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Optical properties of pyrolytic Silicon Nitride SiNx enriched with silicon

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Non-stoichiometric silicon nitride SiN_x, enriched with silicon, is a promising material for the non-volatile resistive memory development. The current studies devoted to investigation of the optical properties of SiN_x synthesized in a low-pressure reactor at 800°C at different ratios of dichlorosilane (SiH_2Cl_2) to ammonia (NH_3). It was found that for films synthesized at $SiH_2Cl_2/NH_3 = 1/1$, 1/2 and 1/3, the corresponding bandgap values are 3.83, 4.17 and 4.40 eV. At the same time, the corresponding values of the parameter x, found according to the theoretical dependence of the bandgap value on x for SiN_x calculated from the first principles, are 1.26, 1.30 and 1.32. Thus, by increasing the SiH_2Cl_2/NH_3 ratio, it is possible to create non-stoichiometric SiN_x films with a controlled silicon enrichment degree with high uniformity of chemical composition and thickness.

Keywords: silicon nitride, memristor, absorption coefficient, ellipsometry, quantum chemical modeling.

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Introduction

The development of non-volatile memory based on reversible switching of dielectric thin films from high-resistance state to low-resistance state under the action of current pulse (resistive or memristor memory) is an actual direction of the information technology development [1]. This type of memory is a promising candidate for the role of universal memory that combines high speed is better tgan fast resoinse, unlimited number of overwriting cycles, and nonvolatility, for the role of high-speed more appropriate and radiation-resistant flash memory of the new generation, as well as for the role of synapse in the neuromorphic electronics for the development of artificial intelligence [2]. Among plenty of dielectric materials that are potentially suitable for the use as the active medium of memristors, one of the most promising is non-stoichiometric silicon nitride, SiN_x, enriched with silicon [3–7]. The advantage of SiN_x over other dielectric materials is its compatibility with standard microelectronics processes. A modern method to synthesize thin films of silicon nitride is pyrolysis of the mixture of dichlorosilane (SiH_2Cl_2) and ammonia (NH_3). By varying the ratio of dichlorosilane to ammonia, thin non-stoichiometric films of SiN_x with various compositions can be synthesized. The controlled varying of parameter x of SiN_x, in turn, opens the possibility to vary electrophysical characteristics of SiN_x as well. Depending on the value of parameter x, SiN_x bandgap value is changed in the range from 1.6 eV of amorphous Si [8] to 4.6 eV of stoichiometric silicon nitride Si_3N_4 [9]. Refractive index of SiN_x depends on the parameter x as well: the more is SiN_x enriched with silicon, the higher is its refractive index.

An effective non-destructive method of characterizing the dielectric films playing the role of storage medium of memristors is spectral ellipsometry and scanning ellipsometry. The spectral ellipsometry allows determining the dispersion of refractive index and absorption coefficient, which analysis, in particular, gives the possibility of indirect determining of chemical composition of films. The scanning ellipsometry allows obtaining information on distribution of refractive index and thickness over the plate area. This information is critically important for the development of resistive memory, because fluctuations of thickness and refractive index (and, respectively, the chemical composition) result in the dispersion of memory properties of memristors, specifically, the memory window value, the time of information storage, the energy consumption, and the maximum number of reprogramming cycles.

The purpose of this work is to study optical properties of the pyrolytic silicon nitride SiN_x, enriched with silicon, synthesized at different dichlorosilane-to-ammonia ratios. Methods of the study are the spectral and scanning ellipsometry with engaging for analysis the results of quantum-chemical modelling of atomic and electronic structure of SiN_x.

