonds in aromatic-like compounds.

Keywords: silicon carbide, interfaces, surface, nanostructures, photoelectron spectroscopy, electronic structure.

Introduction

The development of a high-quality wide-band gap silicon carbide semiconductor is one of the key issues in micro- and nanoelectronics. Silicon carbide shows promise for electronic devices that can perform under extreme conditions such as high temperature, high voltage, high power and frequency. Besides, SiC is a promising material for biophysics applications (Eddy, Gaskill 2009). The majority of applications are oriented toward thin film geometries. The main obstacle to growing low-defective films on Si is the elastic stress due to the mismatch between the lattice parameters of a semiconductor layer and a silicon substrate. To obtain stress-free SiC films, an original method was proposed for the synthesis of epitaxial layers: the substrate is involved in a chemical reaction and the reaction product grows inside the substrate layer (Kukushkin, Osipov 2013; Kukushkin, Osipov 2014).

It was found that the most advantageous location of the dipoles is the direction (111) in crystals with cubic symmetry. In this condition, the elastic energy is relaxed due to the attraction of point defects formed during the chemical reaction in anisotropic media. The theoretical and experimental evidence for a completely new method of growing defect-free silicon carbide films on silicon substrate was proposed in the review (Kukushkin, Osipov 2014) and references therein. The integration of new-grown SiC nanolayers into silicon technology requires studies of surface properties, and, in particular, the interface formation.

Surface electronic properties of brand new SiC nanolayers are still poorly understood. This gives rise to a controversy with regard to surface state spectra, interface formation, band-bending, and the effect of 2D phase transition. These surface and interface boundary regions are crucial which is why these data are so valuable. However, the surface, near surface and interface electronic structure of SiC remains unclear and needs further investigation. Alkali-earth metal and alkali metal adsorbates are good candidates for the formation of metal-semiconductor interfaces and Schottky barrier compositions. The relevant electronic properties were studied for Sc/3C-SiC(111) interface (King et al. 2015), Rb and Cs adsorption on graphene on SiC(0001) (Watcharinyanon et al. 2011) and Na on graphene on SiC(0001) (Watcharinyanon et al. 2012). It was found that Rb, Cs and Na deposited on monolayer graphene samples produce an *n*-type doping with the electron transfer from the metal to the graphene layer.

Photoelectron spectroscopy (PES) is an effective tool to study the electronic structure of both the semiconductor bulk and surface. The electronic structure of SiC grown conventionally has been the focus of a number of experimental and theoretical investigations (Virojanadara et al. 2008; Su et al. 2012; Bechstedt, Furthmüller 2004; Wang et al. 2009). Photoelectron spectroscopy was used to study the surface-related properties in the energy range of the valence band (VB). The obtained conditions were reported to be correlated with the Si dangling bonds and the interaction between the Si top atoms and C atoms. This outcome was predicted in the investigations based on the density functional theory within the local density approximation. Moreover, these calculations showed that the surface electronic states below the Fermi level may originate from the Si-dangling bonds of the SiC surface (Abavare et al. 2013). Only a few studies focus on the valence band and Si 2*p*, C 1*s* core level spectra for SiC(111) as well as the vicinal SiC(111)-4° and SiC(111)-8° surfaces (Su et al. 2012; Takahashi et al. 2011; Bosi et al. 2013). Recently, photoelectron spectroscopy was used to study the Ba/SiC(111)-8° and Cs/SiC(111)-8° interfaces. The study revealed significant changes in surface electronic properties (Benemanskaya et al. 2019a; 2019b).

This paper reports the results of the study of the evolution of electronic structure of the Ba/Si(111)-8° interface as a function of Ba coverage. The data were collected using synchrotron-radiation based photoemission spectroscopy.

Materials and methods

Photoemission studies were carried out at BESSY II (Helmholtz Zentrum Berlin) using the synchrotron radiation with photon energies in the range of 100–450 eV. The PES experiments were performed *in situ* in an ultrahigh vacuum of 5×10^{-10} Torr at room temperature. The SiC sample was preliminary heated *in situ* at a temperature of ~900 K. The spectra were measured in normal emission. For the new SiC nanolayer the photoemission spectra of Si 2*p*, C 1*s*, Ba 4*d* core levels were recorded. The main elements presented in the PES overview of the clean SiC surface were Si, C and negligible O. No other elements were detected in significant amounts. A total energy resolution of better than 100 meV was used.

