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# Possibilities of C 1s XPS and *N*(*E*) C KVV Auger spectroscopy for identification of inherent peculiarities of diamond growth

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**Abstract**

The interaction of C-atoms and $CH_n$-radicals with uncleaned and argon cleaned silicon substrate and with diamond surface after H-treatment have been studied in situ by XPS and Auger spectroscopy. It was found the formation of a new chemical surface state of carbon atoms in the case of carbon atoms and radicals interaction with cleaned silicon. The same chemical state was revealed on the H-treated diamond surface. Graphite-like structure of carbon atoms was observed on the surface of unlearned silicon and H-treated diamond after interaction with carbon atoms and radicals. *N*(*E*) C KVV Auger spectrum for the new chemical state of carbon atoms significantly differs from typical spectra for $sp^2$- and $sp^3$-bonded carbon materials. The high energy part of this spectrum was interpreted under the hypothesis of $sp^3$-bonded carbon atoms but with shifted fermi level position.
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*Keywords:* XPS; XAES; Diamond; Nucleation; Growth

## 1. Introduction

The growth mechanism of CVD diamond films is a continuing subject of debate [1–3]. While the gas-phase reaction mechanism is based on the known rate coefficient of elementary chemical reactions [2] and experimental measurements [4,5], the surface reaction mechanism brings up a few problems. The main of them is the identification of chemical state of carbon atoms on a growth surface. According to Goodwin and Butler [1] "the fundamental goal is to identify the chemistry occurring on the surface during CVD growth. This is difficult experimental problem, since the electron spectroscopies used in surface science are not directly useful at the high gas pressures encountered in chemical vapor deposition".

The early stages of CVD diamond nucleation and growth on silicon substrates have been studied by XPS and AES [6–11]. The chemical shift of C 1s and Si 2p XPS spectra shows SiC layer formation. Undoubtedly, the formation of SiC layers is followed by the growth of layers with C–C interaction. Different C–C interactions (hybridizations) cannot be distinguished by C 1s XPS based of chemical shift. The C KVV Auger spectroscopy is more suitable technique for identification of a chemical state of carbon atoms on upper most layers because the Auger line shape is a probe of valence band electronic structure [11–15].

In [6–10] an analysis of CVD diamond films using d*N*/d*E* C KVV spectroscopy was carried out. The d*N*/d*E* C KVV Auger spectral features were used for the identification of SiC and diamond formation during carbon deposition. However, the differentiation destroyed the shape and width of the spectra, which did not allow obtaining the all possible information from the d*N*/d*E* C KVV spectra. Therefore, the *N*(*E*) C KVV Auger spectroscopy is preferred over d*N*/d*E* one.

The purpose of this work is to study in situ chemical reactions of C-atoms or $CH_n$-radicals with Si and diamond substrates by C 1s, Si 2p XPS and *N*(*E*) C KVV Auger spectroscopy.

## 2. Experimental

XPS and AES data were obtained using the MK II VG Scientific spectrometer with non-monochromatized Al Kα X-ray source (1486.6 eV). The base pressure both in the main and preparation chambers was equal to $5 \times 10^{-10}$ mbar. All spectra

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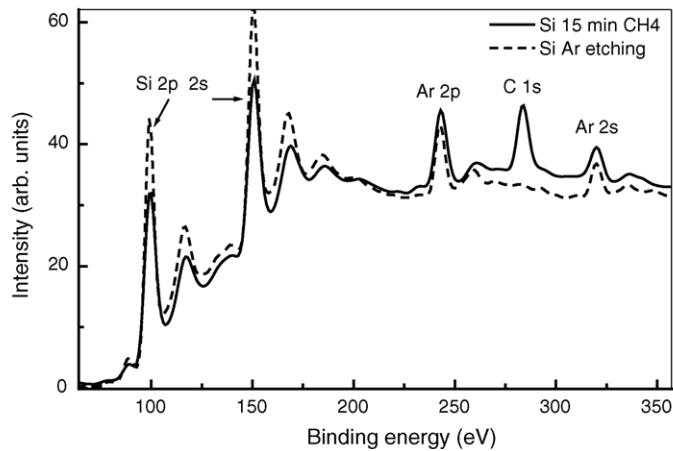


Fig. 1. The wide XPS spectra for silicon substrate before and after carbon deposition.

were charge referenced to the C1s XPS peak (284.4 eV). Si-substrate was cleaned by Ar ions with $E_p = 1$ keV during 5 min.

