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Research Article

Synthesis of silicon-carbon films by induction-assisted plasma-chemical deposition

Alexander A. Temirov[1], Ilya V. Kubasov[1], Andrei V. Turutin[1], Tatiana S. Ilina[1], Alexander M. Kislyuk[1], Dmitry A. Kiselev[1], Elena A. Skryleva[1], Nikolai A. Sobolev[1,2], Igor A. Salimon[3], Nikolai V. Batrameev[4], Mikhail D. Malinkovich[1], Yuri N. Parkhomenko[1]

1 National University of Science and Technology "MISIS", 4-1 Leninsky Ave., Moscow 119049, Russian Federation

2 Departamento de Física and i3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal

3 Skolkovo Institute of Science and Technology, territory of the Innovation Center "Skolkovo", 30-1 Bolshoy Blvd, Moscow 121205, Russian Federation

4 JSC "Piezo", 16 Buzheninova Str., Moscow 107023, Russian Federation

Corresponding author: Alexander A. Temirov (temirov.alex@yandex.ru)

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Abstract

Silicon-carbon films are of great interest as diamond-like materials combining unique properties, e.g. high hardness, adhesion to a wide range of materials, abrasion resistance, chemical resistance, low friction coefficient and biocompatibility. The presence of silicon in the films significantly reduces their inner mechanical stress as compared to diamond films. Currently, the films are used in industry, primarily, as solid lubricants and protective coatings. There are a large number of silicon-carbon film synthesis methods the most widely used of which are various options of chemical vapor deposition. A new silicon-carbon film synthesis technique has been suggested and tested. The technique is based on the use of high-frequency induction for obtaining plasma of silicon and carbon vapors supplied to the reaction chamber from an external source. Impurity-free silicon-carbon films containing 63–65 % carbon atoms with sp^3 orbital hybridization have been synthesized on Sitall substrates. The composition, surface roughness and friction coefficient of the impurity-free silicon-carbon films synthesized using the suggested technology have been studied. The possibility of implementing resistive switching in thin silicon-carbon films in cross-bar structures with metallic electrodes has been analyzed.

Keywords

silicon-carbon films, diamond-like materials, plasma-chemical deposition, thin film technologies

1. Introduction

Diamond-like silicon-carbon films **(SCFs)** combine unique useful properties: high hardness and strength, chemical and radiation resistance, biocompatibility and low friction coefficient [1]. SCFs are amorphous matrices (plasma-polymerized polyphenylmethylsiloxane, **PPMS**) [2] which can be doped with metallic or other impurities to different concentrations up to 20 at.%, thus providing the possibility of controlling the electrophysical and mechanical properties of the material in a wide range. The films have found wide application in industry,

mainly as solid lubricants and protective coatings. Also of interest is the possibility of SCF application as functional layers of memristor structures. Currently, there is a need for materials that can be used as a basis for the fabrication of neuromorphic computing devices and resistive memory **(RRAM)** while being compatible with complementary MOS **(CMOS)** IC technologies [3]. From this viewpoint, the absence of the necessity of high-temperature substrate heating during SCF synthesis is an important advantage [4]. The synthesis of resistive switching structures based on a similar type of materials, i.e., amorphous oxidized carbon and graphite-like (a-GCL) films, was described earlier [5–7]. However, large differences between the resistances in the high **(HRS)** and low **(LRS)** resistance states (by 10 times) could only be achieved at 80–150 K.

The films contain carbon atoms with sp^3 orbital hybridization (which are typical of diamond) and with sp^2 orbital hybridization (typical of graphite). The combination of these two hybridization types affects the properties of the SCF synthesized. The content of carbon atoms with *sp* orbital hybridization in diamond-like materials is low and is therefore often neglected [8, 9].

