OPTICAL PROPERTIES OF SILICON-NITRIDE-BASED CERAMICS WITH MOLYBDENUM AND ALUMINUM ADMIXTURES

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The specimens of the Si_3N_4-based ceramics are investigated by X-ray diffractometry and spectroellipsometry. An influence of admixtures on the phase composition and optical properties of the ceramics has been studied. It has been found that the defects of the crystalline structure are responsible for the reduction of the band gap. It has been shown that, by analyzing the dispersion of the refractive index in the effective medium approximation, it is possible to estimate the amount of oxygen in the Si_3N_4-based ceramics.

Introduction

The silicon nitride Si_3N_4 is an important ceramic material which is widely applied in power, chemical, and automotive industry, in manufacturing the cutting tool, and as components of machines and mechanisms. Silicon nitride and silicon oxynitride are also widely applied in electronic industry in manufacturing the integrated circuits [1] and fiber-optic devices [2, 3].

The products made up of Si_3N_4 are produced, as a rule, with the help of reactions of high-temperature synthesis or methods of powder metallurgy (PM): sintering or hot pressing (HP) at high temperature and pressure. Therefore, they are always polycrystalline samples with defects of crystal structure and admixtures. Since it is not possible to derive products from a pure silicon nitride, the admixtures of oxides or pure metals are added to initial powders. Those admixtures are necessary for forming the stable connections between grains during sintering or HP. The admixtures can create an extra intergrain phase or form the solid solutions of an impurity and the basic phase of Si_3N_4 [4]. If Al_2O_3 is used as an admixture, a solid solution Si—Al—O—N is formed, which is called sialon. The specimens of Si_3N_4 prepared by chemical precipitation have a structure close to the amorphous one.

Single-crystalline Si_3N_4 has two forms: α and β, with the β-phase being thermodynamically more stable [5]. Both phases have identical base elements with a tetragonal bond Si—N_4 for Si, and the bonds in a plane for N—Si_3. An elementary cell in α-Si_3N_4 is twice as large than that in β-Si_3N_4, and the phases differ by a sequence of layers which make up the crystal along the axis C. A sequence ABAB... is realized for the α-phase, whereas the β-phase has a sequence ABCDABCD... . The crystalline structure of silicon oxynitride Si_2N_2O can be regarded as an intermediate phase between Si_3N_4 and SiO_2. The vitreous phase Si_2N_2O can appear both at the edges of the silicon nitride grains and because of the replacement of nitrogen by oxygen during HP or sintering. The oxygen can also diffuse into the interstitial space of the Si_3N_4 lattice [6].

Results of Research and Their Discussion

The specimens of Si_3N_4-based ceramics with molybdenum and aluminum admixtures were produced by hot pressing. The HP occurred under the pressure of 25 MPa at a temperature of 1750—1800° C. The molybdenum admixture in the amount of 8% was taken equal for every specimen. The aluminum admixture quantity was different for different specimens and changed from 0.5 to 3.5%.

The phase composition of the specimens was studied by X-ray diffractometry on a DRON-3 setup (Cu K_α-radiation). The researches were carried out in a range of angles $2\theta = 13 \div 51°$. An example of the X-ray diffraction pattern for specimen Si_3N_4+2.5%Al is shown in Fig. 1.

It was established by analyzing the X-ray diffraction patterns that specimens consist basically of the β-phase of Si_3N_4, and the phase of molybdenum disilicide $MoSi_2$ is also available in all specimens. Molybdenum disilicide is obviously formed at the edges of Si_3N_4 grains during HP. The constants of the $MoSi_2$ crystal lattice for different specimens lie in the ranges $a = 3.2062 \div 3.2160$ Å, $c = 7.8223 \div 7.8435$ Å. The scatter of the crystal lattice parameters can be explained by the formation of molybdenum disilicide with a disturbed crystal structure during HP. In specimen Si_3N_4+0.5%Al, in addition to the above-indicated phases β-Si_3N_4 and