The single-crystal SiC/Si(111)-8° epitaxial layer of the thickness of ~100 nm was grown on vicinal Si(111)-8° substrate using the original method (Kukushkin, Osipov 2013; Kukushkin, Osipov 2014). The structure of the SiC sample was ascertained by angle spectroscopic ellipsometry and electron microscopy. The surface morphology of the sample was characterized by atomic force microscopy. Atomically pure barium was adsorbed onto the SiC/Si(111)-8° surface from a standard source. Step-by-step deposition of Ba coverage was used. Note that the Ba sticking coefficient is equal to one up to 1 monolayer (1 ML). The Ba overlayer corresponding to 1 ML can be estimated from the dependence of the Ba 4*d* core level peak intensity as a function of the Ba deposition time (Okuda et al. 2005). This made it possible to determine the Ba coverage deposited onto the sample to better than 10%. Note that 1 ML is defined as one complete layer of Ba atoms and as equal to $\sim 6.25\times10^{14}$ atoms/cm^2.

Results and discussion

Figure 1 represents the C 1*s* core level spectra taken from the clean vicinal SiC(111)-8° surface (Fig. 1, curve 1) and from the Ba/Si(111)-8° interface at different Ba coverages (Fig. 1, curves 2, 3). The C 1*s* core level spectrum for the clean SiC(111)-8° surface is found to be composed of two main peaks B and S1 (Fig. 1, curve 1). One peak B at the binding energy (E_B) of ~282.5 eV is observed from the bulk of SiC substrate and the other peak S1 at the higher binding energy of ~284.3 eV may originate from the surface C-C bond, namely, the S1 component may indicate the presence of s-p^2 hybridized C-C bonds. Consequently, the peak S1 may be associated with the C-enriched surface.

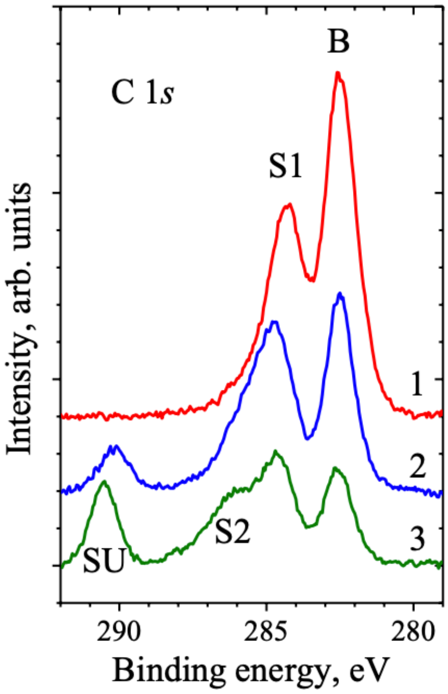

Fig. 1. Photoemission spectra of the C 1*s* core level recorded from the Ba/SiC/Si(111)-8° interface at different Ba coverages: 1—clean surface (Ba-free surface), 2—0.5 ML, 3—1.0 ML. Excitation energy $h\nu$ = 450 eV

A cardinal change in the C 1*s* core level spectrum is revealed upon Ba adsorption on the SiC(111)-8°surface (Fig. 1, curves 2, 3). The appearance of an additional surface component S2 at the binding energy of ~286.0 eV is found at the initial stage of Ba adsorption at 0.5 ML (Fig. 1, curve 2). An odd effect is the appearance of a new peak SU at the E_B of ~290.5 eV at the highest binding energy side of the B, S1 and S2 peaks. It can be seen that the binding energies of S2 and SU components show a weak dependence on the Ba coverage and the relative intensities are equally modified with the increase of Ba coverage. Several components appear at the higher binding energies that indicate a degree of interaction between C-C atoms and an increase in the ionicity of C. The presence of S1 and S2 components is an evidence for the corrugation of the vicinal SiC(111)-8°surface. The positive shift of the S2 component under Ba adsorption is obtained to be ~3.5 eV. This indicates a higher charge transfer from the C surface atoms to the Ba adsorbed atoms.

An uncommon modification of the C 1*s* spectrum is observed after one monolayer of Ba adsorption on the SiC(111)-8° surface (Fig. 1, curve 3), namely, a supplementary SU peak at the energy of ~290.5 eV. Note that both the S2 and SU peaks arise simultaneously and increase in intensity. The SU peak is peculiar as it differs from the traditional C 1*s* core level spectrum. The SU component can be identified as a shake-up satellite. The shake-up satellite is a well-known characteristic of the photoemission process in graphitic and aromatic systems. The shake-up is a two-electron phenomenon; the emitted photoelectron with E_B of 286.0 eV (peak S2) can excite a transition resulting in an additional peak SU at the higher binding energy of 290.5 eV (peak SU). Graphitic systems show a shake-up peak shifted toward higher binding energy from the main peak. Therefore, the modification of the surface structure of the vicinal SiC(111)-8° surface due to Ba adsorption indicates 2D phase transition. It is found that 2D surface phase transition from the C-enriched SiC(111)-8° surface to the aromatic-like one originates from the Ba atomic layer deposition. The result may be due to the charge transfer to C atoms located in interface area in the process of Ba adsorption.

