Semiconductor Physics, Quantum Electronics & Optoelectronics. 2001. V. 4, N 4. P. 301-306.

PACS: 68.55; 73.50; 78.66; 81.15

Experimental investigations and computer modelling of the photochemical processes in Ag-As_2S_3 structures using surface plasmon resonance spectroscopy

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Abstract. Surface plasmon resonance (SPR) was first applied for investigation of the initial stage kinetics of the chemical processes in inorganic resist based on thin-film Ag-As_2S_3 structure. This method enabled to measure optical constants for the super-thin layers (from 0.2 up to 50 nm) and to study the changes in structure and thickness of the films after their exposure with different doses of UV radiation. Computer matching of the experimentally obtained SPR curves enabled to justify the assumption concerning the presence of a thin (close to 0.7–1 nm) intermediate layer with the parameters similar to Ag_2S, which is created during formation of the Ag-As_2S_3 structure, and also estimate its evolution in the course of layers interaction.

Keywords: surface plasmon resonance, chalcogenides, computer matching of curves.

Paper received 19.10.01; revised manuscript received 28.11.01; accepted for publication 12.12.01.

1. Introduction

Investigation of the photostimulated processes in inorganic resist - thinfilm structures metal-chalcogenide glass (Me-ChG) is important for fundamental science and for their practical applications as inorganic resists. Such processes are typically pronounced in Ag-As_2S_3 structure, which in most investigations is used as a model one. Of substantial interest is the formation process of such structure by vacuum evaporation of Ag and As_2S_3. There are known investigations of the vapor phase and freshly evaporated As_2S_3 films using mass-spectrometry [1], and photoemission analysis [2] methods, as well as nuclear magnetic resonance [3], which demonstrate the presence of isolated molecular fragments, mainly As_4S_4, S_2 and As_4S_3. These fragments under influence of thermal annealing or exposure by photoactive light are polymerized into structural network of As_2S_3 glass. It can be assumed that the process of As_2S_3 vapor phase condensation on the Ag layer previously deposited on a substrate at the initial moment will be somewhat different from the process of their deposition on the substrate without the Ag layer. Due to dissociative character of the As_2S_3 evaporation, in this case the chemical interaction between Ag and vapor molecular fragments can take place. Especially, this concerns S_2 fragments (-S-S-) that are very active in respect to silver and easily create chemical compound — silver sulfide — Ag_2S. As the deposition of the ChG layer proceeds, the probability of this interaction becomes lower, because the Ag layer surface is blocked by other fragments. Thus, the formation of the Ag-As_2S_3 structure is accompanied by the chemical interaction preferably between Ag and S_2, as a result of which the intermediate layer is created between main layers of the structure (Ag and As_2S_3), this layer being enriched by Ag_2S. Despite that, the creation of the intermediate layer during formation of Ag-As_2S_3 structure is the experimental fact [4,5]. In most cases, it is not taken into account in the models of photodoping phenomena mechanism, that is, the initial structure is considered as the contact of two layers [6]. From the application point of view, such simplification is not always justified, and thus this intermediate layer deserve more detailed consideration. The fact that the X-ray diffraction analysis did not confirm the presence of Ag_2S [7], is explained by the localization of the reaction of its creation on the molecular level in the scale $\leq$ 1 nm, which this method is not capable to detect. But there exist direct evidences of the Ag_2S creation in the As_2S_3-Ag structure, which were obtained using photoelectron spectroscopy [8].

