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Transition from amorphous semiconductor to amorphous insulator in hydrogenated carbon–germanium films investigated by IR spectroscopy

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ABSTRACT

Thin a-Ge$_x$C$_{1-x}$:H plasma polymerized films, depending on deposition conditions, can be produced in two very different structures, namely amorphous semiconductor and amorphous insulator. The transition from amorphous insulator to amorphous semiconductor is related to the formation of germanium nanoclusters due to ions bombarding the surface of the growing material. This paper concentrates on investigations of the transition by means of IR spectroscopy. To this end a quantitative analysis of IR spectra obtained for thin films deposited on silicon substrate has been described and used for estimation of hydrogen atom concentration and bonding in the investigated material. It was found that the probability that a given H atom is bonded to a germanium or to a carbon atom is almost the same. This conclusion is true both for a-S and a-I films. The average concentration of hydrogen in the investigated material was found to be about 2.4–3.4 × 10^{22} cm^{-2} which means that there are two times more atoms of the carbon family than hydrogen atoms in the film structure.

1. Introduction

An interest in plasma deposited hydrogenated carbon–germanium films is mainly related to the fact that their electronic structure can be easily controlled by a choice of deposition parameters. Changing only the energy of ions bombarding surface of the growing layer, two distinct materials, namely amorphous insulator (a-I) and amorphous semiconductor (a-S), can be produced from single precursors (e.g. tetramethylgermane – TMGe) [1,2]. The differences between a-S and a-I films can be illustrated by a comparison of values: specific electrical conductivity (10^{-4} S/m and 10^{-18} S/m) [3], transport gap (0.3 eV and 0.9 eV) [2] and optical gap (2 eV and 3.2 eV) [1]. This spectacular change of electronic structure can be caused by a small variation of plasma deposition parameters that are responsible for the impact energy of ions bombarding surface of the growing film [4]. On the other hand, values characteristic of deposited materials such as: material density, crosslinking, elementary composition display no rapid change related to the transition [5,6]. It is very interesting to find out how the electronic structure of a-Ge$_x$C$_{1-x}$:H films is related to their chemical composition.

An important insight has been provided by the results of Raman spectroscopy investigations [7]. It has been shown, against expectations, that carbon structures are not responsible for the observed change in electronic structure of the material, and the creation of sp^2 bonds cannot be correlated with the a-I/a-S transition. The main mechanism identified as a origin of the transition is the formation of nanometers-sized clusters of a-Ge. Both kinds of material (a-S and a-I) contain clusters of amorphous germanium with a diameter of about 2 nm embedded in the film matrix. In a-I material only a small fraction of Ge atoms is incorporated into the clusters. Most of them are molecularly dispersed in the material so that an average distance between clusters can be assumed to be much larger than cluster size. On the contrary, the structure of a-S material is dominated by amorphous germanium phase. Most probably ion bombardment of depositing film, which is responsible for deposition of a-S material, promotes phase separation. As a result, the density of amorphous germanium clusters is sufficient to influence the material electronic structure [7].

This hypothesis has been strongly supported by impedance spectroscopy measurements carried out over a broad range of temperatures [3]. It has been found that the electrical conductivity dependence on temperature and frequency fits the hopping model, which is common for percolation transport in heterogeneous systems. The direct correlation between obtained results and material nanostructure has been shown. A hopping mechanism related to jumps between neighboring clusters as well as charge transport inside germanium clusters have been identified. It was also shown that a-Ge clusters form larger domains (size of about 100 nm). Inside these domains charge transfer is more efficient than between neighboring domains, hence the last one is responsible for dc

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conductivity [3]. This specific nanostructure of a-S films deposited from TMGe seems to be particularly interesting due to its possible application in the area of nanocatalysis.

Further investigations on relations between electronic structure and nanostructure of a-Ge_XC_{1-X}:H films were carried out by means of FTIR spectroscopy. Preliminary results, obtained already in 1993, demonstrate that a-S samples are more cross-linked and can be characterized by higher concentration of germanium; however, no rapid changes in the chemical structure between a-S and a-I, contrary to their electronic structure, were observed [6].

FTIR spectroscopy can be employed to determine both a concentration of hydrogen atoms in the material and a way they are bonded to the material structure [8]. In this purpose measurements of IR spectroscopy were carried out on thin films deposited on silicon wafer. The concentration of hydrogen in the films attached to carbon and germanium atoms was determined from the area under the absorption bands using the relationship

$$N_S = A \cdot Ia = A \int \frac{\alpha(\omega)}{\omega} d\omega, \tag{1}$$

where $\alpha(\omega)$ is the absorption coefficient at frequency ω, N_S is the number of corresponding hydrogen bonds contributing to the absorption band, Ia is integrated absorption and A is the inverse absorption cross section [9–12]. The concentration of hydrogen attached to carbon was calculated from the stretching vibration peak C–H around 3000 cm^{-1} assuming the corresponding value of the A parameter equal to 1.35×10^{21} cm^{-2} [13]. To estimate the concentration of Ge–H bonds in samples both stretching and vibrations bands intensity could be used. However, the strength of wagging modes is assumed to be proportional to hydrogen concentration (with constant $A_w(Ge) = 1.1 \times 10^{19}$ cm^{-2}) while the strength of the stretching modes ($A_{S1}(Ge) = 5 \times 10^{19}$ cm^{-2}, $A_{S2}(Ge) = 14 \times 10^{19}$ cm^{-2}) are often not due to the different oscillator strength of GeH_X stretching mode for different neighboring atoms bonded to Ge [14].

