

ON SILICON ALLOTROPY

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Experimental results obtained by the methods of electronography and X-ray spectroscopy testify to the possibility that elemental silicon, like carbon, can exist in several allotropic modifications. Experimental data are in good agreement with the results of non-empirical quantum and chemical calculations for silicon clusters. Possible models are suggested for new structural forms of silicon. A new material, silicyne, was obtained by annealing hydrogenated amorphous silicon in vacuum at 500°C. It is in the form of thin amorphous silicon films with atoms located linearly. Some factors that determine the effectiveness of structural changes during the annealing are discussed, as well as the results of studies of some properties of silicyne.

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1. Introduction

It is well known that in Mendeleev's Periodic Table silicon and carbon are in the same group and they have similar configurations of their outer electron shells. Therefore, it seems that their properties should also be similar. Five principal allotropic forms of carbon are known: diamond, graphite, carbyne, lonsdaleite and fullerene. In contrast to carbon, silicon atoms in all compounds including amorphous silicon, display the valence of four. Valence electrons in these atoms are in sp^3 -hybrid state and until recently it was considered that no compounds can exist where silicon atoms would have sp^2 and/or sp hybridization.

How can one explain this difference in the capacity of silicon and carbon atoms to form chemical bonds?

As it was noted earlier, the atoms of silicon and carbon have four valent electrons each and the electron configuration of the outer electron shell $3s^2p^2$ and $2s^2p^2$, respectively. However, in silicon atoms $3p$ -orbitals are more prolate than $2p$ -orbitals in carbon atoms. Due to this, when molecules are formed under normal conditions, the overlapping of $3p$ - orbitals in silicon is small, π - bond is weak and, hence, the probability of creation of multiple bonds of the type $Si = Si$ or $Si \equiv Si$ is low [1].

Despite this, in 1980s theoretical predictions were made, and later some silicon-containing compounds were obtained that were stable under certain special conditions. These included tetramethylsilane, disilene and disilyne with double silicon-silicon bonds [2, 3]. The above-mentioned compounds were synthesized from polysilanes by substituting some hydrogen atoms in them by phenyl, vinyl or alkyl substituents. The most important factor contributing to the stabilization of double silicon bonds is the large amount of such substituents in silicon. By changing the configuration of the electron cloud of silicon atoms, they contribute to the emergence of a π -component of the chemical bond. However, it was not possible to obtain elemental silicon, both crystalline and amorphous, with the atoms that were not only in sp^3 - hybrid state, under the conditions of thermodynamic equilibrium.

In this paper we present the results of some experiments aimed at studying the effect of exposure to external factors, in particular, annealing at temperatures close to the recrystallization temperature, on the properties of amorphous silicon films. In our opinion, these results cannot be explained even in the framework of quasitrahedral structure of the short-range order of amorphous silicon. It should be noted here that the results we have obtained are an exception rather than a rule, since only

in three cases out of 10, when we used different methods for producing original amorphous silicon film, some effects were observed that found no explanation in the framework of traditional knowledge of silicon structure.

2. Preparation of specimens

Original films of hydrogenated amorphous silicon $a\text{-Si:H}$ ≈ 80 and 400 nm thick were obtained by Professor Bayer at the Nuclear Research Centre in Julich (Germany) by the decomposition of silane in a high-frequency glow discharge. A freshly cleaved NaCl crystal and monocrystalline silicon were used as substrates. Deposition rate did not exceed 0.15 nm/s. Substrate temperature during the deposition process was 250 °C. Isothermic annealing was conducted in vacuum at $\sim 10^{-5}$ torr at temperatures 350 to 700 °C for 30 minutes. Structural measurements were made with the use of EMR-102 recording electronograph.

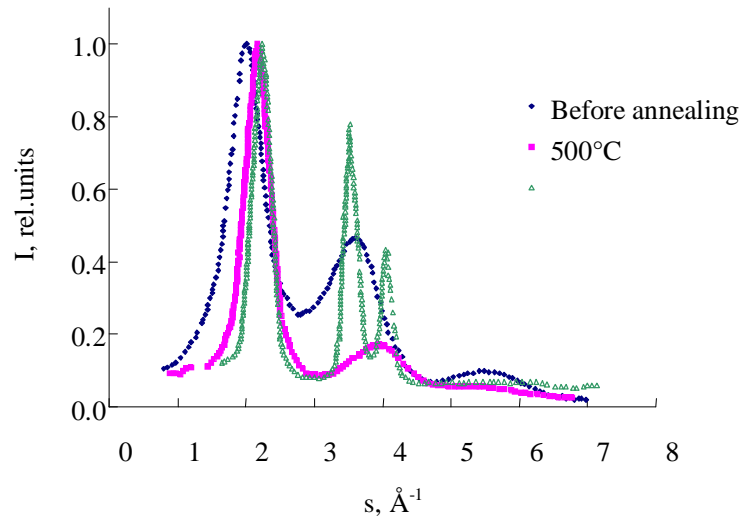


Fig. 1. Angular dependencies of electron scattering intensity for $a\text{-Si:H}$ films before and after annealing.

