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Ion plasma deposition and optical properties of SiC films

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SiC films have been obtained by direct deposition from a C and Si ions flow at energy values in the 30 to 1.500 eV range. The films deposited at the substrate temperature 600°C were chemically and structurally disordered. The deposition energy increase resulted in a reduced optical slot of the film and increased Urbach parameter. The dependence is non-monotonous in the energy range 30–250 eV. The maximum value of the film optical gap (2.2 eV) is close to the band gap for cubic SiC (2.4 eV). The non-monotonic dependence of the film optical properties and structure parameters on the ion deposition energy in the 30–250 eV range can be connected with difference in behavior of C and Si sublattices in SiC under low-energy ion bombardment.

Методом прямого осаждения из потока ионов C и Si с энергиями в диапазоне 30–1500 эВ получены пленки SiC. Осажденные при температуре подложек 600°C пленки являлись структурно и химически разупорядоченными. Повышение энергии осаждения приводило к уменьшению оптической щели пленок и увеличению параметра Урбаха. В диапазоне энергий 30–250 эВ эта зависимость является немонотонной. Максимальное значение оптической щели пленок (2.2 эВ) близко к величине запрещенной зоны кубического карбида кремния (2.4 эВ). Немонотонная зависимость оптических свойств и структурного состояния пленок от энергии осаждения ионов в диапазоне 30–250 эВ могут быть связаны с различным поведением углеродной и кремниевой подрешеток карбида кремния в условиях низкоэнергетичной ионной бомбардировки.

Recent years are characterized by dramatic rise of public interest in low temperature methods of obtaining silicon carbide films, owing to outstanding potential applicability of said material [1]. Synthesis of silicon carbide films under substantially nonequilibrium conditions, specified by decrease of the process temperature, makes it possible to provide the SiC layers of different crystalline states, since amorphous till crystalline. According to the available publications, in the course of silicon carbide synthesis at near room temperatures, amorphous SiC layers are formed, with no relevance to methods of transporting the carbon and silicon atoms to the substrate [2–5]. At the same time, the substrate temperature at which the crystalline phase is formed within SiC films, depends to some extent on the film deposition methods. So, in conventional methods of carbon and silicon deposition from vapor or gaseous phases, the substrate temperature exceeding 1300°C is necessary for the silicon crystalline phase formation [6]. When the magnetron, ion beam and other sputtering methods are used to deposit SiC films, formation of the crystalline SiC phase has been identified in 700 to 800°C substrate temperature range [5, 7]. While obtaining the SiC films by laser ablation, as is shown in [8], the occurrence of SiC crystalline phase is only possible in

Table. Preparation conditions and calculated electron structure parameters of SiC films

Sample No.	Deposition energy, eV	Substrate temp., °C	Film thickness, nm	Approximation by Urbach		Approximation by Tautz		
				α_0	E_u	B	E_{g1} (A)	E_{g2} (D)
7052.33	30	600	990	307.4	0.95	19700	1.49	2.127
7049.23	30	600	880	122.8	0.78	16444	1.43	2.17
7048.23	40	600	790	231.96	0.93	15421	1.49	2.14
7053.11	80	600	775	27.23	0.84	1866	1.51	1.92
7043.12	90	600	990	22.24	0.67	3282.9	1.55	1.87
7041.12	100	600	960	4.85	0.5	3482.9	1.48	1.75
7054.33	150	600	805	181.1	0.84	11984	1.82	2.08
7055.45	190	600	805	208.8	0.9	15345	1.84	2.169
7044.11	200	600	840	97.2	0.76	9225.2	1.53	1.98
7046.13	260	600	756	174.74	0.73	18938	1.54	1.99
6985	1500	650	1000	300.7	0.99	15586	1.44	1.95
6986	1500	650	1700	262	1.072	7160	1.41	1.68

Notes: 1. Approximation by Urbach $\alpha = \alpha_0 \exp(h\nu/E_u)$, Approximation by Tautz $\alpha \cdot h\nu = B(h\nu - E_g)^2$.
2. in Figures, the samples characterized in the Table are denoted as follows: 7046.13 (1), 7054.33 (2), 7041.12 (3), 7044.11 (4), 7049.23 (5), 7043.12 (6), 6986 (7), 7053.11 (8).

the substrate temperature range of 600 to 700°C. In [9, 10], it is reported that to decrease the substrate temperature necessary for SiC film formation by chemical deposition from vapor, the plasma activation of the process with negative bias on the substrate has been used. It was shown that crystalline phase in the films can be identified at the substrate temperature of 600 to 800°C.

