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Structural and optical characteristics of disordered silicon carbide films

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Using spectrophotometry and electron microscopy, the properties of disordered SiC films have been studied. A nontrivial character of spectral absorption has been revealed depending on the structural and polytype constitution of the films. SiC polytypes forming the film and the band gap widths have been determined. It has been shown that in this case, it is possible to obtain the information on the optical band-to-band transition modification depending on the film structure property and phase composition as well as on the influence of various phases and SiC film crystallinity extent on the band gap width.

С использованием методов спектрофотометрии и электронной микроскопии изучены свойства неупорядоченных плёнок карбида кремния. Обнаружен нетривиальный характер спектра поглощения, зависящий от структуры и политипного состава плёнок. Определены политипы карбида кремния, входящего в состав плёнки и величины оптической ширины запрещённой зоны. Показано, что при этом можно получить информацию о видоизменении оптических межзонных переходов в зависимости от изменения структуры и фазового состава плёнок и о влиянии различных фаз и степени кристалличности плёнок SiC на ширину запрещённой зоны.

Thin silicon carbide films demonstrate some properties that make these materials rather promising for application in fields of optics and electrooptics. The modern ion-plasma technology of SiC film fabrication provides deposition of thin silicon carbide films (either in crystalline or amorphous state) onto dielectric substrates [1]. Amorphous films are peculiar in possessing the density-of-state "tails" with the explicit form being defined by value of deviation from ideal periodicity; and edges of mobility zones which separate localized states from non-localized ones. The above films are a main experimental material for working up the manufacturing technology of polycrystal and single-crystal SiC films [2]. To study such films, complex measurements of their micro-structure, phase (i.e., polytype) composition and optical characteristics are necessary. The goal of this work is to study the most informative characteristics such as spectral dependences of absorption and reflection of silicon carbide films in connection with their microstructure and polytype composition.

Subjected to these studies were two series of silicon carbide films of about 100 nm thickness prepared by direct ion deposition onto KCl substrates being at room temperature for the first series (I) and heated up to $T = 500^{\circ}\mathrm{C}$ for the second one (II). Influence of sapphire substrate temperature (as well as energies of ions being deposited) on structure and properties of thin films have been investigated in detail before [3]. The microstructure and phase composition of silicon carbide films were studied using transmission electron microscopy (a PEM-U electron microscope, 80 kV acceleration voltage, with subsequent photometric scanning of blackened photo-

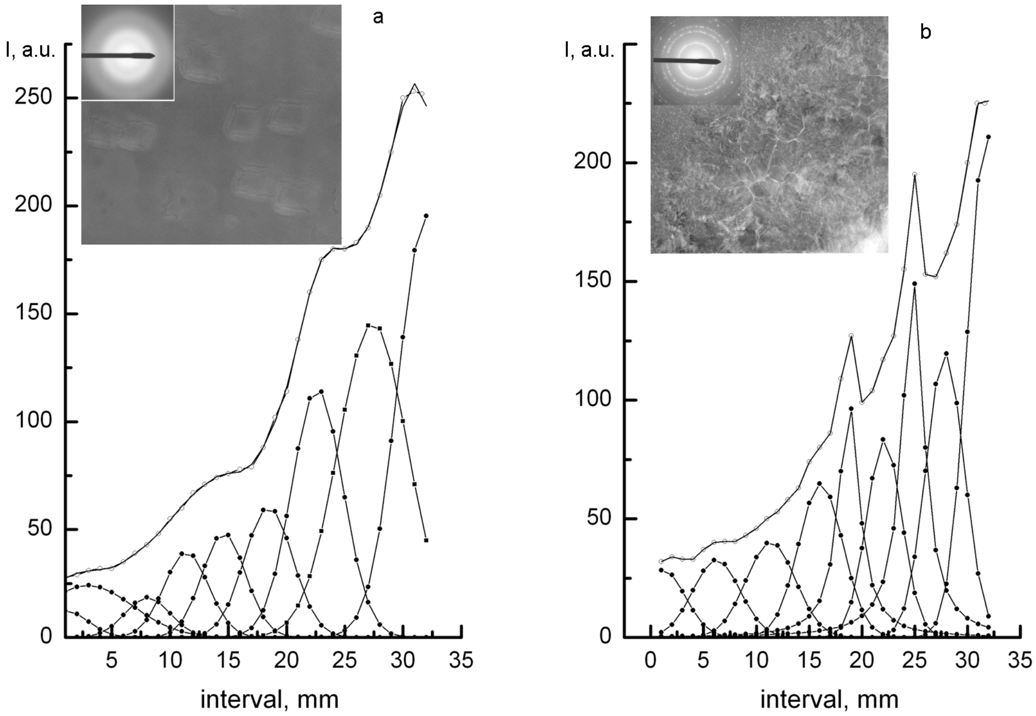

Fig. 1. Photometric curves of electron diffraction for the films of Series I (a) and II (b). Insets: electron microscopic images of the films from Series I and II and diffraction micropatterns from these films.

film) and plotting the dependence of photofilm blackening intensity on the scanning step length along diffraction ring diameter. To evaluate the diameters of diffraction rings, the blackening of photometric curves was approximated by a set of Gaussians. The above method was consisted in search for resultant approximation curves that would agree with experimental curve at a minimal error. In fact, the optimal approximation was attained using 9 to 12 Gaussians. In that cases, the r.m.s. deviation of calculated results vs experimental ones made up $2 \cdot 10^{-3}$. The use of approximation techniques made it possible to determine the diameters of halo rings and to evaluate the degrees blurring and intensity of diffraction reflections from the height and semi-width of Gaussians. This addition by-product of the above-mentioned method is especially useful at investigation of disordered and amorphous films in cases when boundaries of halo are significantly blurred off (i.e., diffused). The optical properties of deposited SiC-films were studied by measuring the reflection and transmission spectra in 190–1100 nm spectral range, using a Perkin Elmer "LAMBDA-35" spectrophotometer with a diffusion light reflection adapter.