In comparison with diamond-like carbon a-C:H and a-C films without silicon **(DLC)**, the SCFs have lower hardness and lower internal mechanical stress, providing the possibility of depositing protective coatings with thicknesses of up to 100 μm [10], whereas the DLC undergo fracture due to internal stress at as small thickness as 2 μm. The SCFs also exhibit better adhesion to various surfaces than the DLC and can have a lower friction coefficient, down to 0.01 [11]. Furthermore, silicon-doped DLC exhibit higher heat stability than carbon films [12]. It was shown [13] that in silicon-carbon coatings and in nanocomposites on their basis, structural changes showing themselves in an increase in the concentration of sp^2-hybridized carbon bonds and caused by material degradation occur at 300–400 °C in air, and in argon the degradation temperature increases to 600 °C.

There are a large number of silicon-carbon film synthesis methods the most widely used of which are various options of chemical vapor deposition **(CVD)** [8–10]. The precursors used are either condensed materials containing carbon, silicon, oxygen and hydrogen (most often, siloxanes, silicates and silanes) or mixtures thereof with gases (methane, acetylene, oxygen etc.) [17, 18]. Liquid siloxanes are preferable to gaseous mixtures for storage and usage safety reasons. Furthermore, precursors of that type are relatively cheap and their application requires simpler technologies.

The main current SCF synthesis method from liquid siloxanes implies the use of a massive tungsten cathode heated to approx. 2000 °C [19, 20] inevitably causing contamination of the synthesized film with background tungsten impurity. Moreover, the cathode requires a current of 100 A from a high-power source causing growth chamber heating, and hence a cooling system is needed.

Below we present a new SCF synthesis technique based on the use of high-frequency induction for obtaining plasma of silicon and carbon vapors supplied to the reaction chamber from an external source and analyze data on the composition, surface roughness and friction coefficient of impurity-free silicon-carbon films synthesized using the suggested method and the possibility of their use as functional layers in memristor structures.

2. Experimental

Impurity-free SCF specimens were obtained by plasma-chemical deposition of polyphenylmethylsiloxane **(PPMS)** vapors in a universal vacuum plant. The working pressure in the chamber was set at about 10^{-3} torr.

