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Holographic investigation of the corona discharge effect on the photo-doping of Ag, Au and Cr into nano-sized As_2S_3 films

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

The paper presents the results of holographically investigated photo-diffusion of Ag, Au and Cr ions into nano-sized As_2S_3 films. Evanescent wave's holographic recordings with spatial resolution 2 500 mm^{-1} in chalcogenide/metal sandwich like structures with 50 nm thick As_2S_3 layer, were performed. When the exposure was switched off at the maximum point of the diffraction efficiency during the holographic recording, 5 kV corona discharge was applied. During the holographic recording 5 kV corona discharge was applied. The maximum measured value of the diffraction efficiency was greater than 8%. The metal ions (Ag, Au and Cr) mobility in thin chalcogenide films was investigated. The mobility of the metal ions, μ, at temperature 17°C was calculated by the Nernst-Einstein equation. The diffusion coefficient D is obtained using the method of holographic grating spectroscopy (Forced Rayleigh Scattering). The values of the mobility and the diffusion coefficients for Ag, Au and Cr ions were discussed.

Key words: chalcogenide glasses, Forced Rayleigh Scattering, metal electromigration, diffusion coefficient, metal ions mobility

INTRODUCTION

The diffusion of silver into thin semiconductor layers is reported for the first time by Kostyshin and co-authors [1] in 1966. In this study the photographic properties of thin semiconductor layers of lead (II) iodide and As_2S_3, deposited on silver substrates were investigated. The authors observed that the layers become photosensitive in the red region of the visible light (the region that usually the layers are non-sensitive) and the hidden image turns visible without feature processing. They assumed that this phenomenon is caused by diffusion of the metal ions from substrate into layers, thus causing a chemical reaction leading to the occurrence of new chemical compounds. Subsequent studies revealed that the same effect is observed in different kind of photosensitive layers deposited on substrates made from Cu, Zn, Pb, Cd, Al, Fe, Ni and others.

Despite of the numerous models which have been proposed, the mechanism of metal photo-doping in chalcogenide glasses is still not clear. To solve this problem it is necessary exact knowledge of the diffusion coefficients of the metal atoms in the glassy network. This is reason to apply different methods for their determination. Investigations on a diffusion of Au and Ag into As_2S_3 chalcogenide glasses are carried out by Suptitz and Willert [2]. They use radioactive tracers Ag^{110} and Au^{198} to make evaluation of the diffusion coefficient of these metals into bulk As_2S_3 and its temperature dependence.

In [3] for investigation of photo-induced diffusion of Ag in As_2S_3 the method of direct weighting is used. The authors have been using the fact that the compounds which are a product of the reaction of Ag with As_2S_3 are resistant to alkalis and it can be dissolved only in HF at 180°C. They have etched removed the non-reacted silver by etching in acid (HCl) after illumination. By measuring the mass of As_2S_3 layer and the mass of silver layers before the illumination, the authors determined the amount of silver that had penetrated into the chalcogenide layer. They have found that the amount of silver increases with exposure increasing.

In [4,5] a technique for measuring the metal diffusion kinetics in As_2S_3 by changes in the electric conductivity of the layer is proposed. The

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results show a connection between the exposition energy, the wavelength used for illumination, the thickness of metal layer, the thickness of chalcogenide glass and the conductivity.

Terakado and Tanaka [6] demonstrated that the photo-doping rate can be controlled by applying bias voltage of ~0.1 V. This rate modulation can be attributed to modulation of an effective internal electric field in the photo-doped layer.

Despite of the studies made, there is not enough systematic, reliable and modern data on these photo-induced processes. This article is continuation of our previous researches [7,8] related to the diffusion of metal ions in the amorphous layers. The aim of this paper is to investigate the electro-stimulated diffusion of Ag, Au and Cr ions into As_2S_3 films and to provide new exact data for diffusion and mobility coefficients.

EXPERIMENTAL

Sample preparation

We performed holographic recording in an As_2S_3/Metal/Cr multilayer system. Firstly, a thin transparent chromium electrode with 10 nm thickness was deposited on a glass substrate by radio-frequency sputtering in argon plasma. A thin metal layer (d ~ 20 nm) was sputtered over the chromium film in the same vacuum cycle. Thin As_2S_3 films with thicknesses 50 nm were deposited on the metal coating by high vacuum thermal evaporation in a Leybold Heraeus A 720 Q deposition system. The chalcogenide films were prepared in a vacuum of 10^{-3} Pa, at a deposition rate of 0.1 nm/s. The constant thickness of the obtained layers was guaranteed by the planetary rotation of the substrate holders.

