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Interface features of SiO_2/SiC heterostructures according to methods for producing the SiO_2 thin films

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Abstract. In this work, we studied comparative characteristics of the SiO_2/SiC heterostructures. The following two techniques were used for SiO_2 formation: thermal oxidation in water vapor (i) and oxidation in solution (ii). According to experimental results obtained from optical absorption and photoluminescence spectra as well as from measurements of internal mechanical stresses, one can conclude that the thin SiO_2 films prepared using the technique (ii) possess SiO_2/SiC interface with a less number of defective states than that for SiO_2 films prepared using the technique (i).

Keywords: SiO_2/SiC, thermal oxidation, oxidation in solution, optical absorption, photoluminescence, internal mechanical stresses.

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1. Introduction

Development of new methods for preparing the structured thin films on silicon carbide compatible with integrated-microcircuit technology offers the challenge for making new devices and equipment with improved parameters. For instance, decrease of the gate insulator thickness provides in CMOS GSI speedup [1, 2]. One of the most preferable insulators for instrumental structures based on silicon carbide is SiO_2 due to its dielectric properties. This choice isn't due to only its insulators properties, but SiO_2 can be grown using thermal oxidizing techniques which are compatible with microelectronics technology [3-7]. The main problem of such technology still is preparation of a high-quality interface SiO_2/SiC with a minimal quantity of impurities.

Though dielectric properties of the SiO_2 layer grown on the silicon carbide are similar to SiO_2 on Si, but SiO_2/SiC interface has different from SiO_2/Si one-electronic properties. These properties are the result of interface impurities formed by high-temperature oxidation. Silicon-carbide-based device structures are intended for operation at higher temperatures, higher dissipated power, and these structures possess higher radiation resistance than that of silicon-based device structures [2, 8]. In this relation, search for further ways of the SiO_2/SiC interface enhancement seems to be a topical problem.

The defect concentration in this interface depends on heating temperature, duration of thermal oxidation, SiC substrates quality and also on growth conditions [5, 7].

2. Sample preparation and investigation technique

In this work, we studied thin SiO_2 films based on *n*-type silicon carbide substrate (6H-SiC polytype) grown using the Lely technique. The free electron concentration was $\sim 10^{18}\,cm^{-3}$. SiO_2 films were formed on the Si side of the silicon carbide substrate. The following two techniques were used: thermal oxidation in water vapor for 5 hours at the temperature $T = 1150$ °C and oxidation in solution where films from film-forming solution were deposited on silicon carbide substrate at room temperature in centrifuge. The solution is composed of butyl alcohol (C_4H_9OH), ethyl alcohol (C_2H_5OH), solution of hydrochloric acid (HCl), tetraethoxysilane ($(C_2H_5O)_4Si$) in the ratio $C_4H_9OH : C_2H_5OH : HCl : ((C_2H_5O)_4Si) = 5:1.5:1:2.5$. Then SiO_2/SiC structures were annealed in air for 3 min at $T = 800$ °C. The thickness of SiO_2 layer reached the values $d_{SiO2} \approx$ 70 nm (i) and $d_{SiO2} \approx$ 170 nm (ii).

We studied the optical absorption and photoluminescence (PL) spectra of SiO_2/SiC structures, measured also was the value of internal mechanical stresses (IMS) in these films.

3. Experimental results and discussion

The absorption spectra for both types of heterostructures SiO_2/SiC practically did not differ in the 400 to 800 nm wavelength range (Fig. 1). The absorption band observed at 630 nm is typical to absorption spectra of silicon carbide doped with nitrogen [9-12]. Since thin SiO_2 film was transparent in the observable wavelength range, absorption in the structure was the result of silicon carbide substrate and SiO_2/SiC interface [13, 14], so differences in absorption spectra were not observed.

According to the literature data [9-12], the wide band at 630 nm (Fig. 1) is related to the ground state of donor centers resulted from presence of nitrogen impurities in silicon carbide crystals. This band is observed on wide general background and is in coincidence with [12]. Existence of background absorption is explained by partial overlapping of the wide band (maximum at 630 nm) and two absorption bands: the more intense and wide boundary band and short-wave tail of the infrared absorption band. The bands mentioned above are determined by photoionization of the nitrogen with electron transition to the minimum of conduction band.

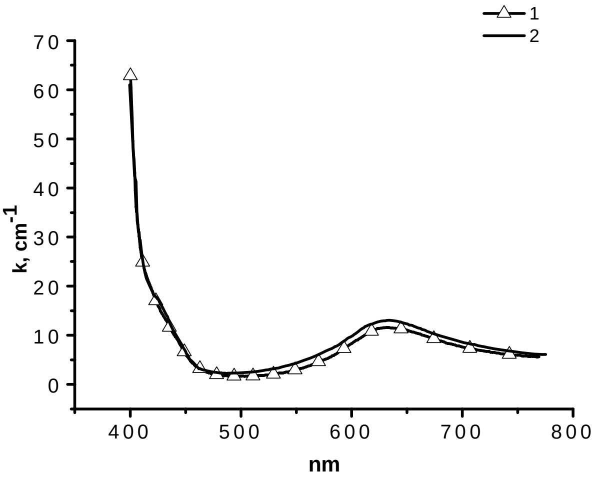

Fig. 1. Absorption spectra of the SiO_2/SiC heterostructures: 1 – SiO_2 layer was deposited using the thermal oxidation technique, 2 – SiO_2 layer was deposited using oxidation in solution technique.

