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Study by X-Ray Photoelectron Spectroscopy of Rice Husk and the Products of Its Processing

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Abstract—The rice floral glume (husk) and its processing products were studied using X-ray photoelectron spectroscopy. We established that the rice husk contained silica in two non-equivalent forms in 1:3 ratio. The predominating form is silicon dioxide, while the minor component contains the silicon bound with the organic component which is stable up to ~350°C.

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A promising source of chemical compounds is a waste of renewable agricultural products, in particular, the waste of the rice production. The rice husk is concentrated in the enterprises producing rice. Its chemical composition differs from that of the husk of other cereals by a high content of amorphous silica, and it can be used to produce some silicon-containing products, as well as other useful substances [1–7]. Creation of an integrated line of processing rice husk to produce materials with different functional properties requires knowledge of the composition and properties of both the raw material and its processing products, which are poorly reviewed in the literature. Thus, an open question remains about the presence of organosilicon compounds in the rice husk. It should be noted that the organic form of silicon, whose existence in plants was foreseen even in the 19-th century was the least studied to date [8–10]. In [11–12] was also shown that the decomposition of volatile components of the husk at 120–600°C proceeds ununiformly: the curve characterizing the material mass loss has varied slope in the temperature range 320–420°C, and two exothermic effects of uncertain nature appear in the heating differential curve.

The purpose of this paper is to study rice husk and the products obtained by its thermal decomposition, using the method of X-ray photoelectron spectroscopy (XPS).

The XPS spectrum of core electrons of the rice husk carbon (sample I, Table 1) is typical of organic compounds (Figs. 1 and 2a). The line of C1*s*-electrons is inhomogeneously broadened and includes components from carbon atoms bonded with oxygen-containing functional groups (–OH, =O, –O–, etc.). In the spectra of rice husk is also registered a line with E_b ~399.8 eV, corresponding to the nitrogen atom bonded with a carbon in organic compounds [13], including amino groups. However, due to the low content of nitrogen in the sample (~2%) it is difficult to identify correctly the respective carbon line in the band of C1*s*-electrons. In Fig. 2a, in the experimental spectrum of C1*s*-electrons the arrows indicate the possible position of the line, which could be attributed to the C–Si bond, however, when a smoothing procedure [14] is applied this "peculiarity" of the spectrum disappears (Fig. 1).

The spectrum of Si2*p*-electrons of the sample I (Figs. 1 and 3a) contains two components with E_b = 101.7 eV (Si^1) and 103.4 eV (Si^2). The component with a higher E_b refers to SiO_2. The low-energy component Si^1 can be attributed to the silicon atoms in organic fragments. Integral intensities of the Si^1 and Si^2 signals are 1:3. The difference $\Delta E_{C–Si}$ between Si^1 and the "peculiarity" in the experimental spectrum of the C1*s*-electrons is ~181.3 eV. The position of the "peculiarity" in the carbon spectrum in the energy scale, the difference of E_b of Si^1 and $\Delta E_{C–Si}$ values in the sample I from the relevant characteristics of the XPS spectrum of SiC can be explained by the difference of the band structure of these compounds due to the essentially different nature of the objects.

