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Absorption edge of nanocrystalline cubic silicon carbide films

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The optical absorption edge of nanocrystalline films of cubic silicon carbide polytype (*nc*-SiC) obtained by direct ion deposition have been studied using optical spectroscopy. Within the 1.12–6.5 eV, three optical absorption regions have been found with different (exponential, power, and oscillating) dependences of the film absorption coefficient on the photon energy. Basing on the proposed structure model, the spectral dependence of absorption coefficient has been related to the defect states of *nc*-SiC, to direct and indirect optical interband transitions, and with dimensional quantization effects.

Методом оптической спектроскопии изучен край оптического поглощения нанокристаллических плёнок кубического политипа карбида кремния (*nc*-SiC), полученных методом прямого ионного осаждения. В диапазоне 1,12–6,5 эВ выделены три области оптического поглощения с различной зависимостью коэффициента поглощения пленок от энергии фотона: экспоненциальной, степенной и осциллирующей. На основе предложенной структурной модели плёнок спектральная зависимость коэффициента поглощения связывается с дефектными состояниями *nc*-SiC, с оптическими прямыми и непрямыми межзонными переходами и эффектами размерного квантования.

Silicon carbide (SiC) is a semiconductor with a wide band gap, this fact provides its applications in high-temperature and superpower electronics [1]. The existence of polytypes and an extra resistance against hard radiation are the SiC properties of great importance. Therefore, it is possible to use SiC films in sensors being operated in hard conditions or in UV range. For applied purposes, it is just the low-temperature SiC deposition techniques (<1400°C) that are of a special good promise, because that way provides a widened range of supports in technical use and an integration with silicon technology. It has been shown before [2] that at low temperatures, the SiC films on supports can be formed as amorphous phases, polycrystals, and single crystals. The SiC films deposited in some low-temperature conditions show a complex phase composition and are nanocrystalline [3]. The structural variety causes some difficulties in studies of the structure and properties of such films. The study of the fundamental absorption edge makes it possible to investigate the electron transitions in the silicon carbide films and to obtain information on electron levels related to short-range and intermediate-range atomic order in the SiC films and thus to characterize the absorption peculiarities in those nanostructured films. That is why the purpose of this work is to study the optical absorption of the nanocrystalline SiC films in the region of the fundamental absorption band followed by the study of the structure properties thereof.

For the study, selected were nanocrystalline SiC films of predominant cubic polytype 3C-SiC structure used widely in electrooptics. The silicon carbide films were deposited onto Al_2O_3 (0001) dielectric substrates using the direct ion deposition technique [4]. To obtain the films of predomi-

nant 3C-SiC structure, the conditions determined before [5] were used: the ion energy $E \approx 100$ eV at the substrate temperature $T_s \approx 1000$°C. The absorption and reflection spectra within the 190 to 1100 nm range were measured using a Perkin-Elmer Lambda 35 spectrophotometer according to known procedures [6]. The structure of deposited SiC films was examined by X-ray diffraction (XRD) method using a diffractometer with copper anode (CuK_α: $\lambda = 1.54176$ Å) in $\theta - 2\theta$ geometry. The morphology of the films was studied by atomic force microscopy (AFM).

The photoelectron spectroscopy (PES) spectra [5] have shown that the atomic concentration ratio of Si and C in the SiC films is about 0.9. The silicon carbide content is 60 % as calculated basing on the peak areas. Besides of the SiC phase, the homobound Si and C phases as well as small amounts of SiO_x and CO_x compounds are revealed in PES spectra.

Fig. 1 shows a typical X-ray diffraction spectrum for a structure selected from the series of films deposited on Al_2O_3 (0001) substrates. In the spectrum, lines related to crystalline silicon, Si (111), Si (220), Si (311) are clearly identified at $2\theta = 28.3°$; 42.8°; 56.01°, respectively. The crystalline silicon is like to be formed from silicon unreacted with carbon. The free carbon is also capable of a carbon phase formation, but no diffraction reflections from carbon phases