Optical arrangement

The general optical arrangement for holographic recording is given in Fig. 1.

In the optical system a crown K-8 glass 45-90-45 prism for the holographic recording is used. The refractive index of the prism at wavelength $\lambda = 442$ nm was $n = 1.526$ and the calculated critical angle was $\varphi_{cr} = 40.9°$. Therefore the incidence angle $\varphi = 41.5°$ was selected for the experiments. The total light intensity of the recording He-Cd laser was 10 $\mu W/cm^2$. For real-time diffraction efficiency monitoring a He-Ne laser with 23 $\mu W/cm^2$ intensity was used. The reconstructed red light beam was measured with “ThorLabs” PM 130 powermeter. Signal to noise ratio was higher than 100:1. Microscope oil with refractive index 1.53 was used as a matching liquid between the substrate and the prism’s reflecting wall. When the exposure was switched off at the maximum point of the diffraction efficiency (DE), high voltage with different polarity (±5 kV) was applied to the corona electrode (needle), situated at a distance of 10 mm from the As_2S_3 film. The Cr sub layer was used with a spring contact as a second electrode and to improve the adhesion of the other metals to the glass substrate. The corona discharge occurred between the needle and the grounded electrode (Cr sub-layer).

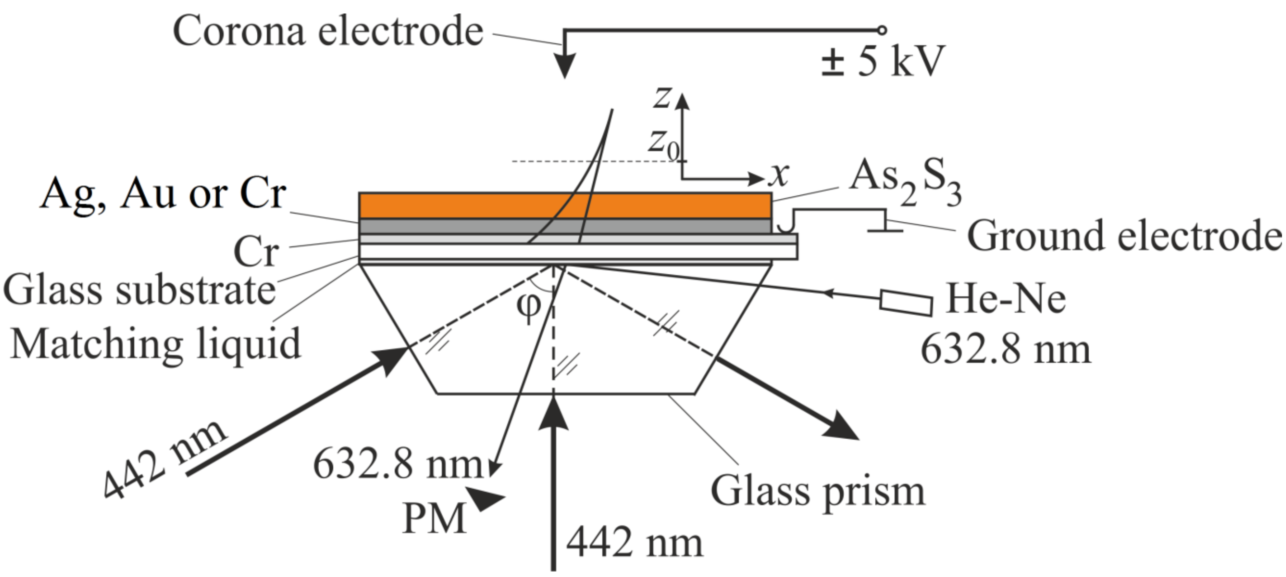

Fig. 1. Optical set-up for evanescent-wave holographic recording.

RESULTS AND DISCUSSION

The time dependences of the diffraction efficiency during the holographic recording at the presence of positive or negative corona discharge of As_2S_3/Ag/Cr multilayer system are shown in Fig. 2.

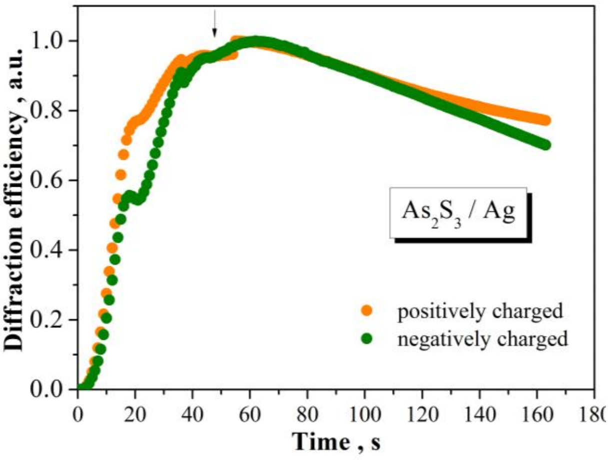

Fig. 2. Normalized diffraction efficiency of holographic recording in As_2S_3/Ag films the presence of a corona discharge.