Table 1. Samples studied by XPS method

Sample	Method of preparation	Characteristics[a]
I	Rice husk with a particle size of no less than 2 mm rinsed with water and dried in air	Content: H_2O 2.8%, SiO_2 16.5%
II	Rice husk (sample no. 1), crushed in a mill	Content: H_2O 2.8%, SiO_2 16.5%
III	Unripe rice grains present in the waste rice husk[b]	Content: H_2O 2.9%, SiO_2 10.5%
IV	Carbonized silica from sample no. 1 after thermal annealing at 350°C	Black, amorphous[c]; content: H_2O 3.8%, SiO_2 46.5%
V	Rice husk after acid leaching with 0.1 N hydrochloric acid at 90°C for 1 h, then filtered off, washed with water and dried in air	Content: H_2O 2.9%, SiO_2 18.5%
VI	Carbonized silica from sample no. 5 obtained by thermal annealing at 350°C	Black, amorphous; Content: H_2O 3.8%, SiO_2 46.5%
VII	Carbonized silica from sample no. 3 (after acid leaching with 0.1 N HCl) after thermal annealing at 350°C	Black, amorphous; Content: H_2O 2.0%, SiO_2 48.5%
VIII	Silica from sample no. 6 after thermal baking at 700°C	White, amorphous; Content: H_2O 0.8%, SiO_2 99.95%
IX	Silica from sample no. 7, thermal baking at 700°C	White, amorphous; Content: H_2O 0.5%, SiO_2 99.0%
X	Carbon obtained from sample no. 1 by treatment of rice husk with conc. HF solution to remove the silicon, followed by annealing at 350°C	Black, amorphous[c]

[a] Analysis of samples was carried out according to procedures specified in [3, 4]. [b] The amount of grains in the rice husk formed at the rice processing depends on the farming conditions of plant growth. [c] The maximum of X-ray-amorphous halo in the samples no. 4, 6–10 is at $2\Theta = 22°$.

Besides, in this case cannot be determined whether silicon is bonded directly to carbon in organic fragment, or through other atoms, for example, through oxygen.

The E_b in Si^2 also differs from the binding energy of the Si2*p*-electrons in SiO_2 which we used as a reference sample. The silica in the rice husk probably is not contained as large clusters. Therefore, the external electrostatic potential on the silicon oxygen atoms of the SiO_2 molecule in the sample differs from the Madelung potential in the reference sample. The same reasons determine the difference in the energies of the extra-atomic relaxation of core holes, which is also reflected in the values of the measured E_b values of O1*s*- and Si2*p*-electrons. Therewith, the difference $\Delta E_{O–Si}$ between the corresponding components of the spectra of silicon and oxygen is close to that of SiO_2 (reference).

The presence of silicon in two chemical states confirms the assumption stated in [9] on the existence of silicon in plants at least in two forms, one of which is organosilicon compound.

The spectrum of O1*s*-electron of rice husk is also a multi-component (Figs. 1 and 3a). A computer simulation (Fig. 3a) provided us a possibility to identify a line of the oxygen of carbonyl groups O^1 with E_b = 531.2 eV (Table 2). The O^2 line with higher E_b includes a signal from the oxygen of silica and the oxygen bound to carbon by a single bond, e.g., the oxygen of hydroxy groups. The separation in O^2 group of individual components for this compound as a whole is conditional, since they may have close values of bond energy. Nevertheless, we can verify the correctness of assignment of the O^2 line when quantifying the contributions to it from oxygen in SiO_2 and in groups bonded with carbon by a single bond. Thus, when we use the “reduced” integral intensities of the signals of chemical elements (the corresponding components in the spectra), the following condition is fulfilled: $I(O^2) \approx I_{C–OR} + 2ISi^2$, where $I(O^2)$, $I_{C–OR}$, and $I(Si^2)$ are “reduced” integral intensities of the O^2 line, the signal of the carbon bonded with the oxygen, and the Si^2 line of 2*p*-electrons of silicon in SiO_2,

