NANOSTRUCTURE OF PLASMA-POLYMERIZED CARBON-GERMANIUM GLASSES

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A b s t r a c t. The dependence of electronic structure and electrical properties on molecular and supermolecular structure in the case of plasma deposited carbon-germanium glasses is reported. Particular attention is devoted to thin films produced from tetramethylgermane in the three-electrode reactor. An attempt is done to correlate the differences in electronic structure with changes of molecular structure. To this end, investigations of chemical constitution, mass density, infrared absorption and Raman spectroscopy are realized. The obtained results allow to state that the transition from amorphous insulator to amorphous semiconductor proceeds due to appearance of specific nanostructure consisting in separation of germanium reach clusters from carbon matrix. Based on XPS spectroscopy and scanning probe microscopy (SPM) it is proved that germanium clusters are not randomly distributed in the carbon matrix but agglomerate forming domains with size of 60 - 100 nm. An average distance between grains inside the domain is respectively shorter than that separating two domains.

K e y w o r d s: plasma deposited thin films, carbon-germanium alloys, nanostructure, atomic force microscopy.

INTRODUCTION

Plasma deposited hydrogenated carbon-germanium glasses ($a-Ge_xC_{1-x}:H$) have been intensively investigated recently [1-3]. Particular attention has been devoted to thin films produced from tetramethylgermane (TMGe) in the three-electrode-reactor [4]. Depending on the energy of ions bombarding the surface of the deposited film the obtained material can be characterized by one of two qualitatively different electronic structures, namely amorphous insulator (a-I) and amorphous semiconductor (a-S) [5]. The contrast between these two kinds of material can be characterized, for example, by values of specific electrical conductivity, which at room temperature are of the order of 10^{-4} and 10^{-18} S/m for a-S and a-I, respectively [5]. Also values of their optical gap (3.2 eV for a-I and 2.0 eV for a-S), transport gap (6.3 eV for a-I and 3.4 eV for a-S) and activation energy

of electrical conductivity (0.89 eV for a-I and 0.26 eV for a-S) reflect transformation in the electronic structure. It should be mention, that these dramatic changes in the electronic structure of a-Ge_XC_{1-X}:H films (a-S—a-I transition) can be caused by a very small changes of the deposition parameters that are responsible for the impact energy of ions bombarding the growing film [4].

Attempts were made to correlate the a-S—a-I transition with changes in the chemical structure of the material. Detailed analysis performed by means of chemical microanalysis, electron spectroscopies (ESCA and Auger) and IR spectroscopy revealed, however, that chemical structure is practically unchanged when the step transition in the electronic structure occurs [6,7]. The only evidence of rapid structural changes come from XPS and SPM investigations [7]. Two phases with identical molecular composition but different electronic structure have been identified. The semiconducting phase exists in the form of domains (60 - 100 nm in size) which are embedded into insulating matrix. It has been found that the transition from a-I to a-S is realized by a rapid increase of the amount of semiconducting domains. While in the a-I material only sparsely distributed domains exist a packed structure is formed in the case of a-S films. The nanoscopic size and distribution of semiconducting domains determines charge transport in the a-Ge_XC_{1-X}:H films. Recently, importance of the nanostructure and its influence on electronic properties of the material has been confirmed on the basis of Raman spectroscopy. This paper is devoted to presentation of these results and comparison with results of XPS measurements.

EXPERIMENTAL

Thin a-Ge_XC_{1-X}:H films were produced from tetramethylgermane (TMGe) by plasma enhanced chemical vapor deposition in the three-electrode-reactor worked at the audio frequency (af) range [4]. In the reactor the small electrode, on which samples are prepared, is placed horizontally between two main perpendicular electrodes maintaining a glow discharge. The small electrode is coupled with the powered main electrode by a variable capacitor. Its capacitance, C_p, which was the only operational parameter in this study, controls the af potential of the small electrode and in consequence the ion impact energy. For C_p < 75 pF and C_p > 75 pF, insulating (a-I) and semiconducting (a-S) films were fabricated, respectively.

The films were deposited from TMGe on silicon (for Raman measurements) or glass substrates. The reactor worked at a frequency of 20 kHz with the power of approx. 50 W supplied to the system. Before deposition the reactor was evacuated down to 0.1 Pa, and then the stationary flow of 11 sccm and the initial pressure of 13 Pa were established. Temperature of the substrate was approx. 380 K during the

deposition. Film thickness (about 1 μm) was measured by Rudolf 431A ellipsometer working at incident light wave of 632.8 nm.

