

# SOL-GEL GLASSY ANTIREFLECTION $\text{GeO}_2 - \text{SiO}_2 - \text{Ag} - \text{RE}$ FILMS FOR SOLAR CELLS AND IR-DEVICES

Dmitry Kovalenko, Vladimir Gaishun, Alina Semchenko, Vitaly Sidsky, Nikolay Aleshkevich, Vasili Vaskevich

## Abstract:

Optically homogeneous double-coated of  $\text{GeO}_2\text{-SiO}_2$  films, doped by ions of silver and cerium were fabricated with use sol-gel of a method, using tetraethylorthogermanate (TEOG) and tetraethylorthosilicate (TEOS) as precursors for germania and silica, respectively. According to data IR-spectroscopy of a coat are glassy. Refractive indices for the materials were obtained the following:  $\text{GeO}_2$ ,  $n = 1.687$  at thickness  $d = 530.5$  nm and  $\text{SiO}_2$ ,  $n = 1.512$  at  $d = 998.2$  nm. They demonstrate good adhesion to the glass, germanium, silica and metal substrates. Introduction of Re-earth ions  $m$  allows to control refractive index within the limits of from 1,2 up to 1,6, that is important for deriving the multilayer antirefractive coats for the infra-red optics. Introduction silver nanoparticles allow using the yielded coats for magnification of efficiency of solar cells.

**Keywords:**  $\text{GeO}_2\text{-SiO}_2$  films, antirefractive film, solar cells, IR-devices.

## 1. Introduction

Series of works are devoted to investigation of germaniumsilicate materials (glasses and films). Silica glass doped with  $\text{GeO}_2$  has been investigated due to of the ultraviolet (UV)-induced refractive index change that is responsible for the formation of distributed Bragg gratings [1]. Also wide-band gap transparent materials are at demand for antireflection coatings of night vision devices, solar cells and manufacturing of planar wave-guides.  $\text{GeO}_2$  is widely used for these purposes. Now widely used vacuum deposition and colloidal methods for fabrication of  $\text{GeO}_2$  films with application in solar cells and planar wave-guides.

Use direct sol-gel of a method and organic compounds of germanium, can provide high optical quality and an opportunity of more flexible check of properties of films as compared with other existing methods [2], and also it is essential to simplify production engineering of their deriving. The films doped with europium demonstrate the intensive luminescence about 600 nm. This issue is of importance for possible blue shift of the spectral range for silicon-based solar cells those possess the maximum sensitivity at 600-620 nm. Silver ions and nanoparticles in the germania matrix are efficient absorbers at 300-500 nm due to the plasmon resonance band, and they can pass the light energy to  $\text{Eu}^{3+}$  emission centers [3]. In the present work, we have developed the sol-gel technique for preparation of  $\text{GeO}_2$ ,  $\text{GeO}_2\text{-Re}_2\text{O}_3$ ,  $\text{GeO}_2\text{-Ag}$ ,  $\text{GeO}_2\text{-Re}_2\text{O}_3\text{-Ag}$  (Re=Eu, Ce, etc.) films by incorporation of Ag, Eu and Ce-compounds into precursor sol followed by

deposition of films onto silicon and germanium wafers. Homogeneous and transparent films of thickness in the range 0.2-2  $\mu\text{m}$  were produced after the heat treatment at 500°C in air with good adhesion to the surface of glasses, silicon and germanium wafers. Thus, sol-gel derived germania coatings incorporated with silver and rare earth elements show perspective optical features aimed at the application for antireflective film and materials for solar cells sensitization.

### 1.1. Subsections

The germanium films with silver nanoparticles and rear earth ions were produced by spin coating on silica wafers from precursor sols prepared by mixing tetraethylorthogermanate (TEOG) in water-ethanol solution.  $\text{HNO}_3$  was used as the catalyst of TEOG hydrolysis. The solution was self-heated up to temperature 30°C due to exothermic hydrolysis and polycondensation reactions. A ripening of sols passed at  $22 \pm 2^\circ\text{C}$  for 4-5 days in closed vessels. Ripened sols were stable at  $\sim 20^\circ\text{C}$  for 2 months. Silver was incorporated by adding of  $\text{AgNO}_3$  (0.5-1 wt.%) in the precursor sols. Also was added  $\text{EuNO}_3$  (0.5-1 wt.%) and  $\text{CeCl}_3$  (0.5-1wt.%). After the spin-coating step, samples were heated up to 500°C in air for 15 min.

