

Formation of Cr ohmic contact on graphitized 6H-SiC(0001) surface

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Ohmic electrical contacts were formed at room temperature on *n*-type, Si-oriented 6H-SiC substrates, with Cr layers vapor-deposited under ultra-high vacuum conditions on the samples being graphitized prior to the deposition. The contacts reveal a very good linearity of the local I - V characteristics. This method of ohmic contact formation does not require the use of samples with high doping concentration and the application of high-temperature annealing during the processing of contacts. Results of characterization of the contacts and of the *in situ* graphitization process of the SiC substrates, obtained by X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and atomic force microscopy (AFM) with conducting tip, are given in this paper.

Keywords: silicon carbide, chromium, electric contacts, graphitization.

1. Introduction

Metal/semiconductor contacts are an important technological issue. Silicon carbide (SiC) is a wide-band-gap semiconductor which gives a great promise of uses in high-power, high-frequency and high-temperature electronic devices [1, 2]. High quality ohmic contacts are especially crucial. In general, metals form Schottky contacts as-deposited on SiC at room temperature. Ohmic contacts are difficult to achieve. Their formation requires high temperatures during annealing and SiC substrates with a high doping concentration. The same applies to chromium used as a material for electrical contacts with SiC. Chromium, as-deposited at room temperature on the 6H-SiC(0001) surface, forms a rectifying contact with a Schottky barrier height (SBH) of the range between 1.1 and 1.3 eV, which was previously reported [3, 4]. To produce the ohmic contact type, a prolonged annealing at temperatures up to 2000 °C is needed [5].

Application of high temperature, which is usually required for electrical contact formation, can destroy the results of preceding technological steps of the electronic device fabrication process performed before the formation of the ohmic contact. Therefore, a low-temperature technology of obtaining the ohmic electrical contact is highly desirable. In our previous studies of Cr/SiC contact it has been shown that the task is possible by using Ar⁺ ion bombardment of the semiconductor surface prior to deposition of a metal layer [6]. The surface becomes graphitized during the bombardment process and, as a result, carbides are formed with the deposited metal (at a temperature as low as ~850 °C), which are responsible for the ohmic contact formation. Following the graphitization trail to facilitate the procedure of ohmic contact formation, it is worth looking at how a thin layer of carbon in the form of graphite affects the properties of the junction under formation. It is well known that an intermediate graphite layer, which is present between the SiC substrate and a metal adlayer, lowers the SBH [7, 8]. Epitaxial growth of good quality graphite films is easy to achieve on SiC surfaces by annealing the SiC substrates in vacuum at temperatures around 1000 °C [9].

Investigation under discussion in the present report was intended to check if the formation of a graphite ultra-thin film between a Cr thin layer and the SiC substrate surface at room temperature would result in the ohmic contact. Accordingly, suitable conditions for the substrate graphitization were searched for, and also the electric properties of the Cr adlayer as-deposited onto the graphite layers were characterized on the nanometer scale by using atomic force microscopy (AFM).

2. Experimental details

Samples, around 10×7 mm² in size, were cut out of the nitrogen-doped *n*-type (resistivity 0.1 Ω·cm) 6H-SiC single crystal {0001}±0.25°-oriented, Si-terminated wafers (Cree Research Inc.). Prior to placement in ultra-high vacuum (UHV), samples were washed with alcohol, next the crystals were *ex situ* hydrogen etched in a tubular reactor to obtain clean and smooth vicinal 6H-SiC(0001) surfaces [10].

The Cr/graphite/6H-SiC interfaces were formed and initially characterized in the UHV chamber at operating pressure of 3×10⁻¹⁰ torr or lower. The substrate surface was modified by cycles of annealing at temperatures in the range 950–1550 °C to produce the graphite/6H-SiC system. The chromium layers were deposited from an electron beam evaporator. The Cr/graphite/6H-SiC(0001) contacts were characterized *in situ* by the UHV atomic force microscope (AFM; Omicron) operating in contact mode with conducting tip (Pt–Ir; Nanosensors). A local behavior of the contact was investigated by measurement of *I*–*V* characteristics in a grid mode. The areas of probed region were covered by 6400 measurement points. The analysis of the substrate and the interface formation were also carried out by X-ray photoelectron spectroscopy (XPS; Specs) using Mg Kα radiation (*hν* = 1253.6 eV) and low-energy electron diffraction (LEED; Omicron).