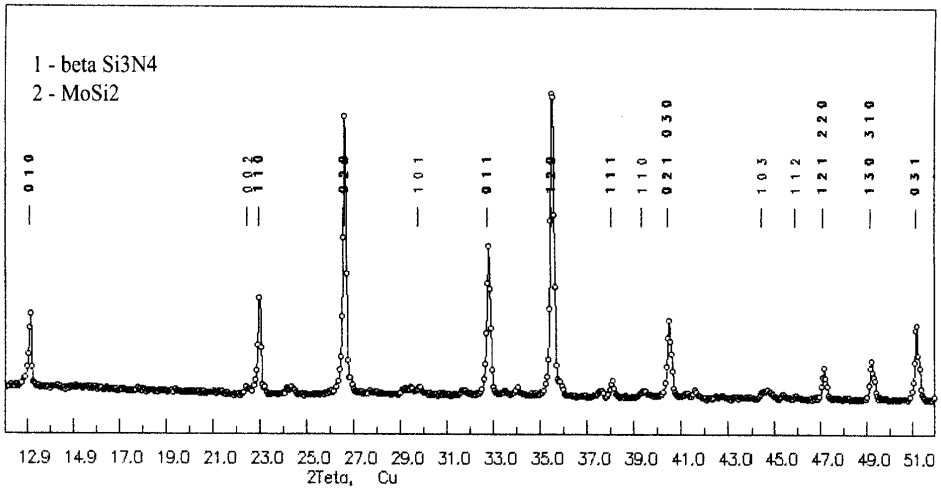

Fig. 1. Example of X-ray diffraction pattern, specimen Si_3N_4+2%Al

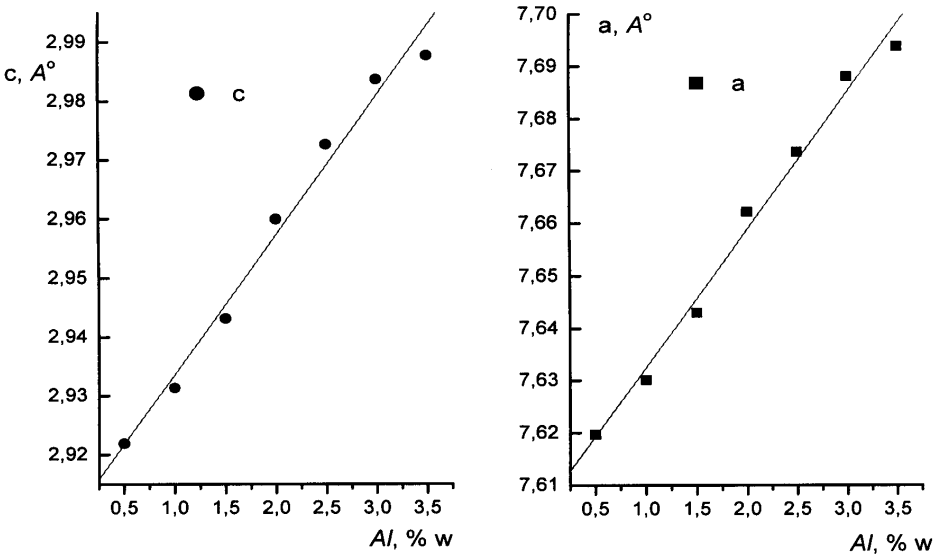

Fig. 2. Dependences of the Si_3N_4 crystal lattice constants on the Al-admixture concentration

$MoSi_2$, there are phases α-Si_3N_4 (about 5%) and silicon oxynitride (about 2%). In specimen Si_3N_4+2%Al, the phase Al_2O_3 is present explicitly. In other specimens, namely, Si_3N_4+1%Al, Si_3N_4+1.5%Al, Si_3N_4+2.5%Al, Si_3N_4+3%Al, and Si_3N_4+3.5%Al, the phases which contain aluminum or oxygen are not formed and do not reveal themselves at X-ray diffraction analysis.

The calculations of the crystal lattice constants for the β-phase of Si_3N_4 carried out by us on the basis of the X-ray diffraction patterns show that, as the content of aluminum increases, the lattice constants grow linearly. For example, the constant a increases from 7.6197 Å for Si_3N_4+0.5%Al to 7.6621 Å for Si_3N_4+3.5%Al. The same is analogously valid for the constant c: from 2.9133 Å to 2.9599 Å. The dependences of the crystal lattice parameters on the Al content are shown in Fig. 2. This makes it possible to conclude that Al does not form a new phase during HP but diffuses into the crystal lattice of Si_3N_4, thus resulting in an interstitial solid solution, contrary to Mo which forms an extra phase. After the establishment of a phase composition of the specimens, we studied their optical properties in a spectral range of 1—5 eV (1200—253.6 nm) by a Beattie ellipsometric method [7]. The research was carried out