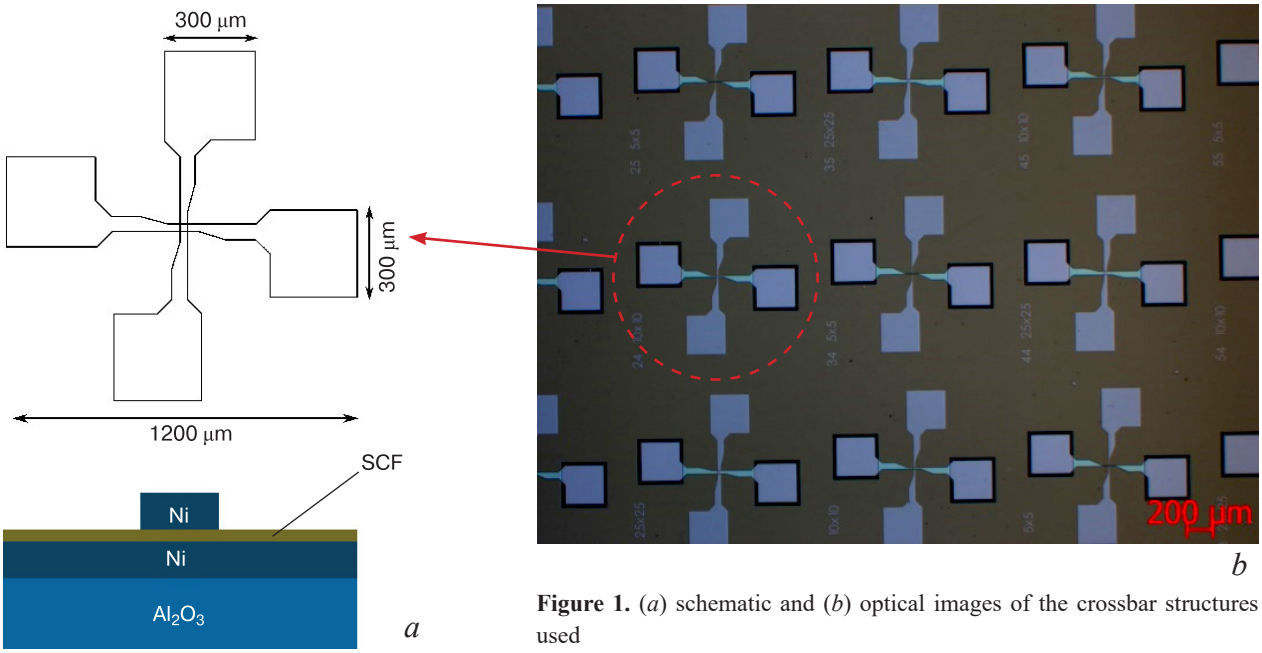

Figure 1. (*a*) schematic and (*b*) optical images of the crossbar structures used

The method used for the synthesis is based on the ionization of PPMS vapors heated in a special stainless-steel chamber to ~350 °C and supplied to a quartz tube with a 13.56 MHz 500 W inductor, and deposition of the resultant plasma onto a substrate at an extracting AC voltage of up to 500 V and a frequency of 299 kHz. In order to simplify the multi-stage fragmentation process of heavy PPMS molecules and increase their ionization rate, a tungsten wire cathode 300 μm in diameter and 100 mm in length was placed in the induction-affected region. The current through the cathode was 10 A, and hence tungsten evaporation and chamber heating could be neglected. The substrate holder rotated at a 2 rpm speed during deposition for improving the homogeneity of material deposition onto the substrate. The substrates were 250 μm thick Sitall wafers cut into 5×20 mm^2 rectangles. The choice of dielectric Sitall substrates was dictated by their low surface roughness (about 2 nm) and availability. The condensation of non-ionized PPMS vapors was prevented by heating the substrates during deposition in a resistive furnace to the boiling points of the liquid siloxanes used (~200 °C). For studying the effect of substrate holder