The crystal plane (1 1 0) of a natural diamond of size 6 mm × 5 mm and 1.5 mm thickness was mechanically polished by means of a cast iron wheel. The roughness was equal to about 1 nm. An ultrasonic rinse in acetone and then in alcohol was performed prior to the mounting of the sample in the vacuum chamber.

Tungsten hot-filament at 2100 K was used for decomposition of $CH_4$. The temperature of tungsten filament was measured by a pyrometer. The distance between the hot-filament and the sample was 10 mm. The temperature of samples was measured by thermocouple deposited alongside and was equal about 1100 K. The surface of Si-substrate was studied in analysis chamber by XPS before and after $CH_4$ treatment at $10^{-6}$ mbar in the preparation chamber of the spectrometer. The information depths of C 1s, Si 2p photoelectrons and C KVV Auger electrons are equal 3, 3.5 and 0.8 nm, respectively, according to our estimation with using of Powell–Jablonski data [12].

At interacting of $CH_4$ with tungsten filament is supposed to form C-atoms and $CH_n$-radicals. In [4,5] only $CH_3$ radicals were detected at a distance about 1 cm from a source at 20 torr of the reactor pressure. These data are not suitable in our case

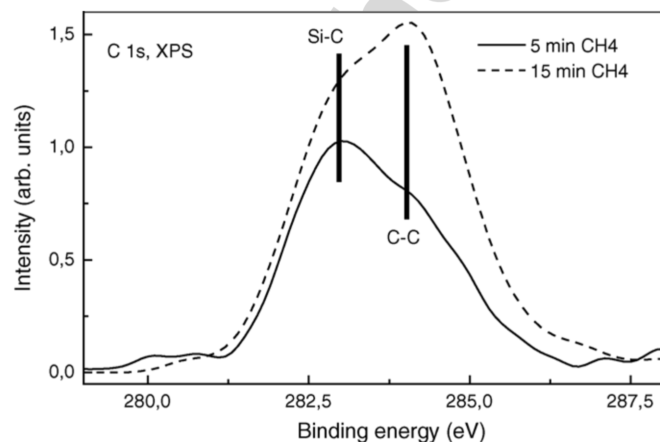


Fig. 2. The C 1s XPS spectra alteration with C-atom deposition on Si-substrate.

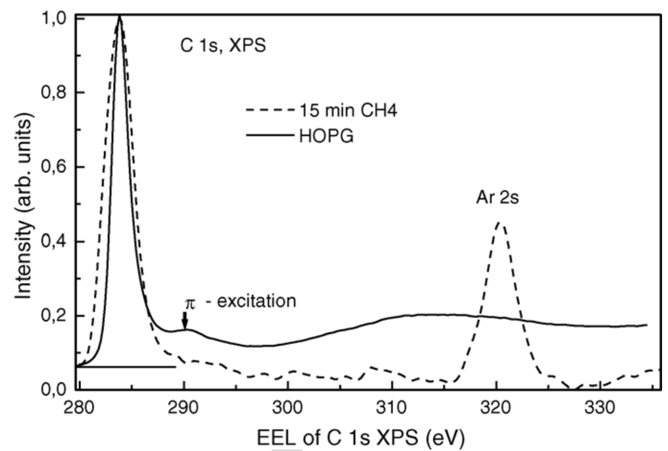


Fig. 3. Electron energy loss of C 1s photoemission for the carbon film and HOPG.

because there is not interaction between atoms and $CH_4$ radicals in the gas phase at $10^{-6}$ torr. Tungsten filament remained the source of C-atoms during a few minutes after methane had been pumped. We consider there is not a principal difference between C-atoms and $CH_n$-radicals because when the radicals interact with atoms on a surface the dissociative adsorption takes place. We say "C-atoms" having in mind possible partial presence of $CH_n$-radicals.

