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Properties of Ge_XO_Y:H Thin Films Produced by Plasma-Assisted Chemical Vapor Deposition

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Amorphous germanium oxide (Ge_xO_y:H) films, 0.2 μm – 1.2 μm thick, produced by plasma-assisted chemical vapor deposition from a mixture of tetramethylgermanium (TMGe) and oxygen (O_2) in radio-frequency (13.56 MHz) glow discharge, were investigated. Highly transmitting (> 80 % at wavelength 300 nm – 800 nm) Ge_xO_y:H films grew at rate of approx. 0.8 nm/s. The film structure and morphology were determined by XPS, X-ray diffraction and atomic force microscopy. The thickness of the films was evaluated by ellipsometry. Optical interferometry was used, in turn, to measure the residual stress in the Ge_xO_y:H films. The correlation between the residual stress and chemical composition of the films was analyzed.

Keywords: germanium oxides, residual stress, XPS, AFM.

INTRODUCTION

Germanium oxides are very interesting materials both from the point of view of their chemical properties and wide possibilities of electronic applications. Thin germanium oxide films are frequently encountered in many coatings on various supports [1]. Among the applications of such coatings are antireflective coatings, solar heat control coatings and switchable coatings [2].

Plasma enhanced chemical vapor deposition (PECVD) is one of the most useful methods for preparing thin films. This method is engaged in production of a wide range of new materials with the structure control at atomic or nanometer scale level. Moreover, it can produce single layers, multilayer systems, composites, nanostructured and functionally graded coating materials with well controlled dimension and unique structures at low processing temperatures. PECVD takes advantage of the huge base of precursors that have been used for the various deposition processes. The precursors can be solid, liquid or gas at ambient conditions, but they are delivered to the reactor as vapor (from a bubbler or sublimation source, as necessary). There are many good examples of the application of the PECVD technique in the recent literature [3]. However, very often this method is prone to induce undesirable compressive or tensile stresses in the deposited films [4]. A lot of methods are currently available for the estimation of residual stresses [e. g. Refs [5, 6]): X-ray and neutron diffraction, strain/curvature measurements, hole drilling, layer removal, optical fluorescence, chemical etching, etc. Stress in thin films may affect a variety of phenomena, including the physical properties of the films, adhesion, generation of crystallographic defects, and formation of surface growth such as hillocks and whiskers.

Excessive tensile stress may produce cracking of the film and/or substrate, and compressive stress can cause buckling. Therefore, determination and control of the stress is an important scientific issue for both functional thin films and engineering coatings from the viewpoint of performance and integrity. Basically, the experimental techniques for measuring stress in thin films on substrates can be classified into two large categories: (a) lattice strain based methods, including X-ray and neutron diffraction; and (b) physical surface curvature-based methods [7]. The curvature techniques based on the Stoney equations [8] can be readily applied to both crystalline and non-crystalline thin films. Optical interferometry [9], have been used to determine curvatures of thin film-substrate composites.

This paper, which is a continuation of our work on plasma deposited hydrogenated germanium oxide (Ge_xO_y:H) films [10], concentrates on the optimization of the deposition parameters with emphasis on achieving the films of high visible transmittance and minimal residual stress.

EXPERIMENTAL

The Ge_xO_y:H films, 0.2 μm – 1.2 μm thick, were produced from a mixture of tetramethylgermanium (TMGe) and oxygen (O_2) by plasma-assisted chemical vapor deposition using a parallel plate r. f. (13.56 MHz) glow discharge reactor. The power supplied to the system was 80 W, the flow rate of the oxygen and TMGe mixture (with 10 % TMGe concentration) was 10 sccm, and the pressure in the reactor chamber was 10 Pa. The substrate temperature was controlled by a standard thermocouple. Highly transmitting Ge_xO_y:H films (> 80 %) at wavelength 300 nm – 800 nm were grown at a rate of approx. 0.8 nm/s. The thickness of the films was determine from the optical measurements carried out by a Rudolf 431A null ellipsometer working at an incident light wave of 632.8 nm. Films were deposited onto 0.27-mm-thick glass substrates.