SPR spectroscopy enables to determine the optical parameters or the thickness of the thin (up to 200 nm) molecular layers [9]. Under that usually used is the displacement of the minimum of reflection spectra (SPR-spectrum, SPR curve) as the only parameter obtained from the SPR experiment. Several works were devoted to the mathematical treatment of the form of SPR curve (all the curve, not only in the minimum region) [10-12], but in these works by means of the matching of the experimental and theoretical curves only one parameter (thickness of the film or refractive index) was determined. For example, applying the matching procedure for SPR curve the thickness of the Langmuir-Blodgett film of polyaniline was determined [10]. But, using the original matching procedure, in the conditions of the proper experiment [13], it is possible to extract several parameters from the one SPR spectrum. Such method enabled to determine the effective values of the optical parameters and the thickness of the adhesive Cr and Mn sublayers in Cr-Ag and Mn-Ag structures [14]. It is necessary to note that this method did not provide the possibility to obtain the exact values of these parameters simultaneously, taking into account their large number. In the mentioned method at each next step of matching procedure the parameter is introduced which is determined at a previous stage. Such decrease of the number of simultaneously treated parameters results in increase of the data accuracy. The use of the additional methods, for example atomic force microscopy (AFM) or profilometry, which give the exact values of the one parameter (in the case — the layer thickness) also increase the reliability of the results. AFM method also gives possibility by means of the registration of the profile for the investigated surface to determine the effective values of the refraction of the intermediate layers, which are necessary for the development of the more reliable mathematical model for the multilayer structure. As the development of the described approach in the present paper the SPR experiment and application of the computer matching of SPR spectra for the Ag-As_2S_3 structure is presented. According to our data, this is the first attempt to carry out similar work. Other goal of the investigation is in study of the interaction of molecular fragments present in the As_2S_3 vapor phase with the Ag film and also in the evaluation of the kinetics of the investigated photochemical reaction.

2. Experiment

SPR experiments were performed using SPR attachment (0.2 mW GaAs laser $\lambda = 664$ nm) with the optical system of the Kretschmann configuration. The use of 45° prism with $n = 1.51$ enable to obtain SPR spectra, that is to register the process of layers interaction in Ag-As_2S_3 structure at initial (induction) stage. The specific peculiarity of the study of the photochemical reaction between Ag and As_2S_3 using SPR spectroscopy is the impossibility to carry out direct measurements without influencing the parameters of photochemical reaction under laser exposure of a sample. Thus the samples with the Ag-As_2S_3 structures deposited on the glass substrates by vacuum evaporation were exposed by the radiation of UV DRSh-250 lamp. After exposure the samples were treated in 5 % solution of KOH with the following thoroughful part of ChG layer which did not reacted with silver was removed, and the structure silver-layer of products of photochemical interaction between Ag and As_2S_3 (Fig. 1) was left on the substrate. This structure is insensitive to the laser radiation during SPR measurements. The samples prepared in this manner were placed at the prism surface (Fig. 2). SPR spectra for each dose (Fig. 4) were fixed and specially developed computer program for matching experimental and calculated curves were used.

At the end matching procedure the value of the goal function was obtained, which was the criteria of the reliability for the chosen model of multilayer structure.

The investigations of silver surface and interaction product between Ag and As_2S_3 microrelief were carried out using Nanoscope III (Digital Instrument, USA).