## 3. Results

### *3.1. Deposition of carbon atoms on silicon substrate after Ar ion etching, Figs. 1–5*

Fig. 1 shows wide spectrum of a silicon substrate surface after Ar etching and deposition of carbon atoms by $CH_4$ decomposition. The Si 2p and Si 2s intensity were attenuated by the carbon layers. The thickness of the layer is equal to about 1.1 nm for 5 min and 2.8 nm for 15 min deposition according to our estimation on the base of Powell–Jablonski [16] formula for attenuation. So the speed of deposition is equal to about 0.2 nm/min. As one can see in Fig. 1, the Ar 2p intensity practically did

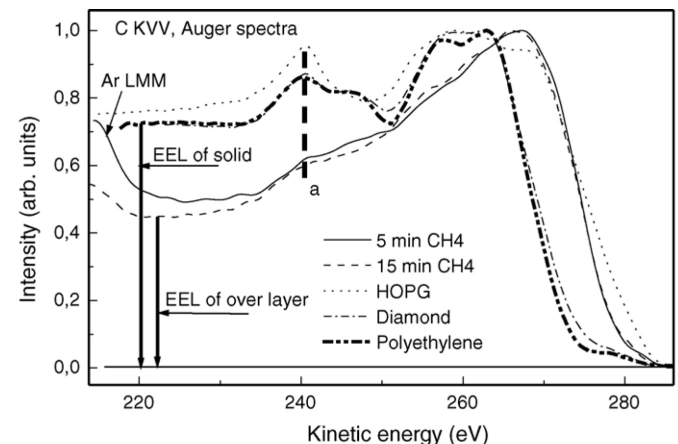


Fig. 4. Comparison of C KVV Auger spectra for carbon layers, HOPG, polyethylene and diamond. The arrow emphasizes the difference in electron energy loss of Auger electrons. The intensities of spectra are normalized.

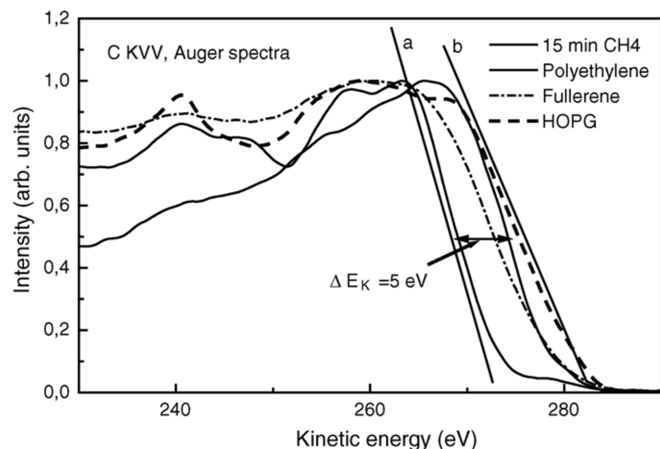


Fig. 5. The $N(E)$ C KVV spectra for the carbon film, HOPG, polyethylene and Fullerene. (a) and (b) shows the characteristic slope of the right part of $N(E)$ C KVV Auger spectra for sp$^2$- and sp$^3$-bonds. The intensities of spectra are normalized.

not change opposite to that of Si 2p. It is very strange phenomena. But it is experimental data and one should suppose a diffusion process of Ar-atoms from upper silicon layers into new carbon film. Incorporation of C-atoms into Ar-atoms sites also may take place and as a result of this process upward motion of Ar-atoms is observed. The Si 2p XPS spectra show an insignificant modification with C-atom deposition. It testifies that C-atoms interact with Si substrate only in a thin layer, which the thickness less than the information depth of the Si 2p photoelectrons.

The spectra of C 1s in Fig. 2 show two chemical interactions: Si–C and C–C. The result coincides with the data [5–10]. One can see an increase of the C–C feature with C-atom deposition. It means that the growth of the upper layers takes place only with C–C interaction. The C 1s XPS spectrum in Fig. 3 has not π-excitation which is inherent peculiarity of sp$^2$-bonds [17]. This is why we cannot attribute this chemical state to sp$^2$-bonds. In order to determine the chemical state of carbon atoms in this case we did qualitative interpretation of $N(E)$ C KVV Auger spectra.