Materials and methods

Films of silicon nitride SiN_x with variable composition were deposited by the method of pyrolysis of the mixture of dichlorosilane SiH_2Cl_2 (DCS) and ammonia NH_3 in a horizontal reduced-pressure reactor at a temperature of 800°C. The composition was varied by changing the DSC/NH_3 ratio in the range of 1/5, 1/3, 1/2, 1/1. Silicon

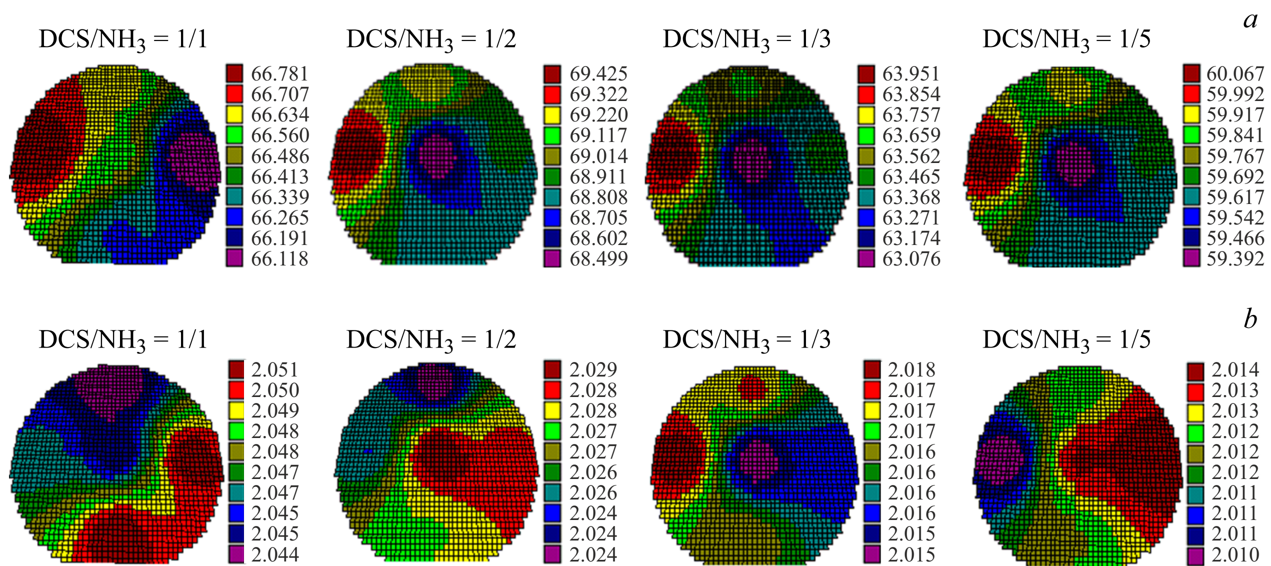

Figure 1. Distribution maps of (*a*) thickness (values are in nm) and (*b*) refractive index over the area of SiN_x films synthesized at various DCS/NH_3 ratios.

plates with a diameter of 150 mm, *p*-type, with orientation of (100), and a specific resistance of $4.5\,\Omega\cdot$cm were used as substrates.

Ellipsometric measurements were conducted with Uvisel 2 spectral ellipsometer by HORIBA/Jobin Yvon in the spectral range of 258–2100 nm at 70° angle of light incidence onto the sample and a size of light spot of 0.7×2 mm. With this setup the refractive index n, the absorption index k, and the thickness of layers were determined by means of multiple solving of the direct ellipsometry problem on the basis of the created mathematical model of the sample and comparison of fitting efficiency of the theoretically calculated sample to the real experimental data. The spectral data were recorded, the mathematical model of the sample was built up, and calculations were performed using built-in software of the ellipsometer.

To calculate parameters of the film we used the model of $Si/SiO_2/SiN_x$. Thickness and optical characteristics of the SiN_x layer were determined in the process of search. Thickness and optical characteristics of the SiO_2 layer were considered as fixed (thickness was taken equal to 1.8 nm).

Atomic and electronic structure of SiN_x was calculated within the density functional theory (DFT) in a model of periodic 3D-cells in the Quantum ESPRESSO software package [10]. We used PBEsol exchange-correlation functional of parametrization, pseudopotentials calculated in the approximation of the projector augmented waves (PAW), the cut-off energy of the plane-wave basis was 680 eV. The method used gives the bandgap of Si_3N_4 close to experimental data: $E_g = 4.55$ eV. The structure of SiN_x ($x < 4/3$) was created by removal of all possible combinations of nitrogen atom pairs in the 28-atom lattice cell α-Si_3N_4 (spatial group P31c) with addition of appropriate number of hydrogen atoms for the charge neutralization and to find a structure with minimum total energy. The electronic structure of SiN_x was calculated for 5 compositions: $x = 1.33$ (stoichiometric silicon nitride), 1.17, 1.0, 0.83, and 0.67.

