Drastic change in surface electronic properties and creation of a new carbon-based nanostructure on the vicinal SiC(111)-4° surface

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Abstract. Novel carbon based nanostructure on the vicinal SiC(111)-4° surface has been found as effect of Cs adsorption. The SiC(111)-4° sample was grown by method of epitaxy of low-defect unstressed nanoscaled silicon carbide films on vicinal Si(111)-4° substrate. Electronic structure of the SiC(111)-4° surface and the Cs/SiC(111)-4° interface has been detailed studied in situ in an ultrahigh vacuum using synchrotron-based photoelectron spectroscopy. The C 1s and Si 2p core level spectra have been investigated as a function of Cs submonolayer coverage. A unique fine structure of the C 1s core level spectrum was revealed to appear under Cs atomic layer deposition. The effect was ascertained and shown to be originated from the interaction of the silicon vacancy with adsorbed Cs atoms that leads to both the redistribution of electron density and surface reconstruction with formation of a new type of the C-enriched aromatic-like nanostructure.

1. Introduction

At present, silicon carbide is a promising wide-gap semiconductor, since there is a possibility of using this substance for the manufacture of semiconductor devices for high-temperature and high-frequency power electronics [1, 2]. SiC is already widely used as a substrate for the growth of III-nitrides, providing much less lattice mismatch than sapphire. Despite the effective technological progress in the growth of high-quality materials, theoretical and experimental data on the electronic structure of SiC are insufficient. The properties of surface states, the formation of interfaces, and band bending in SiC are important both in practical and cognitive aspects. These individual features of the silicon carbide surface affect the electronic properties and technical parameters of electronic devices.

One of the most promising methods for growing epitaxial silicon carbide films is a method that is based on replacing a part of silicon atoms with carbon atoms with the formation of silicon carbide molecules. The method is based on the relaxation mechanism of elastic energy due to the creation of dilatation dipoles. This method can be used to grow non-dislocation films ~100 nm thick. It is also possible to grow different polytypes of silicon carbide and vicinal surfaces with various angles of surface misorientation. Vicinal surfaces can be useful for facilitating stress relaxation due to a significant mismatch in the lattice constants at the initial stages of nitride nucleation on SiC.
Photoelectron spectroscopy (PES) is a powerful tool for studying the properties of materials and obtaining the most complete information about the band structure of occupied electronic states due to its high sensitivity to chemical states. Recently, photoemission studies of various SiC polytypes have been presented. Many aspects of metal/SiC interfaces remain unresolved today. This gives rise to a discussion of surface states, formation of interfaces, band bending. There are several studies on the adsorption of metals Rb, Cs [3], Na [4], Sc [5] only on the surface of the hexagonal SiC polytype. We recently investigated the electronic structure of the vicinal SiC(111)-8° surface and the ultrathin Ba/SiC(111)-8° interface [6, 7].

In this article, we present a detailed study of changes in the electronic and photoemission properties of the vicinal surface of SiC(111)-4° during the adsorption of Cs in the mode of submonolayer coatings. It is shown that the spectrum of surface states and the spectra of the core levels of Si 2p and C 1s are significantly modified due to the adsorption of Cs. The data show that the adsorbed Cs atoms activate the 2D phase transition following both the electron density redistribution and surface reconstruction. This effect leads to the creation of a new type of C-rich aromatic-like nanostructure.

2. Experimental
The epitaxial SiC(111)-4° layer was grown on the vicinal Si(111)-4° surface inclined at angles of 4° to the (111) base orientation. The SiC(111)-4° layer was synthesized by method of chemical atom substitution [8]. The epitaxial SiC(111)-4° layer was studied by X-ray diffraction analysis, atomic-force microscopy, and the electron diffraction technique. The layers thickness is to be ~150 nm.

Photoemission studies were carried out at synchrotron BESSY II (Helmholtz Zentrum Berlin) using the synchrotron radiation with photon energies in the range of 150-450 eV. PES experiments were performed in an ultrahigh vacuum of 5x10^-10 Torr at room temperature. The SiC sample was preliminary heated up to a temperature of ~1100 K. The spectra were measured in normal emission. The photoemission spectra from the C 1s, Si 2p, Cs 4d core levels were recorded for the vicinal SiC(111)-4° surface with Cs submonolayers. For the clean SiC sample the PES overview exhibits the main elements Si, C and micro amount O and no other elements were detected in significant amounts. A total energy resolution of 50 meV was used.

Atomically pure Cs was deposited onto the clean sample from a standard source. Step-by-step deposition of Cs coverage was performed onto the SiC(111)-4° sample. It should be noted that the Cs sticking coefficient is equal to one at least up to 1 monolayer (ML). To ascertain the Cs coverage, the Cs source was preliminary calibrated to dosage using the original technique [9]. This made possible to determine the Cs coverage deposited onto the sample to better than 20%. Note that 1 ML is defined as one complete layer of Cs atoms and equal to ~5.2 x 10^{14} atoms/cm² [10]. Moreover, the Cs overlayer corresponding to 1 ML can be estimated using dependence of the Cs 4d core level peak intensity as a function of the Cs deposition time [11]. It should be noted that we deal with rough surfaces which are remarkable for steps and buckling. Therefore it should be indicated as a relative 1 ML coverage.