Qualitative analysis of the SiC formation conditions in the above-mentioned papers enables us to argue that:

— first of all, the average kinetic energy of the particles being deposited (in abovesaid cases) increases consecutively from its thermal extremes (such as at gas phase or vapor deposition processes) to values being set forth by the electric field (such as at deposition of ionized particles);

— second, a trend is obvious here that formation temperature of silicon carbide crystal phase decreases with energy elevation of the particles being deposited.

Therefore, we may assume that one crucial factor in the process of SiC film synthesis on substrates, at deposition of carbon and silicon particles under elevated energy rate, is a contribution of the particle kinetic energy to energy balance of the process of SiC films formation and crystallization on the substrate. As it follows from the above data, this is the very contribution that can be employed to reduce the substrate temperature at which the SiC crystal phase is formed. In fact, in most of papers dedicated to low-temperature methods of the SiC film preparation, the comparative analysis of the particle energy influence on the SiC films structural formation processes is restricted dramatically by some technological features. These are: (a) different concentrations of ionized particles, or (b) troubles in determination of mean energy value of particles that reach the substrate, etc. For this reason, this paper illustrates an endeavor of authors to study the effect of condensable particle energy on structure and optical properties of SiC films obtained by direct deposition of silicon and carbon ionic flow, within 30 to 1500 eV energy range.

The SiC films were deposited from the flow of carbon and silicon ions generated by a plasma based ion source containing a cathode of polycrystalline silicon carbide (this product has been synthesized by the Institute for Materials Science Problems, National Academy of Sciences of Ukraine) (Table). The deposition process pattern has been presented before in [11]. In the course of deposition process at this experiment, vacuum level was less than $4 \cdot 10^{-4}$ Pa. The ion energy was set by the potential difference between the substrate and the plasma source cathode, within 30 to 1500 eV energy range. The average film deposition

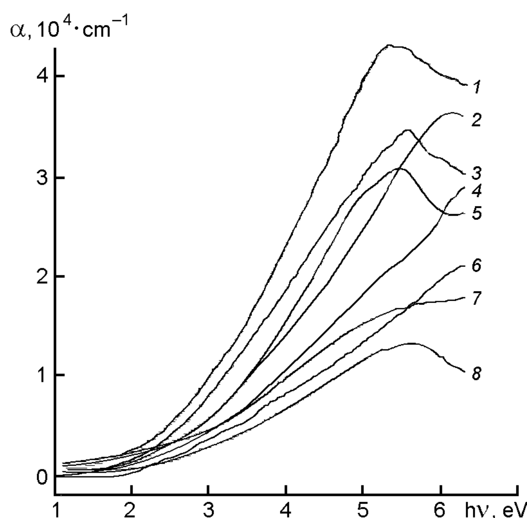

Fig. 1. Adsorption spectra of SiC films deposited at different energies of ions (eV): 260 (1), 150 (2), 100 (3), 200 (4), 30 (5), 90 (6), 1400 (7), 80 (8).

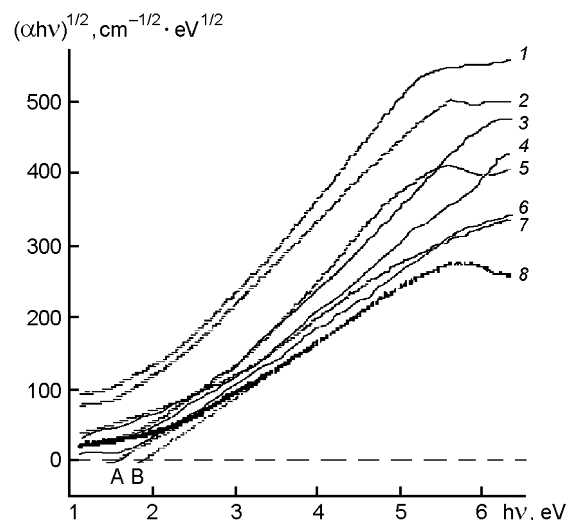

Fig. 2. Approximation of adsorption spectra of SiC films deposited at different energies of ions, by aid of Tautz power function $\alpha = B(h\nu\ E_g)^2$. Curves are numbered as in Fig. 1.