3. Results and discussion

We have discovered (Fig. 1) that for the original film the angular dependence of electron scattering $I(s)$ has three peaks. Two of them (at $s = 2.00$ and 3.60 \AA^{-1}) are prominent and the third one (at $s = 5.60 \text{ \AA}^{-1}$) is weak and diffuse. This kind of diffraction picture means that the original film's structure is amorphous.

After the annealing at 350 и 500°C the film remained amorphous. The diffraction picture for $a\text{-Si:H}$ annealed at 350 °C is almost the same as that for the original film.

At the same time, the annealing at 500°C leads to a substantial decrease (almost by the factor of three) of the intensity and to the shift ($s = 3.78 \text{ \AA}^{-1}$ instead of 3.60 \AA^{-1}) of the second maximum. The first peak's location remains practically the same, and the third peak was not found after annealing. Such changes in the diffraction picture cannot be explained by experimental error and demonstrate a significant change in the short-range order structure of the amorphous material after high-temperature annealing.

The annealing at 700°C leads to a partial recrystallization of the film. One can judge about this by the double lines at the site of the second maximum for the amorphous state of the material.

A more complete information on structural changes in the amorphous material was obtained from the analysis of the radial distribution function (RDF). Taking into account the importance of the results and in order to avoid any errors that might arise from the calculation procedure, the transition from the intensity of electron scattering to RDF was made by two methods: using traditional techniques (TT) [4] and using the method of information functional optimization (IFO) [5].

According to the data presented in Table 1, original *a-Si:H* films retain the short-range order characteristic of the crystalline silicon. The disordering of the structure is shown by a small change in the first coordination number ($k_1 = 3.8$ instead of 4) and the average angle between bonds ($\varphi = 112^\circ$ instead of $109^\circ 28'$).

Table 1. Parameters of near-order structure of *a-Si:H* films.

$T_{\text{ann}}, ^\circ\text{C}$	k_1	$r_1, \text{\AA}$	$\varphi, ^\circ$
20	3.8 ± 0.2	2.34 ± 0.04	112 ± 9
500	2.2 ± 0.2	2.10 ± 0.04	176 ± 9

The most significant change in the structure of the still amorphous film occurs under the annealing at 500 °C. Although the material remains amorphous after such a thermal treatment, it has a totally different structure of the short-range order compared to the material that has not been annealed or has been annealed at a lower or higher temperature. The first coordination number in this case is close to 2 ($k_1 = 2.2$), the average angle between the bonds becoming almost 180° ($\varphi = 176^\circ$), and the inter-atomic distances *Si-Si* are smaller than in a crystal ($\approx 2.10 \text{ \AA}$).

The results of structural transformation of the amorphous hydrogenated silicon under annealing are of fundamental nature and cannot be explained in the framework of quasi-tetrahedral near-order structure of amorphous silicon. The fact that k_1 is reduced to almost 2 and the valence angle is increased to 180° means that, on the average, each silicon atom has two rather than four neighboring silicon atoms located along the same line, i.e. the random grid is formed from linear atom chains rather than from tetrahedrons.

Although essential changes in parameters of the short-range order structure rule out the explanation of our results as an experimental error, to decrease calculation error resulting from the break of the series when using traditional techniques, we also used IFO method for the transition from intensity curves to RDF $\rho(r)$. The function of optimal (from the point of view of information) radial distribution was constructed in this case on the basis of optimization of Shannon's information functional:

$$H(\rho) = - \int \rho(r) \log \rho(r) dr \rightarrow \max \quad (1)$$

and the condition of non-negativity of solution of the form:

$$\rho(r) \geq 0 \quad (2)$$

This allowed to reduce the calculation error to almost zero, thus reducing the overall experimental error. The results of application of this technique for calculating the short-range order structure of *a-Si:H* annealed at 500°C are shown in Fig. 2.