3. Results and discussion

LEED patterns of as-prepared surfaces exhibit hexagonal structure (see Figure 1a). The residual contaminant on SiC(0001), recorded on XPS spectra as a small peak, was oxygen. The surface got slightly contaminated during carrying over the sample from the hydrogen reactor to the vacuum apparatus. Positions of peaks in the XPS spectrum were typical, *i.e.*, 283.7 eV for C-1s, 101.5 eV for Si-2p, and 532.8 eV for O-1s. The contaminants of surface oxygen and hydrocarbons can be removed by a thermal impulse; however, heating the semiconductor 6H-SiC(0001) sample at a temperature of ~ 1000 °C, *i.e.*, a relatively low temperature vs. the melting/sublimation point of SiC, leads to Si-deficiency of the surface. This results from the fact that silicon carbide exceptionally easy undergoes the thermal graphitization due to the high pressure of Si vapor compared with C vapor at the crystal's surface. The phenomenon is easy to observe from the diffraction patterns as the lowering of the lattice parameter (*cf.* Fig. 1b). The heating procedure, however, was intentionally applied to produce a metal/SiC ohmic contact by using the intermediate layer, because the graphite/6H-SiC junction was known to be characterized by a low Schottky barrier suitable for formation of ohmic contacts [7, 8].

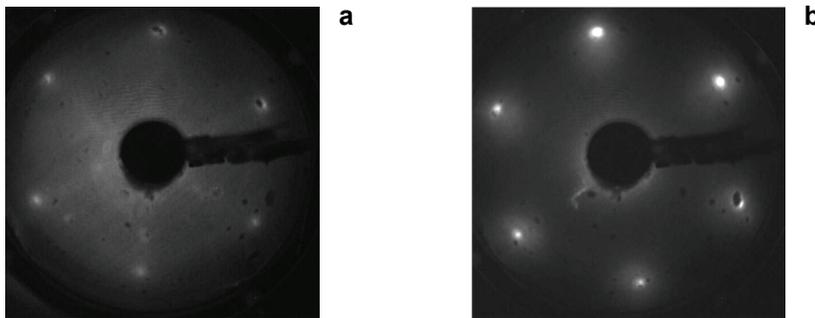


Fig. 1. LEED patterns illustrating the change in lattice parameter of 6H-SiC(0001) surface due to heating. Diffraction pattern corresponding to hexagonal structure of 6H-SiC(0001), obtained after etching the sample *ex situ* in H₂; 50 eV (a). Diffraction pattern of graphite (1×1) structure obtained after heating the sample in UHV; 70 eV (b).

It is worth inspecting the process of annealing the sample for its effect onto the physicochemical properties of subsurface layers, which determine the parameters of the interface under formation. Let us look at the successive stages of heating a sample at different temperatures (see Fig. 2). The sample was subjected to 20-minute heating cycles in the range from 950 to 1500 °C. Differences in position and shape of C-1s and Si-2p peaks become revealed, which is due to a change in chemical interactions between the carbon and silicon atoms. The C-1s spectrum of carbon drifts toward the high bond energy to stop at an energy of 284.7 eV corresponding to the bond energy of carbon in graphite [11]. The Si-2p silicon spectrum line gets shifted

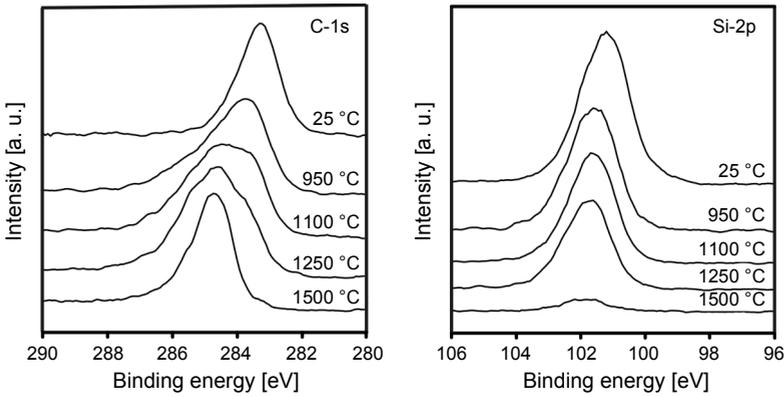


Fig. 2. Changes in position and shape of C-1s and Si-2p peaks due to heating the sample 6H-SiC(0001). Heating at 1500 °C leads to formation of a relatively thick graphite layer. For a thickness of ~7 nm, the spectral line of Si-2p disappears.

toward the high bond energy to about 101.8 eV upon the first heating. Succeeding heating leads to a gradual decay of this peak. The results under discussion demonstrate how a high quality, contaminant-free graphite layer can easily be produced on the SiC substrate.

