SURFACES, INTERFACES, AND THIN FILMS

The C 1s Core Level Spectroscopy of Carbon Atoms at the Surface SiC/Si(111)-4° Layer and Cs/SiC/Si(111)-4° Interface

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Abstract—Photoemission studies of the electronic structure of the Cs/nano-SiC/Si(111)-4° nanointerface are for the first time carried out with the use of synchrotron radiation in the photon energy range 120−450 eV. The in situ experiments are conducted in the case of submonolayer Cs coating of the surface of an epitaxial SiC layer grown on the vicinal surface Si(111)-4° by a new method of substrate-atom substitution. Modification of the valence-band spectra and the C 1s and Si 2p core levels is studied. The appearance of Cs-induced surface states, with binding energies of 1.2 and 7.4 eV, and a sharp change in the spectrum of the C 1s core level with the appearance of two additional modes are found. The evolution of the spectra shows that the Cs/nano-SiC/Si(111)-4° interface is formed due to charge transfer from Cs adatoms to surface atoms at terraces and steps of the vicinal surface. It is found that the structure of the C layer is nontrivial and involves energetically different carbon states.

At present, silicon carbide (SiC) is attracting particular interest within the context of a tendency toward the production of high-temperature, high-power, and high-frequency electronic devices. The high electron mobility and high electric-breakdown field combined with excellent thermochemical parameters and high radiation stability of silicon carbide are promising characteristics for the development of electronic and optoelectronic devices [1−3]. At the same time, the electronic properties of metal/SiC interfaces are extremely important for the functioning of devices. Unfortunately, the corresponding studies are few, and all of them are concerned mainly with metal/SiC(0001) interfaces [4−9]. However, the realization of the high potential of silicon carbide is hampered by serious problems that arise during the growth of SiC crystals or epitaxial layers by various methods.

In this study, we for the first time study the electronic properties of the surface of an epitaxial nano-SiC(111) layer grown on the vicinal surface Si(111)-4° inclined at an angle of 4° to the (111) base orientation. The SiC films are synthesized by a new method of atom substitution [10−13]. This method and the technology of growth of SiC are fundamentally different from currently available methods and technologies of the growth of single crystals, films, and nanostructures. The method is based on "the assembly" of a new silicon-carbide matrix by the partial substitution of carbon atoms for silicon atoms located in the substrate crystal matrix. To implement such a procedure, a carbon atom is preliminarily incorporated into an interstitial position of the silicon lattice, and a neighboring silicon atom is removed to create a silicon vacancy. In this case, an ensemble of dilatation dipoles, i.e., stable complexes consisting of dilatation centers, specifically, an interstitial carbon atom and a silicon vacancy, are formed in the surface region of the silicon lattice. In cubically symmetric crystals, these two dilatation centers elastically interact with each other. Specifically, if the dilatation dipoles are arranged along the [111] direction in silicon, these dipoles attract each other, and the almost total elastic dilatation energy associated with the introduction of a carbon atom and the formation of a vacancy dissipates. Such elastic dipoles are synthesized through a chemical reaction
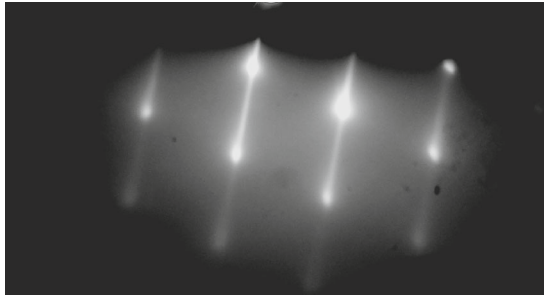
Fig. 1. RHEED pattern for the SiC/Si(111) surface inclined at an angle of 4° to the base orientation towards the [100] direction.

between silicon and carbon monoxide. The rate of this chemical reaction is maximum along the direction in which the dilatation dipoles attract each other, i.e., along the [111] direction in the Si substrate. After termination of the process of chemical transformation, the mechanical dipoles break down with the formation of a silicon carbide layer and pores under its surface. The orientation of the layer is defined by the "old" crystal structure of the initial Si matrix and not just the substrate surface, as it commonly is in traditional methods of film growth. The formation of carbon-atom–silicon-vacancy elastic dipoles makes possible the production of high-quality nano-SiC films, of which one of the most important properties is the unique possibility of growing not only the cubic polytype, but a number of hexagonal polytypes as well [11, 12]. It should be noted that, during the growth of SiC films by the above method, two-layer films commonly grow. In this case, one of the layers is the 3*C*-SiC cubic polytype, and the other is one of the hexagonal polytypes, either 6*H*-SiC or 4*H*-SiC. It was shown that there exists a strong dependence of the formation of a certain type of SiC polytype on the crystallographic orientation of the initial Si surface and a slighter dependence of the type of polytype on the temperature of synthesis and the pressure of carbon monoxide [12, 13].