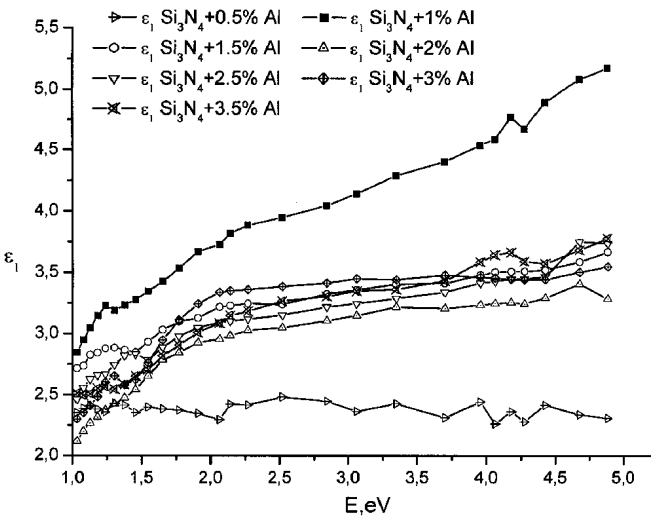

Fig. 3. Spectral dependences of the real part of the dielectric permittivity ε_1 of silicon nitride with various contents of Al

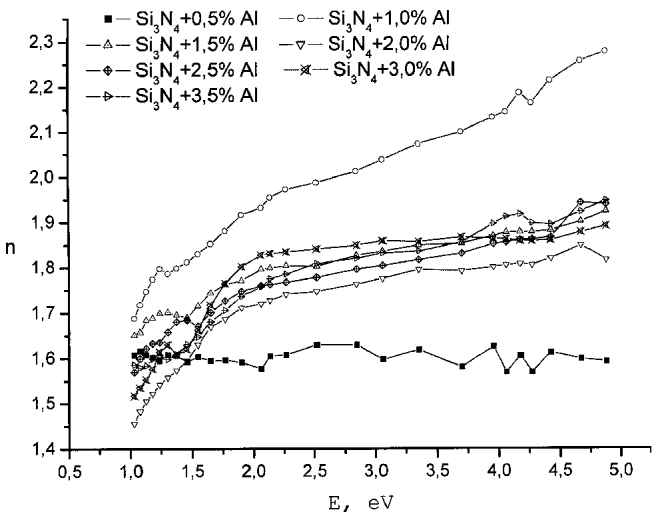

Fig. 4. Dispersion of the refractive index in the specimens of silicon nitride with various contents of Al

in the vicinity of the principal angle of incidence of 60°. The azimuth of the incident beam polarization was equal to $\psi_A = 80°$ rather than 45° because of a small value of the reflection factor with respect to the p-component of the light wave. The intensity of light reflected from a specimen was measured at three fixed angles of the polarizer: 0, 45, and 90°. Making use of the obtained values for the intensity, I_0, I_{45}, and I_{90}, the amplitude ratio ρ and the difference of phases Δ between p- and s-components of the vector of the electrical field of a wave reflected from the specimen were calculated as

$$\cos\Delta = \frac{2I_{45} - I_0 - I_{90}}{2\sqrt{I_0 I_{90}}}, \quad \tan\rho = \sqrt{I_0/I_{90}}\tan\psi_A.. \quad (1)$$

The optical constants, the refractive index n, and the absorption coefficient κ, as well as the value of the dielectric permittivity, were determined according to general metallographic formulae [7]. The experimental spectra of the real part of the dielectric permittivity ε_1, the refractive index n, and the optical conductivity σ vs. the photon energy $h\nu$ for specimens with various Al contents are displayed in Figs. 3–5, respectively.

Figs. 3 and 4 show that the dependences of ε_1 and n on $h\nu$ are increasing functions for all specimens. Fig. 3 shows also that $\varepsilon_1 > 0$ in the IR region for all specimens, and, in addition, the latter possess a small optical conductivity σ, which evidences for that the free electrons of Al and Mo slightly affect the optical properties of ceramic specimens. The Al and Mo admixtures give a small contribution to the concentration of free electrons in the conduction band of the crystal.

The maxima of the curves $\varepsilon_1(h\nu)$ and $n(h\nu)$ in the range of 1.2–1.3 eV are observed for all specimens in Fig. 4. A band corresponding to a hexagonal modification of molybdenum disilicide [8] becomes apparent in this range, and it is possible to assume that just this modification brings about the above-stated maximum. In specimens Si_3N_4+1%Al, Si_3N_4+1.5%Al, and Si_3N_4+3.5%Al, the bands with maxima at 1.9 and 3.8 eV are revealed, being also the bands of the hexagonal modification of $MoSi_2$. They are not observed in spectra of other specimens, although the X-ray phase analysis testifies to that $MoSi_2$ is present in all specimens. It can be explained by a forming of the crystal modification of molybdenum disilicide with a distorted crystal structure (closer to the amorphous state), which has no well-pronounced maxima [8].