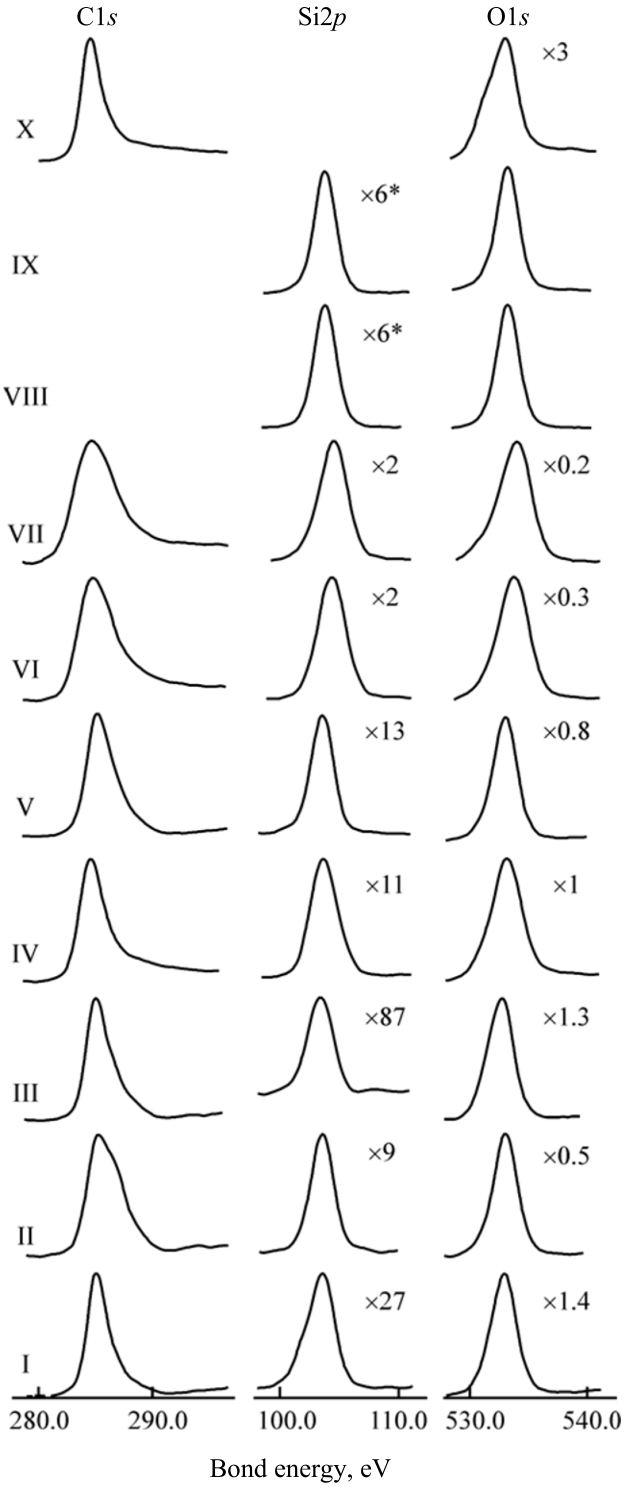

Fig. 1. Smoothed X-ray photoelectron spectra of C1*s*-, O1*s*-, and Si2*p*-electrons of the samples (numbered according to Table 1). Peak intensities of the spectra of core electrons of silicon and oxygen are reduced to the peak intensity of the corresponding line of carbon. (*) Peak intensity of the silicon lines in the spectra of VIII and IX is reduced to the peak intensity of the O1*s*-electrons.

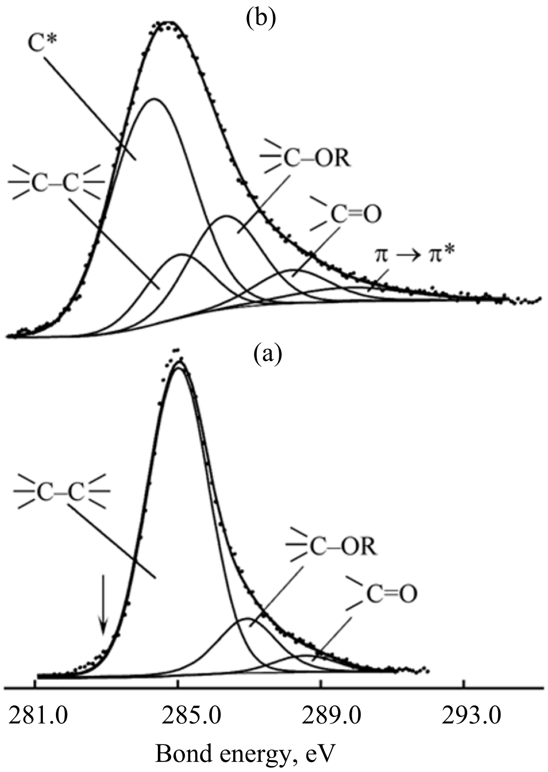

Fig. 2. Experimental XPS spectra of C1*s*-electrons of the samples (a) I and (b) VI, separated into components (arrows indicate the possible position of the line, which could be attributed to the C–Si bond).

