

## Ellipsometric investigation of $\beta$ - $\text{Si}_3\text{N}_4$ ceramics with Mo and Al additives

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Ceramic  $\text{Si}_3\text{N}_4$  samples with Mo and Al admixtures have been investigated by spectroellipsometry. The influence of admixtures on the ceramics optical properties have been studied. The local defects of  $\text{Si}_3\text{N}_4$  crystal structure are responsible for the band gap reduction. The silicone oxynitride amount in the studied samples has been estimated numerically by Bruggeman effective medium approximation.

Методом спектродипсометрии исследованы керамические образцы  $\text{Si}_3\text{N}_4$  с добавками Mo и Al. Изучено влияние добавок на оптические свойства керамики. За сужение запрещенной зоны ответственны локальные дефекты кристаллической структуры  $\text{Si}_3\text{N}_4$ . Количество оксинитрида кремния в исследованных образцах численно оценено с применением приближения эффективной среды по Брюггеману.

Silicone nitride ( $\text{Si}_3\text{N}_4$ ) is a structural ceramics of importance in numerous modern applications.  $\text{Si}_3\text{N}_4$  is used in automotive engine parts, cutting tools, machine components, etc. Silicone nitride and silicone oxynitride play an increasingly important part in electronic industry [1] and in optoelectronics [2, 3].  $\text{Si}_3\text{N}_4$  is usually prepared by high-temperature reaction binding or hot-pressing sintering process and therefore it is always in polycrystalline form with many defects and imperfections. Often, various sintering admixtures of metals and oxides are often added to the initial  $\text{Si}_3\text{N}_4$  powder. Those admixtures are necessary to provide stable intergranular joining in the course of sintering. Those may give rise to additional intergranular phase or solid solution of the admixture in the  $\text{Si}_3\text{N}_4$  phase [4]. Silicone nitride films prepared by chemical vapor deposition are likely to be amorphous. The polycrystalline  $\text{Si}_3\text{N}_4$  exists in two forms,  $\alpha$  and  $\beta$ , with  $\beta$ - $\text{Si}_3\text{N}_4$  to be thermodynamically more stable in the latter [5]. Both the  $\alpha$  and  $\beta$  phases have the same basic structural units with a tetrahedral binding for Si ( $\text{Si}-\text{N}_4$ ) and a binding for N ( $\text{N}-\text{Si}_3$ ). The unit cell of the  $\alpha$ - $\text{Si}_3\text{N}_4$  is twice as large as that of the  $\beta$ -phase, and the

phases differ in the stacking sequence of layer subunits along the  $c$  axis. The  $\text{Si}_2\text{N}_2\text{O}$  crystal can be considered as an intermediate phase between  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  [6]. Silicone oxynitride may appear as a secondary phase in the interfacial grain boundary of  $\beta$ - $\text{Si}_3\text{N}_4$ , and as a result of oxygen substitution for nitrogen during sintering process. This phase influences heavily the overall performance of silicone nitride-based structural ceramics.

The ceramic samples of  $\beta$ - $\text{Si}_3\text{N}_4$  were prepared by hot pressing at 1750–1880°C and 25 MPa. Al and Mo were used as the sintering additives. The Mo amount was the same for all samples (about 8 %), the Al one was varied (from 0.5 % to 3.5 %). The phase structure was studied by X-ray diffraction. All samples, except for  $\text{Si}_3\text{N}_4 + 0.5$  % Al, were identical in the phase structure consisting of  $\beta$ - $\text{Si}_3\text{N}_4$  and molybdenum disilicide  $\text{MoSi}_2$ . The aluminum did not produce a separate phase, but formed an interstitial solid solution in silicone nitride. In the sample with 0.5 % Al, the third phase of silicone oxynitride is present, too. The optical constants of  $\beta$ - $\text{Si}_3\text{N}_4$  ceramics in visible and ultraviolet region were measured by ellipsometry (Beatty method) [7] in