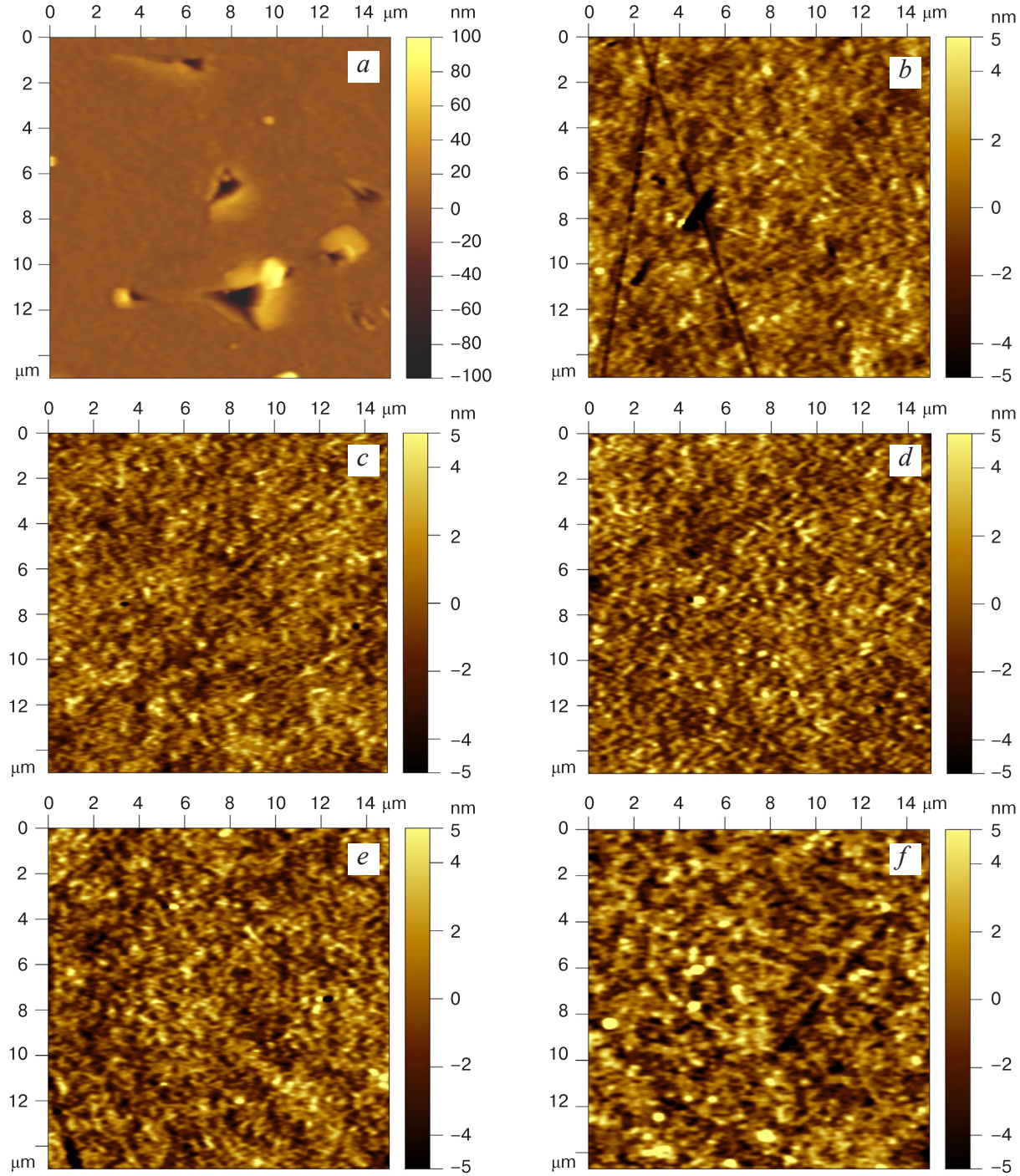

Figure 2. Surface images of SCFs grown at different substrate temperatures: (*a*) room, (*b–f*) 100, 150, 200, 250 and 300 °C, respectively

heating on the morphology of the film surfaces we synthesized films at other temperatures: 100, 150, 250 and 300 °C and at room temperature. The synthesis duration was 60 min for each of the temperatures chosen.

The surface roughness of the synthesized specimens was studied using scanning probe microscopy **(SPM)** in semi-contact mode. The rms roughness data were calculated with the Gwyddion software by processing 15×15 μm^2 scans.

The friction coefficient and the abrasion resistance of the specimens were studied using a CETR universal tribometer at a relative humidity of 40% for a steel ball on a plane setup separately for Sitall substrates without films and for those with undoped SCFs. A 6.3 mm diam. metallic ball was pressed into a specimen with a 2N force and moved through a distance of 4 mm in reciprocating movement mode during 1300 s at an average speed of 10 mmps.

The elemental compositions of the doped and undoped SCFs were determined using X-ray photoelectron spectroscopy **(XPS)** on a PHI5500 VersaProbeII instrument in monochromatic AlK_α radiation ($h\nu = 1486.6$ eV) at a power of 50 W. The atomic concentrations were determined from survey spectra using the method of relative elemental sensitivity factors. Depth profiling was implemented by etching the specimens with 2 keV Ar^+ ions from an ion gun. The etching rate was about 20 nm/min.

The electrophysical properties of the films were studied using optical lithography for substrate/electrode/film/electrode crossbar structures [21] schematic and optical images of which are shown in Fig. 1. The electrode material was nickel, the substrate being a sapphire wafer. The thickness of the top and bottom electrodes was 150 nm, the thickness of the SCF being 40 nm. The measurements were conducted on a stationary probe instrument with a Keithley 2611A source/measuring unit.