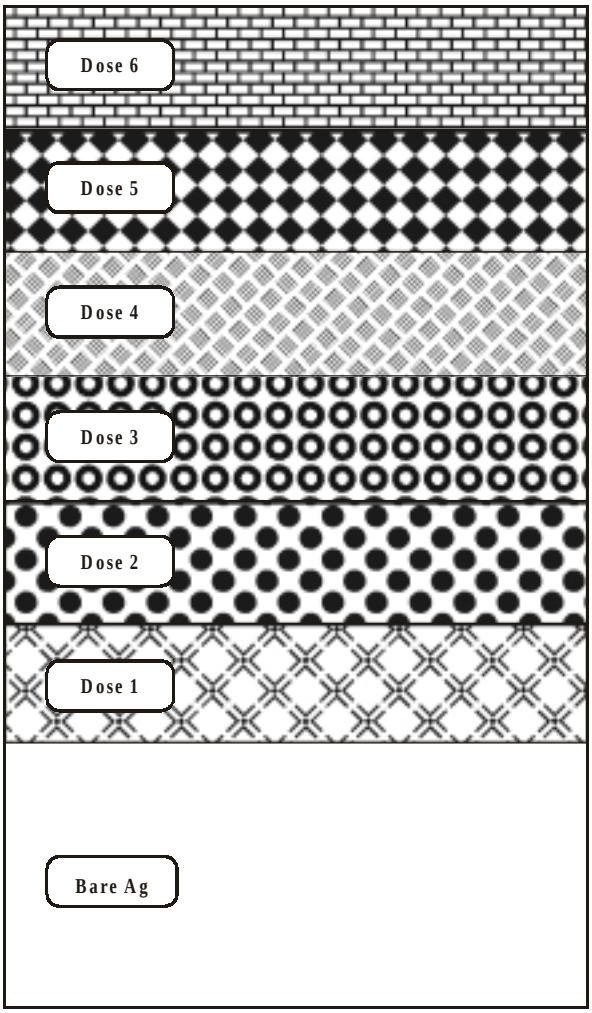

Fig. 1. Location of measured sectors on the glass substrate.

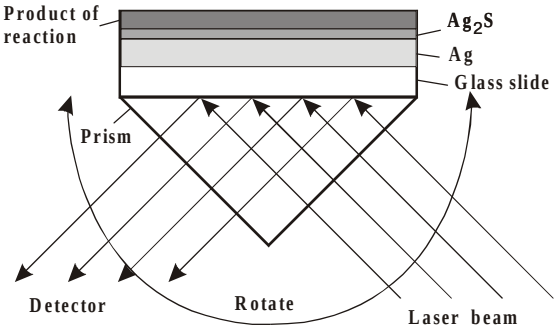

Fig. 2. Schematic illustration of the sensor block and multylayer structure for surface plasmon resonance measurements.

3. Theoretical considerations

The main requirements for the experimental attachment and matching procedure of SPR spectra were published earlier [13]. As the base of the program for modeling of the theoretical SPF spectra serve calculations baesd on scattering matrix formalism [15]:

$$S = I_{10}L_1I_{12}L_2....I_{(j-1)j}L_j....L_mI_{m(m+1)} \quad (1)$$

where I_{ab} is the Jones matrix for the interface between a and b layers. L is the matrix of the layer.

$$I_{ab} = \begin{bmatrix} 1 & r_{ab} \\ r_{ab} & 1 \end{bmatrix} \qquad L = \begin{bmatrix} e^{j\beta} & 0 \\ 0 & e^{-j\beta} \end{bmatrix} \quad (2)$$

where r_{ab} is the reflection coefficient for the respective interface, β is the phase thickness of the respective layer.

$$\beta = 2\pi\left(\frac{d}{\lambda}\right)N\cos\varphi \quad (3)$$

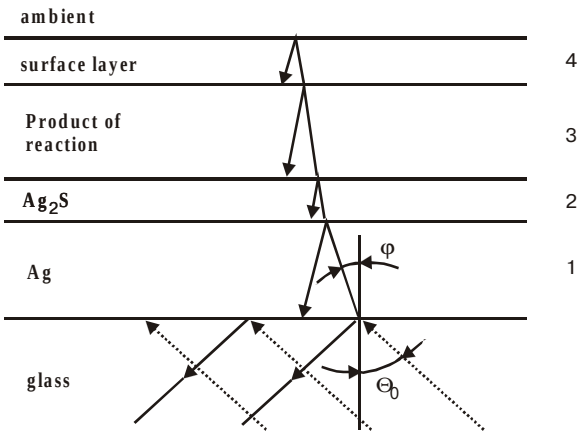

Fig. 3. Scheme of multilayer system for the fitting procedure selected.

where d means thicknesses of respective layers, φ – angles of refraction for them, λ – wavelengh, N – complex refraction coefficient for them respective layer. Integral reflection coefficient R of the structure is determined by the elements of the first column in the matrix:

$$R = S_{21}/S_{11} \quad (4)$$

The accuracy of matching was determined by the goal function $G(x)$, which was obtained using the specially developed minimization algorithm. The fitting procedure accuracy was estimated using the goal function $G(x)$. $G(x)$ for minimization was used in the form:

$$G(x) = \frac{\sum_i [R_i^e(x) - R_i^t(x)]^2}{\sum i} \quad (5)$$

where R_i^e is an experimental reflection, R_i^t is a calculated one.

