Bulgarian Chemical Communications, Volume 45, Special Issue B (pp. 86-89) 2013

On silver electromigration in nano-sized As_2S_3 films

I. Bodurov[1*], R. Todorov[1], T. Yovcheva[2], G. Spassov[1] and S. Sainov[1]

[1]*Institute of Optical Materials and Technologies "Acad. J. Malinowski", Bulgarian Academy of Sciences, "Acad. Georgi Bonchev" str., block 109, 1113 Sofia, Bulgaria*
[2]*Plovdiv University "Paisii Hilendarski", 24 "Tsar Asen" str., 4000 Plovdiv, Bulgaria*

Received October 17, 2013; Revised November 25, 2013

In this paper the silver mobility in thin chalcogenide films is investigated. The diffraction gratings in 96 nm thick As_2S_3 films are holographically recorded using evanescent wave, created by total internal reflection and normally incident plane one. The grating step Λ is 447 nm and corresponding spatial frequency is 2237 mm^{-1}. 5 kV corona discharge is applied during the holographic recording. The maximum measured value of the diffraction efficiency is greater than 8%. The mobility of silver, μ, at temperature 17°C is calculated by the Nernst-Einstein equation. The diffusion coefficient D is obtained using the method of holographic grating spectroscopy (Forced Rayleigh Scattering). The dependence of the diffusion coefficient and the mobility of silver on corona charge polarity are investigated.

Keywords: Chalcogenide glasses, Forced Rayleigh Scattering, Silver electromigration, Diffusion coefficient, Silver ion mobility

INTRODUCTION

Seven years after the pioneer work of Kostyshin and co-workers [1], the conductivity increase of the As_2S_3 bulk samples was observed in an electric field [2]. As a result of this investigation, one quite natural question is raised: How the external electric field will influence the silver transportation into the chalcogenide glasses? As far as we know, the answer was given for the first time by Lebedev and co-workers [3, 4] in 1975. For As_2S_3 samples it was found that the migration of the noble atom in singly charged ionic form was accelerated by the application of the external electric field.

The main futures of these investigations are:

1. The ionic mobility was obtained in high temperature region 120 °C – 180 °C.
2. The time-consuming radioactive tracer is applied for the diffusion coefficient determination.
3. The investigations was carried out in bulk As_2Se_3 samples.

In the present work the electromigration of silver is studied in following different conditions:

1. The nanometer thick samples are used.
2. The electromigration is studied by corona discharged electric field.
3. The diffusion is studied by holographic method of Forced Rayleigh Scattering.
4. The experiments are carried out at temperature, 17 °C.

EXPERIMENTAL

Sample preparation

We performed holographic recording in an As_2S_3/Ag/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 silver layer (d_{Ag} ~20 nm) was sputtered over the chromium film in the same vacuum cycle. Thin As_2S_3 films with thicknesses 96 nm were deposited on the silver coating by high vacuum thermal evaporation in a Leybold Heraeus A 702 Q depositing system. The chalcogenide films were prepared in a vacuum of 10^{-3} Pa, at a deposition rate of 0.1 $nm.s^{-1}$. 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 was used. The refractive index of the prism at wavelength λ = 442 nm was n = 1.526 and the calculated critical

---

[*] To whom all correspondence should be sent: E-mail: bodurov@uni-plovdiv.net

angle was φ_{cr} = 40.9°. Therefore the incidence angle φ = 41.5° was selected for the experiments.

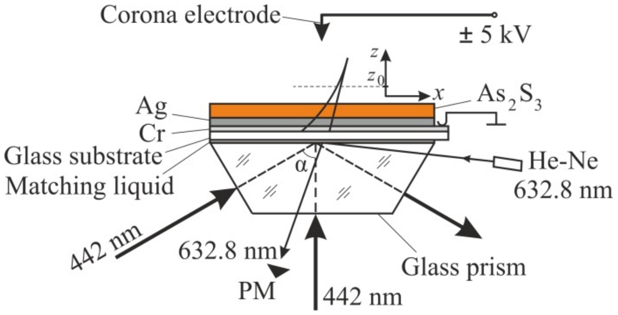

Fig. 1. Optical set-up for evanescent-wave holographic recording.

The total light intensity of the recording He-Cd laser was 10 µW.cm^{-2}. For real-time diffraction efficiency monitoring a He-Ne laser with 23 µW.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 silver to the glass substrate. The corona discharge occurred between the needle and the grounded electrode (Cr sub-layer).

Auger characterization

The AES analysis is performed with a microprobe (including a cylindrical mirror analyzer with a coaxial electron gun), mounted in a stainless-steel bell year at a working pressure 1.3×10^{-8} Pa. The analyzer’s energy resolution is about 0.3%. It uses 0.08 µA current and 3 keV electron beam with a diameter 10µm, directed normally to the surface. The spectra are differential; the modulation voltage is 4 $V_{p.t.p.}$ The profiling is performed with a 3 keV Ar^+-ion sputtering at an angle of 79° to the surface normal. The following Auger peaks were monitored S (152 eV), C (272 eV), Ag (356 eV), O (510 eV), Cr (529 eV) and As (1228 eV). Their intensity was measured peak-to-peak.