The purpose of this paper is to present quantitative results of IR spectroscopy measurements realized for a-Ge_XC_{1-X}:H films and correlation of these results with described above material nanostructure. The calculations are approximate, but give a general idea of the film chemical structure.

2. Experimental details

Thin hydrogenated carbon–germanium films (a-Ge_XC_{1-X}:H) were produced from tetramethylgermane (TMGe) by means of plasma enhanced chemical vapor deposition in the three-electrode reactor working at audio frequency (20 kHz) [15]. In the reactor a small electrode, on which the sample is prepared, is placed between two basic electrodes and coupled with one of them by a variable capacitor. The capacitance controls the negative amplitude $V_{(-)}$ of the voltage with respect to the ground electrode and in consequence energy of ions bombarding the small electrode [4]. The negative amplitude $V_{(-)}$, was the only variable parameter in this study and could be changed in the range 0–1200 V. For values of $V_{(-)} < 450$ V and $V_{(-)} > 450$ V materials ranking among amorphous insulator (a-I) and amorphous semiconductor (a-S) were produced respectively [1,2]. The flow rate and initial pressure were 11 sccm and 13 Pa, respectively. Other deposition parameters were the same for all samples and can be found in earlier paper [7]. Samples were deposited both from pure TMGe and its mixture with argon (TMGe concentration was 50% mol) carrying gas. Samples, thickness of about 1 μm, were deposited on silicon substrate. Film thickness after preparation was controlled by means of Rudolf 431A null ellipsometer working at incident light wave 632.8 nm.

Infrared spectra were taken with the help of ATI Mattson Infinity FTIR 60 spectrophotometer working at resolution of 4 cm^{-1}. The recorded absorbance was a result of averaging of 128 subsequent scans. The PeakFit™ version 4 software has been then used for decomposition of obtained spectra to Gaussian–Lorentzian peaks.

2.1. IR absorption by a multilayer structure

To derive expressions for the normal incidence transmittance of light through a multilayer structure an approach known from ellipsometry has been adopted [16]. Propagation of plane waves in every single layer, which is assumed to be an isotropic absorbing medium, is described by the complex index of refraction n_i. Inside every single layer the electric field is a superposition of two waves (Fig. 1), namely traveling in positive direction of the x-axis (with amplitude A) and traveling in negative direction of the x-axis (with amplitude B). Hence, electric field in every point of the structure can be described by the vector $\begin{bmatrix} A \\ B \end{bmatrix}$. The vector value changes at the planar interface between neighboring layers (e.g. numbered by indexes; i and $i+1$) according to the formula

$$\begin{bmatrix} A_i \\ B_i \end{bmatrix} = \begin{bmatrix} 1 & \frac{r_{i,i+1}}{1-r_{i,i+1}} \\ \frac{r_{i,i+1}}{1-r_{i,i+1}} & 1 \end{bmatrix} \begin{bmatrix} A_{i+1} \\ B_{i+1} \end{bmatrix}, \quad \text{where} \tag{2}$$

$$r_{i,i+1} = \frac{n_{i+1} - n_i}{n_{i+1} + n_i}. \tag{3}$$

Inside layers the vector $\begin{bmatrix} A \\ B \end{bmatrix}$ changes due to absorption. The change can be expressed in the way similar to the expression (2) by the matrix $\begin{bmatrix} a_i^{-1} & 1 \\ 1 & a_i \end{bmatrix}$, where a_i is the complex parameter describing a change of the amplitude and phase of electric field due to transition through the layer i.

Applying that formalism to the double layer (indexes 1 and 2) embedded in a homogenous medium (index 0) propagation of IR wave can be described by the equation

$$\begin{bmatrix} 1 \\ R \end{bmatrix} = \begin{bmatrix} 1 & \frac{r_{0,1}}{1-r_{0,1}} \\ \frac{r_{0,1}}{1-r_{0,1}} & 1 \end{bmatrix} \begin{bmatrix} a_1^{-1} & 1 \\ 1 & a_1 \end{bmatrix} \begin{bmatrix} 1 & \frac{r_{1,2}}{1-r_{1,2}} \\ r_{1,2} & 1 \end{bmatrix} \times \begin{bmatrix} a_2^{-1} & 1 \\ 1 & a_2 \end{bmatrix} \begin{bmatrix} 1 & \frac{r_{2,0}}{1-r_{2,0}} \\ \frac{r_{2,0}}{1-r_{2,0}} & 1 \end{bmatrix} \begin{bmatrix} T \\ 0 \end{bmatrix}. \tag{4}$$

If the amplitude of incident wave is normalized to 1 then parameters R and T denote the amplitudes for reflected and transmitted waves, respectively. Hence, the value of parameter T, which in general is a complex number, can be then written in the form

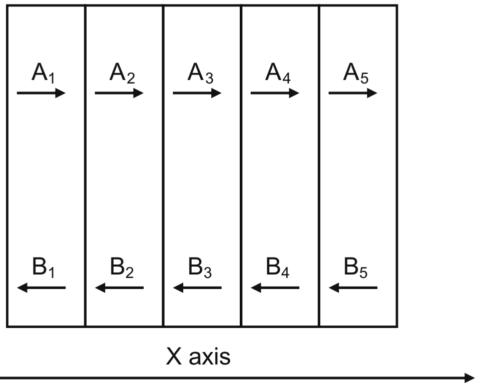

Fig. 1. Light propagation in a multilayer structure. Inside every single layer electric field is a superposition of two waves, namely traveling in positive direction of the X-axis (with amplitude A) and traveling in negative direction of the X-axis (with amplitude B).