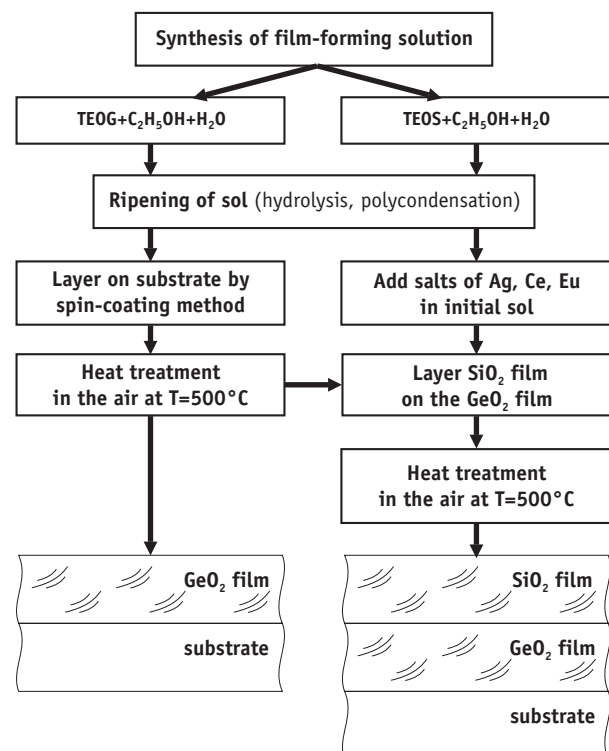


Fig.1. Scheme of formation  $\text{GeO}_2\text{-Re-Ag}$  and  $\text{GeO}_2\text{-SiO}_2\text{-Re-Ag}$  antireflection film.

By sol-gel method also were the two-layer antireflective coat (Fig. 1.) is obtained. And for decrease of reflectivity index it is possible to synthesize nanosized systems of two types; in one case the multilayered antireflection system consists from layer with periodically changed of a refractive index which thickness can be identical. In other case the system consists from too layers with difference in a refractive index, but thickness of such layers are changed. The second layer was hydrophobic  $\text{SiO}_2$  sol-gel film.  $\text{SiO}_2$  film also will be obtained from film-forming (sol) solution, prepared by hydrolysis of tetraethylorthosilicate. Sol superimposed on the surface by spin-coating method. Additively,  $\text{SiO}_2$  films were deposited as protective layers (Fig. 1).

Refractive indices for the materials were obtained the following:  $\text{GeO}_2$ ,  $n = 1.687$  at thickness  $d = 530.5$  nm and  $\text{SiO}_2$ ,  $n = 1.512$  at  $d = 998.2$  nm. They demonstrate good adhesion to the glass, germanium, silica and metal substrates.

### 1.2. Subsections

Refractive index of clear  $\text{GeO}_2$  films was equal 1,6. Preliminary theoretical calculations have shown, that the coefficient of reflection of such films  $R$  makes no more than 3 % Introduction in initial sol salts of silver, cerium and europium will allow decrease value of refractive index up to 1.2.

In Fig. 2 are shown infrared spectrums of a transition of  $\text{GeO}_2$  sol - gel of films superimposed on polished plates of single-crystal silicon wafers. There is an expressed absorption band in the field of  $3300 \text{ cm}^{-1}$ , the bound with presence of hydroxyl groups OH. Bands of  $1008\text{-}1040 \text{ cm}^{-1}$  largely depend on bridge bonds of germanium with oxygen Ge-O-Ge, and bands of  $1059\text{-}1156 \text{ cm}^{-1}$  correspond to the valent antisymmetric oscillations Ge-O-Ge. As a result of heat treatment of films developing process of hydroxyl groups essentially varies, and basic  $\text{GeO}_2$  bands store position and intensity.

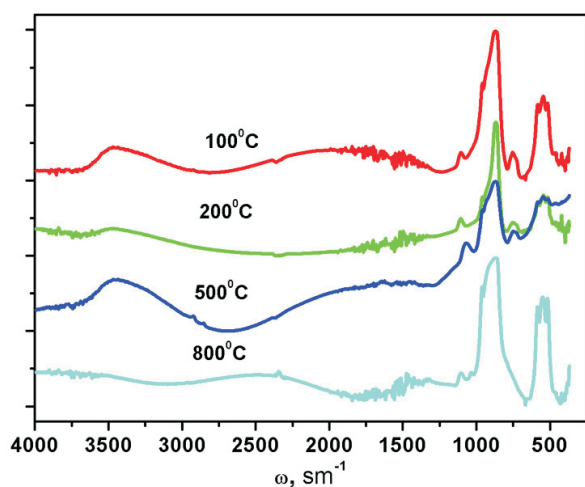


Fig. 2. IR-spectrum of  $\text{GeO}_2$ -Re-Ag film.