In Table 2 are shown the results of approximation of this curve by a sum of five normal distribution functions. A detailed discussion on the applicability of this technique for the processing of RDF is given in [6]. The data on the parameters of coordination spheres given in Table 2 will be used later for the construction of the structural model for the new allotropic form of silicon.

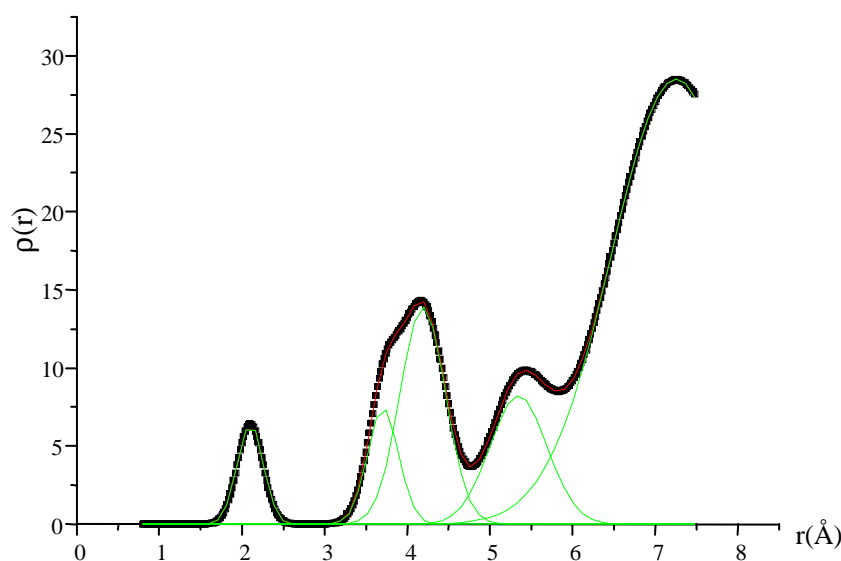


Fig. 2. Radial distribution function of atoms for *a-Si:H* annealed at 500°C, and the results of its approximation by the sum of five radial distribution functions (Table 2).

Table 2. The parameters of the first coordination spheres in *a-Si:H* (Fig. 2).

Peak	Area	Center	Width	Height
1	2.5003	2.1000	0.31008	6.4337
2	3.5243	3.7078	0.37799	7.4392
3	9.5074	4.1883	0.54487	13.922
4	7.1364	5.3453	0.69170	8.2320
5	55.811	7.2524	1.5608	28.531

RDFs obtained by means of IFO method have narrower peaks and do not contain any negative values. The parameters of the first coordinate sphere coincide with those calculated using TT. Due to the narrower peaks, the shape of the second maximum in RDF allows to measure the radii of the second and third coordination spheres directly. For the films annealed at 500°C the values of the first coordination sphere parameters differ slightly from those calculated by means of TT. However, the trends of structural transformations (decrease of k_1 to almost 2, decrease of the average bond length by 0.2 – 0.3 Å, increase of the valence angle to almost 180°) remain after annealing, and the observed differences in absolute value are not of fundamental nature and are within the limits of experimental error.

It should be noted, however, that the second peak on the RDF curve has a structure. One can observe an additional maximum from the side of the small r at $r = 3.7$ Å having the area of approximately 3.5. The value of $k_1 = 2.2 \div 2.5$ thus obtained demonstrate that some silicon atoms in the random network have three or four rather than two neighbours.

Since such changes in the atomic structure of the material under annealing should be accompanied by changes in the nature of silicon bonds, we have studied the effect of annealing on the shape of X-ray emission $Si K_{\beta}$ - и L_{23} spectra obtained on amorphous silicon films.

For all the samples the X-ray spectra have a fine structure, while K_{β} lines are asymmetrical (Fig. 3). These features were reproduced quite well in repeated measurements.

The principal maximum of K_β -line for all the samples is at the energy ≈ 1836 eV and corresponds to $3p$ -states of the electrons in silicon molecular orbitals. For $Si L_{23}$ -spectra, the principal maximum responsible for the contribution in the density of the $3s$ -states of the electrons is at the energy level ~ 92 eV. The fine structure observed in both spectra is explained quite well by the ordering of the atoms in the materials under investigation. Thus, the location of peaks in the low-energy region of the spectra is directly related to inter-atomic distance d :

$$\Delta E(\text{eV}) = 8.0 - 2.2 \times d(\text{\AA})$$

where ΔE is the energy gap between the peaks A_L and B_L in $Si L_{23}$ spectra.

The only exception is the peak (bend) of the K_β -line in the high-energy region which is observed only in the spectra obtained from amorphous silicon films annealed at 500°C .