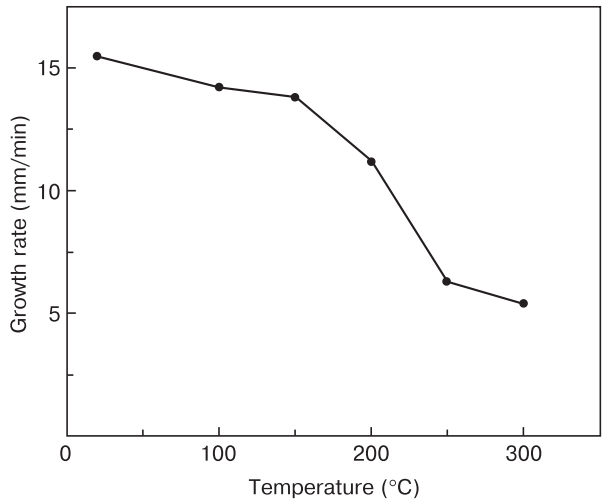

Figure 3. SCF deposition rate as a function of substrate temperature

3. Results and discussion

SPM studies of the surfaces of the synthesized SCFs showed the presence of defects (condensed PPMS particles and holes in the surface) in all the specimens synthesized at substrate temperatures below 150 °C inclusively. Beginning from a substrate temperature of 200 °C the SCF specimens had uniform continuous surfaces. By and large, the entire series of specimens synthesized at higher temperatures exhibited a trend of lowering the content of contaminants and holes (Fig. 2). All SPM scans of the specimens synthesized at room temperature showed the presence of defects.

Along with a decrease in the number of defects, an increase in the substrate temperature also reduced the SCF growth rate. The latter is shown as a function of substrate temperature in Fig. 3.

Since substrate heating to 200 °C prevents defect formation on specimen surfaces, it can be concluded that growing SCFs at that temperature is preferable. Therefore further measurements were conducted on specimens synthesized at 200 °C.

SCF formation reduces the roughness of the specimen surfaces. For a 670 nm thick film the roughness decreased by more than 2 times, from 2.3 nm for the uncoated substrate to 1.1 nm for the SCF-coated substrate (Fig. 4).