Al has a clearly expressed maximum at 1.5 eV, which is observed nicely only in specimens Si_3N_4+3.5%Al and Si_3N_4+2.5%Al.

The growth of σ in the range of the photon energy of 3.9–4.9 eV is observed for all ceramic specimens (Fig. 5). Such a behavior of the optical conductivity is caused by interband transitions in Si_3N_4 in this spectrum interval.

The spectral dependence of the absorption factor is described by an empirical formula [9]

$$\frac{4\pi\kappa}{\lambda}h\nu \sim (h\nu - E_g)^k, \quad (2)$$

where λ is a wavelength, E_g is a band gap, k accepts values from 1 to 3, depending on a material. For Si_3N_4-

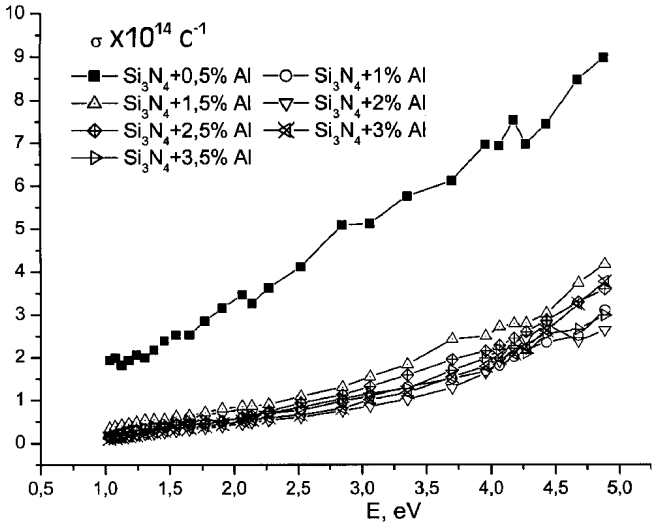

Fig. 5. Spectral dependences of the optical conductivity of the silicon nitride ceramics

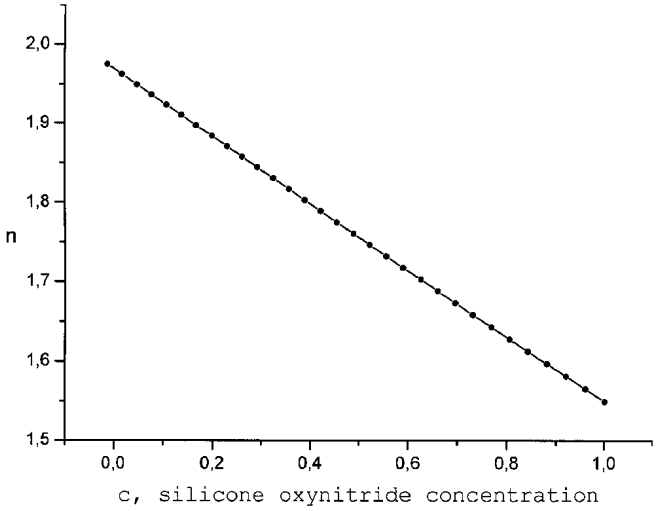

Fig. 6. Dependence of the refractive index of the silicon nitride ceramics on the silicon oxynitride concentration at $\lambda = 632.8$ nm

based ceramics, the value $k = 2$ is adopted [10]. Using relation (2), the band gap was calculated. The results of calculation are shown in the table. The obtained values for E_g, taking into account the experimental errors, can be considered identical for all specimens, except for Si_3N_4+3.5%Al one, for which it is somewhat less. The calculated band gap for ceramics is smaller than the theoretically determined E_g for the single-crystalline β-Si_3N_4. The minimal value quoted in [6] equals 4.96 eV, which corresponds to an indirect transition from point Γ in the Brillouin zone into point A, the energy of 5.25 eV corresponds to a direct transition $\Gamma \to \Gamma$. The experimental value of E_g for the single-crystalline β-Si_3N_4, determined in [11] by X-ray spectroscopy methods, equals 4.4 eV. The results obtained by us for the band gap agree well with the results of [10,12], where E_g was determined for ceramic specimens [10] and powders [12]. The investigation of Si_3N_4 films in the amorphous and α-phase states found that the band gap monotonously changes from 1.7 to 4.6 eV, depending on the stoichiometric composition of $Si_{1-x}N_x$ [13, 14]. This is explained by a violation and break of the Si—N bonds, which results in a forming of defect states located near to the edges of the valence and conduction bands. Since the forming of ceramics occurs at high temperatures and pressures, the specimens are obviously created with distortions of the crystalline structure of Si_3N_4 [1]. Since the value of E_g is almost independent of the Al content for the specimens under investigation, local distortions of the Si_3N_4 crystal structure are therefore responsible for its reduction.

