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FORMING NANOCRYSTALLINE SnO_2 FILMS ON SILICON AND SILICON DIOXIDE BY LASER-PLASMA DEPOSITION METHOD

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Abstract. The method of laser-plasma deposition of a tin thin layer on silicon substrates and SiO_2/Si structures in the combination with subsequent two-stage heat treatment to form a thin nanocrystalline layer of tin dioxide was used. This procedure can be valuable one for the fabrication of transparent conductive coatings and other optoelectronic devices.

1. INTRODUCTION

Tin dioxide (SnO_2) has a number of specific and unique properties, which makes this material suitable for various applications (Wang H. and Rogach A.L., 2014). It is often used to make conductive coatings on solar cells and other optoelectronic devices because it is a wide-gap semiconductor that is optically transparent in the visible wavelength range. The surface of grains in SnO_2 films has high absorption properties and reactivity, which is due to the presence of free electrons and oxygen vacancies in the crystal lattice of SnO_2. Therefore, nanocrystalline tin dioxide films are sensitive to the presence of various organic and some biological molecules in the surrounding atmosphere. Gas-sensitive SnO_2 layers are widely used in the production of sensors for monitoring poisonous and flammable gases (Gorley P.M et al., 2005). It is known that the optical, electrophysical and sensor properties of SnO_2 strongly depend on its structural and phase characteristics. This is depended on the conditions of its formation: type of substrate, deposition method, temperature and annealing environment.

In this work, for the first time, the method of laser-plasma deposition of a tin layer on silicon and a SiO_2/Si structure was used in combination with subsequent two-stage heat treatment to form a thin nanocrystalline layer of tin dioxide. The advantages of the laser-plasma method for applying nanocoatings include high sterility, the ability to obtain plasma from any substance, and guaranteed reproducibility of conditions during the deposition of coatings, which allows you to control their composition and structure (Pulsed laser deposition of thin films, 2007, Goncharov V.K et al., 2021).

2. INSTRUMENTS AND TECHNIQUE OF EXPERIMENT

The LOTIS-TII pulsed YAG:Nd^{3+} laser with a wavelength λ = 1064 nm and a pulse duration τ = 20 ns (as a full width at half maximum - FWHM) was used for experiments. Laser pulse was focused on a target which is placed in a vacuum chamber under pressure of 2.6×10^{-3} Pa. The target was mounted at angle of 45° with respect to the laser beam propagation and was constantly rotated to provide initial surface for ablation. The laser beam intensity was 3.8×10^{8} W/cm^2 and the diameter was about 2 mm. The sample deposition was carried out at room temperature. The target was made from technically pure tin. The laser pulse frequency was 5 Hz. The optically transparent silicon wafers in IR range (polished front and back sides) and the SiO_2(100 nm)/Si structures were used as substrates.

The control of electron and ion flows in erosive laser plasma was carried out according to the scheme (Goncharov V.K et al., 2021). The distance between the substrate and the target was 12 cm. The grid for cutting off the flow of electrons was located at a distance of 6 cm from the target surface. The transparency of the grid was 90%. The exposition of tin films deposition on various samples was lasted for 30-60 minutes. The experimental scheme is shown in Figure 1.

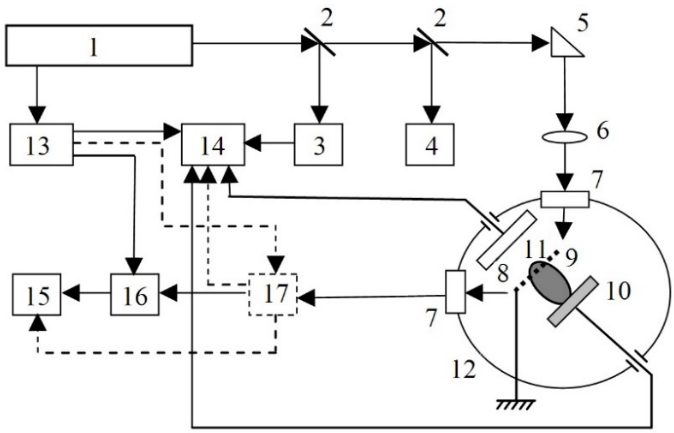

Figure 1. 1 – laser; 2 – beam splitting plates; 3 – photodiode; 4 – energy meter; 5 – total internal reflection prism; 6 – lens; 7 – windows; 8 – substrate; 9 – mesh; 10 – target; 11 – plasma torch; 12 – vacuum chamber; 13 – synchronization block; 14 – oscilloscope; 15 – computer; 16 – CCD - camera; 17 – spectrometer

The topological and structural-phase characteristics of the tin oxide layer were studied by transmission and scanning electron microscopy using a Hitachi H-800 transmission microscope with a Hitachi H-8010 raster attachment. Optical spectra (reflection, transmission) were recorded using a Lambda 1050WB spectrometer.