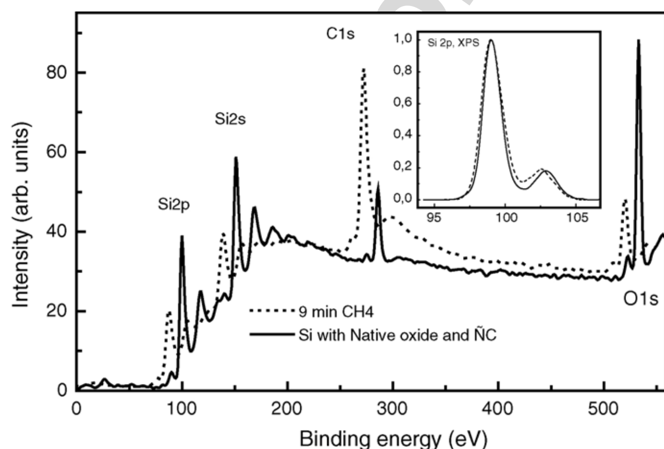


Fig. 6. The wide XPS spectra for Si-substrate with native oxide and carbon contamination before and after C-atoms deposition. The inset shows Si 2p XPS spectra for this sample.

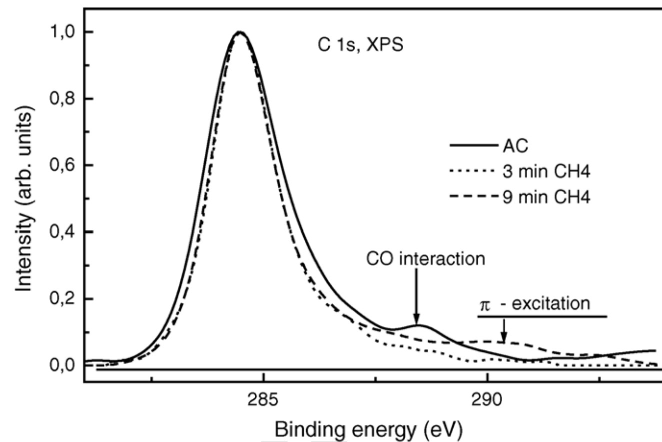


Fig. 7. The C 1s XPS spectrum modification with carbon atom deposition on the Si-substrate with native oxide and carbon contamination.

C KVV Auger spectrum of carbon layers (Fig. 4) significantly differs from that of high oriented pyrolytic graphite (HOPG) and diamond. The preparation of diamond surface which would reflect bulk diamond structure is a big problem. The shape of the diamond spectra usually shows the mixture of sp$^2$/sp$^3$ features [18]. The polyethylene surface is more stable and one should use this C KVV Auger spectrum as standard spectrum of sp$^3$-bonds. Our spectrum of polyethylene coincidences with that obtained by Beamson and Briggs [19].

An important result can be derived from Fig. 5. The right parts of C KVV spectra of polyethylene, H-treated diamond and carbon film are parallel. This fact allows supposing a chemical state of C-atoms in the carbon film to differ from both standard sp$^2$- and sp$^3$-bonds spectra. The position of the right part of the carbon film spectrum is close to that for sp$^2$-bonds but it has the slope as the standard sp$^3$-spectrum.

The right part of a C KVV Auger spectrum is a convolution of the uppermost occupied levels in the valence band therefore the slope of the right part of the spectrum depends on number of electrons on that levels [11,12]. The coincidence of the right part slopes of the C KVV spectra of polyethylene and the carbon film allows supposing that the highly occupied levels of