rate was 10 nm/s. As substrates, polished plates of quartz, leucosapphire, etc. were used. The substrate temperature was varied from 20 to 800°C by a resistive substrate holder heater. The optical transmission and reflection spectra of experimental films were measured by an SF 56 type spectrophotometer. The structural characteristics of experimental films were determined using a JEOL 200Cx type transmission microscope. The following techniques were used for identification : characteristic loss of electron energy (CLEE), scattered electron diffraction effect and plotting the function of atomic radial distribution. Moreover, the SiC film composition was determined using the photoelectron spectroscopy techniques by aid of standard set of calibration standards.

A series of SiC films on quartz and leucosapphire substrates were obtained from carbon and silicon ions flow with energies within 30 to 1500 eV range. The durations and conditions of the film deposition as well as the film thickness values are represented in the Table. The photoelectron spectroscopy data evidence that in the SiC films so obtained homogeneously bound C–C and Si–Si atoms are present alongside with heterogeneously bound C–Si atoms. Oxygen is also present oxygen being generally bound with silicon, which in our opinion, penetrates the just-deposited film at its first contact with atmosphere. This assumption comes out from the fact that during the deposition process the rate of residual oxygen atom flow and carbon + silicon ions flow did never exceed 10^3 level. Features of homogeneously bound carbon and silicon atoms are a subject to further discussion. Fig. 1 represents adsorption spectra α of the SiC films deposited at the substrate temperature 600°C, with ion energies within 30 to 1500 eV range. Note that said spectra are represented with respect to reflection factor. It is obvious from the relevant diagrams that adsorption spectra of films deposited at different ion energies are characterized by their individual specific features across the whole range of optical adsorption. In particular, the long-wave spectrum zone (< 2 eV) is featured by the fact that adsorption curves tend to converge, thus demonstrating a sufficiently active adsorption of SiC films within IR area located at 10^3 cm^{-1}. At this time, the visible spectral band is featured by differences in adsorption rates, which differences are triplicated in UV zone, thus gaining (> 4 eV) level. To facilitate the analysis procedures, we will conditionally split the adsorption spectrum into two areas. One of those is the short-wave bend, whereby the adsorption effect is specified by interband transitions. This adsorption band can be described by [13]:

$$\alpha(h\nu) = B(h\nu - E_g)^m ,$$

where $m = 1/2$ and $m = 2$ correspond to direct and indirect allowed electron transitions, respectively; B is defined by combined density of states associated together

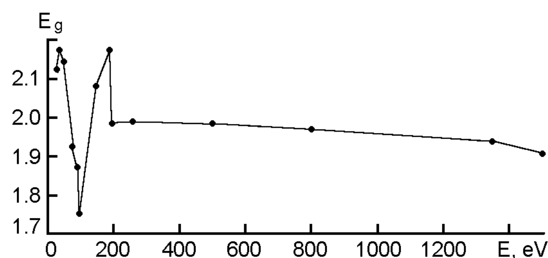

Fig. 3. Dependence of calculated SiC films optical slot width E_g on the ion deposition energy.

by direct and indirect transitions through optical slot E_g.

The other spectral area is the long-wave one, which can by approximated by aid of Urbach exponent [13] as:

$$\alpha = \alpha_0 \exp(h\nu / E_u),$$

where E_u and α_0 are parameters defined by concentration of localized states (LS) and degree of overlapping hereof within the band gap.