3. RESULTS AND DISCUSSION

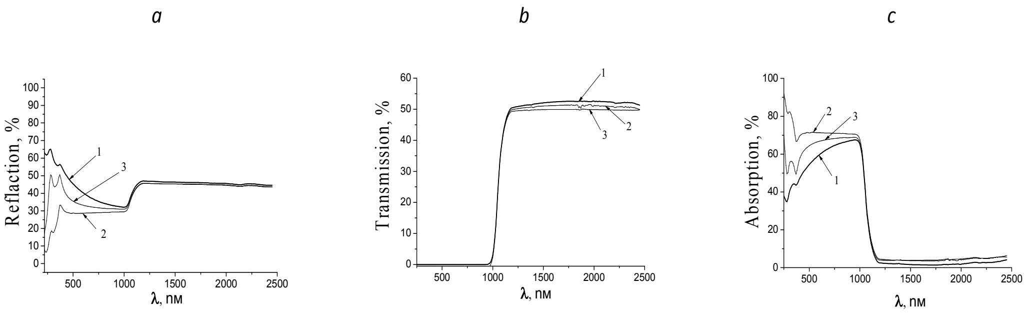

Figure 2. Optical spectra of reflection *a*, transmission *b* and absorption *c* from structures: Si, Sn/Si, SnO_2/Si
1- original Si, 2- film Sn on Si, 3- annealing 200ºC 120 min +500ºC 120 min

Figure 3 shows the results of optical studies of the formed structures: Si, Sn/Si, SnO_2/Si. The reflection and transmission spectra were measured, and the absorption spectra were calculated using the formula: A = 100% - T – R (where A is absorption, T is transmission, R is reflection). Films of amorphous tin and nanocrystalline tin dioxide are almost completely (98%) transparent in the near-IR range. In the ultraviolet and visible ranges, due to absorption, the transparency of the SnO_2 layer is about 80%.

Structural studies has shown that the tin layer after laser deposition has a high degree of thickness uniformity over a large area of the substrate. The droplet fraction was not detected on the surface of the samples. The formed films had an amorphous structure. It has been, found the formation of a nanocrystalline SnO_2 phase for two types of substrates: Si and SiO_2/Si after annealing. Figure 3 presents the results of structural studies.

The thickness of the SnO_2 layers was in the range from 20 to 40 nm, depending on the duration of deposition (Figure 3, *a*). It can be noted that when using a silicon wafer as a substrate, the structure of the SnO_2 film was more perfect: faceted crystals with an average size of 5-10 nm are observed (Figure 3, *b*). A detailed analysis of electron diffraction patterns showed that the crystal structure of the SnO_2 layer corresponds to a tetragonal system with the space group $P4_2$/mnm (Figure 3, *c*).

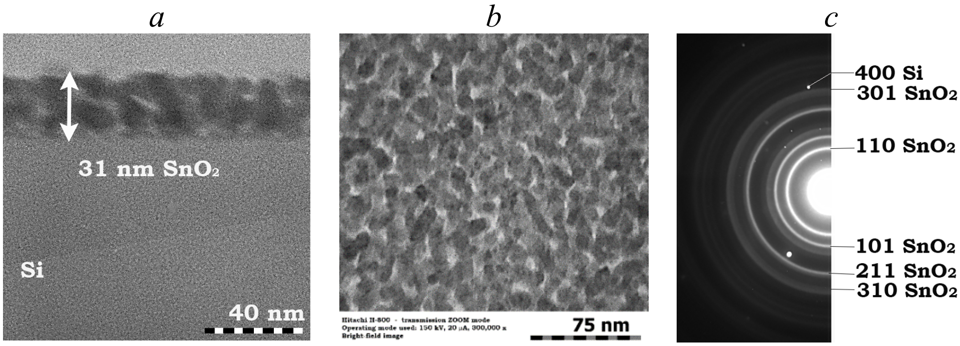

Figure 3. TEM micrographs of cross section *a* and planar *b* sections of the SnO_2/Si structure. *c* – electron diffraction pattern from the SnO_2 layer

CONCLUSION

Thus, the presented work shows the fundamental possibility of using the method of laser-plasma deposition of thin layers of tin on silicon structures, followed by two-stage annealing to form high-quality, in terms of structure (high uniformity in thickness, homogeneity of grain sizes) transparent layers of nanocrystalline tin dioxide.

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