The Raman spectra were obtained using a Jobin Yvon Raman spectrometer T64000 equipped with a microscope. As a light source an argon laser (λ = 514.5 nm and power ca. 200 mW) was used. All measurements were done at room temperature and the integration time for every single spectrum was equal to 120 minutes. For every kind of material the measurements was realized at eight different spots to ascertain reproducibility of the results.

The XPS measurements were realized by means of a Surface Science Instruments SSX-100 spectrometer, which used monochromated Al Ka (1486.6 eV) as the exciting radiation. The X-ray beam was focused to a 600 μm diameter spot. The samples were directly mounted onto a conductive holder electrically connected to the spectrometer earth. For all samples wide scan spectra including C1s and Ge3d were acquired. The both lines, for all samples, consist of two components related to semiconducting domains and insulating matrix, respectively. The fraction of material volume occupied by the domains (parameter Y) was evaluated as a ratio of the XPS signal related to the domains to the total XPS signal (assuming area of C1s and Ge3d bands). More details concerning the XPS measurements can be found in the paper [7].

RESULTS AND DISCUSSION

Figure 1 presents representative Raman spectra for all types of a-Ge_XC_{1-X}:H films investigated in this work. For comparison a spectrum of liquid TMGe is also added (spectrum (a)). The spectra (b) and (c) are typical for a-I and a-S films deposited at C_p < 75 pF and C_p > 75 pF, respectively. As one can see, in both the cases no signals in the carbon typical region (1200 - 1800 cm^{-1}) are visible. The fact that no Raman signals of sp^2 carbon are observed for films under study is indicative of a carbon network only tetrahedrally (sp^3) bonding. This observation leads to an important conclusion; namely the carbon matrix does not determine here the electronic structure and therefore is not responsible for the a-S—a-I transition. The search for a reason of the transition on the molecular level should be focused hence on Ge atoms and the way how they are incorporate into the material structure.

The germanium region of Raman spectra (50-350 cm^{-1}) is presented in Fig. 2. The spectra have been analyzed according to numerical peak fitting algorithm (PeakFit^{TM} software by Jandel), in which Gaussian and Gaussian-Lorentzian peak function were used. The analysis of the germanium region of all investigated spectra shows that in all these cases typical a-Ge bands, such as TO-like, LO-like, LA-like and TA-like, [8] can be distinguished. Beyond a doubt this is indicative of

the existence of a-Ge several-nanometer-sized clusters in the film. One sees at once, however, that the signal for a-I is much lower than for a-S. Due to the low intensity of the Raman signal and its noise in the case of a-I films, only two main a-Ge bands (TA-like and TO-like) were used to fit the spectrum (Fig. 2b). In this case an additional band c-Ge at approx. 300 cm^{-1} appears. The origin of the band is in dispute [9].
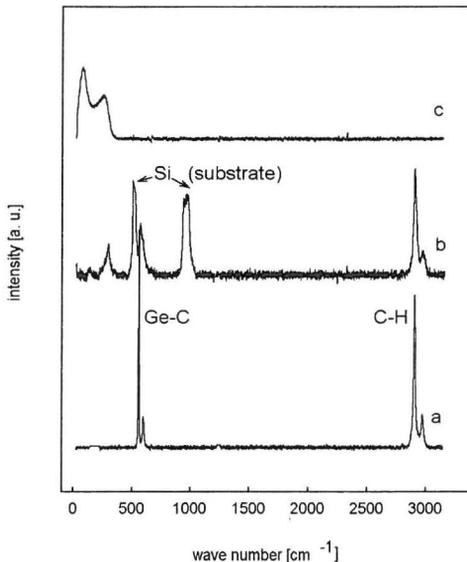
Fig.1. Raman spectra for (a) tetramethylogermane (TMGe) and a-Ge$_X$C$_{1-X}$:H films: (b) a-I film and (c) a-S film.

has been estimated according to the method described by Tsu at al. [10]. The values of $\Delta\theta$ are approx. 12.0° and 8.0° for a-S and a-I samples, respectively. As one can see, the molecular structure of a-Ge clusters in the a-S films is more disordered than that of the a-I material. This effect is probably related to stress induced in a-Ge clusters by more crosslinked carbon matrix including these clusters in the case of a-S films.