In a general case the structure of the thin film can be considered as the multilayer struture. In modeling of such structures first of all it is necessary to determine the number of layers. This parameter can not be substantial, taking into account limited computer and time resources, but on the other hand, it must contain information upon the basic physical properties of the structure. Of peculiar attention are the interface surfaces and internal intermediate layers, as it is not taken into account it can result in substantial errors. The effectivness of taking it into account in the computer modeling of the surface relief and intermediate layers, was estimated further through comparison of goal function $G(x)$ values. In our case we found as optimal for consideration the four-layer model of the investigated structure, which includes intermediate Ag_2S layer and surface layer with taking into account the geometry of its relief (Fig. 2). It is known, that the roughness of the surface can substantially change form of SPR-spectra [16]. The necessary data on the surface relief (for

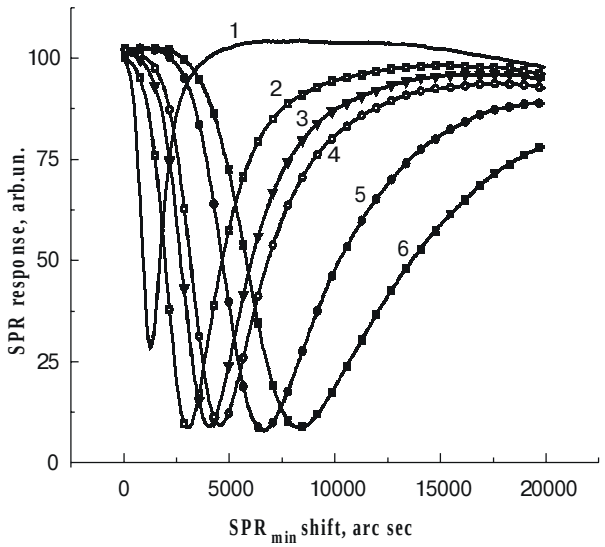

Fig. 4. Experimental reflectance SPR-curves vs. angle of light incidence. 1 – pure Ag, 2 – 3.4, 3 – 6.9, 4 – 10.4, 5 – 13.8, 6 – 20.1 J/cm^2.

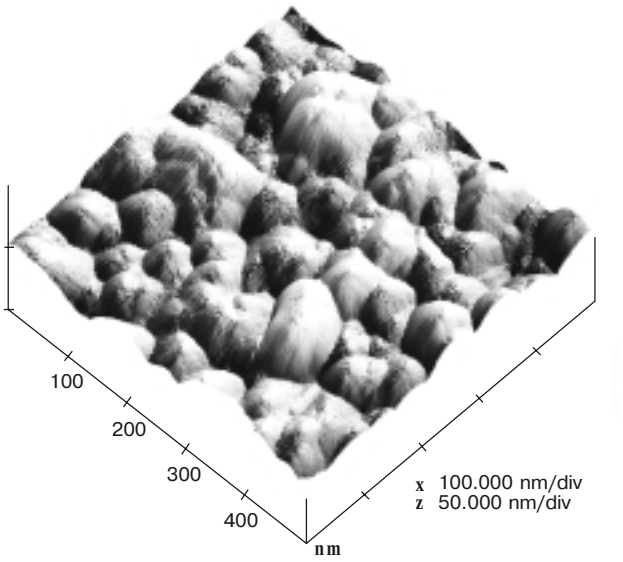

Fig. 5. AFM image of the studied surface (dose 5).