The experimental results show that the diffraction efficiency time dependences are not influenced by the corona polarity. That is why the subsequent experiments are carried out with applying only negative voltage to the corona electrode. The time dependences of the diffraction efficiency during the holographic recording at the presence of negative corona discharge for As_2S_3/Au/Cr and As_2S_3/Cr/Cr multilayer system are shown in Fig. 3 and Fig. 4.

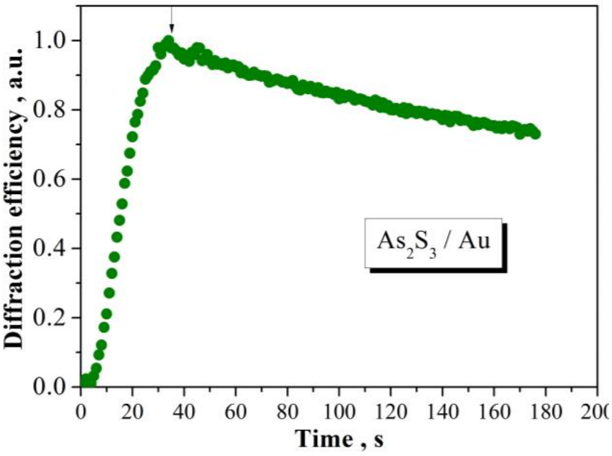

Fig. 3. Normalized diffraction efficiency of holographic recording in As_2S_3/Au the presence of a negative corona discharge.

The results observed show that the diffraction efficiency changes more drastically in the first 30 s of the holographic recording process. The time-dependent decay of the diffraction efficiency is proportional to the interference term and its time constant τ can be obtained by fitting of the experimental data with time dependent expression described in [9].

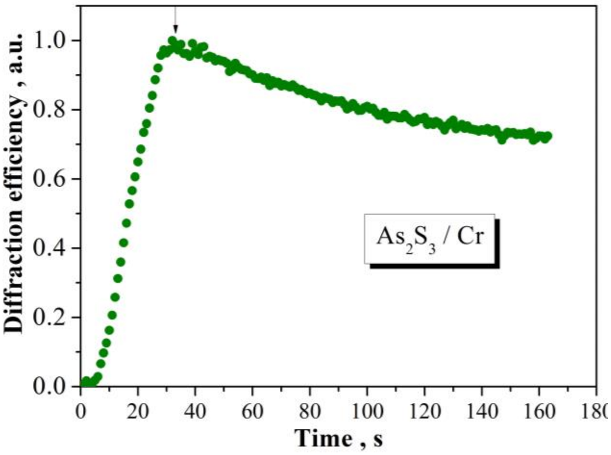

Fig. 4. Normalized diffraction efficiency of holographic recording in As_2S_3/Cr in the presence of a negative corona discharge.

The diffusion coefficient D are calculated by the method of the holographic grating relaxation spectroscopy (Forced Rayleigh Scattering) [7] by the following relation using already obtained values of the time constant τ:

$$D = \frac{4.84}{\tau} 10^{-11}\ \text{cm}^2/\text{s}, \quad \text{for } \lambda = 442\ \text{nm} \qquad (1)$$

With the obtained values of the diffusion coefficient, the mobility of metal ions are calculated using the modified Nernst-Einstein relation:

$$\mu = D\frac{q}{kT} = D\frac{e}{kT}\left(1+\Delta\right) \qquad (2)$$

where:

e is the elementary charge of the electron;
q is the metal ions charge;
k is the Boltzmann constant;
T is the absolute temperature;
Δ is the correlation coefficient [10] and in our case it is defined as:

$$\Delta = \frac{(\varepsilon_0 - 1)}{2(2\varepsilon_0 + 1)} \tag{3}$$

For As_2S_3 the constant ε_0 is 7.8 [11,12] and the correction coefficient was calculated from eqn. (3) to be Δ = 0.205. This result is in very good agreement with the experimentally obtained value of the silvers ion charge

$$q = (1.2 \pm 0.2)e.$$

The results obtained by eqn. (1) and eqn. (2) are presented in Table 1.

Table 1. Calculated values of the coefficients of diffusion and mobility.

