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Short Communication

Temperature Influence on the Properties of Thin Si_3N_4 Films

V.S. Zakhvalinskii[1], P.V. Abakumov[2], A.P. Kuzmenko[2], A.S. Chekadanov[2], E.A. Piljuk[1], V.G. Rodriguez[1], I.J. Goncharov[1], S.V. Taran[1]

[1] *Belgorod National Research University, 85, Pobedy St., 308015 Belgorod, Russia*
[2] *South-West State University, 94, 50 let Oktyabrya St., 305040 Kursk, Russia*

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Applying Raman spectroscopy, small-angle x-ray scattering, and atomic force microscopy it were studied phase composition and surface morphology of nanoscale films Si_3N_4 (obtained by RF magnetron sputtering).

Keywords: Raman spectroscopy, Small-angle x-ray scattering, Atomic force microscopy.

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1. INTRODUCTION

Si_3N_4 is one of the most widely used in microelectronics materials. One of possible application of silicon nitride is solar elements (SE). Usually the silicon nitride films are applied in SE and other microelectronic devices as passivation layers, that reduces the rate of surface recombination of charge carriers [1]. Another typical application of silicon nitride films is obtaining anti-reflection layer of SE [2]. Reduced production cost of solar cells can be achieved by simplification of the manufacturing technology and construction SE. It has been recently obtained uni-junction SE on the basis of Si_3N_4. Thin film of Si_3N_4 thickness 20 nm of hetero-structure solar cells Ag/n-Si_3N_4/p-Si (100)/Cu is forming a potential barrier and at the same time acting as a passivation layer and anti-reflector layer. The energy conversion coefficient (ECC) of the photovoltaic stricture was 6.4 % [3, 4].

One of possible ways to improve EEC is increasing of solar energy absorption due to developed relief and increasing the relative surface of the up-per layer of the heterostructure. The main purpose of this work was to investigate the influence of the substrate temperature of high-frequency magnetron sputtering films Si_3N_4 on the phase composition and the relative surface area of the film.

Applying improved BH-2000 magnetron sputtering unit it was installed an optical substrate sample heater, that allows to set the temperature during deposition in the range of 40 °C up to 800 °C. Non-reactive RF magnetron sputtering of films was carried out using solid-state target Si_3N_4.

To analyze the changes in the distribution of particles according to their size in magnetron films it was applied the method of small-angle x-ray scattering (SAXSees mc[2], Anton Paar, Austria). The investigations were conducted in the linear collimation mode, providing characterization of structural features of objects, ranging in size from 0.1 to 100 nm, with a resolution of up to 0.03 nm^{-1}, which is substantially higher than the best examples of spectral instruments. During analyzing of the distribution it was performed subtraction of the spectrum from conducted single-crystal silicon scattering with the same orientation. The obtained scattering curves were processed using the program GIFT (PCG Software Package). The calculated volume distribution function of particle size $D_V(r)$ for coating Si_3N_4 on the cold substrate and the silicon substrates at a temperature of 500 and 750 °C are shown on Fig. 1. The analysis shows that a large part of the volume in silicon nitride Si_3N_4 film on the substrate at room temperature is occupied by particles with a radius of about 2 and 7.5 nm. These data are consistent with earlier researches for magnetron coating on glass [5]. In films Si_3N_4 while heating the substrates, it was ob-served increasing minimum size of occurring structural formations and the emergence of structures with different average static dimensions (for the sub-strate at 500 °C – 5, 12, 20.5, 29 nm), aalso there is a significant increase in the maximum size of above 50 nm.

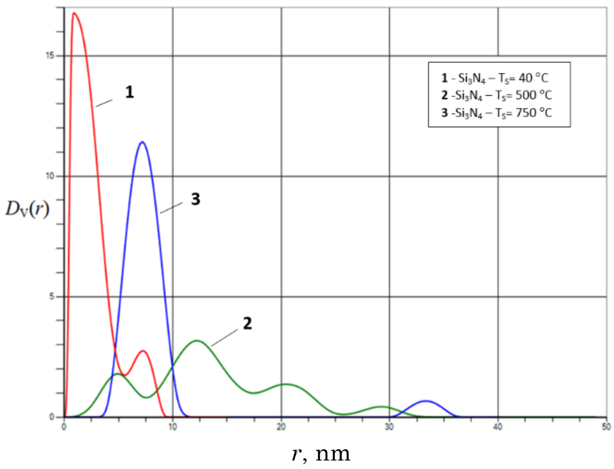

Fig. 1 – The calculated volume functions $D_V(r)$ particle distribution according to their size r for coatings Si_3N_4 on substrates Si (100) at temperature T_S = 40 °C, 500 °C and 750 °C