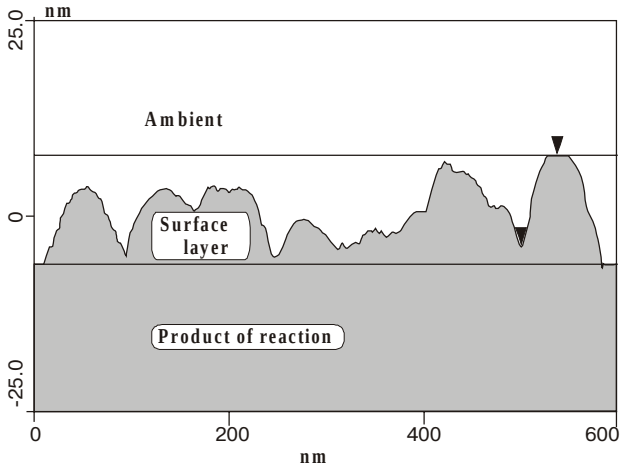

Fig. 6. AFM-section and scheme of the surface layer profile for SPR-curve fitting procedure (dose 5, filling factor V = 0.4).

each dose separately) were obtained using AFM (Figs 5, 6). The substantial size of the surface granules for product of photochemical reaction (up to 10 nm, Fig. 6) and their repeatability lead to the necessity to take into account the products surface as a layer with the effective refractive index neff. Calculation of neff for the rough surface layer was carried out using equation [16]:

$$\frac{n_{eff}^2 - 1}{n_{eff}^2 + 2} = \frac{n_{prod}^2 - 1}{n_{prod}^2 + 2} V + \frac{n_{amb}^2 - 1}{n_{amb}^2 + 2}(1 - V)$$

where: n_{eff} – complex effective refraction index, n_{prod} – refractive index for the reaction product, n_{amb} – refractive index of the ambient medium, V – filling coefficient. In our case, the exact value of the refractive index n_{prod} for the reaction product is not known, besides that it can change with the change of exposure dose. Thus, the values of the effective refraction index for the surface layer of the product was calculated during the carrying out of the matching procedure in dependence on the obtained n_{prod} values specific for each dose in the matching process.

4. Results and discussion

The result of the matching of SPR spectra mainly depends on two factors: accuracy of the experiment and correspondence of the chosen computer model to the experiment. The final result of matching becomes more reliable if it is possible to include preliminary known parameters for each of the layers. The matching (adjustment) of the SPR spectra for the silver without resist coating has shown values of the complex refraction index $n_{Ag} = 0.08 + 4.3i$. This parameter during the further matching procedure for all cases did not change.

To estimate more accurately the chosen number of layers, goal functions were calculated for two cases taking into account the intermediate Ag_2S layer and without it. The initial values of the refraction coefficient and Ag_2S layer thickness $n = 2.8 + 0.2i$, d = 1nm were taken from. It is necessary to note that under calculation of the one and the same SPR spectrum in some cases, several minima were observed as depended from initial parameters of the layers chosen for the matching. In this case, as the right one the deepest was taken. In Table 1 the values of the goal function $G(x)$ for different doses of UV radiation obtained as a result of matching are presented. As seen from the table, taking into account the Ag_2S layer leads to the substantially smaller values of the goal function, which enables to say about the existence of intermediate layers in investigated samples, optical parameters of which are close to the initial values of Ag_2S.

Most important dependencies of the thickness and refractive index for the investigated structure are shown in Figs 7, 8. Here the dependence for the thickness of each of

Table 1.