3. Results and discussion
Figure 1 presents the C 1s core level spectra taken from the clean SiC(111)-4° sample and from the Cs/SiC(111)-4° interface at various Cs coverages (θCs = 0.3 ML and 0.9 ML). The photon energy corresponds to hν = 450 eV. The C 1s core level spectrum for the clean SiC surface is obtained to be composed of two distinct components B and S1. The one peak B at the binding energy of ~282.8 eV is originated from the bulk of the SiC substrate and the other peak S1 at the higher binding energy of ~284.5 eV can be assigned to the surface C-C bond. In agreement with the observations [12, 13], it should be noted that the component S1 is related to the presence of s-p^2 hybridized C-C bonds. Then the peak S1 can be considered as a signature of the C-enriched surface.
Figure 1. The C 1s core level spectra for the Cs/SiC(111)-4° interface at various Cs coverages.

The Cs adsorption on the SiC(111)-4° surface is found to induce a drastic change in the C 1s core level spectrum. The appearance of additional surface component S2 at the binding energy of ~285.6 eV is revealed as an effect of initial stage of Cs adsorption at 0.3 ML. It can be seen at 0.9 ML Cs coverage the presence of a new peak SU at the binding energy of ~289.4 eV on the highest binding energies. The components S2 and SU appear at the higher binding energies indicating a stronger degree of interaction between C-C atoms and increase of the C ionicity. The presence of S1 and S2 components is widely proved a corrugation of the vicinal SiC(111)-4° surface. The positive shift of the S2 component under Cs adsorption is obtained to be ~ 2.8 eV. This means a higher charge transfer from the C surface atoms to the Cs adatoms.

An unusual C 1s spectrum is found upon 0.9 ML Cs coverage on the SiC(111)-4° surface. Namely, a supplementary peak SU at the binding energy of ~289.4 eV is distinctly revealed. This marked peculiarity SU, which differs from the traditional C 1s core level spectrum, can be identified as a shake-up satellite. The shake-up satellite is a well known characteristic of photoemission process in graphitic and aromatic systems. The shake-up is a two electron phenomenon; the emitted photoelectron switch energy of 285.6 eV (peak S2) can excite a transition resulting in an additional peak SU at the higher binding energy of 289.4 eV (peak SU). Graphitic systems show a shake-up peak shifted toward higher binding energy from the main peak by approximately 6.5–7.0 eV [14]. Therefore the modification of surface structure of the vicinal SiC(111)-4° surface due to Cs adsorption was obtained indicating 2D phase transition. It is found that 2D surface phase transition from the C-enriched SiC(111)-4° surface to aromatic-like one is originated from an effect of the Cs atomic layer deposition.

Figure 2 shows the evolution of the Si 2p spectrum recorded at the excitation energy of $h\nu = 150$ eV for Cs coverages ($\theta_{Cs} = 0$ ML, 0.3 ML and 0.9 ML) on the SiC(111)-4° surface. The bulk-related
peak B at the binding energy of ~100.5 eV corresponds to the Si 2p peak. One surface-related component S is detected for the clean vicinal SiC(111)-4° surface. The component S at the binding energy of ~102.1 eV is most probably associated with the so-called interfacial states provided by Si atoms in the buffer layer between the C-enriched surface layer and the SiC substrate. It should be noted that the component S is significantly shifted toward higher binding energies (by ~0.6 eV), as the Cs coverage approaches 0.9 ML. It is found that the Si 2p spectrum is only slightly modified upon adsorption of Cs. This is indicative of charge transfer between adsorbed Cs atoms and Si atoms underneath. Recently, the similar modification of the Si 2p spectrum was observed in the case of the Ba/SiC(111)-8° interface [15].

Figure 2. The normal photoemission spectra of the Si 2p core level for the Cs/SiC(111)-4° interface at various Cs coverages.

Thus, upon adsorption of Cs metal atoms on the vicinal SiC(111)-4° surface, a new, previously unknown carbon nanostructure involving carbon rings structurally similar to aromatic-like compounds is formed. The weak change in the Si 2p spectrum under Cs adsorption testifies in behalf of C-rich surface, when the Si layer lies under the superficial layer of carbon atoms.

4. Conclusions
To summarize, the Cs/SiC(111)-4° interface have been investigated in situ using photoelectron spectroscopy with photon energies in the range of 150-450 eV. The vicinal SiC(111)-4° sample was grown by a new method of epitaxy of low-defect unstressed nanoscaled silicon carbide films. The C 1s and Si 2p core levels photoemission spectra were studied as a function of Cs submonolayer coverage. A special fine structure of the C 1s core level spectrum was revealed to appear under Cs adsorption. The drastic change in the C 1s core level spectrum is found to originate from the interaction of silicon vacancies with adsorbed Cs atoms that leads to the redistribution of surface electron density and to the
2D phase transition from the C-enriched SiC(111)-4° surface to the aromatic-like one. It is found that Cs adsorption causes a charge transfer with increasing ionicity of the C surface atoms.

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