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Optical absorption measurements were performed by a transmission spectrophotometer in the region of wavelengths 200 nm – 800 nm using samples prepared on quartz glass substrates. X-ray diffraction (DRON - 3.0 powder X-ray diffractometer using Cu K_α radiation) was also carried out in order to examine the crystalline structure of the films. Surface composition of the films was investigated by X-ray photoelectron spectroscopy (XPS). The KRATOS ANALYTICAL XSAM800 spectrometer with nonmonochromatized Al K_α radiation ($h\nu = 1486.6$ eV) was used. Energy scale of the system was calibrated according to the Au4f7/2, Cu2p3/2 and Ag3d5/2 peaks position. The XPS spectra were recorded at the pass energy of 20 eV with the energy increment of 0.1 eV for C1s, Ge3d and O1s spectra, and 0.2 eV for Ge2p spectra; the analyzer was in the fixed analyzer transmission (FAT) mode. The samples were analyzed as received – no surface cleaning procedure was applied. Charge effects were compensated assuming carbon C1s peak at 284.6 eV position. The carbon, oxygen and germanium relative atomic concentrations were calculated from the appropriate peak area with respect to sensitivity factors, using original KRATOS software DS800.

The film morphology was determined by atomic force microscopy measurements (Atomic Force Microscope NT-206). The residual stress in the deposited thin films was calculated using a Stoney formula. The residual stress of Ge_xO_y:H thin films deposited at different conditions was measured using a panoramic interferometer [11].

RESULTS AND DISCUSSION

It has been found, on the basis of XRD measurements, that the germanium oxide films are amorphous (Fig. 1). Measurements performed by means of AFM have shown that all the films under discussion are morphologically homogeneous. As it is seen from Fig. 2, the thickness of the film as a function of the deposition time is linear.

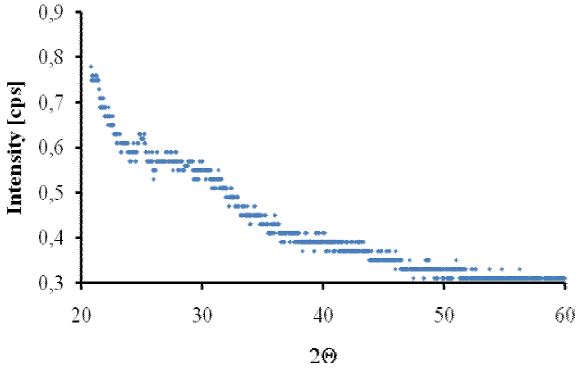

Fig. 1. Typical XRD spectrum for germanium oxide films discussed in this work

The fluctuation in the refractive index was about 1 % in all ranges of the deposition time and its average value was 1.64. Similar results have been reported for GeO_2 films produced by reactive DC magnetron sputtering, for which the refractive index in the visible range is between 1.63 and 1.58 [12].

The optical gap E_{OPT} was calculated according to the following relation [12]:

$$\alpha h\nu = B(h\nu - E_{OPT})^2, \qquad (1)$$

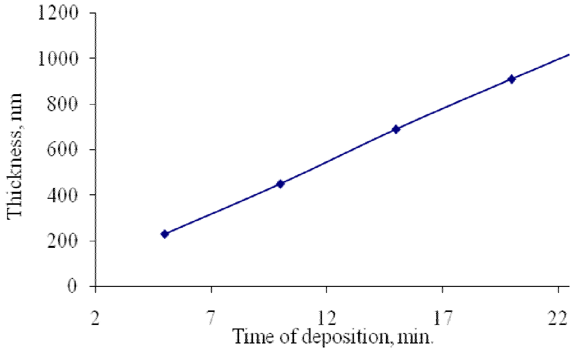

Fig. 2. The thickness of Ge_xO_y:H films as a function of the deposition time

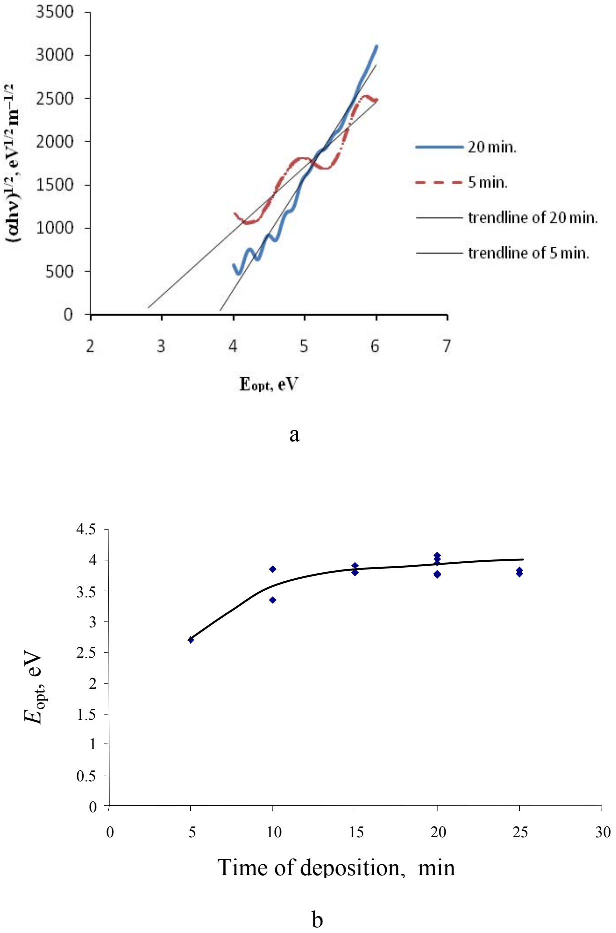

Fig. 3. (a) – the absorption edges plotted according to Eq. 1; the intercepts of the straight lines with the abscissa determine E_{OPT}, (b) – the obtained values of E_{OPT} presented as a function of the deposition time

where α is the absorption coefficient, hν is the energy of absorbed light, B is the proportionality factor. Fig. 3, a, presents examples of the absorption edges (for the films deposited for 5 min and 20 min) plotted according to Eq. (1). From such plots we can evaluate the E_{OPT} values. All these values obtained for the samples deposited in the time interval from 5 min to 25 min are put together in Fig. 3, b. As can be seen, the optical gap increases with the deposition time, and in consequence, with the growing thickness of the films. It means that the density of localized states in the bandgap has to decrease when the thickness grows. This interesting result can be explained by considering that the sample temperature increases during the deposition process. Roughly estimation indicates that the temperature grows from 295 K at start to about 330 K after 20 min deposition.

We should pay attention added that the stabilized value of E_{OPT} (3.8 eV) is in good agreement with the values obtained by other authors [13].

Amorphous germanium oxide films deposited on glass substrates, as it was investigated by AFM microscopy, show the low (~0.3 nm) surface roughness (Fig. 4).

The composition of the film surface was investigated by XPS technique analyzing C1s, O1s, Ge3d, and Ge2p spectra. The Ge3d spectra for the films deposited for 5 min and 20 min are presented in Fig. 5.

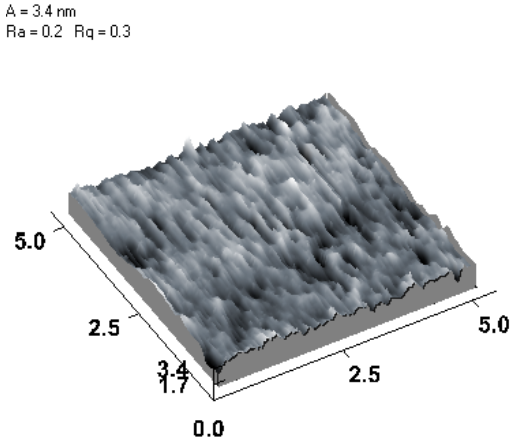

Fig. 4. AFM image of the Ge_xO_y:H film (200 nm thick) deposited on a glass substrate

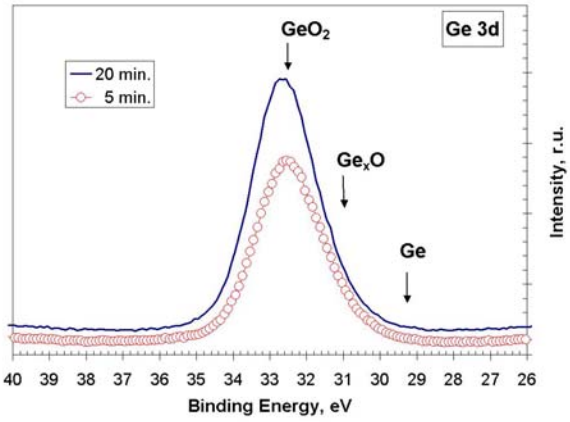

Fig. 5. XPS spectra of Ge3d for Ge_xO_y:H films deposited for 5 min and 20 min. The black arrows illustrate literature data

As one can see, the positions of the main peak Ge3d is at 32.64 eV and 32.7 eV for 5- and 20-min samples, respectively. These values coincide with known position (32.3 eV – 33.6 eV) for GeO_2 reported in literature [14 – 19]. A small shoulder on the right side of the main peak is located at 31.9 eV and 31.8 eV for 5- and 20-min samples, respectively. This shoulder can be assigned to Ge_xO structure, as reported by A. Molle at al. [14]. It should be noticed that for the sample of the 5-min deposition this shoulder is more pronounced. The possible peak position for pure germanium [14, 20] is indicated in the figure, but no peak was found in this area for both investigated samples.