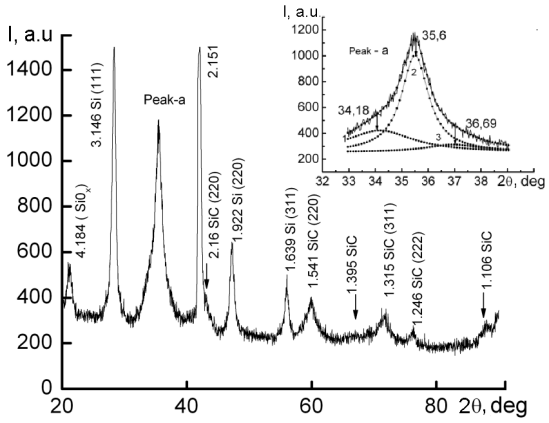

Fig. 1. XRD spectrum of a *nc*-SiC film deposited at substrate temperature 1000°C and ion energy 100 eV. Inset: approximation example of a compound diffraction peak (peak *a*).

are observable. Perhaps this is connected with a low atomic factor of carbon. The consideration of reflection maxima corresponding to silicon carbine phases ($2\theta =$ 35.7°; 42.09°; 59.87°; and 71.49°) has shown that the main polytype in the studied SiC film is cubic 3C-SiC, rhombohedral polytypes 21R-SiC and 15R-SiC being present, too. The analysis results and structure parameters calculations are summarized in Table 1.

The size of silicon carbide and silicon crystallites (or the coherent scattering regions) was determined using the Scherrer

Table 1. Structure parameters.

Position of maxim XRD spectrum $\omega = \theta_0$°	21.2	28.32	35.7			42.09	47.23	56.01	59.87	67.11	71.49	76.32	88.52
			the approximation										
			34.18	35.6	36.96								
Half-width $\Delta\theta$°	0.91	0.526	3.05	1.6	2.65	1.78	0.76	0.652	2.097	1.14	2.21	1.47	4.297
Polytype or the chemical element	SiO_x	Si(111)	21R-SiC	3C-SiC	51R-SiC	3C-SiC	Si (220)	Si (311)	3C-SiC	15R-SiC	3C-SiC	15R-SiC	15R-SiC
Interplanar The distance d_{hkl}	4.184	3.146	2.62	2.51	2.424	2.16	1.922	1.639	1.54	1.395	1.310	1.246	1.106

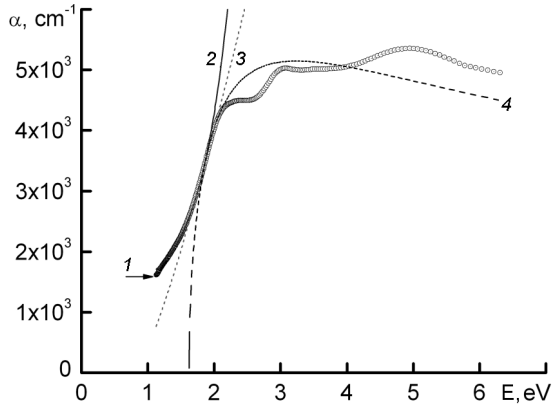

Fig. 2. Absorption coefficient of a *nc*-SiC film as a function of the photon energy. Curve *1* — experimental, curves *2*, *3*, *4* — calculated. Curve *2* is calculated according to the Urbach formula: $\alpha = 1225.6 \exp[(h\nu - 1.7)/0.42]$. Curves *3* and *4* are calculated according to the Tauc formula. Curve *3* — $(\alpha\nu h)^{1/2} = A(h\nu - E_g)$, $A = 4766.7$ cm$^{-1/2}$·eV$^{1/2}$, $E_g = 1.09$ eV; Curve *4* — $(\alpha\nu h)^2 = B(h\nu - E_g)$, $B = 13097$ cm^{-2}·eV^2, $E_g = 1.7$ eV.

formula [7]. The SiC film can be presented as a set of cubic 3C-SiC polytype nanocrystals of about 7.0 nm size, some amount of rhombohedral 21R-SiC and 15R-SiC polytype nanocrystals of about 4.0 nm to 10.0 nm size, and silicon nanocrystals with interboundary region containing disordered phases of silicon carbide and oxides (SiO_X, CO_X). The structure peculiarities of the SiC films define the spectral characteristics thereof. Fig. 2 presents the spectral dependence of absorption coefficient α on the photon energy $h\nu$ for a silicon carbide film. The α values for SiC films deposited onto a transparent dielectric substrate were calculated taking into account the reflection coefficient as described in [6]. Three regions of optical absorption can be distinguished basing on behavior of the fundamental absorption edge. The first region corresponding to the photon energy range of 1.124–1.88 eV demonstrates an exponential dependence and is due to optical transitions including directly the defect states [8]. It has been shown [9] that account for the scattering on impurities results in a change in the state density functions at the gap edges that correspond to formation of the final state density "tails" decreasing exponentially into depth of the band gap. The optical transitions between the parabolic part of a band and the tail of another one result in a shift of the fundamental absorption edge towards longer wavelengths where the absorption corresponds to the following empirical rule [9]:

$$\alpha = \alpha_0 \exp[(h\nu - E_g)/E_u]. \qquad (1)$$

Here α_0 is a constant; E_u, the logarithmic slope of the absorption coefficient that characterizes the Uhrbach tail width and means that the absorption below the direct band is contributed by both static structure disorders and dynamic thermal ones. It has been shown [10] that at room temperature, the structure disorder due to grain boundaries and other defects provides the dominating contribution to the Uhrbach tail. The approximation results of the $\alpha(h\nu)$ curve are presented in Fig. 2. The exponential absorption region is described well as $\alpha = 1225.64 \exp[(h\nu - 1.72)/0.42]$. As is seen, for the films described in this work are characterized by rather high E_u values (about 0.42 eV) that evidence the presence of disordered regions in the sample studied.

The second absorption region (1.72 to 2.09 eV) is described by a power function that is due usually to direct and indirect interband transitions. The absorption coefficient dependence on the photon energy for interband optical transitions has the form

$$\alpha E = A(E - E_g)^m, \qquad (2)$$

where A is a constant connected with the band structure features; E_g, the optical band gap width; $m = 1/2$ corresponds to direct interband transitions and $m = 2$, to indirect ones. Having constructed the dependences of $(\alpha h\nu)^{1/m}$ on $h\nu$, we have determined E_g by extrapolating the straight line to intersection with the E axis for two cases, namely, direct and indirect transitions (Fig. 3). In the case $m = 2$, the curve is seen to include a linear section crossing the E axis at $E^i_g = 0.7$ eV. The obtained value $E^i_g = 1.1$ eV corresponds to indirect transitions in the studied SiC film. For direct interband transitions ($m = 1/2$), there are three linear sections. The E^d_g values for those three straightened sections (*a*, *b*, and *c*) of the absorption curve $(\alpha h\nu)^2$ are 1.7 eV; 2.34 eV, and 2.96 eV, respectively. The existence of direct optical band having the value of 1.7 eV cannot be explained by the dependence of the optical band width on the nanocrystal size [12], because the average nanocrystal size for silicon (according to

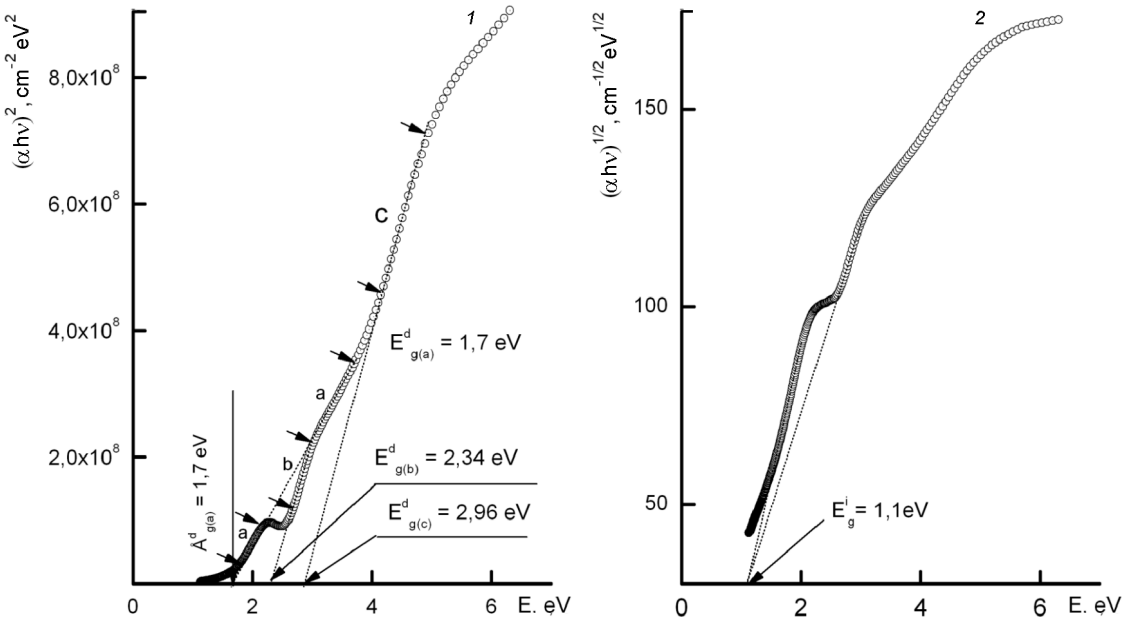

Fig. 3. Approximation of the absorption spectrum of a *nc*-SiC film by functions $(\alpha h\nu)^2$ (Curve *1*) and $(\alpha h\nu)^{1/2}$ (Curve *2*).