To determine the changes in chemical structure was carried out Raman (Raman) scattering of light. Spectral data was obtained using a combination of Omega Scope, including a spectrometer SOLAR TII. Measurements were per-formed in configuration of "reflection»

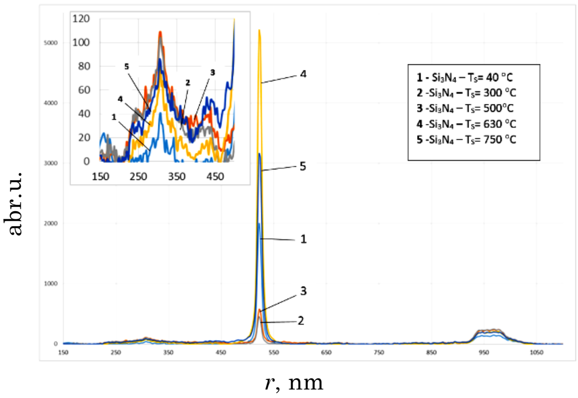

Fig. 2 – Raman spectra of light scattering for the Si_3N_4 films, that were obtained by RF-magnetron sputtering on substrates at temperatures T_S = 40, 300, 630, 750 °C. The inset shows the wavelength range of 150-450 nm

(ZXXZ) applying a solid-state laser source is 532 nm (50 mW) with a diffraction grating 600 lines/mm. Spatial focusing of the probing radiation was about 500 nm, spectral resolution was 3 cm^{-1}. The intensity of the scattered radiation was sufficient for reliable study of all the characteristics in the spectrum of the magnetron coatings, which is illustrated in Fig. 2. Besides responsible for fluctuations lines atoms Si – 528 cm^{-1} and its harmonics in the vicinity of 950 cm^{-1} there are been detected vibrations at frequencies of 288, 307 and 347 cm^{-1} that according to [6] correspond to fluctuations of a cubic silicon nitride. Most clearly they are driven in the Si_3N_4 obtained on a cold silicon substrate (40 °C), while the films obtained by heating the substrates, their intensity increases, but this range is an amorphous halo. The study of electron diffraction was performed at room temperature on a Si_3N_4 thin foil using a transmission electron microscope of high resolution (2 Å) JEOL JEM-2100. The set interplanar distances correspond to cubic Si_3N_4 [b], the nature of the diffraction rings indicates mixed (microcrystal-line and amorphous) state of Si_3N_4 film sputtered onto the substrate *p*-Si (100).

Table 1 – Relative surface area of the films dependence of Si_3N_4 on substrate temperature

The substrate temperature, Celsius	40 °C	300 °C	500 °C	800 °C
The relative surface area of the film,%	0.8	4.1	7.6	8.9

The study of thickness and surface morphology of films Si_3N_4 was conducted on an atomic force microscope NTEGRA Aura, NT-MDT in a controlled atmosphere. The thickness of the film amounted to 20 nm. After processing the results of the study of surface morphology using a software package «Image Analysis P9» (NT-MDT) was found the dependence of the relative surface area of the Si_3N_4 film on the heating temperature of the substrate during the rf-magnetron sputtering (Table 1).

Thus, we have completed a study of nano-sized Si_3N_4 films, obtained by RF-magnetron sputtering at various temperatures of heating of substrate *p*-Si (100). Applying small-angle X-ray scattering method, Raman spectroscopy, electron transmission and atomic force microscopy, it was found that the film is a mixed phase consist of amorphous and cubic Si_3N_4, the average radius of the particles increases from 2 nm to 7.5 nm at temperature increasing from 40 °C to 750 °C, and the relative surface area of the film increases from 0.8 % to 8.6 % when the temperature of the substrate varies from 40° C to 800 °C.

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