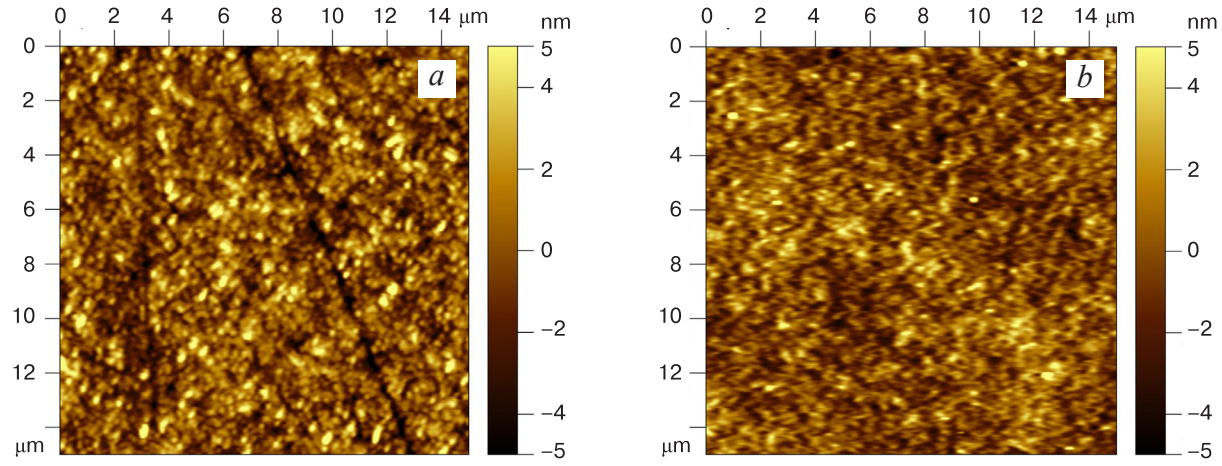

Figure 4. Surface roughness of (*a*) Sitall substrate and (*b*) synthesized SCF

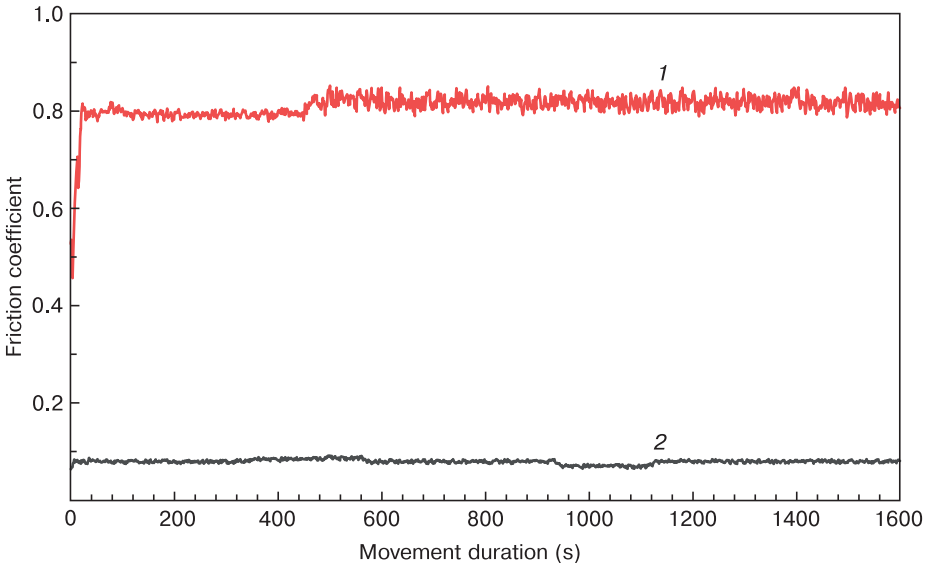

Figure 5. Sliding friction coefficients for (*1*) uncoated Sitall substrate and (*2*) SCF-coated substrate

Friction measurements showed that the sliding friction coefficient of a steel ball on SCF-coated Sitall is almost by an order of magnitude lower compared with that for uncoated substrate. Figure 5 shows the sliding friction coefficients for the uncoated substrate (Sitall wafer) and the SCF-coated substrate.

All the polished Sitall substrates exhibited an increase in the friction coefficient in the first 30–40 s of testing.

Table 1. Elemental composition of silicon-carbon film before and after etching

Etching time (min)	Concentration (at.%)			
	C	O	Si	C/Si
0	87.1	9.5	3.4	25.6
1	91.2	4.6	4.2	21.7
5	92.8	3.5	4.3	21.8

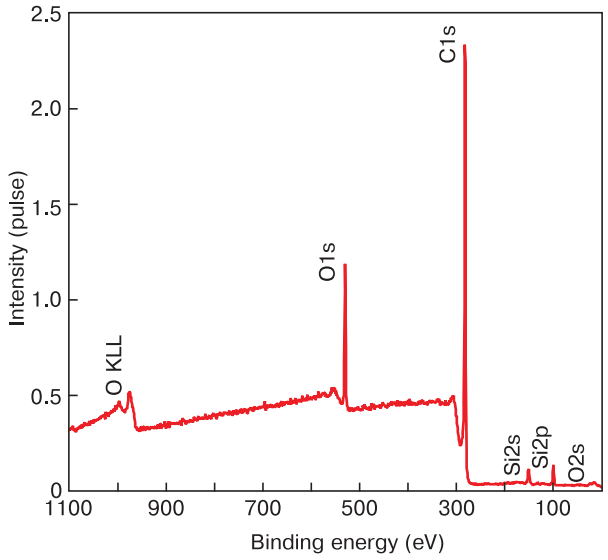

Figure 6. Survey XPS spectrum of SCF

This can be caused by substrate surface degradation during measurements. Scratches and cleaves damage the polished surface Sitall layer and largely increase the friction coefficient (almost twofold, from 0.45 to 0.8). After 400 s of measurement (~500 reciprocation movement cycles) the scratched erosion area increased and the friction coefficient further grew and then remained constant until the end of measurements.

