Optical properties of silicon carbide obtained by direct ion deposition

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Optical transmission, absorption and reflection spectra of silicon carbide thin films deposited on sapphire substrate from the carbon and silicon ionic flows have been investigated. The films have been obtained at various deposition parameters, i.e., under variation of ion energy and substrate temperature. The behavior of optical characteristics of silicon-carbide films depending on influence of changes in technological parameters. It has been shown that direct ion deposition method provides a control of film optical parameters within a wide range.

Исследованы спектры оптического пропускания, поглощения и отражения тонких плёнок карбида кремния, осаждённых из потока ионов углерода и кремния на сапфировые подложки. Плёнки получены при различных технологических параметрах осаждения: при фиксированной энергии ионов и температур подложек. Изучено поведение оптических характеристик плёнок карбида кремния в зависимости от изменения технологических параметров. Показано, что метод прямого ионного осаждения позволяет управлять оптическими параметрами плёнок в широких пределах.

It is known that silicon carbide (SiC) films obtained under various technological conditions differ substantially in the structure, phase composition and hence in the optical features. Application of modern spectroscopy methods makes it possible to measure the important optical parameters that provide qualitative characterization of the material manufactured using a specific technology. This work presents the results of studies for transmission and reflection spectra of SiC-films obtained by direct deposition on sapphire substrates at different technological parameters. This work is aimed at the study of optical absorption characteristics (i.e., extinction coefficients), as well as at the consideration of fundamental absorption edge of SiC films depending on varying deposition conditions.

To produce silicon carbide films on sapphire substrates, a unique setup (developed at the Institute for Single Crystals) intended for direct ion deposition using plasma source with a SiC cathode was used for the first time. Application of the plasma source generating a mixed flow of carbon and silicon ions to deposit these ions (of preset energies) onto a substrate made it possible to obtain, at relatively low temperatures of substrates ($<1000°C$), SiC films having a high content of nanocrystal silicon carbide phase [1]. This method has demonstrated its technological versatility, since it provides a wide independent variation range of both substrate temperature ($30°C$ to $1000°C$), and energy (30 to 2000 eV) of ions being deposited. The possibility to vary these important parameters as well as reliability of their control provides the obtaining of reproducible films with structures varying from merely amorphous to polycrystalline [2]. In this experiment, the films were deposited at different temperatures of dielectric substrate, and at preset optimized values of ion energy. The

substrate temperature was preset by means of a resistive heater and controlled by of an optical pyrometer. The substrate temperature was $T = 800°C$ for series III test samples, $T = 700°C$ for series II ones and $T = 600°C$ for series №7092 ones.

The transmission coefficients (optical density) and reflection ones were measured by a Perkin-Elmer Lambda-35 (USA) and SF-56 type (Russia) spectrophotometers, within 190 to 1100 nm wavelength range. The film thickness for samples with reflection spectra representing interference profile was measured by spectral-extreme method. Authors have also measured spectral dependences of reflection coefficients under forward $[R = f(\lambda)]$ and reverse $[R' = f(\lambda)]$ illumination of the film-substrate system. To calculate the film thickness, we determined the order of interference extreme using a formula for $R' = f(\lambda)$ [3]:

$$m = \lambda_{m+1} / (\lambda_m - \lambda_{m+1}), \qquad (1)$$

where λ_m and λ_{m+1} are wavelengths of two neighboring extremes.

The absolute value of reflection for a given maximum was determined from $R = f(\lambda)$ curve. The spectral dependences of reflection coefficients at forward and reverse illumination of the film/substrate system for a film from series II are presented in Fig. 1. The SiC layer thickness was calculated from the formula [4] :

$$d = \varphi \lambda_{\max} / 4\pi n, \qquad (2)$$

where φ is phase of λ_{max} wave; d, the SiC film thickness; n, refractive index at λ_{max} wavelength; and λ_{max}, the wavelength of interference maximum for reflection coefficient R_{max}. The thickness and refractive index were calculated for the visible spectral region, where the extinction coefficient $\kappa << 1$ for most films. Therefore, the application of formula (2) is justified. The thickness values calculated using formula (2) agreed well with measurement for reference films using a MII-11 microinterferometer. The refractive index of SiC film was calculated using an equation following from ratio of reflection and transmission coefficients within the air-film-substrate system [4]:

$$n^2 - 2(n_s R_{\lambda m})^{1/2} n - n_s = 0. \qquad (3)$$

Here, $R_{\lambda m}$ is the value of $R(\lambda_{max})/T(\lambda_{max})$ function at wavelength
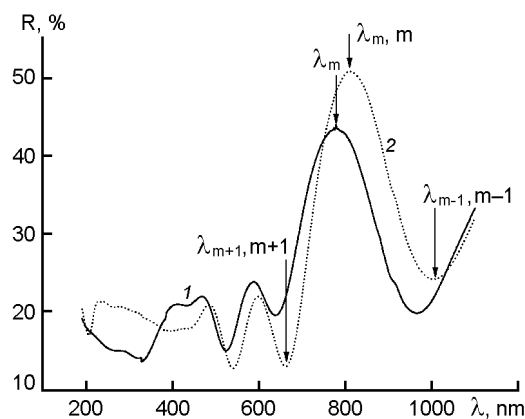

Fig. 1. Spectral dependences of reflection coefficients at direct $R = f(\lambda)$ (curve 1) and reverse $R' = f(\lambda)$ (2) illumination of the film-substrate system.

λ_{max}; n_s, the refractive index of sapphire substrate which, in its turn, can be determined using an equation which includes the sapphire substrate transmission coefficient T_s [4].

When calculating the extinction coefficient κ of films deposited on substrates having a refractive index different from those of the film being studied and of air, the reflection from the film/substrate and substrate/air interfaces should be taken into account. In this case, the extinction coefficient was determined as [5]:

$$\kappa = \lambda / 4\pi d \cdot \ln(B / T), \qquad (4)$$

where B is a pre-exponent taking into account optical properties of the substrate material as well as reflection from interfaces; in the case of strong absorption in SiC film and low absorption in sapphire substrate, this parameter may be expressed as $B = [(1 - R_1)(1 - R_2) (1 - R_{12})$. Here, R_1, R_2, R_{12} are reflection coefficients from film/air, substrate/air and SiC film/substrate interfaces, respectively; d, the SiC film thickness; T, experimental dependence of transmission coefficient on wavelength.

Application of spectral dependence of extinction coefficient $\kappa = \kappa(\lambda)$ is necessary for identification of strong and weak peaks within absorption spectrum structure. It has been found experimentally that curves of reflection and extinction spectral dependences $\kappa = \kappa(\lambda)$ are similar to spectra of imaginary dielectric permeability component, which describe well the features of
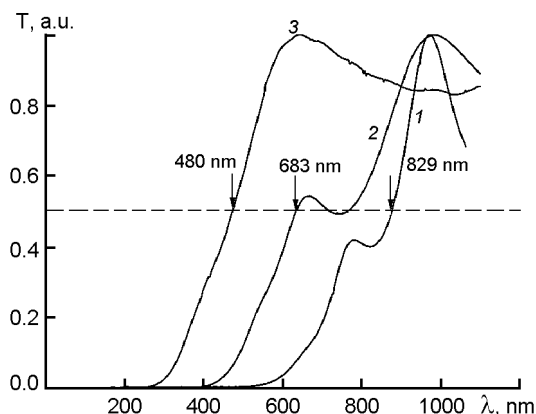
Fig. 2. Dependences of SiC film transmission on wavelength for samples from series №7092 (*1*), №7091 (*2*) and №7049 (*3*). Plots are normalized to a unified scale.

Fig. 3. SiC-film absorption spectra $\alpha = \alpha(E)$ for samples from series I (*1*), II (*2*) and III (*3*). Using test-sample III, demonstrated is an approximation of fundamental absorption edge by curves (a) and (b), according to Urbach and Tautz laws, respectively.

excited state in amorphous and crystal semiconductors [6].