The most comprehensive data on the electronic structure of bulk and surface states can be obtained by photoemission studies, specifically, by photoelectron spectroscopy (PES). The subject of PES investigations is different SiC modifications, i.e., cubic and hexagonal structures [5–9]. The electronic properties of the SiC surface and metal/SiC interfaces have not been adequately explored, which generates discussion concerning the nature of surface states, the formation of interfaces and band bending, and the possibility of charge accumulation. In publications, data on the processes of formation and the electronic properties of metal interfaces on SiC substrates are still very few. The adsorption of some metals (Cs [14], Au [15], Ti
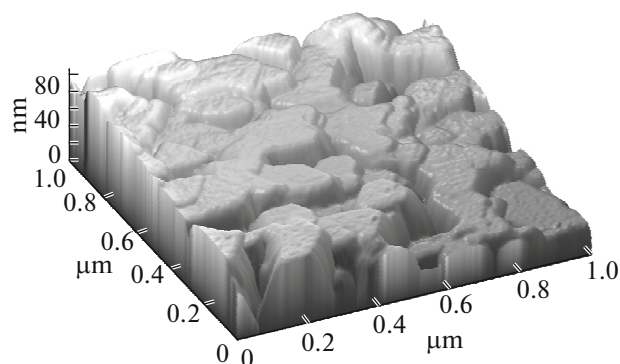
[16]) was studied for the 6*H*-SiC(0001) surface. The Schottky barriers, the energy shifts of the core levels, and the thermal properties were determined. As concerns the SiC(111) surface, there are extremely few PES studies [17, 18]. Nevertheless, performing these studies is one of the most important challenges, since the above-listed properties play a key role in nanostructures, for which the interfaces are of crucial importance in structure formation.

In this study, we for the first time explore the electronic properties of the surface of a nano-SiC sample grown on the Si(111)-4° vicinal surface by the above-mentioned new method. The SiC films were synthesized using a specially designed system for the synthesis of SiC on Si [12]. The SiC films were grown on the surface of B-doped *p*-Si with a resistivity of 10 Ω cm. The temperature in the zone of synthesis was 1250°C; the total pressure of the gas mixture ($CO + SiH_4$) was 79 Pa; the flux rate of the gas mixture was 12 sccm; the silane (SiH_4) percentage in the flux of the mixture corresponded to 45%; and the time of growth was 80 min. The SiC films grown were studied by X-ray diffraction (XRD) analysis, atomic-force microscopy (AFM), and the electron diffraction technique. The full width at half-maximum ($FWHM_{\omega - \beta}$) of the XRD peak observed for the sample with $CuK_{\alpha 1}$ radiation was 40 arcmin, which is indicative of the epitaxial orientation of the structure. The layer thickness was 80 nm.

Figure 1 shows typical reflection high-energy electron diffraction (RHEED) patterns recorded for the (111) surface of the SiC/Si films in the [100] direction using an EPM-100 electron diffractometer at an electron energy of 50 keV. The point reflections observed in this electron diffraction pattern unambiguously suggest that, on the Si surface, there is an epitaxial SiC layer formed from the 3*C*-SiC polytype, with the (111) plane protruding above the substrate surface. It should be noted that the distinguishing feature of the method of atom substitution is that, irrespective of the initial crystallographic plane of Si, on which SiC is synthesized, one of the planes formed is certain to be the (111) plane. Such a transformation in SiC yields substantial changes in the adsorption properties of the SiC film compared to those of the SiC films grown by traditional synthesis upon the entry of reagents from above to the Si substrate surface [19].

Figure 2 shows the three-dimensional AFM image of the sample surface. It can be seen that the surface is covered by terraces mainly triangular or hexagonal in shape with a characteristic size of 150–200 nm. AFM measurements were conducted using a Solver P-47H instrument with NSG11 probes (NT-MDT) in the tapping mode of operation.