Results and discussion

To evaluate homogeneity of samples in terms of film thickness and refractive index, ellipsometric measurements were performed in 5 points (center and for points on edges of the plate), and based on these measurements distribution maps for the measured parameters were compiled (Fig. 1).

The presented data demonstrate high homogeneity of thickness over the area of studied samples: the dispersion of thickness values is not greater than 1 nm for all samples with a root-mean-square deviation of 0.3 nm. In addition, it can be said that the synthesized films have high optical homogeneity: the spread of refractive indices over the area is not greater than 0.006 for all samples with a root-mean-square deviation of 0.003. The data of these measurements indicate a high quality of the produced SiN_x films.

Fig. 2 shows spectral dependencies of refractive index n and absorption index k on the photon energy for the measured samples of SiN_x. It can be seen from the obtained values of refractive index n and absorption index k for the studied samples of SiN_x, that with the growth of quantum energy the refractive index increases monotonously in the studied range of quantum energies. An increase in the DCS/NH_3 ratio (1/5, 1/3, 1/2, and 1/1) at a fixed quantum energy is accompanied by an increase in the refractive index: with the quantum energy of He–Ne-laser the corresponding values of n are 2.015, 2.019, 2.024, and 2.045. In contrary to the expectations, curves of dispersion $n(E)$ for different samples are not parallel to each other, which is caused by

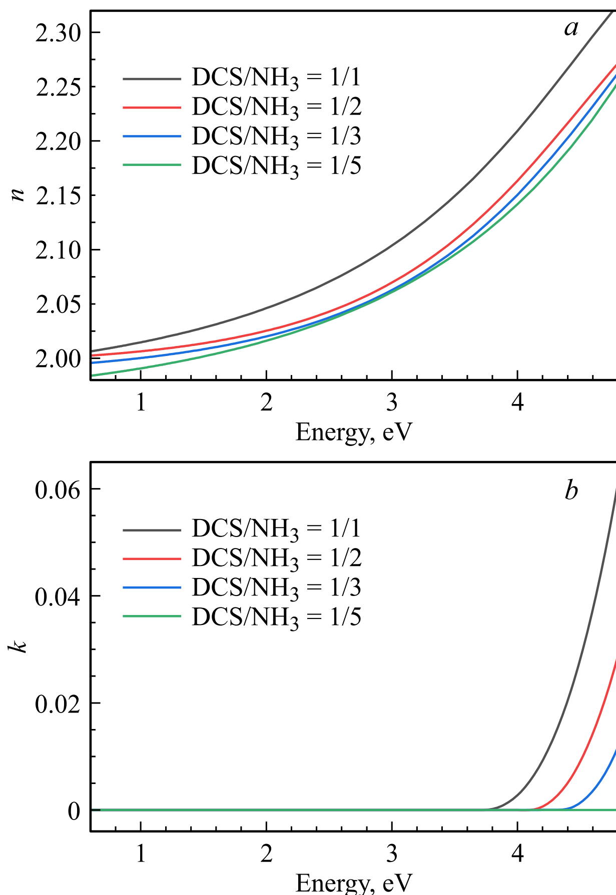

Figure 2. Spectral dependencies of (*a*) refractive index n (*b*) and absorption index k of SiN_x films synthesized with different ratio of DSC/NH_3.