It is possible to suppose that we deal with a graphene-like surface layer comprising a high proportion of *sp*^{3} hybridized C-C bonds at the vicinal SiC surface. It is also possible to assume that the surface reconstruction induced by Ba adsorption can create the *sp*^{2}, *sp*^{3} and π → π* hybridized C-C bonding inherent aromatic-like compounds. Therefore, it can be confirmed that 2D phase transition on the vicinal SiC surface takes place due to Ba adsorption which leads to the creation of the C-C chemical bonds close in nature to the bonds inherent in aromatic-like compounds.

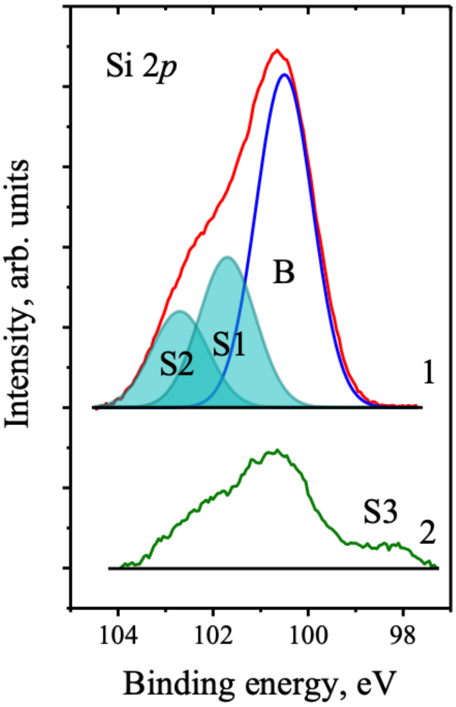

Fig. 2. The Si 2*p* core level photoemission spectra for SiC(111)-8° surface (1) and Ba/SiC(111)-8° interface at Ba coverage of 0.8 ML (2). Excitation energy *hν* = 130 eV

Figure 2 represents the modification of the Si 2*p* core level spectrum under Ba adsorption on the SiC(111)-8° surface recorded at the excitation photon energy of *hν* = 130 eV. The bulk-related peak B at the binding energy of ~100.5 eV corresponds to the Si 2*p* components (the spin-orbit-split Si $2p_{1/2}$ and Si $2p_{3/2}$ states are unresolved in the spectra). Two surface-related components S1 and S2 at higher binding energies are found for the clean SiC(111)-8° surface (Figure 2).

The component labeled S1 (E_B = ~101.7 eV) is most easily seen in the surface sensitive spectra. It most probably originated from Si surface atoms. The S2 component (E_B = ~102.7 eV) appears as a shoulder on the high binding energy side of the B and S1 peaks and, most likely, can be connected with the Si-Si surface dimmers. Ba adsorption leads to the suppression of B, S1 and S2 peaks. The appearance of the component S3 (E_B = ~98.5 eV) is most probably associated with the so-called interfacial states provided by interaction of Ba-Si atoms in the buffer layer between the C-enriched surface layer and the SiC substrate.

Findings

In summary, first, the Ba/SiC(111)-8° interface has been studied in detail *in situ* using photoelectron spectroscopy with photon energies in the range of 100–450 eV. The SiC(111)-8° samples were grown by an original method of epitaxy of low-defect unstressed nanoscaled silicon carbide films. Second, experimental data show that the aromatic-like nanostructure can be created exclusively on the vicinal SiC(111)-8° surfaces in the presence of stabilizing adsorbed metal atoms, specifically, Ba atoms. It is shown that the surface nanoclusters are formed due to the local interaction between silicon vacancies, carbon atoms and Ba adatoms. It is established that the carbon C-clusters are composed of carbon rings and their chemical bonds are similar in nature to the bonds in aromatic-like compounds. Third, the modification of the Si 2*p* core level spectrum with surface-related components indicates a compound surface atomic structure that can provide two features S1 and S2 associated with Si surface atoms and Si surface dimmers. The appearance of the S3 component is most probably associated with the so-called interfacial states due to the interaction of Ba with Si atoms.

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