In this study, we studied the valence-band (VB) spectra and the spectra of the Si 2*p* and C 1*s* core levels using PES with synchrotron excitation. We for the first
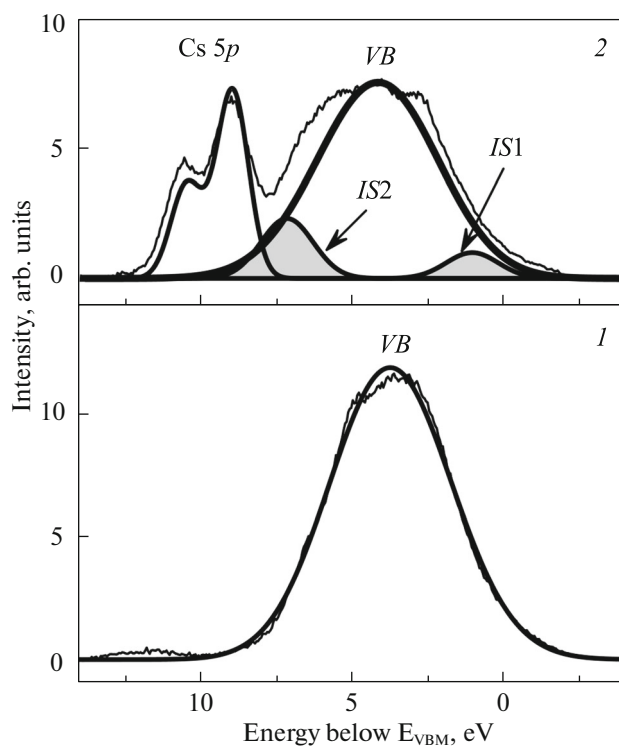
**Fig. 2.** Three-dimensional image of a 1 × 1 μm region of the SiC(111)-4° crystal surface.

Fig. 3. Normal photoemission spectra for the VB region: (*1*) the initial Si(111)-4° surface and (*2*) the surface with 1 ML Cs coating. The excitation energy is $h\nu = 120$ eV.

time studied the modification of the spectra on the formation of the Cs/SiC(111)-4° nanointerface in the case of a Cs monolayer (1 ML) coating. It is found that, as the Cs coating is increased, all of the spectra significantly change and two induced surface states appear in the VB region. It is established that cesium adatoms interact mainly with carbon atoms at the terraces of the SiC(111)-4° surface enriched with carbon; in this case, carbon atoms are in nonequivalent energy states.

Photoemission studies were carried out at the Russian−German beamline of the BESSY II synchrotron, Berlin, Germany, using the high-energy-resolution PES technique with excitation in the photon-energy range 120−450 eV. Photoelectrons were detected within a cone oriented along the normal to the sample surface. The excitation beam was incident on the sample surface at an angle of 45°. The SiC(111)-4° sample and the Cs/SiC(111)-4° interface were studied in situ in vacuum (at a residual pressure of $P < 5 \times 10^{-10}$ Torr) at room temperature. We recorded the normal emission spectra of electrons from the VB and the spectra of the Si 2*p* and C 1*s* core levels at different excitation energies. The overall energy resolution of the analyzer and monochromator was 50 meV.

Directly before the studies, the sample was annealed in situ at a temperature of ~750°C. A lack of foreign impurities at the sample surface was verified using the PES spectra at the excitation energy 450 eV. Atomically pure cesium was sputtered onto the sample surface from a standard source that was previously calibrated against the values of the atomic cesium flux [16]. In assessing the Cs coating, we took into account the fact that it was impossible to deposit more than 1 ML of Cs onto the surface at room temperature. It is worth noting that one monolayer (1 ML) of Cs was thought to correspond to the concentration ~5.2 × 10^{14} atom cm^{-2}, at which a complete layer of Cs atoms is formed [20]. It should be noted that, in the case of

the vicinal surface under consideration, the concept of a monolayer is a matter of convention.

The photoemission spectra in the VB region of SiC(111)-4° are shown in Fig. 3 for the cases of a pure surface (*1*) and a 1-ML Cs coating (*2*). The excitation energy corresponds to $h\nu = 120$ eV. The spectra are brought to the energy of the VB top at the surface, E_{VBM}. This energy is determined from linear approximation of the low-energy edge of the spectrum. For the sample in the initial state, the spectrum presents a slightly structured photoemission band ~7 eV in width. The spectrum is in good agreement with the experimental data known from publications [6, 14, 18, 20−23].

