

## Short Communication

### Temperature Influence on the Properties of Thin Si<sub>3</sub>N<sub>4</sub> Films

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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<sub>3</sub>N<sub>4</sub> (obtained by RF magnetron sputtering).

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

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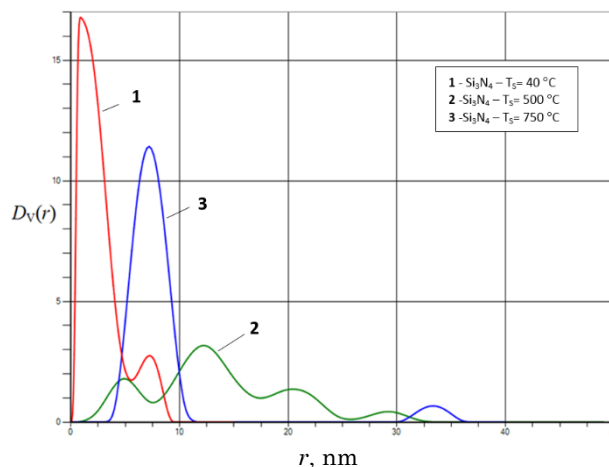
## 1. INTRODUCTION

Si<sub>3</sub>N<sub>4</sub> 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<sub>3</sub>N<sub>4</sub>. Thin film of Si<sub>3</sub>N<sub>4</sub> thickness 20 nm of heterostructure solar cells Ag/n-Si<sub>3</sub>N<sub>4</sub>/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 structure 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<sub>3</sub>N<sub>4</sub> 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<sub>3</sub>N<sub>4</sub>.

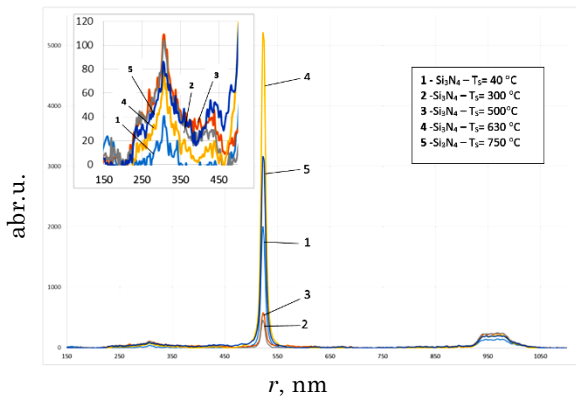
To analyze the changes in the distribution of particles according to their size in magnetron films it was applied the method of small-angle x-ray scattering (SAXS) using mc<sup>2</sup>, Anton Paar, Austria). The investigations were conducted in the linear collimation mode, providing characterization of structural features of objects, ranging in size from 0.1 to 100 nm, with a resolution of up to 0.03 nm<sup>-1</sup>, 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



**Fig. 1** – The calculated volume functions  $D_V(r)$  particle distribution according to their size  $r$  for coatings Si<sub>3</sub>N<sub>4</sub> on substrates Si (100) at temperature  $T_s = 40$  °C, 500 °C and 750 °C

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<sub>3</sub>N<sub>4</sub> 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<sub>3</sub>N<sub>4</sub> 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<sub>3</sub>N<sub>4</sub> while heating the substrates, it was observed increasing minimum size of occurring structural formations and the emergence of structures with different average static dimensions (for the substrate at 500 °C – 5, 12, 20.5, 29 nm), also there is a significant increase in the maximum size of above 50 nm.

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 performed in configuration of "reflection"



**Fig. 2** – Raman spectra of light scattering for the  $\text{Si}_3\text{N}_4$  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  $3 \text{ cm}^{-1}$ . 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 –  $528 \text{ cm}^{-1}$  and its harmonics in the vicinity of  $950 \text{ cm}^{-1}$  there are been detected vibrations at frequencies of 288, 307 and  $347 \text{ cm}^{-1}$  that according to [6] correspond to fluctuations of a cubic silicon nitride. Most clearly they are driven in the  $\text{Si}_3\text{N}_4$  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  $\text{Si}_3\text{N}_4$  thin foil using a transmission electron microscope of high resolution ( $2 \text{ \AA}$ ) JEOL JEM-2100. The set interplanar distances correspond to cubic  $\text{Si}_3\text{N}_4$  [b], the nature of the diffraction rings indicates mixed (microcrystal-line and

amorphous) state of  $\text{Si}_3\text{N}_4$  film sputtered onto the substrate  $p\text{-Si}$  (100).

**Table 1** – Relative surface area of the films dependence of  $\text{Si}_3\text{N}_4$  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  $\text{Si}_3\text{N}_4$  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  $\text{Si}_3\text{N}_4$  film on the heating temperature of the substrate during the rf-magnetron sputtering (Table 1).

Thus, we have completed a study of nano-sized  $\text{Si}_3\text{N}_4$  films, obtained by RF-magnetron sputtering at various temperatures of heating of substrate  $p\text{-Si}$  (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  $\text{Si}_3\text{N}_4$ , 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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