Previous results of As-S-Se/Ag [5] showed that the electron beam induced additional silver diffusion into the chalcogenide glasses composition. In order to avoid the phenomenon the time of electron-beam interaction with matter should be as short as possible. Therefore instead of the conventional, the crater-edge profiling was utilized. The latter approach consists in etching a crater in the studied specimen and successively scanning the fabricated edge by the electron beam. Thus, the duration of irradiation at each scanned spot is reduced to less than 1.5 min and the accumulation of silver is prevented.

RESULTS AND DISCUSSION

Fig. 2 presents Auger profiles of $As_{40}S_{60}$ layers after holographic recording in the presence of the negative and positive corona electric field. The AES profiles reveal uniform distribution of all the elements in the depth (Figs. 2, 3). The AES analysis showed presence significant amount of embedded carbon (it is not shown in figures), due to the immersion fluid used in the process of holographic record. The ratio of S/As for negative electric field treated sample is 2:1, while this ratio varied from 1 (to the surface) to 1.7 in the case of positive electric field treated samples. The results showed that the silver is approximately homogenous distributed in

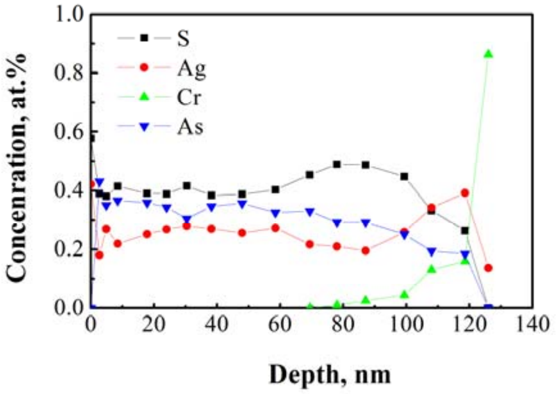

Fig. 2. Auger profiles of silver doped $As_{40}S_{60}$ films obtained by negative corona discharge treatment.

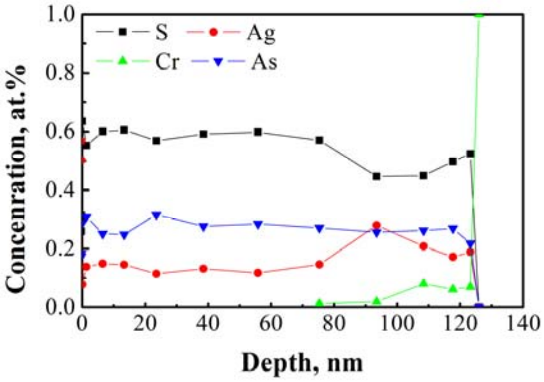

Fig. 3. Auger profiles of silver doped $As_{40}S_{60}$ films obtained by positive corona discharge treatment.

the samples, independently from the electric field's polarity. The composition analysis showed that the ratios (S+As)/Ag are 4.3 and 2.8 for positively and negatively charged samples, respectively.

The time dependencies of the diffraction efficiency during the holographic recording in the presence of negative or positive corona discharge are shown in Fig. 4.

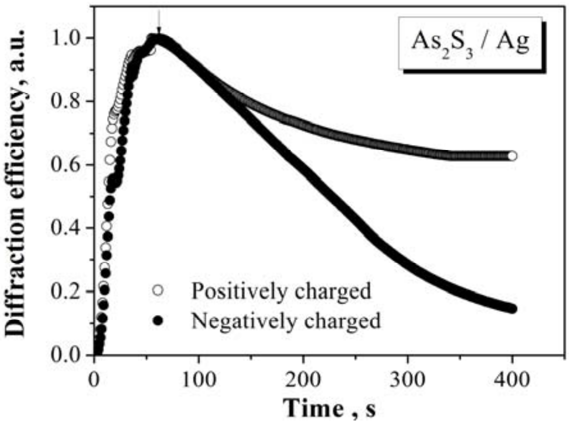

Fig. 4. Normalized diffraction efficiency of holographic recording in the presence of a corona discharge.

The experimental results show that the diffraction efficiency changes more drastically in the first (50-60) s of the holographic recording. 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 [6].

The diffusion coefficients *D* are calculated with the help of 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:

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

and they are found to be $D = 5.1\times10^{-13}$ cm^{2}s^{-1} and 1.7×10^{-13} cm^{2}s^{-1} for negatively and positively charged samples, respectively.