More thorough analysis of the a-Ge bands gives information about the degree of disorder in Ge clusters. Taking values of FWHM (full width at half maximum) for the TO-like band presented in Table 1, the root mean square (RMS) bond angle deviation, $\Delta\theta$,
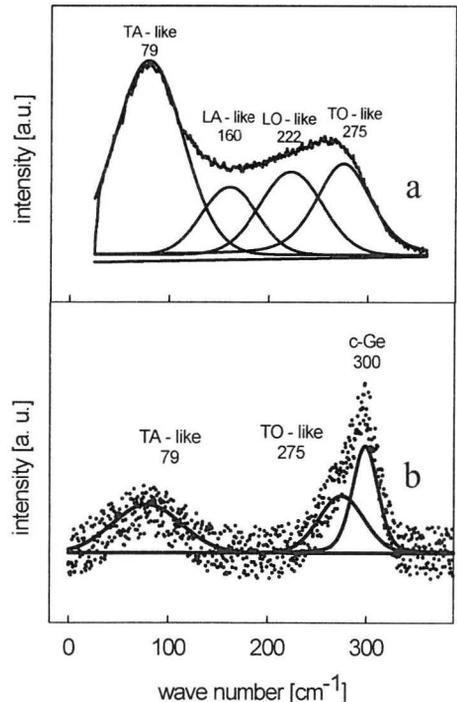
Fig. 2. Raman spectra in the germanium region for: (a) a-S film and (b) a-I film. Peaks separated by a numerical peak fitting procedure are shown
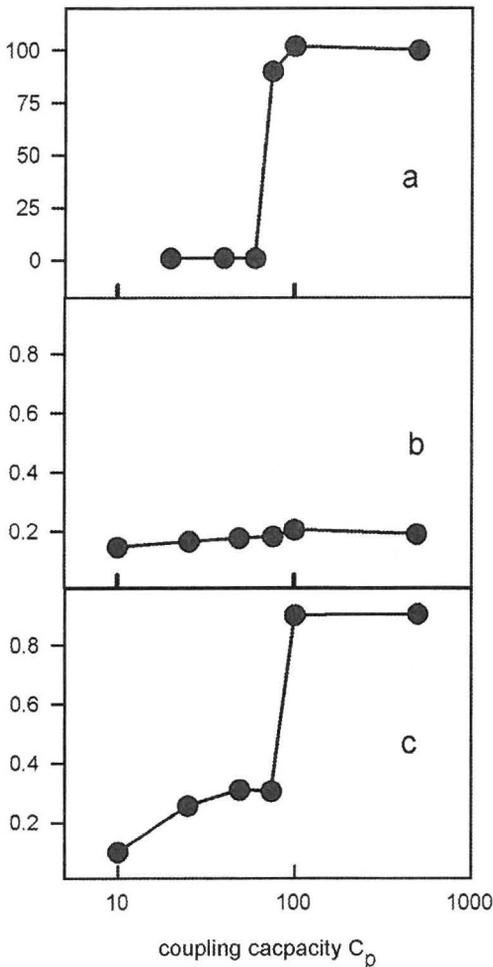
Comparing the integrated areas of Ge bands (TA-like and TO-like) measured for the both materials at the same experimental adjustments, it has been found that the signal in the case of a-S is about one order of magnitude stronger than that for a-I. To compare the Ge-cluster-fraction density for samples deposited at different values of coupling capacity C_p, it is necessary to take into account its different values of the absorption coefficient, α, at 514.5 nm

Table 1. Parameters of Raman peaks in the germanium region for a-Ge_xC_{1-x}:H films.

Raman band	peak position (cm^{-1})	FWHM (cm^{-1})	relative area (a.u.)
a-I films			
TA-like	79	80	39.8
TO-like	275	47	28.5
c-Ge	300	31	31.7
a-S films			
TA-like	79	78	40.8
LA-like	160	95	17.5
LO-like	222	88	23.3
TO-like	275	68	18.4