As is seen from Fig. 4, the refractive index changes within the limits of 1.57—2.1. It is also seen that the presence of admixtures slightly influences the general view of the dependence $n(h\nu)$. The value of the refractive index is less than that for a pure β-Si_3N_4. The value of n is affected by the presence of oxygen [15]. During sintering, there is a replacement of nitrogen by oxygen and a forming of silicon oxynitride Si_2N_2O. The substitution of nitrogen by oxygen does not change strongly interatomic distances in Si_3N_4 and, consequently, the definition of the oxygen availability by methods of X-ray phase analysis is problematic. To estimate the amount of silicon oxynitride, we applied the effective medium approximation (the theory of Bruggeman) [16]. This method was successfully applied in [17, 18] to calculate the dielectric permittivity of hydrogenized films of silicon nitride. The effective value of the dielectric permittivity ε should satisfy the equation

$$(1-c)\frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} + c\frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon} = 0, \qquad (3)$$

where $c = m_2/(m_1 + m_2)$ is the concentration of the admixture with a dielectric permittivity ε_2 in a matrix with a dielectric permittivity ε_1. The refractive index at $\lambda = 632.8$ nm is 1.97 for a pure β-Si_3N_4 and 1.55 for Si_2N_2 [6]. Using Eq. (3), we calculated the dependence of the refractive index of the ceramic specimens of silicon

The band gap of the silicon nitride ceramics

Al content, %	0.5	1	1.5	2	2.5	3	3.5
E_g, eV	3.9 2 3.9		4.04	3.87	3.94	3.95	3.7

nitride on the concentration of silicon oxynitride. The results of calculations are represented by a plot $n(c)$ in Fig. 6.

The refractive index is within the limits of 1.7—1.8 for all specimens except for those with the Al content of 0.5 and 1%. The low value of n for the first specimen is explained by a presence of a great amount of oxygen (the estimated concentration of silicon oxynitride equals 0.88). This is also confirmed by the results of X-ray phase analysis: the phase Si_2N_2O was revealed in this specimen. The maximal value of n for the second specimen testifies to a small amount of oxygen: the concentration of oxynitride is 0.13. For the rest of specimens, the concentration of Si_2N_2O changes within the limits of 0.45—0.6. Therefore, it is possible to check the amount of oxygen, which gets into Si_3N_4 ceramics during the HP process, by ellipsometric methods.

Conclusions

The results of the researches fulfilled testify to that the ellipsometric method is effective in studying the phase composition and electronic structure of ceramics based on silicon nitride. During the process of HP, the aluminum and molybdenum admixtures which are present in initial powders can form both an additional phase (the molybdenum admixture forms the phase $MoSi_2$) and a solid solution of the admixture and the basic phase (aluminum diffuses into the crystal lattice of Si_3N_4 making up a solid solution). Based upon experimental data on the dielectric permittivity and the refractive index, one can make a conclusion concerning the crystal structure of molybdenum disilicide which is formed in the process of HP.

The analysis of the band gap value allows us to make conclusion that the reduction of E_g is connected to a distortion of the crystal structure of Si_3N_4 and to the appearance of defect states located near to the edges of the valence and conduction bands.

The reduction of the refractive index value for Si_3N_4-based ceramics is connected to the presence of oxygen in specimens and to a forming of silicon oxynitride in the process of HP. The analysis of experimental data on the refractive index with the help of the effective medium approximation allows one to estimate the concentration of Si_2N_2O in the specimens.

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ОПТИЧНІ ВЛАСТИВОСТІ КЕРАМІКИ НА ОСНОВІ НІТРИДУ КРЕМНІЮ З ДОМІШКАМИ МОЛІБДЕНУ І АЛЮМІНІЮ

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Р е з ю м е

Зразки нітродокремнієвої кераміки були досліджені методами рентгенівської дифрактометрії та еліпсометрії. Вивчено вплив домішок на фазовий склад та оптичні властивості кераміки. Встановлено, що за зменшення ширини забороненої зони відповідають порушення кристалічної структури. Показано, що з аналізу дисперсії показника заломлення за допомогою наближення ефективного середовища можна оцінити кількість кисню, який присутній у нітриді кремнію.