Thus, differences in adsorption coefficients within the short-wave spectral area (i.e., interband transitions) can be caused by phase or structure differences within films. Differences in exponential spectral area, however, can be explained by differences of defective states within the films. Fig. 2 represents approximated values of adsorption spectra through degree functions with coefficient $m = 2$, selected for its optimal inclination towards linear extrapolation of characteristic curves. Being calculated using the above formulae, values of optical slots E_g within films change depending on the ion deposition energy, which is an evidence for differences within structural states at the level of medium and proximate order of atomic disposition. These data are disclosed in the relevant Table. Fig. 3 represents the calculated values of SiC film optical slot as a function of the ion deposition energy. It is obvious from the data of Fig. 3 and the Table that as the ion deposition energy increases within 30 to 1500 eV energy range, the optical slot size (calculated using Taucz's formula) tends generally to reduce. At the same time, the very complex nature of E_g dependence on the ion energy within 30 to 250 eV energy range enables us to identify three following extremes: (i) a minimum size of optical slot (~ 1.65 eV) near 100 eV deposition energy; (ii) a maximum size of optical slot (~ 2.1 eV) around 30 eV deposition energy and (iii) a maximum size of optical slot (~ 2.2 eV) in 200 to

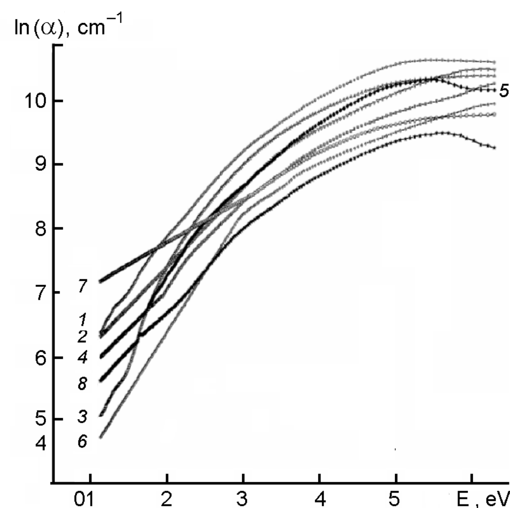

Fig. 4. Approximation of adsorption spectra of SiC films deposited at different energies of ions, by aid of Urbach formula $\alpha = \alpha_0 \exp(h\nu E_u)$. Curves are numbered as in Fig. 1.

250 eV deposition energy range. It should be mentioned that maximum values of optical slot approach the band gap value (2.4 eV) in cubic silicon carbide [14]. Silicon carbide is known to possess three structural modifications: cubic, hexagonal, and rhombohedral, which, despite the identical bonds between carbon and silicon atoms, differ from each other in lattice type, and, correspondingly, position of electron energy levels and the band gap width E_g. Thus, for example, the E_g value is 2.403 eV in 3*C* SiC cubic crystals [14], 3.285 eV in hexagonal 4*H* SiC [14] and 3.05 eV in rhombohedral 15*R* SiC [15].

Therefore, considerable changes of optical slot sizes from 1.65 to 2.2 eV (as is seen in Fig. 3) cannot be explained by phase differences within SiC. We have presumed that a cetrain effect on the film adsorption and, hence, an error in the optical slot value calculation (by method of per degree approximation of adsorption spectra) is contributed by silicon-free carbon in various structural states. In our opinion, approximation of the spectra for most of samples represented in Fig. 2 demonstrates that this effect occurs due to a knee in the linear area at about 3 eV spectral zone. Said knee is indicated in the bottom curve by auxiliary straight lines. The adsorption curves of SiC and of unordered carbon areas formed by homogeneously bound carbon atoms can be supposed to intercross in that point. The Table also represents calculated values of optical slot (presumably, for unordered

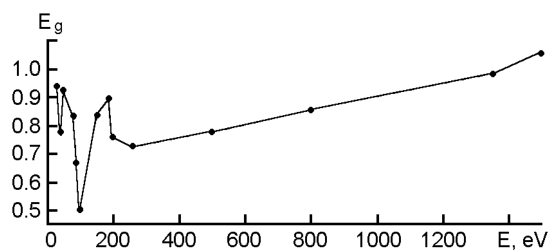

Fig. 5. Dependence of calculated of Urbach's parameter E_u value on the ion deposition energy.

carbon) for 2nd linear area of the spectrum. The so obtained E_{gc} values are typical of known values for band gap in diamond-like carbon films being deposited from high-energy carbon particles. Depending on the diamond-like film preparation method, the E_{gc} values of are determined to be within 1.6 to 2.5 eV energy range [16].