The Series I thin films are non-uniform ones, that is, simultaneously with proper irregularities (which resemble boundaries of grains) clearly seen on background of amorphous matrix, there also exists a crystalline morphology of rather regular rhomb-shaped formations, about 30 nm in size. Fig. 1a presents an electron diffraction pattern taken from a disordered portion of an experimental film. The image shows a diffusion-blurred halo with practically even intensity that makes it impossible to distinguish between the profiles of diffraction rings. Application of approximation methodology used in this experiment made it possible to discern the profiles of diffraction rings and thus to determine coordinates of diffraction maxima for various groups of SiC polytypes. Fig. 1b shows the results of a similar experimental processing of photometric curves for Series II thin films containing about 800 to 1000 nm sized crystalline inclusions. Results of approximation methodology in use are also represented in Table.

As to the disordered areas of Series I thin films, the most typical are reflections with gravity center $d_{hkl} \approx 3.135$ Å which correspond to silicon phase [4]. The remaining atomic interplanar spaces correspond to

Table 1. Structural parameters and polytupes of experimental samples

Sample	d_{hkl}								
Film of Series I	1.132	1.218	1.309	1.54	1.692	1.92	2.17	2.511	2.135
the polytype	6H	6H	3C	3C, 4H, 15R	15R	Si	3C	3C, 6H	Si
Film of Series II	1.139	1.177	1.310	1,54	1.609	1.84	2.36	2.51	3.14
the polytype	4H	4H	3C	3C, 4H, 15R	4H	4H	6H	6H	Si

cubic, rhombohedral, and hexagonal polytypes of silicon carbide (3C-SiC, 4H-SiC, 6H-SiC, and 15R-SiC, respectively) with disordered structures [5].

It is to note that as to Series II thin films, the above-mentioned electron diffraction pattern provides a more clear distinction of diffraction rings. Judging from the Figure showing the approximation curves, some changes can be noted for locations and semi-widths of peaks, which all is an evidence of d_{hkl}. value variation. These results demonstrate that the series II films contain polycrystalline areas with experimentally obtained d_{hkl} values being in agreement with the same parameter for silicon carbide of hexagonal 4H-SiC structure and 6H-SiC inclusions.

Fig. 2 represents the spectral dependences $(\alpha h\nu)^{1/2}$ on the photon energy for two types of thin films. Here, α is the absorption coefficient, its measurement procedure is described in [6]. The Figure clearly shows that spectral curves of absorption differ notably from each other. Thus, values of E_g for optical gap (determined from the function $(\alpha h\nu)^{1/2}$ plot) made up 1.78 eV and 2.45 eV for Series I and Series II thin films, correspondingly.

Moreover, there are further differences in exponential sections of curves. The Urbach energy E_U (which is known as a measure for disorder) evaluated from the spectra made up 0.9 eV and 0.5 eV for Series I and Series II samples, respectively. Thus, values of E_g and E_U demonstrate an ordering of structure, being in a good correlation with results of electron microscopy examinations. It has been shown that with increasing substrate temperature, the crystallization processes become intensified, whereby composition of polytype phases tends to shift towards area of hexagonal polytypes. The optical gap E_g values for Series II samples tend to increase, making up approximately a mean arithmetic value between those values of optical forbidden bands for polytypes silicon carbide 3C, 4H, 6H, 15R and Si.

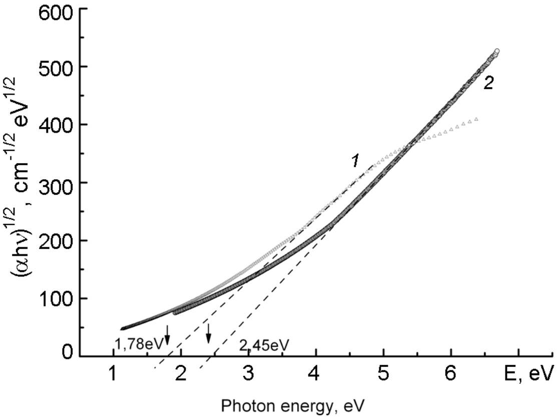

Fig. 2. Spectral dependences of $(\alpha h\nu)^{1/2}$ value on photon energy.

Thus, it has been shown that utilization of independent analysis methods of spectrophotometry techniques and electron microscopy makes it possible to get detailed characteristics of silicon carbide films in various phase and structural states. As a result, the information becomes available on transformation of optical interband transitions, depending on changes in the film structures and phase compositions, influence of different phases on band gap width, and crystallinity degree of SiC films.

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Структурні та оптичні характеристики невпорядкованих плівок карбіду кремнію

О.В.Лопін

З використанням методів спектрофотометрії і електронної мікроскопії досліджено властивості невпорядкованих плівок карбіду кремнію. Виявлено нетривіальний характер спектра поглинання, залежний від структури і політипного складу плівок. Визначено політипи карбіду кремнію, що входять до складу плівки, і значення оптичної ширини забороненої зони. Показано, що при цьому можна отримати інформацію про видозміну оптичних міжзонних переходів залежно від зміни структури і фазового складу плівок, про впливи різних фаз та міри кристалічності плівок SiC на ширину забороненої зони.