The following information was gathered from the detailed analysis of the X-ray spectra:

- all the three low-energy maximums in X-ray spectra correspond to the molecular orbitals that are the superpositions (in different proportions) of $3s$ and $3p$ -atomic orbitals of silicon.

- the increase in the energy gap between A_L and B_L peaks in $Si L_{23}$ spectra for amorphous silicon films annealed at 500°C by 0.4 eV compared to crystalline silicon is caused by the reduction of inter-atomic distance in them by 0.2 \AA.

- instead of the "shoulder" C_L with the intensity of 50% characteristic of c - Si , the $Si L_{23}$ -spectrum of a - $Si:H$ annealed at 500°C displays a maximum with the intensity of $\sim 75\%$.

Such changes in the X-ray spectra and, hence, in the distribution of state density in the valence band of the semiconductor demonstrates a significant change in the character of hybridization of silicon atomic orbitals as the molecular orbitals of σ -type are formed in the investigated material.

- in the high-energy part of $Si K_\beta$ -spectrum a small maximum D_k (of intensity $\sim 11\%$) arises at ~ 1838 eV, which has no corresponding maximum in $Si L_{23}$ spectrum thus, it can be assumed that the fourth peak in $Si K_\beta$ spectrum of a - $Si:H$ annealed at 500°C corresponds to the bonding molecular orbital for which only $3p$ -atomic orbitals of silicon are responsible, i.e. it corresponds to the silicon π -bond.

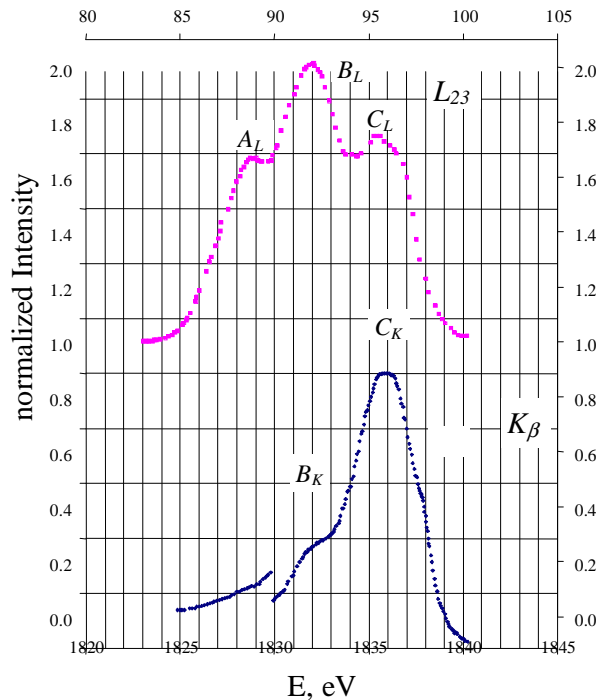


Fig. 3. $Si L_{23}$ and K_β -spectra for a - $Si:H$ annealed at 500°C .

Thus, the data obtained from X-ray spectra confirm the results of the structural experiments noted by us earlier regarding the decrease in the inter-atomic distance in amorphous silicon films under annealing at 500°C and our assumption regarding the change in the chemical bond, in particular, the emergence in it of a substantial π - component and regarding the transition of valence atomic orbital of *Si* from sp^3 hybridization to sp hybridization with the formation of multiple bonds between silicon atoms. In other words, we assume that during the annealing of *a-Si:H* a new allotropic form of elemental silicon is formed. We have called this material silicyne in analogy with carbyne, the third allotropic form of carbon. We believe that in silicyne structure, like in carbyne, macrostructures in the form of *Si*-chains with polyene or cumulene bonds will be predominant.

Silicyne's amorphous structure imposes severe limits on the experimental investigation of its structure, the study of geometrical and electron characteristics of *Si*-chains. That is why quantum and chemical methods of investigation are so important in this case.

Since the specimens of the new allotropic form of silicon had an amorphous structure, quantum-chemical calculations of the geometry and thermodynamic characteristics of silicon atom chains were made with the use of PC GAMESS program by non-empirical SSP method without the account of electron correlation (RHF/6-311G(d)) and with account of electron correlation according to Moller-Plesset second order disturbance theory (MP2/6-311G(d)).