respectively; R is either hydrocarbon group, or H, or Si, in the case of silicon bonded with organic component through oxygen.

Mechanical grinding of rice husk in a ball mill (sample II, Table 1) under atmospheric conditions leads to visible changes in the X-ray photoelectron spectra (Fig. 1). Thus, in the C1*s*-electron band of the treated matter the intensity of the spectrum component of the carbon bonded with oxygen increases significantly. The Si2*p*-electron spectrum is a single line, which we assign to SiO_2. The content of oxygen and silicon in the sample increases. The observed facts can be understood as follows. In the course of crude mechanochemical processing the organic components of the rice husk suffer decomposition with the formation of smaller fragments that can be further oxidized at the sites of the ruptured bonds. The change in the oxygen content in the samples I and II (Table 2) is accompanied by the change in the intensity of lines in the carbon spectrum. A part of the carbon fragments is removed from the substance in the process of evacuation of the spectrometer in a high vacuum. As a

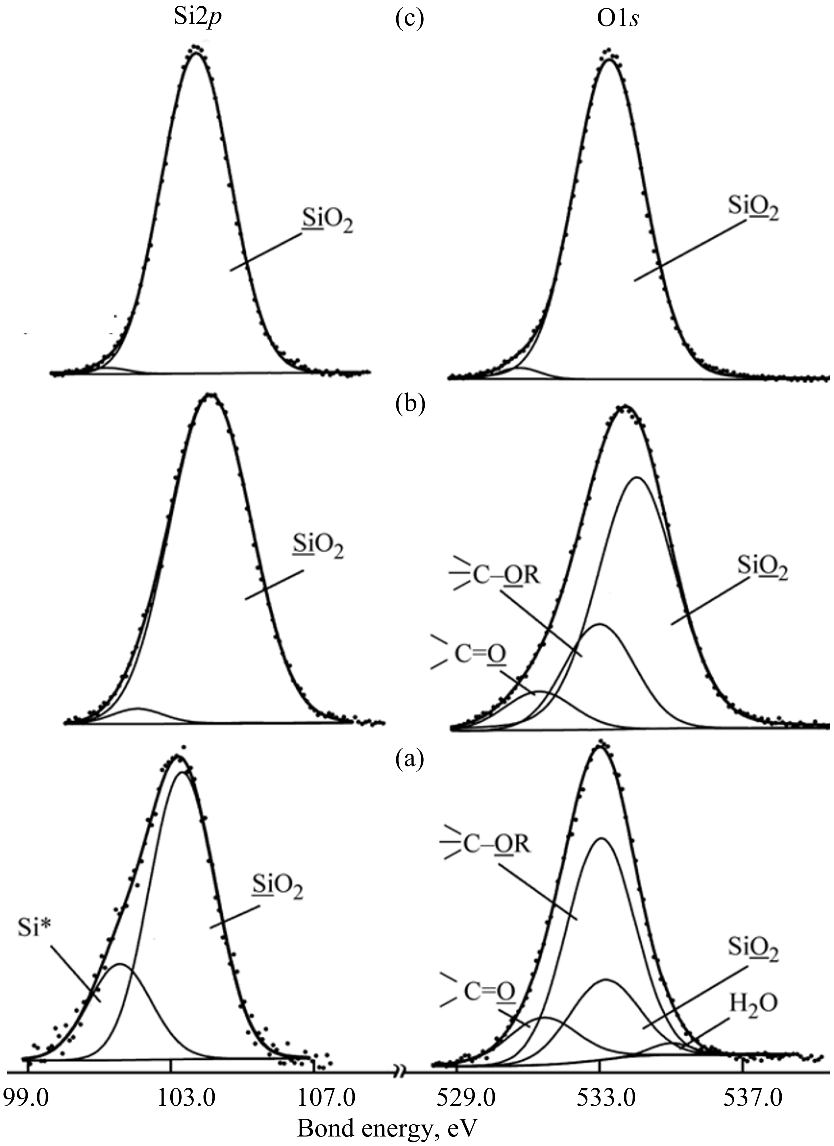

Fig. 3. Experimental XPS spectra of O1*s*- and Si2*p*-electrons of the samples (a) I, (b) VI, and (c) VIII, separated into components. R is hydrocarbon radical, H or Si in the case of bonding silicon with the hydrocarbon fraction through oxygen. Si* is a signal of silicon in the composition of organic fraction.