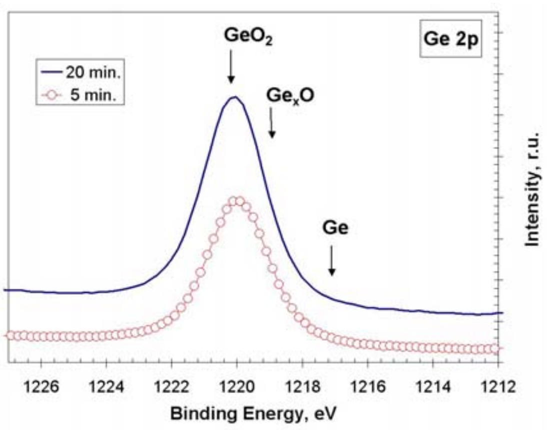

Fig. 6. XPS spectra of Ge2p for Ge_xO_y:H films deposited for 5 min and 20 min. The black arrows illustrate literature data

In Fig. 6, the Ge2p spectra for the same samples (see Fig. 5) are presented. The main peak positions at 1220 eV are in good agreement with the value of 1220.4 eV reported for GeO_2 oxide [20]. The small shoulder on the right side coincides with the features demonstrated in the Fig. 5.

Table 1. Calculated surface atomic concentrations for Ge_xO_y:H films

Element	Deposition time, min	
	5	20
O 1s	58.3 %	55.9 %
C 1s	11.9 %	14.6 %
Ge 3d	29.8 %	29.5 %
	Ge : O ratio	
	0.5107	0.52696

The calculated surface atomic concentrations are listed in Table 1. It is clear on this basis that the surface compositions of both samples are similar and the Ge to O ratio is close to the theoretical value for pure GeO_2.

Summarizing, it can be assumed that the analyzed films consist mainly of GeO_2 with relatively small fraction of Ge_xO. The 5-min films demonstrate, however, large content of Ge_xO fraction (about 32 %, calculated from curve fitting procedure, not shown here) than those produced for 20 min (about 21 %). It is indicative of larger oxygen deficiency in the 5-min films, and consequently, larger density of dangling bonds, which coincides with the decreased optical gap found for these films (Fig. 3).

The residual stress of the Ge_xO_y:H films was determined to identify the possible stress production mechanism. The results of optical interferometry measurements show that the residual stress in these films varies from compressive to tensile when the film thickness increases. This dependence is presented in Fig. 7. The maximal stress is observed for the thinnest films as highly compressive (for 400 nm – –6 GPa) and subsequently it decreases with increasing the film thickness becoming tensile at approximately at 1000 nm. Similar changes of the stress as a function of the film thickness were observed by Carroll et al. [21]. The residual stress changes can be generally attributed to the complicated variation of the film structure with the increasing deposition time. It can be related, for example, with a specific behavior of many amorphous materials that grow in the Volmer-Veber mode of nucleation and coalescence [21]. In our case, it can be also associated with the changes in the chemical structure of the films, which has been found by the E_{OPT} and XPS measurements, as well as thermal relaxation caused by growing temperature of the film during its deposition.

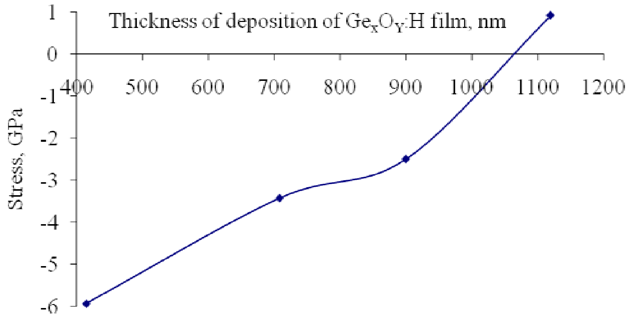

Fig. 7. Residual stress of Ge_xO_y:H films as a function of the film thickness

CONCLUSIONS

The investigations performed on amorphous Ge_xO_y:H films fabricated by PECVD from the mixture of TMGe and O_2 have revealed that the molecular structure of these films, and in consequence, their optical gap and residual stresses closely depend on the film thickness. For the thinnest films (5 min of deposition), the relatively low value of E_{OPT} (2.7 eV) and extremely high compressive stress (about –6 GPa) are observed. With the growing deposition time, E_{OPT} increases up to 3.8 eV and the stress converts from compressive to tensile achieving the resultant value equal to zero for the film thickness of approximately at 1000 nm. These changes can be related to a transformation in the molecular structure of the films, which is suggested by the XPS measurements, and consists in a decrease of the Ge_xO fraction in the GeO_2 matrix with the increasing deposition time. It seems that the growing temperature during deposition can play some role in this process, on the one hand decreasing the density of dangling bonds, and on the other relaxing the compressive stress.

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