Evolution of the photoemission spectrum of SiC(111)-4° covered with a Cs monolayer is shown in Fig. 3, *2*. In addition, Figure 3 shows the result of decomposition of the photoemission spectra with the use of MagicPlot software (www.magicplot.com). As can be seen from Fig. 3, we observe radical changes in the VB region. These changes manifest themselves as the formation of two new peaks, *IS*1 and *IS*2, and as a decrease in the intensity compared to the initial intensity. The principal broad peak at the energy ~4 eV corresponds to photoemission from the VB. This is supported by experimental data [22, 24, 25] as well as by
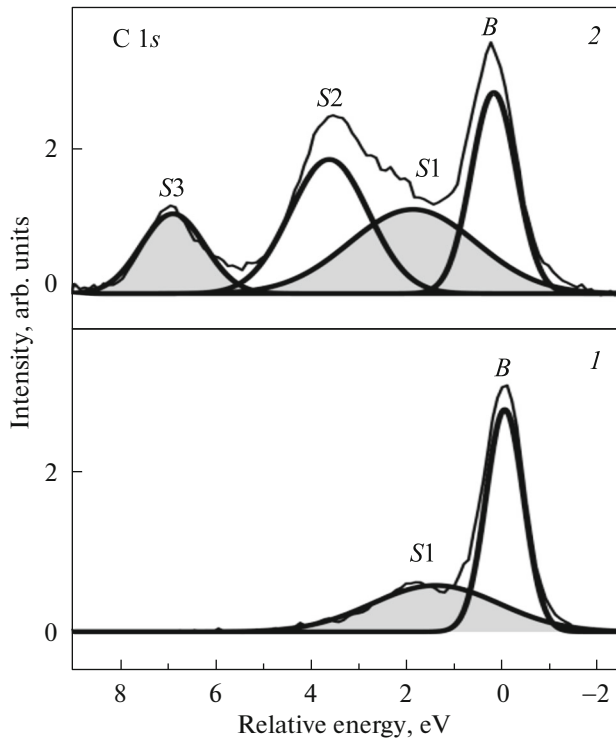
Fig. 4. Photoemission spectra of the C 1s core level for (*1*) the pure Si(111)-4° surface and (*2*) Cs/Si(111)-4° interface with 1 ML Cs coating. The excitation energy is $h\nu$ = 450 eV.

calculations of the density of states (DoS) [26–28]. In the case of the Cs-monolayer coating, we observe the resolved Cs 5p doublet at binding energies of 7–11 eV and new peaks at the binding energies ~1.2 eV (*IS*1) and ~7.4 eV (*IS*2) corresponding to Cs-induced surface states.

In comparing the spectra of the Cs/SiC(111)-4° interface with data on the surface states for the Ba/SiC(111) interface [25], we can see a small decrease in the binding energy of the surface states induced by the adsorption of Cs.

Figure 4 shows the spectra of the C 1s core level for the pure vicinal SiC(111)-4° surface (*1*) and the Cs/SiC(111)-4° interface with the 1 ML Cs coating (*2*). It can be seen that, in the case of a pure surface, the C 1s spectrum consists of two peaks. The principal peak *B* corresponds to carbon atoms in the bulk. The mode *S*1 observed at a higher binding energy corresponds to C atoms located at terraces in the surface layer above Si atoms; when interacting with Si atoms, these C atoms form a C–Si double layer. Quite similar spectra can be observed for the SiC(100), SiC(111), and SiC (0001) surfaces [7, 22, 24, 29]. The position of the mode *S*1 at higher binding energies suggests that, in the case of the pure surface enriched with carbon,

there is charge exchange between the states of the surface C and Si atoms in the C–Si layer.

An extremely unusual C 1s spectrum is observed upon the formation of the Cs/Si(111)-4° interface (Fig. 4, *2*). It can be seen that two new modes, *S*2 (with the binding energy 3.8 eV) and *S*3 (with the binding energy 7 eV) appear in the spectrum. The mode *S*1 is shifted to higher binding energies by ~0.3 eV.