UV dose, J/cm^2	3.4	6.9	10.4	13.8	17.2
$G(x)$ without Ag_2S layer	1.74*E-5	4.63*E-6	1.07*E-6	2.42*E-5	8.41*E-6
$G(x)$ with Ag_2S layer	4.23*E-6	3.71*E-6	8.9*E-7	2.1*E-5	7.99*E-6

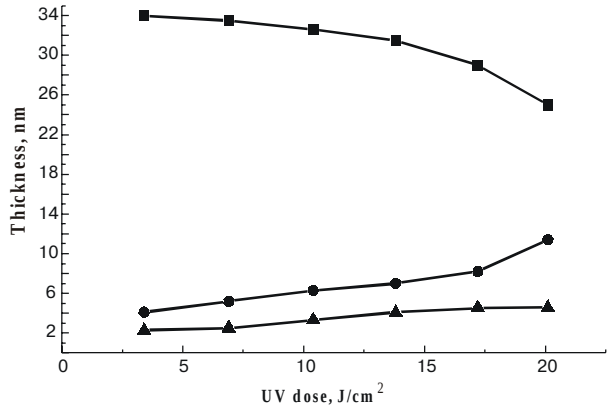

Fig. 7. Measured dependence of the Ag layer thickness (square), product (circle) and Ag_2S (triangle) on the UV irradiation dose.

the layers (Ag, Ag_2S, reaction product) is shown, as dependent on the value of UV radiation exposure (Fig. 7).

It is seen from the figure that the exposure increase leads to the decrease of two silver layer thickness and, respective, to the increase of the product layer thickness, which is concentrated at Ag-As_2S_3 interface. On the other hand, the thickness of the Ag_2S layer is not essentially changed. The complex refractive index for the photodoped by silver As_2S_3 layer is increased with the exposure increase (Fig. 8). It is necessary to note that at the initial stage of reaction the real part of the complex refractive index is growing more rapidly, and at the final stage the imaginary part (absorption index) behaves similarly. The value of the refractive index for Ag_2S $N = 2.8 + 0.2i$, chosen for the initial stage of the matching procedure with the change of UV dose was not essentially changed.

The presented above results support and supplement the photodoping model proposed in [17]. Because the real structure, that was formed by the consequent vacuum evaporation of Ag and As_2S_3 is 3-layer one, this makes

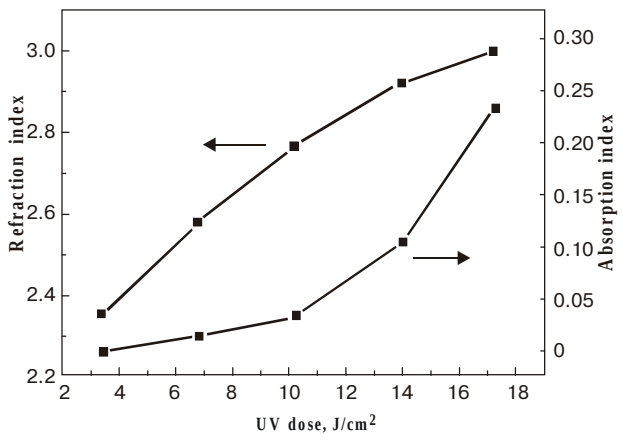

Fig. 8. Dependence of refraction and absorption indexes vs. UV dose. Rate of filling for surface layer $V = 0.4$.

possibility to consider it already at the initial stage as the complex structure (Ag) - heterojunction (Ag_2S-As_2S_3). This heterojunction is the region where the process of photochemical reaction begins: absorbed here atthe initial moment light energy initiates the mechanism of the photostimulated diffusion of Ag into As_2S_3 layer

Conclusions

The matching procedure for theoretical and experimental SPR-spectra enables to obtain data on the complex refractive index for the multilayer structures under high experimental accuracy and right choice of the physical model for layers. The thoroughful SPR experiment and taking into account the basic physical factors during modeling produce the result which leads to the more sophisticated and right understanding of the photochemical processes in complex multilayer structures.

The obtained result shows that during the process of the photochemical reaction the investigated structure can be considered as the system with the four layers: first layer – Ag, second – Ag_2S, third – As_2S_3 doped by silver, fourth – undoped As_2S_3 layer that did not interact with silver. At the initial stage of the photochemical reaction the intermediate Ag_2S layer is formed, the optical indexes and thickness of which do not change almost in the following .

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