When studying the excited states above the absorption band edge in amorphous semiconductors, the Penna model [7] is often used there to describe the band gap; the model makes it possible to determine major features of state density distribution within valence band. This model is very suitable to consider the optical properties of amorphous semiconductors. It is known that in the Penna band gap, the $h\nu_g$ value coincides at a good accuracy with the spectral maximum $k(h\nu)$ [8]. Therefore, measurement of extinction-coefficient dependences $(\kappa = \kappa(h\nu)$ provides the determination of band gap width.

Optical transmission spectra for SiC films deposited onto sapphire substrates are shown in Fig. 2. In all the series, the SiC films were about 1 μm thick. To facilitate comparison of transmission indices $T = T(\lambda)$, the relevant graphs were normalized and converted to a common scale. These graphs demonstrate obviously a shift of spectral dependences towards shorter wavelengths as the substrate temperature rises (600°C, 700°C and 800°C for the samples of series I, II and III, respectively). The shift of transmission curve edge at increase of sapphire substrate temperature from 600°C to 700°C was about 146 nm (the energy of deposited ions being unchanged). A further temperature rise by another 100°C resulted in another 203 nm shift, whereby the total shift value made 349 nm (the transmission coefficient was measured at 50 % of maximum transmission value).
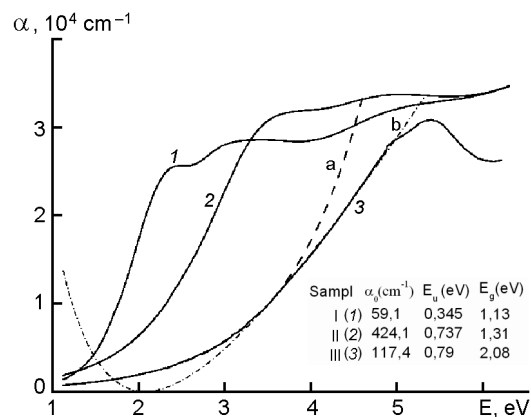
In our opinion, that the increasing film transparence at the substrate temperature elevation is relevant to ordering and possible crystallization of SiC amorphous phase.

To analyze the fundamental absorption edge, we have measured optical density and calculated the absorption coefficient of the film samples. Fig. 3 represents the absorption spectra $\alpha = \alpha(E)$, with values of SiC film reflection spectra being taken into account. As is seen in Fig. 3, the absorption edge has a complex shape. At low energy of photons, the spectral dependence shows a tail, which is presumably an evidence of absorption on defect states of disordered structure. The subsequent phase of the curve shows that the absorption index depends on photon energy exponentially and later on, it changes according to a power law according to Urbach and Tautz laws [6]. Such sort of curve is typical of films that contain amorphous phase, whereas the film structure has no long-range order periodicity. In other words, the SiC films possess the state density tails situated within the semiconductor band gap. Fig. 3 exemplifies an approximation of a complex curve of absorption coefficient $\alpha = \alpha(E)$ by Urbach functions (curve a) $\alpha = \alpha_0 \exp(h\nu/E_u)$, and Tautz functions $\alpha(h\nu) = D\,(h\nu - E_g)^q$ (curve b), for a sample from III series. In the Urbach formula, parameter E_u is Urbach energy, and α_0 is pre-exponential multiplier. In the Tautz formula describing the interband absorption, $q = 1/2$ and $q = 2$ correspond to direct and indirect transitions, re-

spectively. The multiplier D is defined by combined density of states associated with direct and indirect transitions through optical gaps E_g.

The plots in Fig. 3 demonstrate optical absorption shifts along the energy axis, evolution of complex fundamental absorption edge structure, as well as variation of parameters E_u and α_0 (the Urbach energy E_u characterizes the measure of static disorder within crystal lattice caused by accumulation of various defects). The parameters E_u and α_0 (defined by concentration of localized states and by overlap extent thereof in various experimental samples) are different, thus evidencing the different disorder degree in crystal lattice of materials under study. Existence of photon energy intervals $\Delta(h\nu)$ where $\ln\alpha \sim h\nu$ (evidenced by compliance with the Urbach law) demonstrates exponential character of energy-depended density distribution for states localized in the band gap.