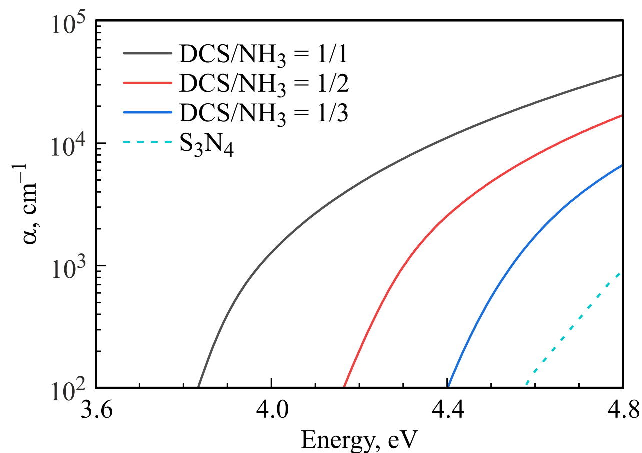

Figure 3. Dependencies of absorption coefficient of SiN_x films synthesized at different ratios of DCS/NH_3, as well as Si_3N_4 films on the photon energy. The data for Si_3N_4 is taken from [11].

the incomplete matching of the mathematical model to real structures and individual features of the samples themselves, such as the presence of SiO_2 sublayer, heterogeneity of thickness of dielectric materials, and roughness. The spectrum of absorption index k shows that films are transparent ($k = 0$) up to the quantum energy, that corresponds to interband transitions, and in this case with an increase in the DCS/NH_3 ratio a shift of the self-absorption edge towards lower quantum energies is observed. For the sample synthesized with a ratio of $DCS/NH_3 = 1/5$, there is no absorption in the measured range of quantum energies (up to 4.8 eV). To all appearances this sample is the closest to the stoichiometric silicon nitride (for Si_3N_4 $E_g = 4.6$ eV), however the sensitivity of the instruments used is insufficient to record the optical absorption.

To determine the bandgap value E_g of the studied samples, curves of absorption coefficient (α) vs quantum energy were plotted (Fig. 3). For the purpose of comparison, the spectrum $\alpha(E)$ for the silicon nitride taken from [11] is also shown in the graph. The value of E_g was determined at the level of $\alpha = 10^2\,\mathrm{cm}^{-1}$, because it is for this absorption intensity the value of E_g for Si_3N_4 is matched to the known data from literature: $E_g = 4.6$ eV [9]. Thus, for a sample synthesized with $DCS/NH_3 = 1/1$, $E_g = 3.83$ eV, with $DCS/NH_3 = 1/2$ $E_g = 4.17$ eV, and with $DCS/NH_3 = 1/3$ $E_g = 4.40$ eV.

To determine the parameter x of the studied films, the atomic and electronic structure of SiN_x with various compositions was calculated and dependence of E_g on the atomic ratio of $x = [N]/[Si]$ was plotted (Fig. 4, *a*). As demonstrated by the calculated spectra of the total density of states (TDOS), with a decrease in x from 1.33 down to 0.67, a monotonous decrease in E_g of SiN_x is observed. At the sane time this decrease is mainly due to the shift of conduction band edge to the bandgap. The valence band top of SiN_x is formed mainly by Si3p-atom orbitals, corresponding to bonding σ-orbitals of Si−Si bonds, and the shift of E_V towards higher energies is explained by the increase in the energy of these orbitals with growth of nitrogen vacancies concentration (decrease in parameter x). The shift of E_C towards lower energies can be explained by the decrease in the energy of bonding σ^*-orbitals of Si−Si bonds.

The determined bandgap values for the samples under study synthesized with ratios of $DCS/NH_3 = 1/1$, 1/2 and 1/3, being superimposed on the theoretical curve $E_g(x)$, yield values of parameter $x = 1.26$, 1.30, and 1.32, respectively (Fig. 4, *b*). The determined values of parameter x are different from each other by not more than 4%, therefore it is difficult to distinguish them by the standard method of chemical analysis with the help of X-ray photoelectron spectroscopy, which typical error is about 5%. The error of the method to determine the parameter x proposed in this work is due to mainly the arbitrariness of choice of the SiN_x structure model. However, it can be expected that this error is small, because the electronic structure of solid bodies is defined by the short-range order. In [12], in the description of SiN_x structure in the model of random bonding (RB), nearly the same dependence of $E_g(x)$ is obtained.