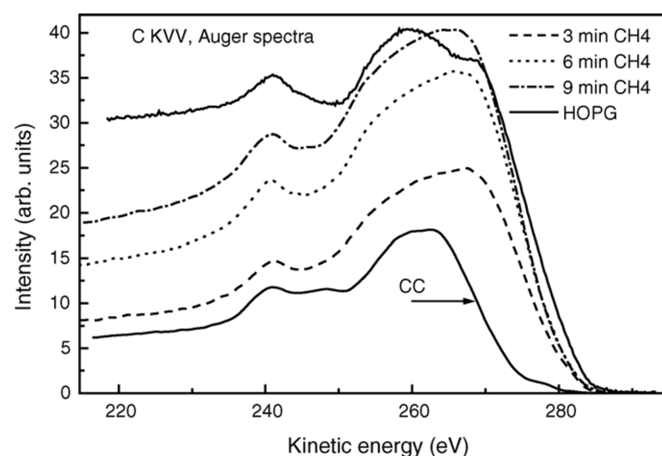


Fig. 8. The C KVV Auger spectra alteration with carbon atom deposition on Si-substrate with native oxide and carbon contamination.

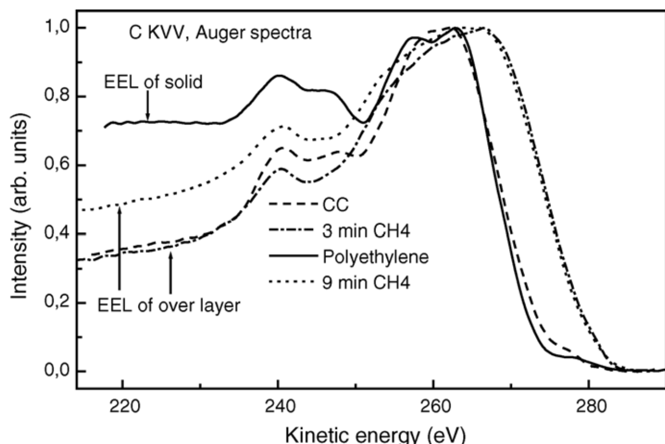


Fig. 9. The C KVV Auger spectra from Fig. 8 with normalized intensities.

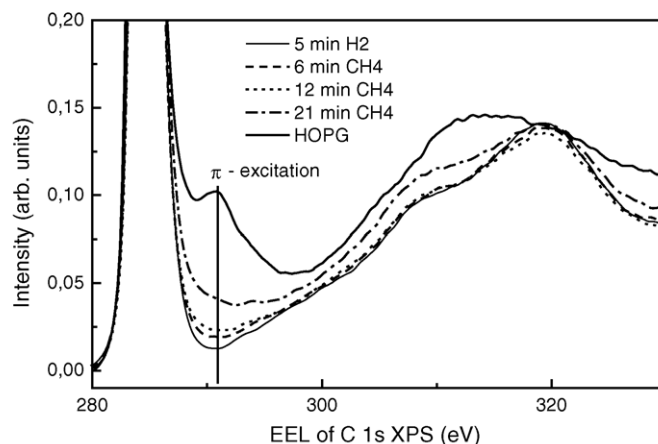


Fig. 10. The comparison of the EEL of C 1s XPS spectra of natural diamond after H-treatment and carbon atoms deposition.

the valence band of the carbon films are populated by three electrons.

The left part of Auger spectrum is conditioned by electron energy loss (EEL). The carbon film is an over layer on Si-substrate while diamond, polyethylene and HOPG are solid.

### 3.2. *Deposition of carbon atoms on silicon substrate with native oxide and carbon contamination (CC), Figs. 6–9*

The interaction of carbon atoms with Si-substrate without cleaning was carried out at the same conditions as explained in Section 3.1. The wide spectrum of Si-substrate in Fig. 6 shows the surface composition before and after C-atoms deposition. The Si 2p XPS spectrum before C-atoms deposition shows two chemical states of silicon atoms: Si–Si and $SiO_2$. This spectrum does not change with C-atoms deposition. This implies that there is no chemical interaction of the C-atoms with native silicon oxide and with silicon substrate. One can see attenuation of the intensities of Si 2p, Si 2s and O 1s peaks. The thickness of the carbon layer after C-atoms deposition is equal to about 2.5 nm according to our estimation on the base of Powel–Jablonsky [20] formula for attenuation. Before the deposition of C-atoms C 1s XPS spectrum (Fig. 7) had not π-excitation. This feature occurs only after C-atoms deposition.