The linearity condition for *Si*-chains in the optimization of the geometry was obtained by means of setting a point group of symmetry of the systems under consideration. As in the case of polymer models, clusters were used in the form of *Si*-chains, that were closed by a fragment containing one or more impurity atoms. The requirement of linearity of *Si* atoms location may lead to the instability of model structures, which was confirmed by the calculation of oscillation frequencies. However, this requirement can be justified here, since experimentally the restructuring of *a-Si:H* and silicyne formation occur in a solid, where considerable limitations for atom shifts exist. Quantum-chemical calculation of the band structure was made at the RHF/STO-3G level in the framework of the model of quasi-expanded elementary cell (QEEC) [6].

Under the above-mentioned conditions we have discovered polyene and cumulene silicon molecules optimized with regard to energy.

The lengths of the ordinary and the triple bond in the polyene structure are, respectively, 2.205 and 1.968 Å, the mean inter-atomic distance $r_{cp} = 2.087$ Å, and the value of bond alternation $\delta_{ce} = 0.237$ Å. The calculated mean value falls within the experimental interval $r = 2.10 \pm 0.04$ Å. The influence of electron correlation, δ_{ces} , decreases but leaves the mean value of the distances unchanged. Hence, by taking electron correlation into account we can confirm the possibility of existence of polyene *Si*-chains in silicyne.

The mean distance between silicon atoms in the cumulene chain $r_{cp} = 2.067$ Å. It also falls within the experimental interval of distances. Calculations at MP2 level for cumulene clusters show a shift of the calculated distance $r = 2.067$ Å closer to the center of the experimental interval $r = 2.10 \pm 0.04$ Å.

The calculation of energy and thermodynamic characteristics (enthalpy and Gibbs free energy) of silicon atom chains has shown that the polyene structure of the silicon polymer is more advantageous than the cumulene one. Thus, $E(-Si-Si-) - E(=Si=Si=) = -11.7$ kJ/mol Si_2 .

The theoretical curve of distribution of states density in the valence band of the polyene polymer consists of two σ - bands: $\sigma_1 = (-20.16$ eV; -17.82 eV), $\sigma_2 = (-16.44$ eV; -11.08 eV) and a twice-degenerated π - band: $\pi = (-8.96$ eV; -5.24 eV). the structure of the valence band of the cumulene polymer practically does not differ from that of the polyene polymer: $\sigma_1 = (-20.15$ eV; -17.82 eV), $\sigma_2 = (-16.43$ eV; -11.07 eV) and $\pi = (-8.95$ eV; -5.24 eV).

To compare the experimental and theoretical data, calculation of the band structure for *c-Si* was made. Model clusters of T_d symmetry were considered where the number of silicon atoms was increasing consecutively (up to 67 *Si* atoms); non-saturated bonds of the boundary atoms were formed with hydrogen atoms. The analysis of the composition and single-electron energies of molecular orbitals shows that with the increase of cluster size the values of the energy of the upper occupied molecular orbitals (*Si-Si* bonds) converge at -7.1 eV. In the cluster approximation this value is estimated for the top of the valence band of *c-Si*. The calculated value of the top of the valence band for silicyne (-5.2 eV) is higher than in *c-Si* (-7.1 eV) by $\Delta_{calc.} = 1.9$ eV, which is in good agreement with

the experimental estimated $\Delta_{\text{exp.}} = 2 \text{ eV}$. The equality $\Delta_{\text{calc.}} \approx \Delta_{\text{exp.}}$ confirms the presence of linear silicon chains in the specimens of silicyne being investigated.

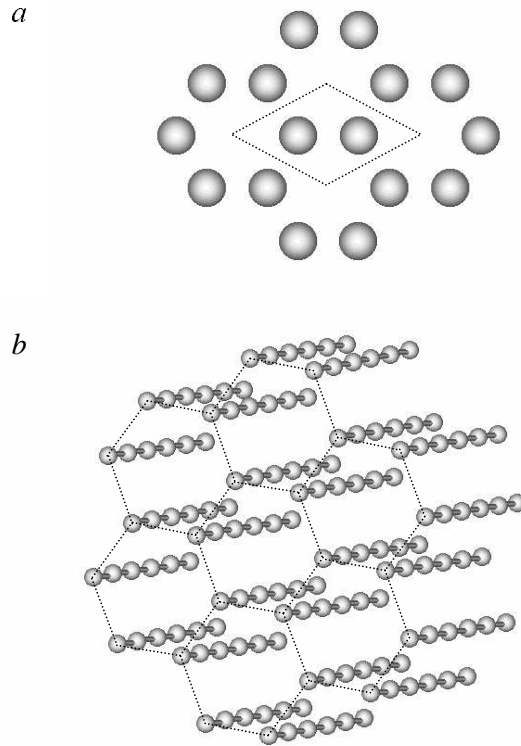


Fig. 4. Possible types of a two-dimensional (a) and a three-dimensional (b) grid of silicyne nanocrystallite.