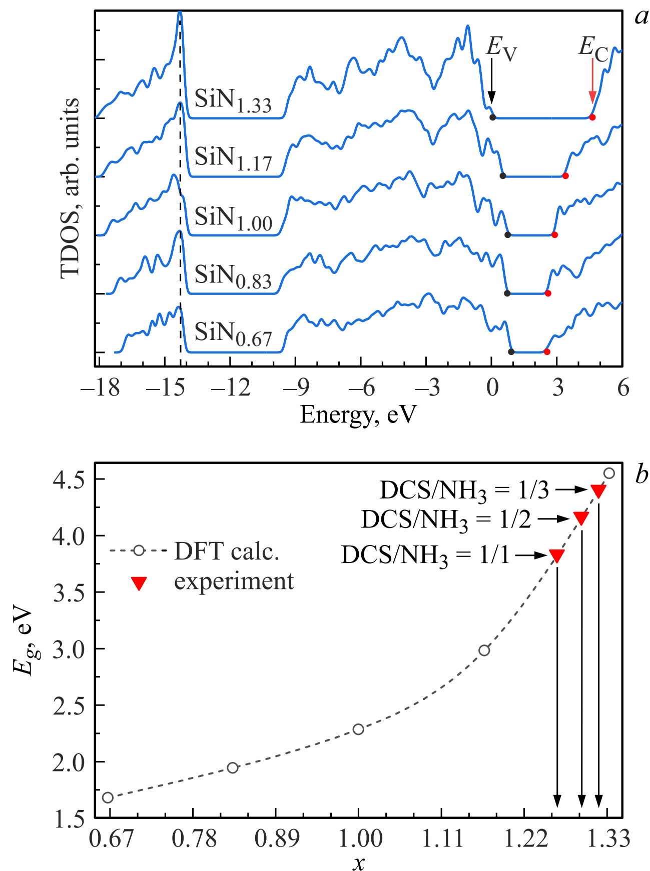

Figure 4. (a) Spectra of total density of electron states for SiN_x with $0.67 < x < 1.33$. The zero energy corresponds to the position of valence band top E_V of α-Si_3N_4, the spectra are coincided by the position of peak of the N2s-level 14.3 eV below E_V and smoothed by the Gaussian function with $\sigma = 0.15$ eV. (*b*) Calculated dependence of SiN_x bandgap value on the parameter x with superimposed values of E_g for the samples under study.

Conclusion

In this study methods of spectral and scanning ellipsometry were used to investigate optical properties of the pyrolytic silicon nitride SiN_x, enriched with silicon, synthesized with four different ratios of dichlorosilane to ammonia: $DCS/NH_3 = 1/5$, 1/3, 1/2, and 1/1. It is shown that the studied films have high homogeneity over the area of the sample (a plate with a diameter of 150 mm) in terms of both thickness and refractive index. The dispersion of thickness values over the area is not greater than 1 nm, while for the values of refractive index it is not greater than 0.006. The film synthesized with $DCS/NH_3 = 1/5$ is close to the stoichiometric Si_3N_4. An increase in the DCS/NH_3 ratio is accompanied by an increase in refractive index and a shift of optical-absorption edge towards lower energies. For the films of SiN_x synthesized with a ratio of $SiH_2Cl_2/NH_3 = 1/1$, 1/2, and 1/3, bandgap value values of 3.83, 4.17, and 4.40 eV, respectively, are obtained. By modelling within the density functional theory a simple structural model of SiN_x with different values of parameter x is developed. First-principles calculations have shown that with decrease in x from 1.33 down to 0.67 a monotonous decrease in the bandgap value of SiN_x is observed, which is due to mainly the shift of conduction band edge to the bandgap. Using the plotted theoretical dependence of bandgap width of SiN_x on the parameter x it is found that for the samples synthesized with $DCS/NH_3 = 1/1$, 1/2, and 1/3 values of the parameter x are 1.26, 1.30, and 1.32, respectively. Thus, by increasing the ratio of SiH_2Cl_2/NH_3 non-stoichiometric films of SiN_x can be produced with high homogeneity and controlled rate of enrichment with silicon. This allows for the qualitative conclusion of applicability of SiN_x films synthesized by pyrolysis of the dichlorosilane/ammonia mixture for manufacture of memristors.

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Conflict of interest

The authors declare that they have no conflict of interest.

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