Fig. 8 depicts the modification of shape and intensity of C KVV Auger spectra with C-atom deposition. The disappearance of the CC spectrum after 3 min of C-atoms deposition testifies that the layer of CC is being covered by a new carbon film. The spectrum of CC has peculiarities that coincidence with that of polyethylene (Fig. 9). It means that the carbon atoms in CC have $sp^3$-bonds. It is the very important spectral feature which can be used for the detection of CC presence on carbon surfaces. The spectra in Fig. 9 are the normalized spectra of Fig. 8. These spectra show alteration of the left tail. This part of spectra results from energy loss of Auger electrons during its escape from surfaces. One can see an increasing of EEL with the thickness of carbon films on the substrate (Fig. 8).

### 3.3. *Deposition of carbon atoms on natural diamond (1 1 0), Figs. 10–12*

Deposition of carbon atoms on natural diamond (1 1 0) was carried out at the same conditions as explained in Sections 3.1 and 3.2 experiments. The diamond surface was H-treated before C-atoms deposition. After the treatment there is only low oxygen impurity concentration detected on the surface.

Fig. 10 shows modification of the EEL of C 1s XPS peak with the deposition time. As one can see the $sp^2$-bonds are not formed. Opposite that the right part of C KVV Auger spectrum in Fig. 11 shifts to graphite with carbon atoms deposition. It is necessary to emphasize the coincidence of the right parts of the Auger spectra Fig. 11 with that of the carbon film Fig. 4.

In the case of diamond we cannot estimate the thickness of the deposited film. With the same deposition rate as in Sections 3.1 and 3.2, the formation of graphite would take place after 5 min. But this is not the case, hence, the incorporation of C-atoms into non-graphite type structure can be supposed. The EEL of Auger electrons feature (left tail) opposite to the results in Figs. 4 and 9 does not differ from solid. Obviously, in this case take place an incorporation of C-atoms into diamond,

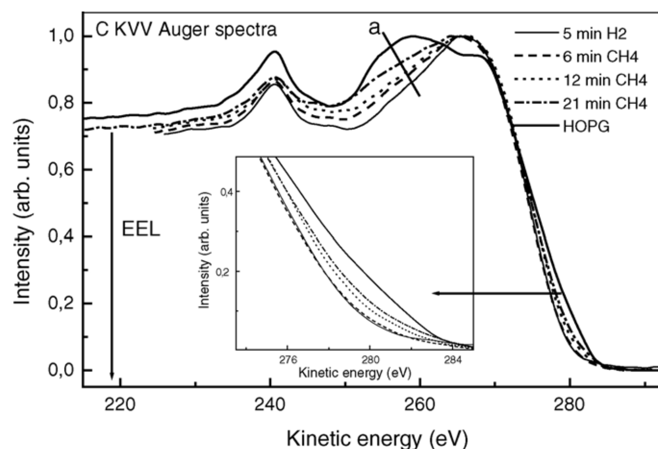


Fig. 11. The $N(E)$ C KVV Auger spectra alteration with C-atoms deposition on diamond after H-treatment.

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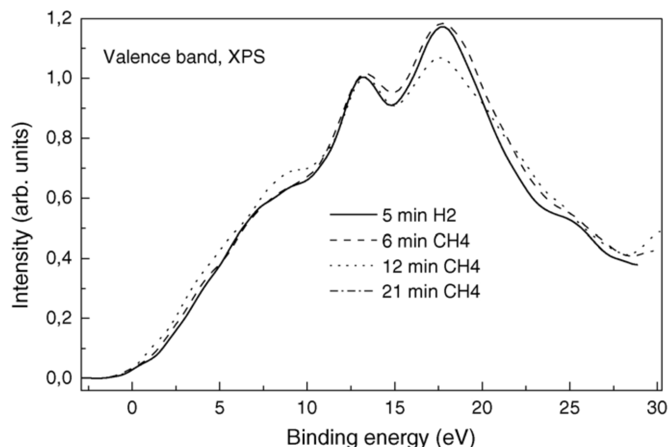


Fig. 12. The valence band XPS spectra for diamond sample after H-treatment and C-atoms deposition.

rather than an over layer formation as in Sections 3.1 and 3.2. The valence band XPS is not modified with C-atoms deposition (Fig. 12).