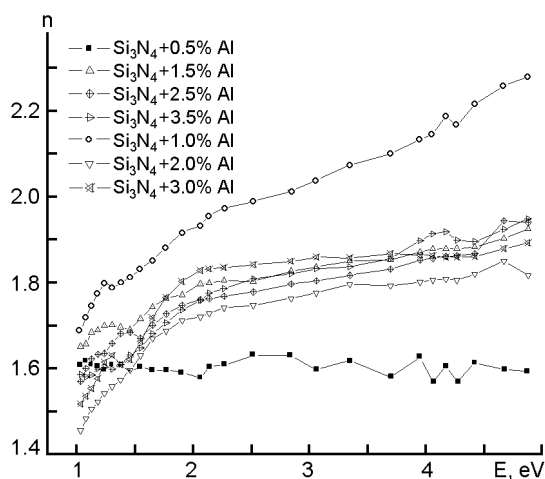


Fig. 1. Refractive index of  $\text{Si}_3\text{N}_4$ .

wavelength range of  $0.26 \mu\text{m}$  to  $1.2 \mu\text{m}$  (1 to 5 eV). The measurements were carried near the main angle of incidence about  $60^\circ$ . The polarization azimuth was  $\psi_A = 80^\circ$ , instead of  $45^\circ$ , because of weak reflection of the  $p$ -component. The reflected light intensity was measured at three fixed positions of the polarizer:  $0^\circ$ ,  $45^\circ$ , and  $90^\circ$ . Using the received light intensity  $I_0$ ,  $I_{45}$ ,  $I_{90}$ , the amplitude ratio and phase difference between  $p$ - and  $s$ -polarized reflected light were calculated. Optical constants, refractive index  $n$  and extinction coefficient  $k$  were calculated using metallographic formulas [7]. Then, using the correlation among the real and imaginary parts of dielectric function, the refractive index  $n$  and extinction coefficient  $k$ , the dielectric function was determined.

The experimental spectra of refractive index, real parts of dielectric function and optical conductivity are presented in Figs. 1, 2, 3. As is seen from Fig. 1 and Fig. 2, the dependences  $n(h\nu)$  and  $\epsilon'(h\nu)$  are rather similar to each other and increase with photon energy. In the IR region,  $\epsilon' > 0$ , and the low value of optical conductivity evidences that Mo and Al free electrons in the ceramics influence only slightly the optical properties. Mo and Al admixtures provide low free electron concentration in the conductive band. A maximum at 1.2–1.3 eV is present in  $n(h\nu)$  and  $\epsilon'(h\nu)$  diagrams (Fig. 1, Fig. 3). In this region, the hexagonal molybdenum disilicide shows a maximum [8] and we can assume that this is the cause of the above-mentioned maximum. In the spectra of samples  $\text{Si}_3\text{N}_4 + 1\%$  Al,  $\text{Si}_3\text{N}_4 + 1.5\%$  Al, and  $\text{Si}_3\text{N}_4 + 3.5\%$  Al, the bands at 1.9 eV and 3.8 eV are observed. Those

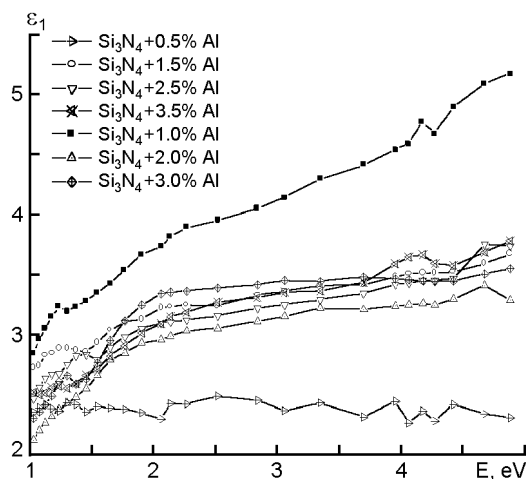


Fig. 2. Real part of dielectric function of  $\text{Si}_3\text{N}_4$  ceramic samples.