Fig. 4 represents the film adsorption spectra in logarithmic scale for consideration of the Urbach "tail". Electronic microscopy investigations have shown that the film structure is significantly unordered, and in adsorption spectra this fact is featured as an exponential "adsorption tail" within the long-wavelength area. The presence of $\Delta(h\nu)$ type energy intervals (where $\ln\alpha \sim h\nu$ is an indication that Urbach's rule is valid) evidences the exponential character of energy distribution of the density of states localized in the band gap [13]. It is obvious from the Table that E_u parameter (defined by LS concentration for films deposited at different energies) varies, thus evidencing different degrees of disordering in crystal lattices of these materials. Fig. 5 presents dependence of Urbach parameter on the ion deposition energy. As is obvious from Fig. 5, the dependence of E_u on the ion energy is non-monotonous and exhibits a broad minimum at about 50 to 200 eV energy range. While within higher energy (> 200 eV) area this increasing disordering can be explained by intensification of defect formation (owing to radiation failures by ions in the course of deposition), the nature of E_u increase within low-energy (< 50 eV) area is still incomprehensible. Perhaps this phenomenon is related to exit of the ion condensation front out of subsurface layers up to open surface, where defect formation energy is lower because the surface atoms possess incomplete bonds.

Fig. 6 represents radial distribution function calculated for SiC films deposited at 200 eV ion energy, which demonstrates availability of homogeneously bound carbon atoms. The film obtained at room temperature was then annealed at 500°C. As is seen in Fig. 5, the atomic distribution maxima in the annealed film are narrowed, thus evidencing the atomic ordering at the short-range level. At certain concentrations of homogeneously bound carbon and silicon, clusters may arise, i.e carbon and silicon based structural components that may contribute to the electron properties of films. Such the components include sp^2-, sp^3-bound carbon phases and silicon ($E_s \approx 1$ eV), which can be formed from free atoms of carbon and silicon. It should be noted that the formation problem of homogeneously bound carbon and silicon atoms at low temperature silicon synthesis is known for years. Homonuclear -C–C- and -Si–Si-bonds can be found in amorphous silicon carbide films obtained either at low temperatures [17], or by virtue of crystalline material amorphization effect [18]. In this work, SiC films have been obtained by direct deposition of carbon and silicon ions flows at pre-specified energies of 30 to 1500 eV. Within this range, formation of structure occurs in the subsurface film layer, its thickness being depended on the ion energy. As is shown in [19], the behavior of C and Si sublattices in silicon carbide under radiation-stimulated processes differs from one another. The same paper states that these differences have been specified by various threshold energies of defect formation in carbon and silicon sublattices. The averaged value of minimum defect formation threshold energy in (3C) cubic and hexagonal (6H) SiC struc-

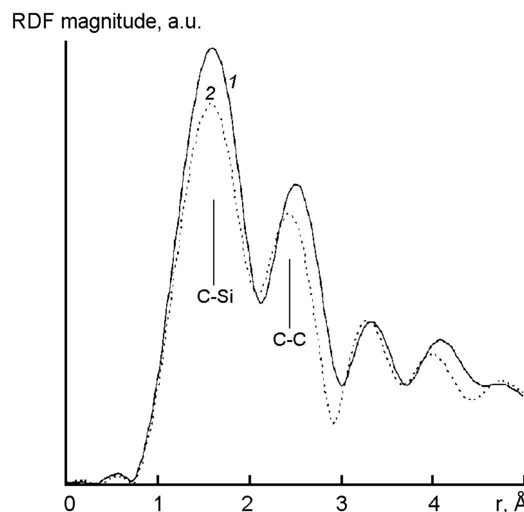

Fig. 6. Calculated function of atomic radial distribution in SiC film deposited at 200 eV ion energy.