The friction coefficient of the SCF-coated substrate was 0.084, and no film surface degradation was observed during the tests: the appearance of the film surface did not change. After 1500 s of measurement (1875 reciprocating movement cycles) the friction coefficient changed but slightly. This suggests that the abrasion resistance of the material increased significantly after SCF deposition. Noteworthy, along with the mechanical properties of the film itself, another cause of the friction coefficient's decrease was a reduction in the surface roughness in comparison with the Sitall wafers without SCF.

A study of the elemental composition of the synthesized specimens showed the presence of three elements: carbon, silicon and oxygen. Background impurities, including tungsten, were absent. The carbon-to-silicon concentration ratio was greater than in the PPMS precursor: ~ 25:1 for the surface and 21:1 after etching. One can assume that part of the oxygen-bound Si atoms forming charged molecular complexes with oxygen were out of the substrate holder area. The measurement results are shown in Fig. 6. Table 1 shows element concentrations in the SCF calculated based on the survey spectra.

The total specimen etching time was 5 min, but after the first minute, the composition of the material remained almost unchanged. Low argon concentrations (to 0.1%) were excluded from the final SCF composition table since their presence was caused by the use of an ion beam gun for specimen surface bombardment with Ar^+ ions. Carbon spectra were recorded separately for assessment of the concentration of atoms with sp^3-hybridized orbitals.

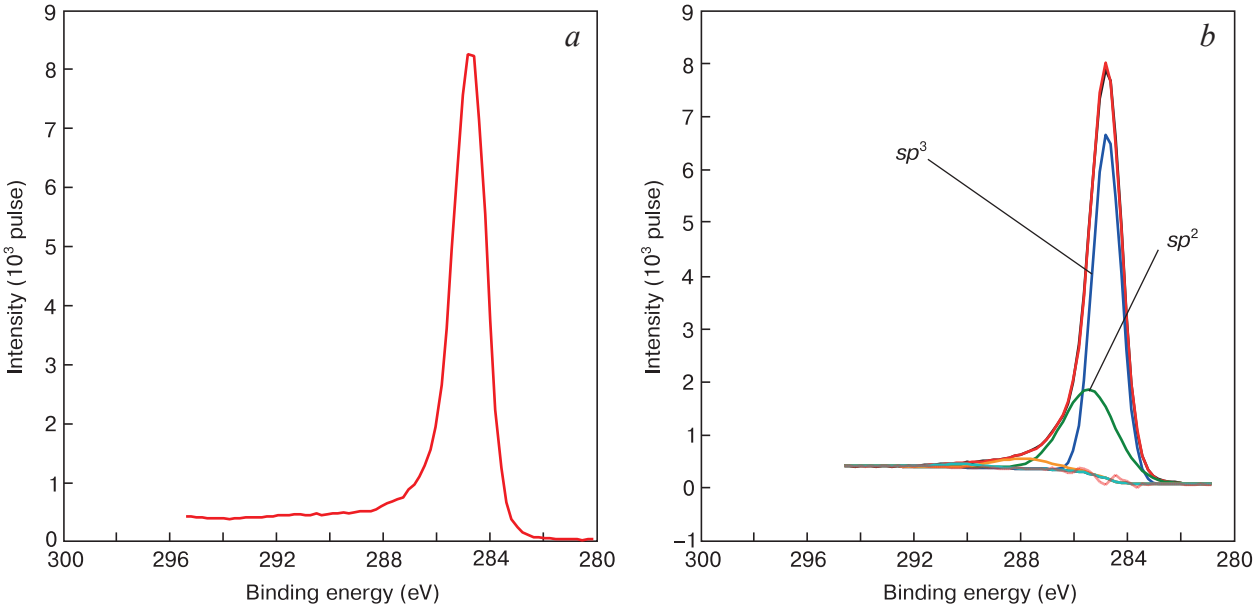

Figure 7. XPS spectra of carbon in SCF (*a*) before and (*b*) after approximation

Measurement results before and after approximation are shown in Fig. 7.