result, the relative content increases on the sample surface of not only oxygen but also of oxidized silicon (Table 2).

The X-ray photoelectron spectrum of carbon 1*s*-electrons of rice grains present in the husk (sample III, Table 1) is analogous to the corresponding spectrum of rice husk (Fig. 1). Semiquantitative elemental analysis using XPS data shows that the silicon content in sample III is 1– 2% with respect to carbon (Table 2). The main signal of Si2*p*-electrons with E_b 103.2 eV is very weak, therefore the reliable identification (with measuring E_b) of the second state of silicon is difficult. The nitrogen content in the sample III is twice compared with the sample I (5.4%).

X-ray photoelectron spectrum of carbon in sample IV (Table 1) contains an asymmetric line with E_b 284.4 eV (Fig. 1) characteristic of condensed carbon like graphite, glassy carbon, etc. [13, 15]. The E_b of the single line of silicon 2p-electrons is equal to 103.5 eV. Within the accuracy of the measurements, the ΔE_{O-Si} value (429.7 eV) is close to that of SiO_2 (reference sample). With accounting for the value of E_b Si2*p*-electrons, one can assume that in this sample of carbonized silica the silica clusters are of small size. In

Table 2. The content of oxygen and silicon (% relative to carbon) and E_b of C1*s*-, O1*s*-, and Si2*p*-electrons (eV) in the rice husk and its processing products