On the basis of the data that we have obtained on the atomic and electron structure of the new material we propose two possible models for the atomic structure of the amorphous silicyne film:

- linear chains of silicon atoms have bends after approximately 5-10 atoms. Silicon atoms at such bends have one or two extra bonds which can be used for forming a continuous random spatial network;
- silicon atoms in sp -hybrid state produce separate inclusions in the form of nanocrystallites (Fig.4) measuring $\sim 15\text{-}20 \text{ \AA}$, which are in the matrix of amorphous silicon with tetrahedral network.

With crystallite sizes as small as that, it is practically impossible to distinguish between the two models.

As we have noted earlier, from the energy point of view it is not possible to obtain silicon layers with non-tetrahedral atomic structure in the conditions of thermodynamic equilibrium. That is why, to obtain silicon in the new allotropic form, we produced initially silicon layers that had quasi-tetrahedral structure, and then, by subjecting this original material to external effects, e.g. high-temperature annealing, we achieved the necessary structural transformations. The final result of such external effects depended on the following factors:

1. Silicon multibonds on annealing of amorphous silicon films occurred only in the films that had structural large-scale inhomogeneities of the pole structure type (Fig. 5) and/or other linear defects and nanocrystalline inclusions, blisters and polysilane chains.

On annealing at 500°C structural changes take place in this material with a high concentration of dangling bonds, that occurs due to intensive evaporation of hydrogen at temperatures $\sim 500^\circ\text{C}$ and to the effect of the existing intense stresses near the walls of the above-mentioned macroinhomogeneities that stimulate the formation of chain silicon structures.

The information about considerable evaporation of hydrogen from amorphous films of hydrogenated silicon was obtained from the experiments aimed at studying temperature effusion of hydrogen on KFA-ISI/ST mass-spectrometer and the data of IR-spectroscopy. The result of the process of formation of silicon multibonds depends on the size of macroinhomogeneities and improves as the concentration of structural inhomogeneities grows.

On the basis of the results of the experimental [7] and the theoretical [8] work aimed at the reconstruction of the interface between amorphous and crystalline silicon on annealing at temperatures ≤ 500 °C, we consider that the presence of structural macroinhomogeneities in the original films of amorphous silicon is exactly the necessary factor that stimulates the forming of chains out of silicon atoms with multibonds;

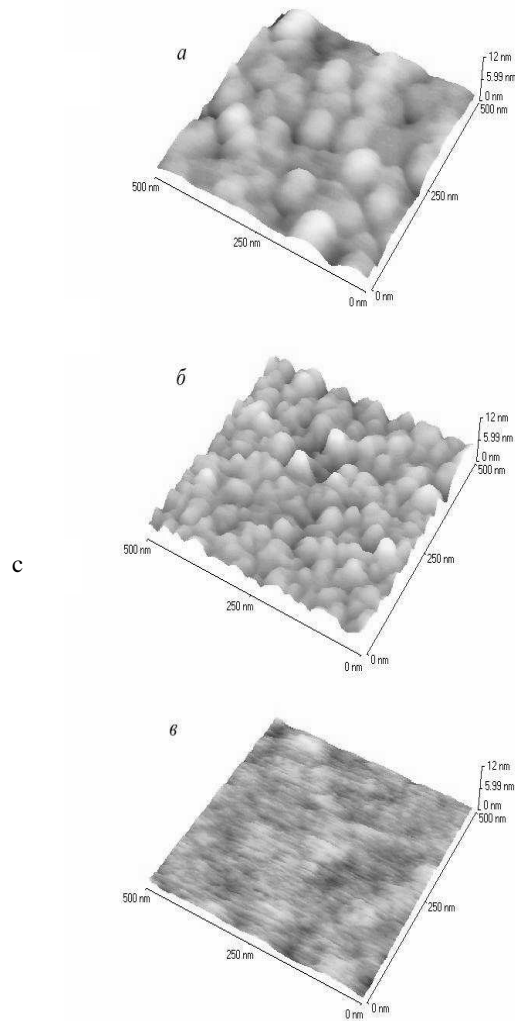


Fig. 5. Surface morphology of silicene (a) и $a\text{-Si:H}$ (b, c) films.
b - original $a\text{-Si:H}$ film used for obtaining silicene;
c - $a\text{-Si:H}$ film whose annealing at 500°C does not yield silicene.