The two main peaks seen in Fig. 7 *b* pertain to carbon atoms with sp^2 and sp^3 orbital hybridization. The concentration of the latter atoms was 63–65 % and it corresponded to that in diamond-like materials described earlier [22].

Data on the electrophysical properties of the SCF are shown in Fig. 8.

The memristor effect observed in the structures was quite clear: the average ratio between resistances for the two conductivity states was about 170 in the tested structures. The LRS to HRS switching was unipolar, i.e., occurred at a voltage of the same polarity.

4. Conclusion

A new method of synthesizing impurity-free SCF from PPMS using plasma-chemical deposition with high-frequency induction was developed and tested and allowed synthesizing specimens that were free from background impurities. The optimum substrate temperature for film deposition proved to be 200 °C. The use of amorphous SCF reduced the ball on the Sitall substrate sliding friction coefficient by almost one order of magnitude, from 0.8 for the Sitall surface to 0.084 for the SCF surface. Abrasion resistance estimation showed an increase in this parameter. The RMS roughness of the SCF-coated substrate surface decreased by almost 2 times. The content of carbon atoms with sp^3 orbital hybridization was 63–65 %. The memristor effect was observed. Unipolar resistive SCF switching yielded an LRS to HRS ratio of ca. 170.

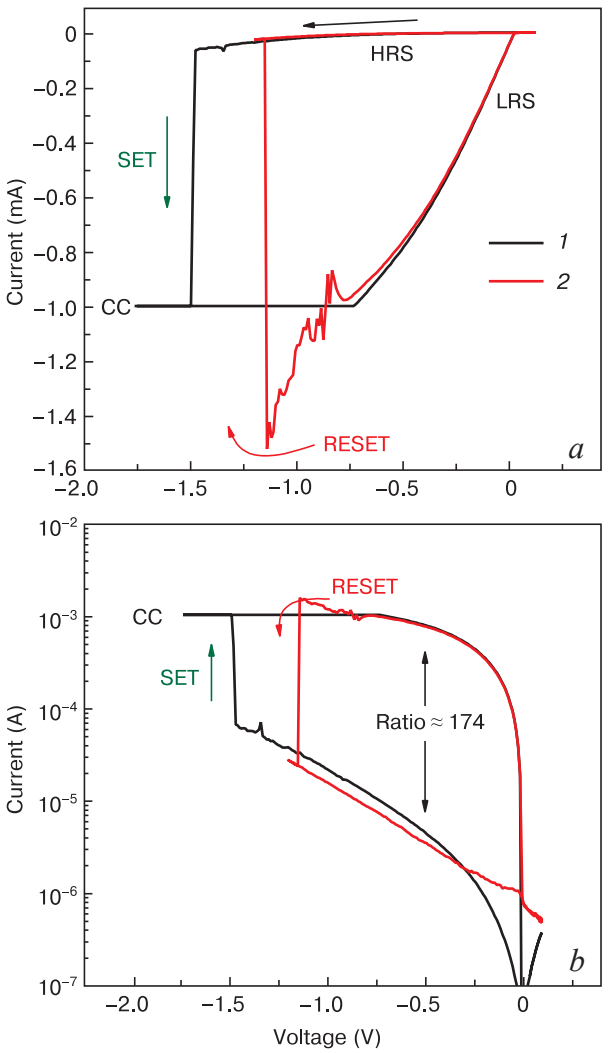

Figure 8. Current-voltage characteristics of SCFs: (*a*) standard and (*b*) semi-logarithmic coordinates

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