With the obtained values of the diffusion coefficient, the mobility of silver ions is 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 silver ions charge; *k* is the Boltzmann constant; *T* is the absolute temperature; Δ is the correction coefficient [8] and in our case it is defined as:

$$\Delta = \frac{\left(\varepsilon_0 - 1\right)}{2\left(2\varepsilon_0 + 1\right)} \qquad (3)$$

For As_2S_3 the constant ε_0 is 7.8 [9, 10] 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 silver ions charge $q = \left(1.2 \pm 0.2\right)e$ reported in [3].

The values of the silver ions mobility are calculated from eqn. (2) to be 2.4×10^{-11} cm^{2}V^{-1}s^{-1} and $0.8\ \times10^{-11}$ cm^{2}V^{-1}s^{-1} for negatively and positively charged samples, respectively.

In our room temperature experiment the mobility of silver's ion is about three orders of magnitude smaller, compared with the high temperatures value of the silver's ion mobility in bulk chalcogenide glass samples. The temperature dependence of the mobility of silver's ion is presented by Lebedev [3] by the following relation:

$$\mu = 9\exp\left(-\frac{U}{kT}\right) \qquad (4)$$

where *U* is the activation energy of the electromigration.

It should be noted that in [3] Lebedev and co-authors have accepted that *U* = 0.80 eV. Most common ionization state of silver is +1. The activation energy in our case is $U = \frac{U_{Lebedev}}{\left(1+\Delta\right)} = \frac{0.80}{1.2} = 0.67$ eV. So, for *T* = 290 K from eqn. (4) we have $\mu = 2.1\times10^{-11}$ cm^2/Vs, that is in good agreement with the experimentally obtained value for 100 nm thick film.

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 nanometer-thick materials. It should be noted the main advantaged as:

1. Negligible Joule heating.
2. The measurements are express.
3. One contact plate electrode is needed.
4. The sub-layer (Cr) electrode could be used for the sample heating for high temperature

electromigration investigations.

REFERENCES

1. M. Kostyshin, E. Mikhaylovskaya, P. Romanenko, *Sov. Phys.Sol. State,* **8**, 451 (1966).
2. J. Shimizu, H. Kokaido, E. Inoue, *Bull. Chem. Soc. Jpn.,* **46**, 3662 (1973).
3. E. Lebedev, P. Suptitz, I. Willert, *Phys. Stat. Sol. (a),* **28**, 461 (1975).
4. P. Suptitz, J. Teltow, E. Lebedev, I. Willert, *Phys. Status Solidi, (A)* **31**, 31 (1975).
5. R. Todorov, J. Tasseva, G. Spassov, K. Petkov, *J. Phys.: Conf. Ser.,* **223**, 012040 (2010).
6. S. Sainov, *J. Chem. Phys.,* **104,** 6901 (1996).
7. S. Sainov, R. Todorov, I. Bodurov, T. Yovcheva, *J. Opt.,* **15** 105705 (2013)
8. E. Katz, *Phys. Rev.,* **99**, 1334 (1955).
9. N. Goyal, A. Zolanvari, S. K. Tripathi, *J. Optoelectron. Adv. Mater.,* **3**, 741 (2001).
10. Z. Borisova, Semiconductrors, Plenum Press, New York, 1981.

ОТНОСНО ЕЛЕКТРОМИГРАЦИЯТА НА СРЕБРО В НАНОРАЗМЕРНИ ФИЛМИ ОТ AS_2S_3

И. Бодуров[1], Р. Тодоров[1], Т. Йовчева[2], Г. Спасов[1] и С. Съйнов[1]

[1]Институт по оптически материали и технологии „Акад. Йордан Малиновски“, БАН, ул. “Акад. Георги Бончев”, блок 109, 1113 София, България

[2]Пловдивски университет “Паисий Хилендарски”, ул. “Цар Асен” 24, 4000 Пловдив, България

Постъпила на 17 октомври 2013 г.; коригирана на 25 ноември, 2013 г.

(Резюме)

В настоящата работа е изследвана подвижността на среброто в тънки халкогенидни филми. Във филми As_2S_3 с дебелина 96 nm бяха записани холографски дифракционни решетки чрез използването на нормално падаща вълна и на затихваща вълна, създадена при пълно вътрешно отражение. Стъпката на решетката Λ беше 447 nm със съответстваща пространствена честота 2237 mm^{-1}. Записът беше осъществен едновременно с прилагане на електрично поле на 5 kV коронен разряд. Максималната измерена дифракционна ефективност беше по-голяма от 8%. Подвижността на среброто, μ, при температура 17°C, беше изчислена с уравнението на Нернст-Айнщайн. Коефициентът на дифузия D беше получен по метода на холографската релаксационна спектроскопия (Форсирано разсейване на Релей). Изследвана е зависимостта на коефициента на дифузия и на подвижността на среброто от полярността на коронния разряд.