According to IR spectroscopy Ag nanoparticles and Re-earth ions not influence on structure of  $\text{GeO}_2$  film.

The absorption spectra of  $\text{GeO}_2\text{-SiO}_2\text{-Re-Ag}$  film have typical plasmon absorption peak of Ag nanoparticles with size 10-20 nm. In the range 1000-2600 nm films have

a minimum sign of absorption  $D = 0,044$ . Such films can be used as antireflection films.

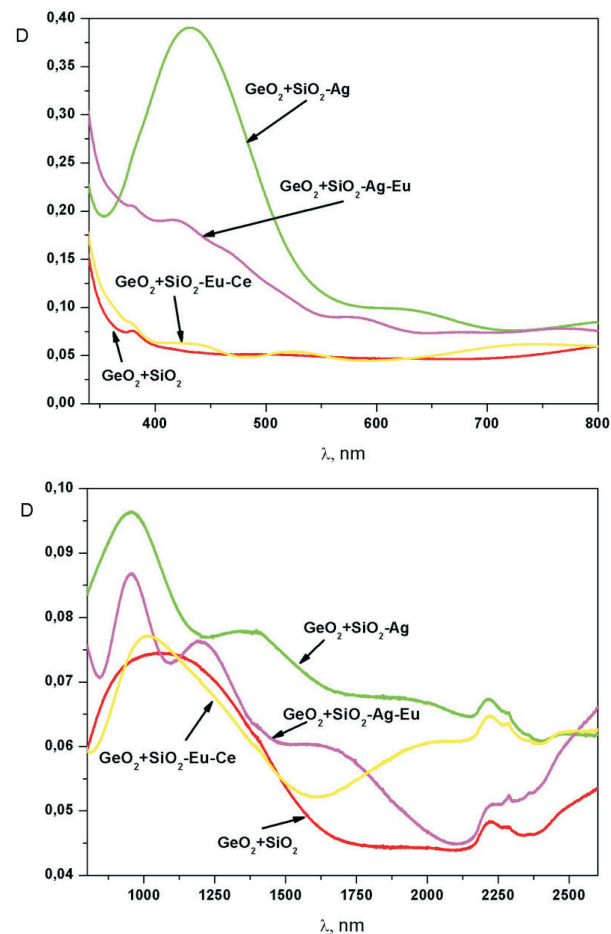


Fig. 3. Absorption spectra of  $\text{GeO}_2\text{-SiO}_2\text{-Re-Ag}$  film.

For checkout of an efficiency of  $\text{GeO}_2\text{-Re-Ag}$  films coats have been superimposed on a surface of a solar battery. Figure 4 presents dependence of a voltage on a solar battery from a wavelength and a composition of antireflection film.

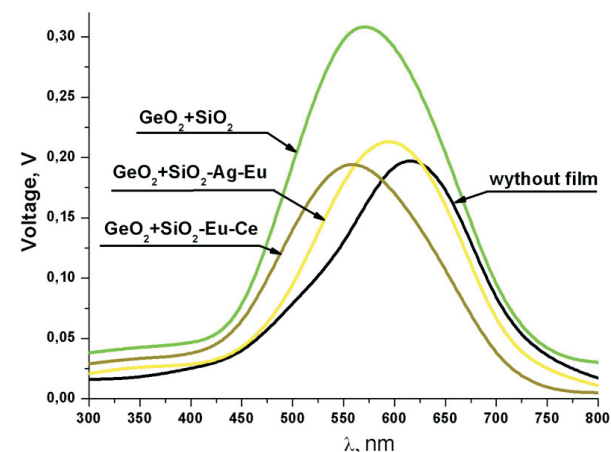


Fig. 4. Dependence of voltage solar battery from wavelength and composition of antireflection films.

From figure follows, that the given coats can serve for increase of work efficiency of a solar device. The efficiency of a solar device is increased and the working area of a solar device expanded in wavelength diapason.

## 2. Conclusion

Changing thickness and sign of a refractive index of antireflection  $\text{GeO}_2\text{-SiO}_2\text{-Ag-Re}$  film allows displacing a minimum of reflection in various sites of a spectrum. Application double-layer antireflection film allows removing almost completely reflection of light from a surface of a detail. Now an important problem is reception of antireflections coats for IR-techniques (thermal imager, night vision equipment etc.). In particular, for germanium lenses. The transmission of germanium plates in the range from 3 up to 12 microns makes 70 %. Drawing antireflection coat allows increasing transition up to 98 %.

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