Scherrer) is 19 nm and exceeds considerably the Bohr radius for electrons and holes (about 3.1 nm). However, it has been shown [13] that when a SiO_x ($0 < x < 2$) interface layer is present in silicon nanocrystals, the band gap width is defined by the transition at the Si/SiO_x interface, depends only slightly on the crystallite size, and has the value $E_g = 1.7$ eV. The next two E_g values are close to those for band gap of cubic 3C-SiC and 21R-SiC polytypes, respectively [14, 15].

In third region (>2.09 eV), the absorption coefficient oscillates. Four maxima are observed in the absorption curve. To identify the maxima, the absorption coefficient curve was approximated by Gaussians (Fig. 4). The 1st maximum ($E_{max1} = 2.34$ eV) has a rather large halfwidth ($\Delta E = 0.88$ eV). The expansion in Gaussians favors identification of next maxima ($E_{max2} = 2.96$ eV, $E_{max3} = 3.6$ eV, and $E_{max4} = 4.45$ eV). The four maxima are nearly equidistant with the average spacing $\Delta E_{int} \approx 0.62$ eV. Such a large ΔE_{int} cannot be ascribed to electron-phonon interaction having usually constants not exceeding 0.2 to 0.3 eV [16]. In our opinion, those oscillations are due to quantum-dimensional quantization of the electron-hole pair energy [17]. To study the absorption coefficient curves in more detail, the derivatives $d\alpha/d\lambda$ were plotted. In the case of dimensional

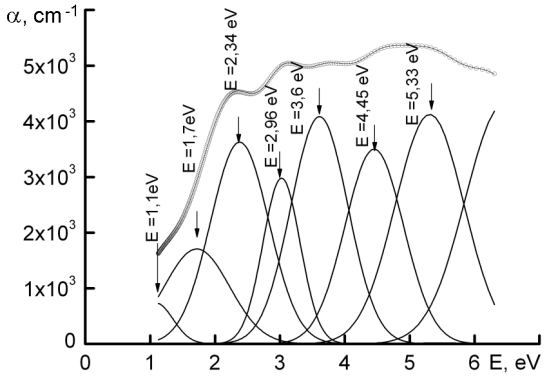

Fig. 4. Approximation of absorption coefficient curve for a *nc*-SiC film by Gaussians.

quantization, as it is shown in [18], the following relationship should be met:

$$n = E_n(d\alpha/d\lambda)_n / E_1(d\alpha/d\lambda)_1. \qquad (3)$$

Here n is an integer; $(d\alpha/d\lambda)_n$, the derivative value at each threshold energy of optical transition, $E_n = h\nu$. Substituting the derivative and transition energy values, n values were obtained to be 2.08 and 3.14 for $n = 2$ and 3, respectively. This can be considered as a confirmation for dimensional quantization. The insignificant discrepancy between the substitution results and integer n values as well as the blurring of absorption peaks is to be explained by the dispersion of SiC nanocrystallite sizes [17].

The dispersion in the nanocrystalls size results in smoothed absorption curve in the high-energy region [20].

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Край поглинання нанокристалічних плівок кубічного карбіду кремнію

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Методом оптичної спектроскопії досліджено край оптичного поглинання нанокристалічних плівок кубічного політипу карбіду кремнію (*nc*-SiC), одержаних методом прямого іонного осадження. У діапазоні 1,12–6,5 еВ виділено три області оптичного поглинання з різною залежністю коефіцієнта поглинання плівок від енергії фотона: експоненціальною, степеневою та осциляційною. На основі запропонованої структурної моделі плівок спектральна залежність коефіцієнта поглинання пов'язується з дефектними станами *nc*-SiC, з оптичними прямими та непрямими міжзонними переходами та з ефектами розмірного квантування.