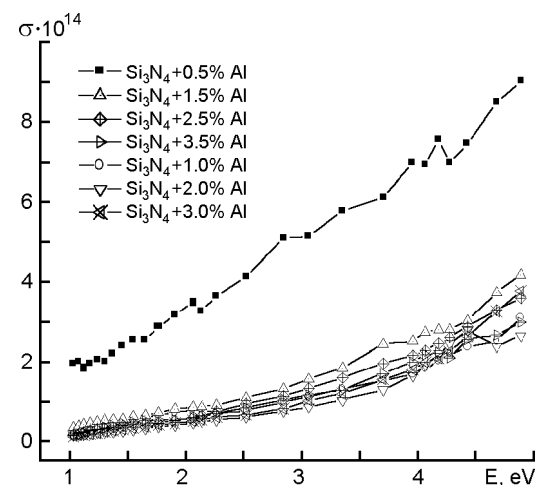


Fig. 3. Optical conductivity of  $\text{Si}_3\text{N}_4$  ceramic samples.

are related to hexagonal  $\text{MoSi}_2$  too. Those bands are absent in the spectra of other samples. This can be explained by formation of a disilicide modification with defect crystal structure (almost amorphous) during sintering. Such modifications show no explicit maxima. Aluminum exhibits a maximum at 1.5 eV which is only observed in the spectra of samples  $\text{Si}_3\text{N}_4 + 3.5\%$  Al and  $\text{Si}_3\text{N}_4 + 2.5\%$  Al.

The spectral dependence of extinction coefficient can be fitted by empirical formula [9]:

$$\frac{4\pi k}{\lambda} h\nu (h\nu - E_g)^k, \quad (1)$$

where  $\lambda$  is wavelength;  $E_g$ , band gap;  $k$  varies from 1 to 3 depending on the sample material. For silicone nitride,  $k$  was ac-

cepted to be 2 [10]. Using the correlation (1), the band gap values for silicone nitride ceramics have been determined.

The band gap width for  $\text{Si}_3\text{N}_4 + 0.5\%$  Al,  $\text{Si}_3\text{N}_4 + 1\%$  Al,  $\text{Si}_3\text{N}_4 + 1.5\%$  Al,  $\text{Si}_3\text{N}_4 + 2\%$  Al,  $\text{Si}_3\text{N}_4 + 2.5\%$  Al, and  $\text{Si}_3\text{N}_4 + 3\%$  Al samples is the same within the calculation error and amounts 3.9 eV. The  $\text{Si}_3\text{N}_4 + 3.5\%$  Al sample has a narrowed band gap,  $E_g = 3.7$  eV. The estimated band gap width is smaller than theoretical value calculated for pure  $\beta\text{-Si}_3\text{N}_4$  single crystal. The minimum band gap value is 4.96 eV, which corresponds to indirect transitions from the valence band top A to the conduction band bottom  $\Gamma$ , the direct transition  $\Gamma \rightarrow \Gamma$  energy being 5.25 eV. The experimental  $E_g$  value for  $\beta\text{-Si}_3\text{N}_4$  single crystal obtained by X-ray spectroscopy is 4.4 eV [11]. Our estimations of  $E_g$  are in good agreement with the results in [10, 12] where the band gap values were determined for ceramic and silicone nitride powders. Investigating of amorphous and  $\alpha\text{-Si}_3\text{N}_4$  films shows that the optical band gap increases smoothly from 1.75 eV to 5.5 eV depending on the stoichiometry of  $\text{Si}_{1-x}\text{N}_x$  [13, 14]. The band gap reduction is caused by the presence of broken Si-N and wrong Si-Si and N-N bonds. Both Si and N defect bonds introduce localized states into the gap. As the ceramics was sintered at high temperature and pressure, the broken crystalline structure of silicone nitride was obtained [1].