- From the data of Auger-spectroscopy and preliminary irradiation of $a\text{-Si:H}$ films by neon, oxygen and carbon ions it has been found that, regardless of the method for producing the original silicon films, the presence of oxygen in these films is the principal factor that inhibits the formation of silicon multibonds during the annealing in vacuum and implantation of superlarge doses of inert gases. The maximum allowable concentration of oxygen in the original films is ~ 0.2 at. %.

The presence of silicon atoms in the original films of amorphous hydrogenated silicon in concentrations $\sim 1 - 2$ at.% does not interfere with the above-mentioned structural changes during the annealing. However, the reduction of the average distance between the atoms to 2.01 \AA instead of 2.10 \AA is observed.

The presence of radiation defects and neon in amorphous silicon films also does not lead to the disappearance of the effect of decreasing the first coordination number and the inter-atomic distance after the annealing. It only leads to the increase in the temperature required for the annealing.

We have studied temperature dependences of conductivity of the original films and the absorption edge of the new material.

Temperature dependences of conductivity of the original *a-Si:H* films prepared at different temperatures and of silicene obtained after the annealing at $500 \text{ }^\circ\text{C}$ of respective *a-Si:H* films are shown in Fig. 6. It can be seen from the figure that regardless of the substrate temperature in the process of sample preparation the conductivity of amorphous hydrogenated silicon is of activation type in the whole temperature range that has been studied and is described by the following expression:

$$\sigma = \sigma_0 \exp(-\Delta E/kT), \quad (1)$$

where $\Delta E = (E_c - E_f)$ is activation energy, E_c and E_f – the energies corresponding to the bottom of the conduction band and the position of the Fermi level. The conductivity is effected by the carriers excited from the Fermi level to the distributed states located higher than the bottom of the conduction band. The values of activation energy depend weakly on the conditions of preparation of the films and for *a-Si:H* prepared at 50 and $250 \text{ }^\circ\text{C}$ equal 0.92 and 0.88 eV , respectively. At the same time, the pre-exponential factor σ_0 in expression (1) increases by two orders of magnitude as the substrate temperature increases from 50 to $250 \text{ }^\circ\text{C}$ and amounts to ≈ 250 and $2.5 \times 10^4 \text{ } \Omega^{-1} \text{ cm}^{-1}$, respectively.

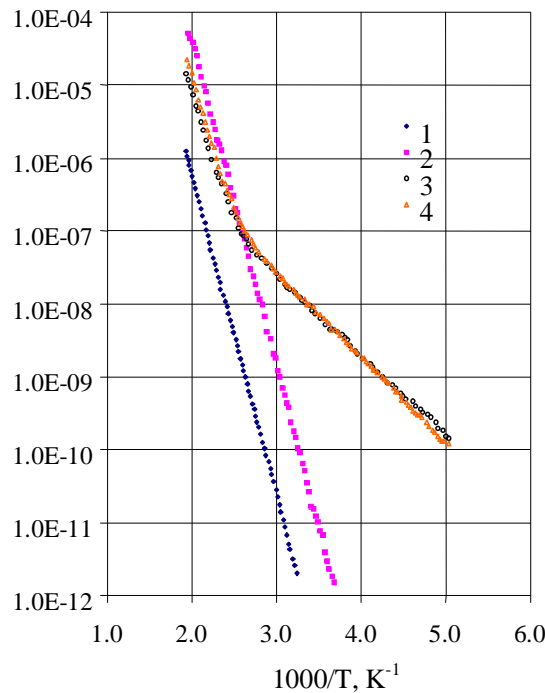


Fig. 6. Temperature dependences of specific conductivity of original *a-Si:H* films obtained at substrate temperatures $50 \text{ }^\circ\text{C}$ (1) and $250 \text{ }^\circ\text{C}$ (2), and silicene (3 and 4), obtained after the annealing at $500 \text{ }^\circ\text{C}$ of respective *a-Si:H* films.

Near the room temperature, conductivity is effected by the jumps of charge carriers excited from the Fermi level to the localized states of the band tails. The temperature dependence of the conductivity in this temperature region is also described by the law of the type (1), however, the respective activation energy is $\Delta E = (E - E_f + W) \approx 0.25$ eV, where E is the energy close to which jumps of charge carriers occur, and $W \approx 0.01$ eV is the jump energy. The presence of the jump component of the conductivity with activation energy ≈ 0.25 eV demonstrates the fact that when amorphous silicene is formed from *a-Si:H*, some defects arise, that produce some localized states in the forbidden gap of silicene, whose energy is 0.2 - 0.25 eV higher than the Fermi level.