Metal	**Atomic number**	**Ion charge**	***D*, ×10^{-13} cm^2/s**	**μ, ×10^{-11} cm^2/V.s**
Ag	47	+1	3.43	1.65
Au	79	+1	2.02	1.01
Cr	24	+2, +3	2.49	1.19

The results for the coefficients of diffusion and mobility indicate that they decrease with increasing of the atomic number as well as increase of the charge of the ions. To explain this result, we applied the Born-Mayer potential, which can be written as follows:

$$U = \frac{-\alpha q_c q_a}{r} + Z\lambda \exp\left(-\frac{r}{\rho}\right) \tag{4}$$

where α is the pseudo-Madelung constant, r is the internuclear distance, Z is the coordination number of metal cations in glassy network, ρ is the repulsion parameter and λ is the empirical parameter, q_c and q_a are the charges of metals cations and anions from the glassy network of the chalcogenide films, respectively.

The second term in eqn. (4) takes into account the bonding interactions as the electronic delocalization of the metal atoms, overlap of the valence electron and bond stretch. And it explains the lower values of the diffusion coefficient of the gold in comparison to that of the silver ions. The ion charge of silver and gold is equal and does not influence on the diffusion coefficient value. The gold atomic number is 1.68 times bigger than the silver atomic number which is in very good agreement with the diffusion coefficient ration of silver and gold that is 1.70.

This first term in the eqn. (4) describes the electrostatic interactions between charged ions and glassy network. It is seen that the increase of the charge of the ions leads to increasing of the electrostatic forces of interaction of ions with anions from the chalcogenide network which the ion's jumps more difficult.

The ratio of the diffusion coefficients of chromium and silver is 0.73 while the atomic number of the silver is 1.96 times higher than the chromium atomic number. The difference between the diffusion coefficients cannot be explained only with the radius of the atoms of both metals. In this case the value of the diffusion coefficient for chromium could be explained if we take into account two terms of the eqn. (4). On the base of the second term the silver atomic number is 1.96 times higher than the chromium atomic number which is not is not in agreement with diffusion coefficient ration of chromium and silver that is 0.73. On the base of the first term if we take into account that the average chromium ion charge is 2.5 times higher than the silver ion charge and multiplied by it the ratio 0.73 we get 1.83 that is close to 1.96.

Analogically, we could compare the diffusion coefficient of chromium and gold. The gold/ chromium atomic number ratio is 3.29 and the chromium/gold diffusion coefficient ratio is 1.23. If we multiply the second ratio by 2.5, we get 3.08 that is close to 3.29.

For more clear understanding and explanation of this phenomenon the good knowledge of the coordination numbers of silver, gold and chromium is necessity.

CONCLUSION

The combination between the holographic grating spectroscopy (Forced Rayleigh Scattering and corona charging seems to be a useful experimental method for electromigration study of metal diffusion coefficient and ion mobility in nanometer-thick amorphous chalcogenide layers. Two coefficient values for three metal ions – silver, gold and chromium were experimentally calculated and analyzed by the Born-Mayer potential equation. It was obtained that the diffusion coefficient and the ion mobility of silver are the highest and of gold are the lowest.

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ХОЛОГРАФСКО ИЗСЛЕДВАНЕ НА ВЛИЯНИЕТО НА КОРОННИЯ РАЗРЯД ПРИ ФОТОДОПИНГ НА СРЕБРО, ЗЛАТО И ХРОМ В НАНОРАЗМЕРНИ ФИЛМИ ОТ As_2S_3

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(Резюме)

В настоящата работа са изследвани подвижността и фото-дифузията на йоните на Ag, Au и Cr в наноразмерни слоеве от системата As_2S_3 при прилагане на коронен разряд. Холографските записи в структура тип сандвич от слой As_2S_3 с дебелина 50 nm и метален слой са направени с помощта на нормално падаща и на затихваща вълна, създадена при пълно вътрешно отражение при пространствена честота 2 500 $мм^{-1}$. При достигане на максималната дифракционна ефективност, записващият лазерен лъч се изключва и се прилага електричното поле на 5 kV коронен разряд. Измеренаат максимална дифракционна ефективност е по-голяма от 8%. Изследвана е подвижността на металните йони (Ag, Au and Cr) в тънки халкогенидни филми. Подвижността на металните йони, при температура 17°C е изчислена с уравнението на Нернст-Айнщайн. Коефициентът на дифузия D е получен по метода на холографската релаксационна спектроскопия (Форсирано разсейване на Релей). Обсъдени са получените стойности за подвижността и коефициента на дифузия за йоните на Ag, Au и Cr.