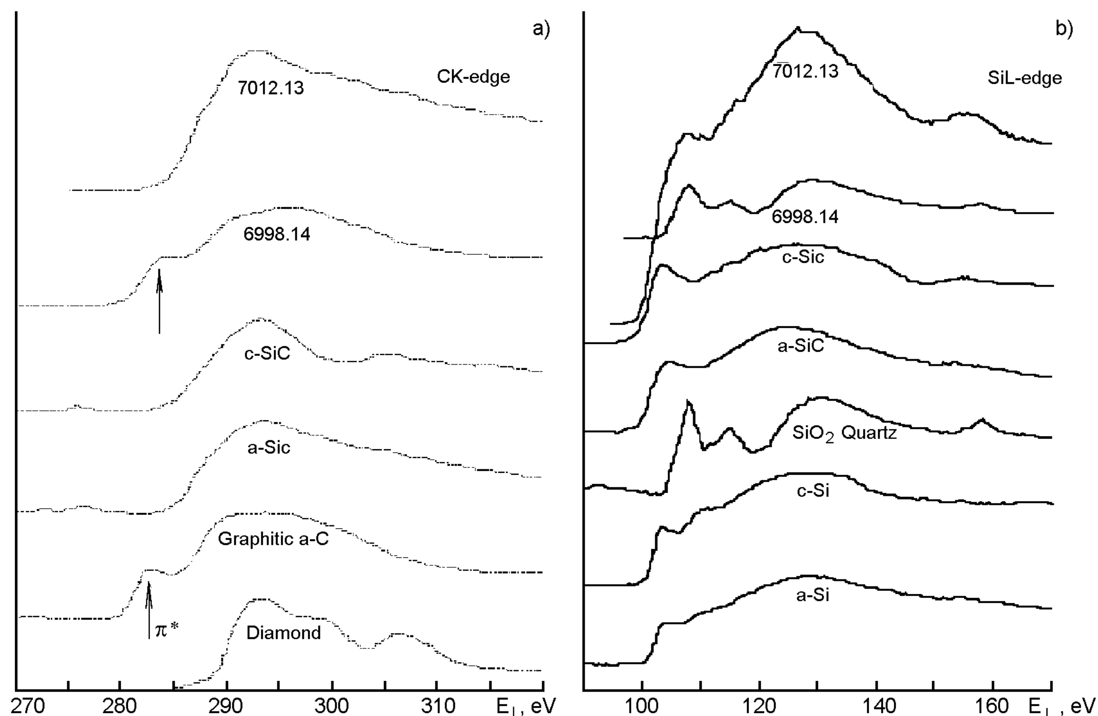

Fig. 7. Spectra of CLEE in binding energy ranges 1*s* electron in carbon (~ 284 eV) and 2*p* electron in silicon (~ 100 eV) in films deposited at 80 eV (#7012.13) and 1500 eV (#6998) ion energies. For comparison sake, presented are CLEE spectra for amorphous and crystalline silicon carbide, graphite, diamond, silicon and quartz. The CLEE spectra are measured in films deposited at 80 eV and 1500 eV ion energy.

tures is 21 eV for carbon sublattice and 35 eV for silicon one [20].

This means that if SiC is bombarded with ions of an energy exceeding the threshold defect formation energy, there will appear numerous carbon atoms knocked of the lattice sites. Thus liberated carbon atoms, owing to their increased mobility, are able to form the homogeneous bonds and to unite together into clusters. Now, non considering the stage of SiC phase formation (under deposition and ion bombardment conditions), let us consider the possible structure of carbon clusters. Said carbon clusters, in our case, are formed under ion bombardment conditions and, therefore, when considering the process, the known dependences of carbon film phase composition on the deposition energy can be used. So, according to numerous experimental data collected, the formation of predominantly sp^3-coordinated carbon (diamond-like) films occurs within 30 to 300 eV deposition energy range [16]. The sp^3 phase formation depends strongly on the substrate temperature which should not exceed 150°C. Beyond the range of the deposition conditions, the sp^2-coordinated carbon films are typically formed. Thus, under conditions of SiC films deposition from ion flow (realized in this work), we may expect an occurrence of sp^3- or sp^2-bound carbon components, depending on ion energy and condensate temperature.

Fig. 7 represents CLEE spectra in areas of 1*s* electron in carbon (~ 284 eV) and 2*p* electron in silicon (~ 100 eV) binding energy. The CLEE spectra have been measured for SiC films deposited at ion energy values 80 eV and 1500 eV. For comparison, in Fig. 7 are shown the CLEE spectra for samples of amorphous and crystalline silicon carbide, graphite, diamond, silicon, and quartz.