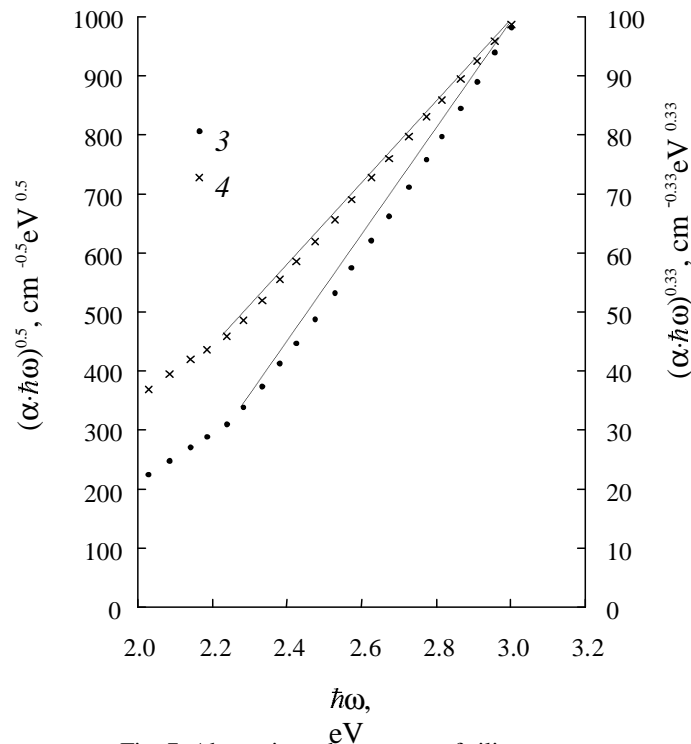


Fig. 7. Absorption edge spectra of silicene.
3 – in Tauc's coordinates; 4 – in Klazes' coordinates

Thus, according to electrophysical studies, silicene is a semiconductor with the forbidden gap at ~ 1.6 eV. Near the room temperature the conductivity is by hopping on localized states situated in the forbidden gap 0.2 - 0.25 eV higher than the Fermi level.

Specific conductivity value at the temperature ≈ 300 K is $\sim 10^{-8} \Omega^{-1} \text{cm}^{-1}$.

The value of the forbidden gap obtained from the conductivity data agrees with the results of optical experiments. As it is known, absorption spectrum for most of the studied amorphous films, in the investigated interval of photon energies, is described by the power law of the form:

$$\alpha \propto (E - E_g)^r \quad (2)$$

$E_g = E_c - E_v$, E – photon energy, and the power parameter r depends on the conditions of preparation of amorphous film. To determine the width of the forbidden band, Tauc's law [9] is used as a rule:

$$\sqrt{\alpha \cdot \hbar\omega} \propto (\hbar\omega - E_g) \quad (3)$$

This law works well if the distribution of delocalized states is described by a simple parabolic law. In our experiments, Tauc's law worked only for the original *a-Si:H* film. In this case the width

of the forbidden gap was 1.86 eV. For silicyne the range of linearity in Tauc's diagram is limited (see Fig. 7) However, the linear dependence will be observed in a wider range of photon energies, if we use Klazes' law [11] for describing the shape of the absorption edge (4) instead of (3):

$$\alpha \propto (\hbar\omega - E_g)^3 \quad (4)$$

In Fig. 7 both plots are shown for silicyne. To demonstrate the above assertion, the straight lines corresponding to the laws (3) and (4) are shown in the same figure as dotted lines.

The fact that the law (4) is satisfied for silicyne absorption edge means that the density of delocalized states near E_c and E_v in this material depends linearly on the energy. The value of E_g , found according to Klazes's law equals ≈ 1.6 eV. As we can see, the optical width of the forbidden zone in silicyne is approximately 0.2 - 0.25 eV smaller than in $a\text{-Si:H}$, and is in a good agreement with the data obtained from the measurement of the temperature dependence of specific darkness conductivity.

4. Conclusions

The results of our theoretical and experimental investigations have shown quite convincingly that there are no limitations in principle for the existence of elemental silicon consisting of atoms that are not in sp^3 - hybrid state. Rather, the problem consists in technical difficulties in the preparation of such a material in crystalline form and separating it from other phases. At present only amorphous films have been obtained that we believe to be a mixture of many allotropic forms of silicon. Regrettably, the data available to us is not sufficient for the complete decoding of the new material's structure.

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