Sample	E_b, eV			Content of the elements , %	
	C1*s*	O1*s*	Si2*p*	O	Si
I	285.0 $\equiv C{-}C\equiv$			23.6	3.9
	286.9 $\equiv\underline{C}{-}OR$	531.2 $>C{=}\underline{O}$	101.7 $\underline{Si}^a$		
	288.6 $>\underline{C}{=}O$	532.9 $\equiv C{-}\underline{O}R$, $Si\underline{O}_2$	103.4 $\underline{Si}O_2$		
II	285.0 $\equiv C{-}C\equiv$			46.6	6.4
	286.7 $\equiv\underline{C}{-}OR$	531.5 $>C{=}\underline{O}$			
	288.5 $>\underline{C}{=}O$	533.0 $\equiv C{-}\underline{O}R$, $Si\underline{O}_2$	103.3 $\underline{Si}O_2$		
III	285.0 $\equiv C{-}C\equiv$			22.4	1.0
	286.9 $\equiv\underline{C}{-}OR$	531.7 $>C{=}\underline{O}$	101.5 Si^a		
	288.4 $>\underline{C}{=}O$	532.8 $\equiv C{-}\underline{O}R$, $Si\underline{O}_2$	103.2 $\underline{Si}O_2$		
IV	284.2 condensed $\underline{C}$			32.2	7.7
	285.0 $\equiv C{-}C\equiv$				
	286.5 $\equiv\underline{C}{-}OR$	531.4 $>C{=}\underline{O}$			
	288.7 $>\underline{C}{=}O$	533.2 $\equiv C{-}\underline{O}R$, $Si\underline{O}_2$	103.5 $\underline{Si}O_2$		
V	285.0 $\equiv C{-}C\equiv$			34.5	5.6
	286.8 $\equiv\underline{C}{-}OR$	531.5 $>C{=}\underline{O}$	102.1 Si^a		
	288.4 $>\underline{C}{=}O$	532.9 $\equiv C{-}\underline{O}R$, $Si\underline{O}_2$	103.5 $\underline{Si}O_2$		
VI	284.3 condensed $\underline{C}$			95.0	34.8
	285.0 $\equiv C{-}C\equiv$	531.2 $>C{=}\underline{O}$			
	286.3 $\equiv\underline{C}{-}OR$	532.9 $\equiv C{-}\underline{O}R$	102.1 Si^a		
	288.2 $>\underline{C}{=}O$	533.9 $Si\underline{O}_2$	104.1 $\underline{Si}O_2$		
VII	284.2 condensed $\underline{C}$			108.0	33.2
	285.0 $\equiv C{-}C\equiv$	530.8 $>C{=}\underline{O}$			
	286.3 $\equiv\underline{C}{-}OR$	532.6 $\equiv C{-}\underline{O}R$	102.0 Si^a		
	288.5 $>\underline{C}{=}O$	534.0 $Si\underline{O}_2$	104.3 $\underline{Si}O_2$		
VIII	285.0 surface $(-\underline{C}H_2{-}\underline{C}H_2-)_n$	533.1 $Si\underline{O}_2$	103.5 $\underline{Si}O_2$		$\approx 50^b$
IX	285.0 surface $(-\underline{C}H_2{-}\underline{C}H_2-)_n$	533.1 $Si\underline{O}_2$	103.6 $\underline{Si}O_2$		$\approx 50^b$
X	284.4 condensed $\underline{C}$	531.3 $>C{=}\underline{O}$		≈ 12	
		532.9 $\equiv C{-}\underline{O}R$			

[a] Silicon in the composition of the organic fraction. [b] The silicon per cent with respect to oxygen.

general, the substance can be regarded as a two-phase system.

After treatment of the rice husk with hydrochloric acid (sample V, Table 1) the amount of silicon bonded with organic fragments on the sample surface decreases. Therewith, the content of the silicon dioxide increases. This fact indicates that the acid leaching leads to the removal of a part of carbon from the sample. The shape of the spectrum of C1*s*-electrons, however, remains characteristic of carbon in organic compounds (Fig. 1).

According to XPS, samples VI and VII (Table 1) are not the single-phase systems. The line shape of C1*s*-electrons from the side of high energy is similar to that for sample IV (Fig. 1). This feature of the spectrum indicates a partial carbonization of the material. Silicon dioxide in the annealed samples is present possibly in clusters, partially isolated from the carbonized phase by the residues of organic fragments. Due to the arising non-uniformity of the charges on the sample surface [13] or the effect of "internal" charging [16] of the silicon dioxide particles, the lines Si2*p* and O1*s* of SiO_2 are shifted toward higher binding energies

(Figs. 1 and 3b, Table 2). The samples of the rice husk and grains were annealed in the atmospheric air. Therefore, due to burning of a part of carbon the relative concentration of other chemical elements increased. Thus, the relative content of silicon dioxide determined by X-ray photoelectron spectra of the surface of samples VI and VII as compared with the starting materials, increases by about an order of magnitude (Table 2). In the sample VII obtained from the rice grains there is a greater amount of carbon bound with oxygen. The partial preservation of organic residues also follows from the fact of the registration in the XPS spectra of the lines nitrogen 1*s*-electrons in the samples VI and VII. Figure 2b shows the experimental spectrum of C1*s*-electrons of the sample VI with a separation into the components. At the approximation of the spectrum were taken into account the "reduced" integral intensities of the spectra of O1*s*- and Si2*p*-electrons.