The deposition temperature lowering at constant ion energy (within 70 to 90 eV range) results in a significant reduction of optical gap E_g. To characterize optical transitions, spectral dependence of SiC film extinction coefficients is of major importance. Fig. 4 shows the spectral dependences of extinction for samples from I, II and III series. Authors attribute the main absorption band near 2.30 eV to excitation of indirect transitions inside cubic silicon carbide (refer to $E_1 = 2.32$ eV for I series sample, curve 1). The transition energy for II series sample is $E_2 = 3.45$ eV. The sample from III series has a plateau near 5.0 eV area in the extinction spectrum. The experimental extinction spectrum has been expanded into elementary components (i.e., Gaussians), with the aim to characterize interband transitions occurring at absorption within the III series film. After a relevant approximation, we can suggest that, as to the above-mentioned sample, two direct transitions occur in the plateau area with interband distances of 5.03 and 5.23 eV (curve 3). It is seen from these plots that these transitions possess a maximum oscillator force, which is a measure of integral intensity of the whole absorption band. The transition with energy $E_1 = 2.32$ eV corresponds to indirect transition $X_{3c} - \Gamma_{15v}$ in the 3C-SiC polytype (i.e., a cubic modification). That with energy $E_2 = 3.45$ eV corresponds to indirect transition $M_{4c} - \Gamma_{5v}$ with interband distance of 3.48 eV, in 4H-SiC polytype. The transition $E_3 = 5.036$ eV approximates direct transi-
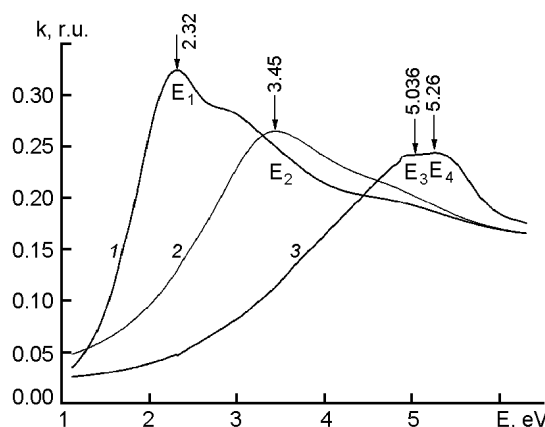

Fig. 4. Spectral dependences of SiC-film extinction for samples from series I (*1*), II (*2*) and III (*3*).

tion $\Gamma_{1v} - \Gamma_{15v}$ (5.03 eV), whereas $E_4 = 5.26$ eV corresponds to transition $X_{3c} - X_{5v}$ in 3C-SiC which makes 5.23 eV [9].

These transitions are involved immediately in formation of SiC-film absorption band edge. The states localized due to accumulation of defects, as well as the interaction of those states, result presumably in formation of subbands within the band gap. Absorption is formed up under involvement of direct and indirect allowed transitions between states of the allowed band and subband. Thus, in samples from II and I series, the band edge is formed under involvement of indirect transitions $E_1 = 2.32$ eV and $E_2 = 3.45$ eV and direct transitions $E_3 = 5.03$ eV (series III). It should be noted that in spectra of films deposited at $T_s = 600$°C (I series), along with the main absorption band ($E_1 = 2.32$ eV), shoulders are seen near 3.0 eV and 5.0 eV, whereas in spectra of films deposited at $T_s = 700$°C (II series), a band at 5.0 eV is present. In other words, the absorption bands near 2.30 eV, 3.00 eV, 3.40 eV, and 5.20 eV are present in every sample, though having significantly different intensity values.

Results of fundamental absorption edge approximation demonstrate the existence of not only exponential area of absorption, but as well of that meeting the power law. In fact, in $(\alpha h\nu)^{1/2} - h\nu$ coordinates, within 1.64 to 2.09 eV, 2.56 to 3.28 eV and 4.0 to 4.82 eV ranges for I, II and III series, respectively, the curves tend to be linear (Fig. 5). Therefore, with account for [5], the long-wave increase of parameter α at such the energy values can be attributed to indirect

transitions. Extrapolation of dependences $(\alpha h\nu)^{1/2} \to 0$ allows to determine E_g. As a result, optical gaps make up 1.13 eV, 1.31 eV, and 2.08 eV for the three cases, respectively. For convenience, the optical absorption characteristics and the electron structure parameters of SiC films depending on the preparation conditions are summarized in Table.