A graphitized intermediate layer ~1 nm thick was applied to investigate formation of the contact, by observing the intensity decay of the Si-2p spectrum line relative to the reference spectrum. Formation of islands started after deposition of chromium onto such a prepared substrate. When the surface was entirely covered with chromium, the deposition of subsequent Cr doses resulted in the growth of a new grain generation. AFM topography measurements unequivocally show that the Cr/graphite/SiC contact has a grainy structure. Typical topography patterns of the surface are shown in Fig. 3. During the course of evaporation, the chromium layers did not undergo oxidation and the positions of Cr spectral lines were 574.4 and 583.7 eV for Cr-2p_{3/2} and Cr-2p_{1/2}, respectively, with their half-intensity width 1.85 and 2.3 eV, respectively (see Fig. 4).

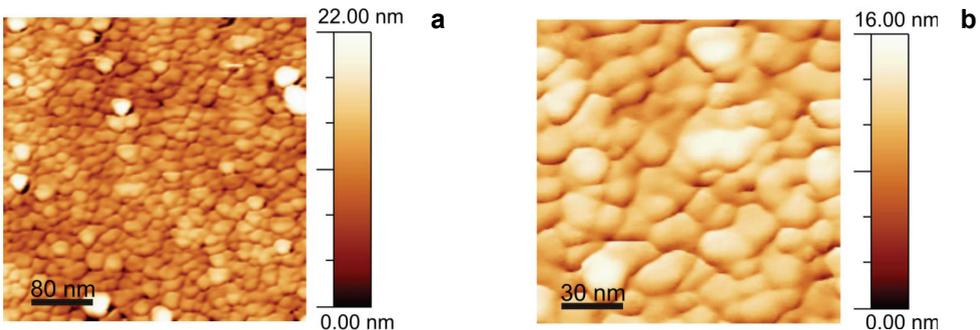


Fig. 3. AFM topography of the surface after Cr deposition, clearly seen is a grainy structure. Surface area 400 nm×400 nm (a), and area 150 nm×150 nm (b).

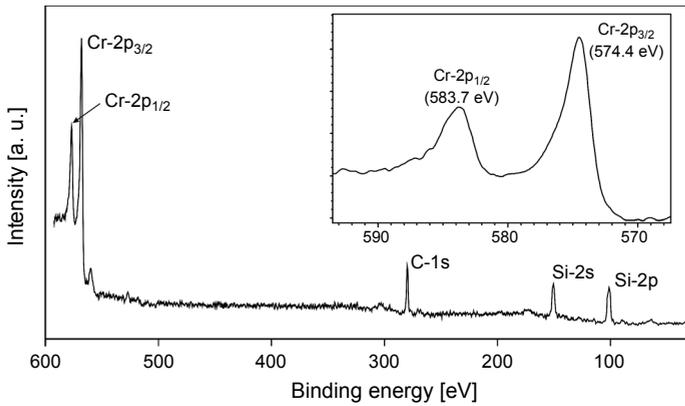


Fig. 4. XPS spectrum of the system Cr/graphite/6H-SiC(0001) in a wide bond energy range from 600 to 40 eV. An enlarged spectrum fragment in the inset shows the doublet Cr-2p in detail.

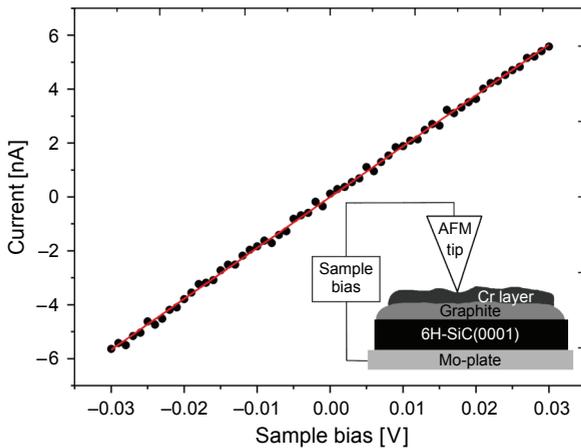


Fig. 5. Current–voltage characteristics illustrating the electric properties of the formed system Cr/graphite/6H-SiC(0001).

Essential data are, apart from the topography, the electric properties of the junction. Atomic force microscopy with a conducting tip enables to collect the latter by yielding the maps of current–voltage characteristics, which permits determination if a given junction has rectifying or ohmic properties. It should be stressed that in the case of the local I – V characteristics survey one deals, in fact, with two junctions – *i.e.*, the tip/Cr and the Cr/graphite/6H-SiC(0001) which are connected in series. The former junction is of the metal–metal type with a linear characteristics and it does not veil the properties of the phase boundary Cr/graphite/SiC. A typical averaging curve obtained from the I – V characteristics taken over a surface area of $400 \times 400 \text{ nm}^2$ is shown in Fig. 5. The I – V curves obtained from the surface are practically equal while the deviation from the mean appears as low as located within the limits of the point marked on the diagram. Assuming that the AFM tip formed a contact with the surface

of the sample having a diameter of about 20 nm, the value of the contact resistivity of the Cr/graphite/SiC system was estimated as $1.7 \times 10^{-5} \Omega \cdot \text{cm}^2$. It is worth noting that in the former report, where the Cr layer was grown on the clean surface with the original stoichiometry, the Cr/SiC contact had a clear diode character which started to faint only after a prolonged heating at a temperature of 700 °C [3].