The PL spectra of the SiO_2/SiC heterostructures (PL was excited from the side of SiO_2 film) have been shown in Fig. 2. As can be seen from this figure, the weak PL band is observed in 450…500 nm region of PL spectra. Since SiO_2 films are transparent in the observable wavelength range and the penetration depth of exciting radiation (λ_{exc} = 370 nm) for *n*-SiC single crystals are approximately 10 μm (silicon carbide substrate thickness ~ 460 μm), it can be considered that the PL spectrum is mainly related with the contribution of silicon carbide at the SiO_2/SiC interface. Consequently, particular changes in the PL spectra of the whole structure is primarily caused by changes in the properties of the oxide film and silicon carbide at the interface SiO_2/SiC, as well as by localization of substrate structural defects at this interface and the presence of IMS. The appearance of silicon carbide additional bands in the PL spectra within the range 400 to 500 nm is associated in literature with the presence of luminescence centers related to intrinsic defects or breach of stoichiometric silicon carbide crystals [15-17]. There is also evidence that centers providing contribution to the short-wave PL band ($\lambda_{max} \approx$ 500 nm) can be considered as point-defect complexes [15-17]. A slight change in the peak position of PL band for the samples with different ways of forming the thin SiO_2 film is the result of redistribution of defects localized at the interface SiO_2/SiC, apparently due to different values of the IMS at the interface SiO_2/SiC and depends on the method of film preparation on the substrate, which correlates with data from the heterostructure curvature (see Table). Localization of the defects caused by the presence of IMS at the interface SiO_2/SiC can be judged by the changes observed only in the PL spectrum that is mainly characterized by the state of the sample surface and the interface SiO_2/SiC. At the same time, the value of the band gap determined from optical absorption spectra that characterize the entire sample bulk remains unchanged.

The value of IMS for double-layer SiO_2/SiC structures can be calculated by Stoney's formula:

$$\sigma = \frac{E \cdot d^2}{6 \cdot (1-\nu) \cdot R \cdot d_1}, \qquad (1)$$

where E and ν are Young modulus and Poisson's ratio of the substrate, d is the substrate thickness, d_1 – film thickness, R – radius of heterostructure curvature. The radius of curvature was measured using the profilometer $\mathrm{P} - 201$ and calculated with the formula

$$R = \frac{m^2}{8l}, \qquad (2)$$

where l is bending deflection of the film-substrate structure, m – chord connecting the ends of the arc of a circle. In the film, compressive stresses will be, if it is on the convex side of the substrate, and expanding, if the film is on the concave side heterosystem. Results of experimental studies are presented in Table.

Table. Comparative characteristics of the SiO$_2$ films obtained using different methods (r_{av} – average value of the deflection radius; T – oxidation temperature; t – oxidation time).

Deposition method	d_1, nm	Sign of deflection	l, mm	m, mm	r_{av}, m	σ, GPa	Oxidation regime	
							T, °C	t, min
Thermal oxidation	70	–	79	3	40.63	7.79	1150	300
Oxidation in solution	170	–	86	2.5	30.82	4.41	800	3

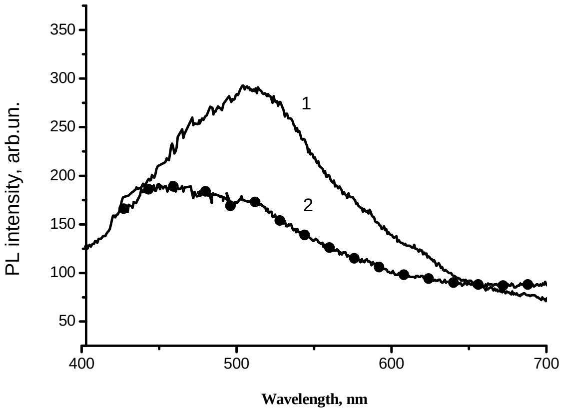

Fig. 2. SiO$_2$/SiC photoluminescence spectrum. 1 – SiO$_2$ layer was deposited using the thermal oxidation technique, 2 – SiO$_2$ layer was deposited using oxidation in solution technique.

According to these data, SiO$_2$ film is on convex side of the substrate. The value of compressive stresses in the sample obtained using the technique (i) is $\sigma = 7.79\cdot10^9$ N/m^2, which correlates with the data [14] for IMS values of the samples obtained by conventional thermal oxidation, and for the sample obtained using the technique (ii) $\sigma = 4.41\cdot10^9$ N/m^2.

In addition, the stresses in the film caused by the difference of thermal expansion coefficients can be estimated using the formula [18]

$$\sigma_{\Delta\alpha} = \frac{E}{1-\nu}\Delta\alpha\cdot\Delta T, \qquad (3)$$

where E and ν are Young modulus and Poisson's ratio of the film, $\Delta\alpha$ is the difference in thermal expansion coefficients of the epitaxial film and substrate, ΔT – temperature difference between the temperature of the film grown at room temperature.

As seen from (3), in this case the ratio of the stresses arising in SiO$_2$ films due to the difference between the thermal expansion coefficients of films grown using various techniques, will be determined by the ratio $\sigma_{\Delta\alpha1}/\sigma_{\Delta\alpha2} = \Delta T_1/\Delta T_2 \approx 1.5$ where the index 1 corresponds to the technique (i), and 2 – to the technique (ii). Thereof, it follows that the film SiO$_2$ obtained by thermal oxidation is more stressful.

Thus, the experimental results show that thin SiO$_2$ films obtained by oxidation in solution allows one to create the interface SiO$_2$/SiC with fewer defect states than the film SiO$_2$ obtained by thermal oxidation.

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