As is seen from Fig. 1, the refraction index of ceramic samples increases from 1.57 up to 2.1. The presence of admixtures has a little influence on the  $n(h\nu)$  dependence shape. The refractive index value is lower than that of pure  $\beta\text{-Si}_3\text{N}_4$ . The presence of oxygen influences strongly the refractive index [15]. The substitution of oxygen for nitrogen in silicone nitride occurs during the sintering process, so silicone oxynitride is formed. We used Bruggeman effective medium approximation [16] to estimate the silicone oxynitride amount. The effective dielectric constant  $\varepsilon$  of the physical mixture is described by the equation

$$(1 - c) \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} = c \frac{\varepsilon - \varepsilon_2}{\varepsilon_2 + 2\varepsilon}, \quad (2)$$

where  $c$  is the concentration of the admixtures with complex dielectric constant  $\varepsilon_2$  in the matrix with complex dielectric con-

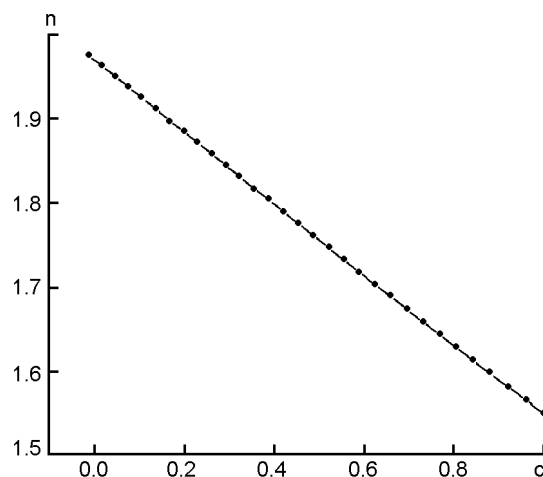


Fig. 4. The dependence of silicone nitride refractive index on silicone oxynitride concentration.

stant  $\varepsilon_1$ . The refractive index of pure  $\beta\text{-Si}_3\text{N}_4$  at  $\lambda = 632.8$  nm is 1.97 while for  $\text{Si}_2\text{N}_2\text{O}$ ,  $n = 1.55$  [6]. Using the equation (4), we have calculated the dependence of refractive index on oxynitride concentration. The result is presented as the  $n(c)$  diagram in Fig. 4.

The refractive index at  $\lambda = 632.8$  nm was within limits of 1.7–1.8 for all ceramic samples, except for  $\text{Si}_3\text{N}_4 + 0.5\%$  Al,  $n = 1.59$  and for  $\text{Si}_3\text{N}_4 + 1\%$  Al,  $n = 1.92$ . The lowered value in the former case is connected with as large amount of oxygen (the silicone oxynitride concentration was 0.88). It was confirmed by X-ray diffractometry: oxynitride phase was detected. The elevated value in the second case can be explained by low concentration of oxygen ( $c = 0.13$ ). The other ceramic samples contain  $\text{Si}_2\text{N}_2\text{O}$  concentrations within limits of 0.45–0.6. Using ellipsometry and effective medium approximation, we can estimate the oxygen amount in the ceramics.

Thus, ellipsometric investigation of silicone nitride ceramics and band gap calculation enable us to conclude that the gap decrease is connected with broken crystalline structure of  $\beta\text{-Si}_3\text{N}_4$  and formation of wrong interatomic bonds. Analyzing the experimental data on dielectric function and refractive index, we have concluded the formation of a crystalline modification of molybdenum disilicide during the sintering. The silicone oxynitride amount present in ceramic samples has been estimated by Bruggeman effective medium approximation.

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## Еліпсометричне дослідження кераміки $\beta$ - $\text{Si}_3\text{N}_4$ з домішками Mo та Al

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Методом спектроскопічного еліпсометрії досліджено керамічні зразки  $\text{Si}_3\text{N}_4$  з домішками Mo і Al. Вивчено вплив домішок на оптичні властивості кераміки. За звуження забороненої зони відповідають локальні дефекти кристалічної структури  $\text{Si}_3\text{N}_4$ . Кількість оксинітриду кремнію у досліджених зразках оцінено з застосуванням наближення ефективного середовища за Брюггеманом.