## 4. Discussion

Our SiC layers identification on the base of C 1s XPS spectra is in a good agreement with data [6–10]. But it is difficult or impossible to compare our *N*(*E*) C KVV spectra with d*N*/d*E* C KVV Auger spectra from [6–10]. The reason is that the spectrum differentiation results the in main features disappears, such as the width, shape and the kinetic energy position of the peak.

One of the main results of this work is the establishing of coincidence of C KVV Auger spectrum after Si–C interaction with that of diamond after H-treatment. This coincidence is an evidence of the same chemical state of carbon atoms in the both cases. Obviously one should suppose that the revealed chemical state of carbon atoms is responsible for diamond nucleation and growth. According to our results the valence band of this chemical state is unusual, with three electrons being on the uppermost levels as in the $sp^3$-hybridization. But the energy position of these electrons is shifted on 2.5 eV in comparison with uppermost occupied levels for polyethylene. This value is obtained on the basis of Auger emission equation [11,12] using 5 eV energy difference shown in Fig. 5.

Our results give a demonstration of the *N*(*E*) C KVV Auger spectra potentialities. In such a way the slope of the right part of *N*(*E*) C KVV Auger spectra is a measure of electron number on the uppermost levels of valence band. Obviously, such unique information can be received only by *N*(*E*) C KVV Auger spectroscopy.

Information depth of C KVV Auger electrons is equal to about 1 nm. If the C-atoms deposition rate was the same as explained in Sections 3.1 and 3.2, the Auger spectrum would be graphite-like after about 10 min. But this is not the case that is an evidence of a certain chemical interaction resulted in transformation of adsorbed C-atoms into the diamond structure in the sub-layer with diamond nucleation and growth states being kept in over layer.

The left tail of *N*(*E*) C KVV Auger spectra is electron energy loss (EEL). The EEL of Auger spectra of HOPG, polyethylene and H-treated diamond differ significantly from that of CC and C-atoms deposited on Si-substrate before and after Ar ion cleaning. Obviously the difference in EEL is evidence of solid state and over layers state. With increasing of the over layer thickness the EEL part approaches to a solid state shape (Fig. 9). The EEL does not change during C-atoms deposition (Fig. 11) on H-treated diamond. These data clearly reveal that C-atoms were incorporated into the diamond substrate but did not form over layers on it. So, there are grounds to believe that the diamond growth takes place in this case.

As Arnault notes in [3]: "Unfortunately, scratching treatment produces damage and contamination of the substrate surface, and leads to a roughened diamond/substrate interface so that produced diamond films are incompatible with requirements of electronic devices". In our experiment explained in Section 3.2 this supposition was confirmed. The native oxide and contamination prevents interaction of C-atoms with the Si-substrate.

In [6–10,21] SiC detection is declared as a certain critical stage of the diamond growth mechanism. However, our Auger results are evidence that the SiC is sub-layer above that take place a formation of the layers with the same chemical state of carbon atoms as on diamond surface after H-treatment. We suppose this chemical state is responsible for diamond nucleation and growth. Certainly, our results did not answer on a lot of questions about Si–C and diamond–C interaction but they show that *N*(*E*) C KVV Auger spectra are the most informative for study of inherent peculiarities of diamond growth.

## 5. Conclusions

The *N*(*E*) C KVV Auger spectra show the coincidence of C-atoms chemical state on the surface of natural diamond after H-treatment with that on the surface of carbon films on Si-substrate at initial growth stage. The qualitative interpretation of these Auger spectra demonstrates that:

- the chemical state of C-atoms differs in principle from $sp^2$- and $sp^3$-bonds;
- the population of the top level of valence band is the same as in the $sp^3$ valence band but its binding energy position is shifted to $E_f$.

The growth of the graphite-like film takes place during C-atoms deposition on Si surface with native oxide and carbon contamination. During C-atoms deposition on H-treated diamond, Auger spectra show the formation of graphite only after a long period of time. A possibility of C-atoms incorporation into diamond structure cannot be excluded.

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