In the case of electric junction its high temperature behavior is of importance, especially from the viewpoint of construction of electronic devices designated to work in harsh conditions. The effect of heating the system of interest under UHV conditions on its physicochemical properties was investigated by the XPS techniques. After a cycle of flashing at 1500 °C, chromium was completely desorbed from the surface and the initial spectrum was obtained with the C-1s and Si-2p lines at bond energies of 283.7 and 101.8 eV, respectively. Cr layers of insignificant thickness were evaporated onto such a surface while the substrate spectrum was clearly visible, and the sample was subjected to heating at a temperature of 700 °C, the stages of which are illustrated in Fig. 6.

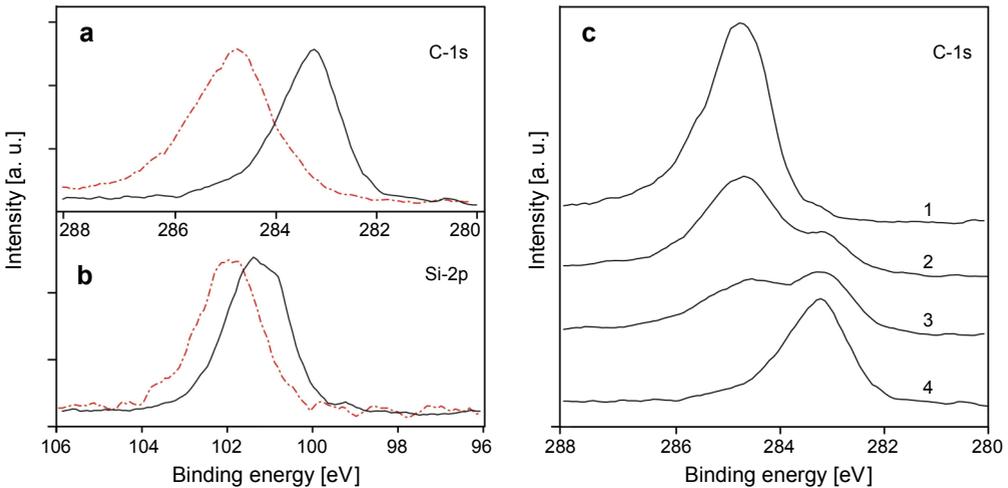


Fig. 6. Reaction stages of chromium with the substrate graphitized to a depth of ~ 1 nm. Spectrum of C-1s (a). Spectrum of SiC-2p, dot-dashed line (red) corresponds to the system before heating, solid line does to that after heating (b). Subsequent stages of chromium dissolving and reacting with carbon: 1 – initial stage, 283.7 eV; 2 and 3 – transient stages; 4 – final stage after Cr dissolution and its reaction with C, 283.4 eV (c).

It has appeared from the investigation that heating the system leads to a reaction of chromium with carbon, or even with silicon, which results in the shifted spectral lines C-1s and Si-2p to bond energies of 283.4 and 101.4 eV, respectively. It is seen from the Si-2p line shift that the chromium must have penetrated to a depth of at least 1 nm to react with silicon. For the contact under heating, a reaction occurs between

chromium and the components of the graphitized substrate. It is worth noting that, for the heating of Cr adlayers on a strongly graphitized surface of 6H-SiC(0001), the carbon peak C-1s was shifted as far as to 283.1 eV after reaction with the adsorbate. (In this case, the graphite layer was more than 7 nm thick; and the signal of Si-2p spectral line almost entirely vanished.)

4. Conclusions

The surface of the semiconductor SiC appears to be very susceptible to thermal modification under vacuum conditions, which leads to the formation of a graphite surface layer. After deposition of metal layers, no heating was necessary to produce the contact. It was observed that during heating the system under formation the chromium chemically reacted with carbon and silicon and diffused into the sample's bulk. The electric contact Cr/SiC, as obtained by using the intermediate graphite layer, has the ohmic character.

The effect of an intermediate graphite layer on the electronic properties of metal/SiC contacts can be utilized to form ohmic contacts. The use of graphite intermediate layer to create a good contact can reduce the temperature up to 1000 °C in comparison with the previous technology. In the next stage of this study, we will check if a well-thin carbon layer like graphene can play the role such as that of graphite present between Cr and SiC, in formation of the ohmic electric contacts.

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