After processing the rice husk and the rice grains with hydrochloric acid and subsequent annealing at 700°C for 20 min (samples nos. VIII and IX, Table 1), the Si2*p* spectrum in both cases contained a single unresolved doublet (Fig. 3c) with E_b 103.5 eV and 103.6 eV, respectively. The oxygen to silicon ratio defined from the data of X-ray photoelectron spectra of O1*s*- and Si2*p*-electrons O/Si is ~ 2. From the E_b Si2*p* value and the O/Si ratio it can be concluded that the investigated sample is silicon dioxide, and its structure, according to the X-ray phase analysis, is amorphous.

When silicon was removed by the action of concentrated solution of HF, the subsequent annealing at 350°C (sample X) resulted in the formation of a form of condensed carbon, as in the case of sample IV, however, without any admixture of the silicon dioxide phase. The spectrum of C1*s*-electrons consists of a strong asymmetric line, typical of conducting materials (Fig. 1). Besides, low-intensity signals of carbon and oxygen connected by a single or a double bond were observed.

Thus, we studied by XPS method the rice husk and its accompanying grains forming as a waste at the processing raw rice. The presence of two forms of silicon in rice husk in the ratio of approximately 1:3 is revealed. Most of the silicon is in the form of dioxide, and the smaller part is contained in the organic fragments. Mechanical grinding of this raw material leads to increased content of oxidized silicon. The rice grains differ from the husk by the higher content of nitrogen and lower content of silicon. The silicon compounds associated with organic fragments in the rice husk and grains are destroyed when heated above 350°C.

The rice husks and accompanying grains can be used as a raw material for obtaining silica and various forms of condensed carbon.

EXPERIMENTAL

The object of the study was rice husk-24 (the number corresponds to the collection of the Institute of Chemistry of Far Eastern Branch of Russian Academy of Sciences) and the products of processing by the methods described in [4]. The material was produced in the Krasnodar Territory in 2005. Characteristics of samples and methods for their preparation are listed in Table 1.

The XPS spectra of core electrons (Figs. 1–3) were recorded on a EC 2401 spectrometer of Russian production using nonmonochromatic AlK_α radiation. The vacuum in the energy-analyzer chamber was maintained at ~10^{-7} Torr. The spectra were calibrated by the 1*s*-electron line of saturated carbon of the organic fragments of the samples, the bond energy (E_b) was assumed equal to 285.0 eV. The accuracy of determining E_b was ± 0.1 eV. Pretreatment of the experimental spectra was done using programs and methods in [14]. In determining the relative concentrations of elements the transmission function of the analyzer, asymmetry of the wave functions and photoionization cross-sections of the core electrons by Scofield [17] were taken into account. As a result, in the calculations were used the integrated intensities "reduced" to the intensity of carbon and taking into account the factors described. For the separation of the experimental spectra into components we used the freely distributed XPSPEAK 4.1 program. Binding energy of the spectral component and concentrations of elements are given in Table 2. Listed in Table 2 silicon E_b values correspond to the $2p_{3/2}$ component of the unresolved spin-orbital doublet. All data on the content of elements on the surface of the samples determined by X-ray photoelectron spectra, are given in percentes relative to carbon.

At the analysis of the spectra of the studied objects silicon carbide and dioxide (chemically pure grade) were used as the references. The signal of Si2*p*-electrons of silicon dioxide is an unresolved spin-orbital doublet. The E_b values of O1*s*- and Si2*p*3/2-electrons equal 533.0 and 103.5 eV, respectively. The ΔE_b difference of O1*s*- and Si2*p*-electrons ($\Delta E_{O–Si}$) is 429.5 eV. The E_b value of Si2$p_{3/2}$-electrons in SiC is 99.9 eV, the difference between E_b of C1*s*- and Si2$p_{3/2}$-electrons ($\Delta E_{C–Si}$) is 182.2 eV. The estimation of the ΔE_b value of core electrons of atoms of different elements helps in some cases to estimate the chemical state of elements, regardless the method of calibration of the spectrometer energy scale.

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