[5]. For the a-S films $\alpha = 2.5$-3.6×10^6 m^{-1} (depending on C_p), hence one can estimate that the effective thickness ($1/\alpha$) is approx. 280-400 nm. On the other hand, in the case of a-I, where $\alpha \approx 10^5$ m^{-1}, and so $1/\alpha \approx 10^4$ nm, laser light can penetrate full film thickness (1.5×10^3 nm) practically without its intensity loss. Then the light is reflected from silicon substrate and once again passes through the film. The effective film thickness in the case of a-I samples is approx. 3000 nm. It is about ten times as thick as the effective layer of a-S. Although at this stage of investigations the absolute number and size of a-Ge clusters can not be estimated, it is evident that the density of Ge atoms in clusters is approximately two order of magnitude higher for the a-S films than that for the a-I films. The rest of Ge atoms in the a-I films are molecularly dispersed, which is confirmed by the band at 570 cm^{-1} attributed to Ge-C bonds (Fig. 1). The results of calculation of the relative density of clustered Ge atoms for all investigated films are presented in Fig. 3a.

It should be emphasized that the transition from the a-I material with a very low density of a-Ge clusters to the a-S material characterized by a very high density of the clusters proceeds rapidly when the coupling capacity surpasses $C_p = 75$ pF. Hence, the a-I—a-S transition takes place when the impact energy of ions bombarding the growing film exceeds some critical value. This is energy sufficient to activate the separation process of amorphous germanium phase in the deposited a-Ge_XC_{1-X}:H films. This is thermodynamically justified in the light of the fact that the mutual solid solubility of Ge and C is negligible in the mixture in the state of equilibrium [11]. As a result, a high density of a-Ge clusters occurs in the film.

In the case of a-S, clusters of a-Ge are not randomly distributed in the material. The process of germanium clusters separation from carbon matrix is correlated with the step change in value of the Y parameter describing volume fraction of semiconducting domains (Fig. 3c). This can be understood as a result of assembling of the a-Ge clusters in the framework of the domains. It is remarkable that during this process atomic composition of the material is almost constant (Fig.3b). The average diameter of the semiconducting domains has been established during former studies to be in the range 100 - 150 nm [7]. However, taking into account that used SPM technique overestimates this value about 30 %, the average domain size can be estimated as being in the range 60 - 100 nm [12].

Fig. 3. Selected properties of a-Ge_XC_Y:H films deposited in the three-electrode-reactor from TMGe, as a function of the coupling capacity C_p: (a) relative density of clustered Ge atoms (from Raman spectroscopy), (b) germanium molar fraction, and (c) volume fraction of semiconducting domains (parameter Y) (from XPS spectroscopy).

CONCLUSIONS

Although the drastic changes in the electronic properties are observed in a-Ge_xC_{1-x}:H films deposited in the three-electrode-reactor when the coupling capacity exceeds the critical value of 75 pF, the investigations performed by means of XPS and IR spectroscopies have not revealed any changes that could explain such a transition (a-I—a-S transition). Recently, a significant progress towards understanding of this problem has been made buy our studies carried out by Raman spectroscopy that enables us to distinguish and analyze carbon and germanium nanostructures. It has been found, against expectations, that carbon matrix does not determine the electronic properties of the studied material. On the other hand, it has been shown that the a-I and a-S films drastically differ in the character of germanium nanostructure from one another. In the case of a-I films most Ge atoms are molecularly dispersed in the carbon matrix while in a-S films the vast majority of germanium is in the form of a-Ge several-nanometer-sized clusters. The clusters are not randomly distributed in the material but aggregate in the form of domains of about 60 - 100 nm in diameter. It is suggested that such a nanostructure of hydrogenated carbon-germanium amorphous semiconductors is responsible for their electronic properties.

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NANOSTRUKTURA POLIMERYZOWANYCH PLAZMOWO SZKLIW GERMANOWĘGLOWYCH

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S t r e s z c z e n i e. Przedstawiono zależność struktury elektronowej i właściwości elektrycznych amorficznych szkliw germanowęglowych wytwarzanych w plazmie niskotemperaturowej od ich budowy chemicznej i nadcząsteczkowej. Szczególną uwagę skupiono na cienkich warstwach produkowanych z tetrametylogermanu w reaktorze trójelektrodowym. Na podstawie badań spektroskopii XPS, mikroskopii sił atomowych SPM, stwierdzono, że ziarna germanu w warstwach półprzewodnika nie są rozmieszczone losowo w matrycy węglowej, ale tworzą strukturę wyższego rzędu skupiając się w domeny o średnicy 60 - 100 nm.

S ł o w a k l u c z o w e : plazmowe osadzanie cienkich warstw, stopy węgiel-german, nanostruktury, mikroskopia sił atomowych .