The C 1s spectrum exhibiting a rather rich series of intense modes in combination with a large width is observed in the case of the adsorption of metal atoms on SiC for the first time. This observation is indicative of the specific structural features of the SiC(111)-4° vicinal surface of the nanolayer, with terraces and steps (Fig. 2). In addition, the above result suggests that surface carbon atoms possess nontrivial electronic and morphological features and possibly form several monolayers. Upon adsorption, three energy positions of carbon atoms on the complex structured vicinal surface enriched with carbon are evident. In this case, the large positive shift of mode *S*2 to larger binding energies and the positive shift of mode *S*1 suggest a decrease in the electron density of surface carbon atoms. The results show that, for the SiC(111)-4° vicinal surface under study, there exist additional positions related to carbon atoms in different energy states. It should also be noted that the peak *S*3 can be a "shake-up" satellite. In this case, the binding energy of the state *S*3 is equal to the binding energy known for the "shake-up" satellite in graphene on the 4*H*-SiC(0001) surface [30].

Figure 5 shows the spectra of the Si 2p core level for the pure SiC(111)-4° surface (*1*) and for the surface covered with 1 ML of Cs (*2*). The excitation energy corresponds to $h\nu$ = 150 eV. In the case of the pure surface (*1*), we observe a peak (*B*) at the binding energy ~101 eV in the spectrum. This peak corresponds to Si atoms in the substrate bulk and consists of two unresolved spin-orbit components, Si 2p1/2 and Si 2p3/2. In the high-energy region, we can see an additional mode *SS*1 attributed to Si atoms at the surface.

As the Cs coating is increased during formation of the Cs/SiC interface, we observe a decrease in the intensities of bulk mode *B* and surface mode *SS*1 and the appearance of an additional mode *SS*2 with a negative energy shift. This result suggests that the adsorption of Cs brings about radical changes in the electronic structure of the SiC(111)-4° vicinal surface and induces the processes of charge transfer between the Cs, Si, and C atoms during the formation of the Cs/SiC(111)-4° interface.

Thus, a SiC sample with the SiC(111)-4° vicinal surface is grown by a new method for the first time. Morphological studies of the sample by the RHEED and AFM techniques show that the vicinal surface features are developed morphology with terraces and steps.
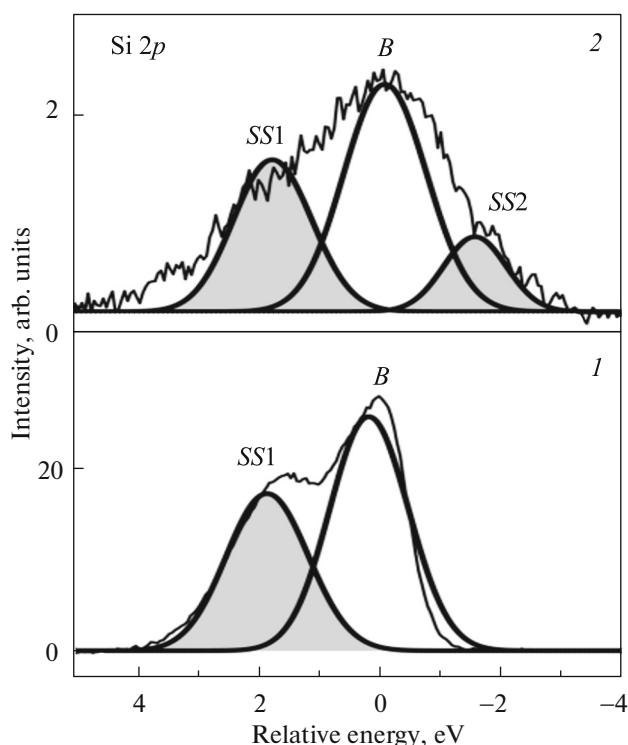
Fig. 5. Photoemission spectra of the Si 2*p* core level for (*1*) the initial Si(111)-4° surface and (*2*) the surface with 1 ML Cs coating. The excitation energy is $h\nu = 150$ eV.

Studies of the electronic structure of the SiC(111)-4° sample and Cs/SiC(111)-4° interface show that the VB spectrum and the spectrum of the Si 2*p* core level only slightly differ from the corresponding spectra of SiC crystals grown by traditional methods. The most striking effect observed on the formation of the Cs/SiC(111)-4° interface is a radical change in the spectrum of the C 1*s* core level. The rich structure of the C 1*s* spectrum with intense modes is not observed in other SiC crystals produced by traditional methods as well as in diamond crystals, graphene films, or graphite. This is indicative of the specific structural features of the vicinal surface of the SiC(111)-4° nanolayer with terraces and steps and suggests that the surface carbon atoms possess nontrivial electronic and morphological features and possibly form graphene islands.

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