The comparative consideration of shapes and positions of maximum losses in above mentioned spectra makes it possible to state a similarity between CLEE spectra of films and those of amorphous silicon carbide. At the same time, the CLEE spectra of films obtained at various energies are characterized by significant differences. So, the film obtained at 1500 eV ion energy has its maximum energy loss near 7 eV, which is due to adsorption of π electrons present in the sp^2-bound carbon (see spectrum of graphite CLEE). Quite in contrast, the

CLEE spectrum of a film deposited at 80 eV does not exhibit this maximum, thus evidencing the predominant formation of sp^3-bound carbon clusters [21]. Although the above-mentioned values of ion energy coincide with the determined values at formation of sp^2- and sp^3-phases of pure carbon, it should be mentioned that at simultaneous deposition of carbon and silicon ions, optimum conditions (such as energy and temperature) of sp^3-coordinated carbon phase can differ from those specified for formation of pure carbon, because of simultaneous involvement of carbon and silicon ions in radiation stimulated processes of the film formation. In our opinion, silicon atoms due to larger size, and hence lower mobility (compared to carbon atoms), which are knocked out of their lattices in the course of ionic bombardment, would tend rather to form defects (like dandling bonds) than become united in clusters. This assumption is supported by the presence of a significant number of –Si–O– heterogeneous bonds in amorphous SiC films. We believe that said heterogeneous bonds are formed due to the contact of thus grown films with atmospheric oxygen.

Reviewing thus obtained results, we come to the conclusion that the kinetic energy of particles deposited during preparation of the SiC films (as well as any other multicomponent systems) should be optimized. On the one hand, the amount of energy being transferred to atoms should be sufficient enough to ensure the atomic mobility required to form chemically ordered structure. On the other hand, the radiation stimulated processes which result in atom offset from their structural lattice cells and in formation of homogeneously bound C–C and Si–Si molecules and clusters, should be restricted. Therefore, the films obtained at high energies of particles, will always include a certain portion of homogeneously bound atoms of carbon and silicon. This statement is well illustrated by results of [22], where SiC films produced under conditions of high energy ion bombardment, tend to contain maximum 70 % of chemically ordered atoms.

The SiC films have been obtained by direct deposition from flows of carbon and silicon ions in 30 to 1500 eV energy range. The films deposited onto substrates heated up to 600°C demonstrate the structural and chemical disordering. Increase of C and Si ion deposition energy within 30 to 1500 eV range resulted in a reduction of film optical gap value and in increase of Urbach parameter. Thereby, within the initial energy range section (30 to 250 eV) the dependence is non-monotonous, whereby two maxima of optical slot width appear at 30 eV and in 200 to 250 eV energy range. The maximum value of the film optical slot (2.2 eV) approaches the band gap value for cubic silicon carbide (2.4 eV). Under conditions of ionic deposition, the silicon-free carbon can form sp^2- or sp^3-clusters, depending on energy of ions. The non-monotonous dependence of optical properties and structural state of films on ion energy within 30 to 250 eV is presumably related to different behavior of C and Si sublattices of SiC under low-energy ion bombardment.

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Іонно-плазмове осадження та оптичні властивості плівок SiC

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Плівки SiC одержано методом прямого осадження з потоку іонів C та Si при значеннях енергії від 30 до 1500 еВ. Плівки, осаджені при температурі підкладок 600°C, є структурно та хімічно розупорядкованими. Підвищення енергії осадження спричиняє зменшення оптичної щілини плівок та збільшення параметра Урбаха. У діапазоні енергій 30–250 еВ ця залежність є немонотонною. Максимальне значення оптичної щілини плівок (2.2 еВ) є близьким до ширини забороненої зони у кубічному SiC (2.4 еВ). Немонотонна залежність оптичних властивостей та структурного стану плівок від енергії осадження іонів у діапазоні енергій 30–250 еВ може бути пов'язана з різницею у поведінці вуглецевої та кремнієвої підграток у SiC в умовах низькоенергетичного іонного бомбардування.