Knowing the extinction coefficient dependence $\kappa = \kappa(h\nu)$, the limiting band gap width can be determined typical of strongly structurized films. The presence of various defects in films results in a gently drop of long-wave absorption edge. The observed E_g variation can presumably be explained by formation of a certain amount of homogeneously tied molecules and clusters of C–C and Si–Si, which emerge at low-temperature (<1000°C) synthesis of silicon carbide films. Moreover, a considerable contribution to E_g variation is due to deep levels of radiation-induced defects (such as vacancies, interstice atoms and complexes thereof) being caused by ion bombardment of film being synthesized. This is, the composition disorder grows up and optical gap reduces, followed by increase of optical constants. Evaluation of refractive index for deposited SiC films shows that its value exceeds considerably that for single crystals within the spectral region in study. For example, at $\lambda = 750$ nm, the refractive index may vary from 2.98 to 4.2, depending on deposition regime. Optical properties of such a material can be described within the frame of effective environment theory. This assumes a necessity to use the diffuse reflection method for film samples, which would facilitate an accurate measurement of SiC film absorption characteristics.
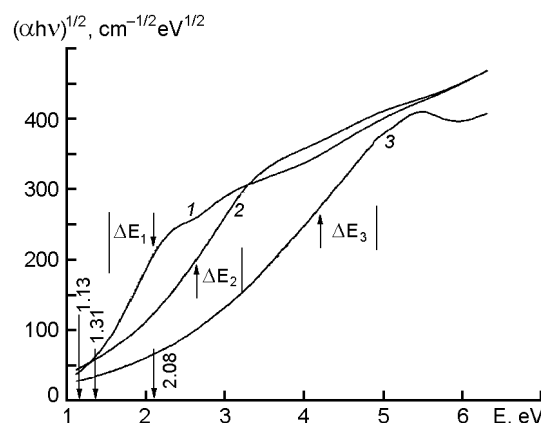

Fig. 5. Dependences $(\alpha E)^{1./2}$–$\hbar\omega$ of SiC-films for samples from series I (*1*), II (*2*) and II (*3*).

Thus, in the work, silicon carbide films with reproducible optical characteristics have been obtained by direct ion deposition. A relatively simple control method for optical characteristics by changing important technological regime parameters (such as substrate temperature and ion energy) has been demonstrated. It was shown that spectral methods provide not only determination of optical mobility gap, but show its variation as well. The spectral absorption curves and intrinsic absorption edge of SiC films are shown to be well describable by exponential and power laws. The variation range of the band gap (1.13 to 2.08 eV) and of intrinsic absorption coefficient is determined (10^4 to 10^5 cm^{-1}). At sapphire substrate temperature change from $T_s = 600$°C to $T_s = 800$°C, intensities of optical transitions that correspond to various modifications (i.e., polytypes) of silicon carbide vary. These facts define widening or narrowing of optical gap, thus changing greatly the possibilities of the film application.

Table. Experimental values of energies of electronic transitions and their interpretation

Series	Temperature of substrate, T_s °C	Transition energy, E, eV	Interpretation of experimental results		Parameter E_g (optical gaps), eV
			Transition type	SiC polytype (modification)	
I	600	2.32	indirect X_{3c}–Γ_{15v}	3C–SiC	1.13
II	700	3.45	indirect M_{4c}–Γ_{5v}	4H–SiC	1.31
III	800	5.03	direct Γ_{1v}–Γ_{15v}	3C–SiC	2.08
		5.26	direct X_{3c}–X_{5v}	3C–SiC	

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Оптичні властивості плівок карбіду кремнію, одержаних методом прямого іонного осадження

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Досліджено спектри оптичного пропускання, поглинання та відбиття тонких плівок карбіду кремнію, осаджених з потоку іонів вуглецю та кремнію на сапфірові підкладки. Плівки одержано при різних технологічних параметрах осадження: при варіації енергій іонів і температур підкладок. Вивчено поведінку оптичних характеристик плівок в залежності від впливу зміни технологічних параметрів. Показано, що метод прямого іонного осадження дозволяє керувати оптичними параметрами плівок у широких межах.