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HOLOGRAPHY

Effect of Corona Discharge on the Optical Properties of Thin-Film $Cu–As_2Se_3$ Structures

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Abstract—The effect that corona discharge has on holographic recording of diffraction gratings in a thin-film $Cu–As_2Se_3$ structure deposited on glass by thermal vacuum evaporation is studied. The use of negative corona discharge during holographic recording enhances the holographic sensitivity of the $Cu–As_2Se_3$ structure and the diffraction efficiency of inscribed gratings. Irradiation of the $Cu–As_2Se_3$ structure with actinic light results in photodarkening in the spectral region in which the structure exhibits a strongly absorption, while the region characterized by a weaker absorption becomes more transparent. The effect of photoinduced transparency is enhanced if samples are treated using positive corona discharge and with negative corona discharge the effect is weakened. The experimental results are explained qualitatively, assuming the diffusion of Cu^+ ions into the As_2Se_3 layer.

Keywords: chalcogenide films, thin-film structure, diffraction efficiency, transmission spectrum, corona discharge

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INTRODUCTION

Despite the fact that semiconducting chalcogenide glasses (SCGs) were discovered a long time ago (in 1956), they are still attracting considerable interest, with the focus mainly being on the electrical and optical properties of thin noncrystalline SCG films [1–3].

The main development of optical technology consists in the search for new materials, including different recording media, and development of new methods for optical recording. Thin noncrystalline SCG films are promising recording structures for use in optical holographic inscribing. Methods most widely used for optical recording in thin SCG films are based on light-induced structural transformation (LIST) and light-induced metal diffusion (LIMD) within a metal–SCG structure [4]; however, there are more contemporary versions of these classical methods [5]. For a metal–SCG structure, a recording method in which exposition was carried out simultaneously with inscription using corona discharge was proposed in [5]. With this method, the sensitivity, diffraction efficiency, and relief depth produced using chemical etching [6] due to the LIST [7–9] and LIMD [10, 11] effects were increased by several times. We note that the effect of corona discharge is more emphasized in thin SCG layers. For instance, for SCG films with thicknesses of 29 and 56 nm, the use of corona discharge—unlike conventional methods for hologram recording (i.e., without corona discharge)—resulted in a 30- and 10-fold increase in the maximum diffraction efficiency, respectively, due to the LIST effect [12].

The aim of this study is to investigate the effect the corona discharge has on photoinduced changes in transmission spectra of $Cu–As_2Se_3$ structure and on the inscribing of holographic diffraction grating into them.

SAMPLE PREPARATION AND CHARACTERIZATION METHODS

Thin-film $Cu–As_2Se_3$ structures were fabricated by depositing Cu and SCG layers onto glass substrates by thermal vacuum evaporation (residual pressure, 3.7×10^{-3} Pa), with the SCG layer deposition rate being around 5 nm/s. The thickness of SCG layer on different samples was either 0.27 or 0.11 μm, while the metallic (i.e., Cu) layer was around 40 μm thick. Transmission spectra were recorded and holographic recording of diffraction grating was performed for the freshly prepared samples of the $Cu–As_2Se_3$ structures. We note that in performing holographic recordings in corona discharge, the copper layer was connected as one of the electrodes, and the transmission of the copper film at a wavelength of 0.63 μm amounted to around 30%.

In studying transmission spectra of the $Cu–As_2Se_3$ structure, the latter was irradiated by a He–Ne laser (wavelength λ = 0.6328 μm and exposure H = 0.5 J/cm^2) from the SCG side, with and without corona discharge (±7 kV) applied. Transmission spectra were recorded using a Specord UV–Vis spectrophotometer controlled by a computer.

A setup producing corona discharge consisted of a high-voltage unit and a corona treater unit. A thin tungsten thread (60 μm) was used as the corona-discharge electrode to which a potential of +7 or −7 kV was applied. A sample was placed at a distance of 17 mm away from the thread.

Holographic recording of diffraction gratings was performed either using corona discharge or without such. Diffraction gratings with a period of 2 μm were recorded in converging beams of the He–Ne laser (λ = 0.6328 μm) using the conventional off-axis method. Diffraction efficiency η was measured as the first-order diffraction in transmitted light with the same wavelength (λ = 0.6328 μm), with a light beam directed at normal incidence to the SCG layer. The diffraction efficiency was calculated as the ratio of intensity of the first diffraction maximum to the intensity of light passed through an unexposed region of the sample.

RESULTS AND DISCUSSION

Figure 1 shows the variations of diffraction efficiency with exposition for holographic diffraction gratings with a spatial frequency of 500 mm^{-1} fabricated using both conventional (curves *2*, *5*) and corona discharge-assisted (curves *1*, *3*, *4*) recording methods (note that a similar figure can be found in [11]). As can be seen, with negative corona discharge, the sensitivity of $Cu–As_2Se_3$ structure was enhanced and the diffraction efficiency of inscribed gratings was raised (compare curves in pairs *1*, *2* and *4*, *5*). In contrast, with positive corona discharge, both the sensitivity and diffraction efficiency diminished (compare curves *2*, *3*).

As in work [11], these results can be easily explained within a known photoelectrical model [4, 13]. This model assumes that the photodiffusion rate is limited by the rate of metal permeation from the doped region of an SCG material into the undoped one. When the interface between the doped and undoped regions of SCG is irradiated with light, electrons and holes are separated in such a way that the electric field they create has a pulling effect on metal ions [4]. The net pulling electric field, which drives positively charged metal ions from the photodoped layer into the undoped one [4, 13], is enhanced when the $Cu–As_2Se_3$ structure is exposed to a negative corona discharge, whereas exposure to a positive corona discharge weakens the field.

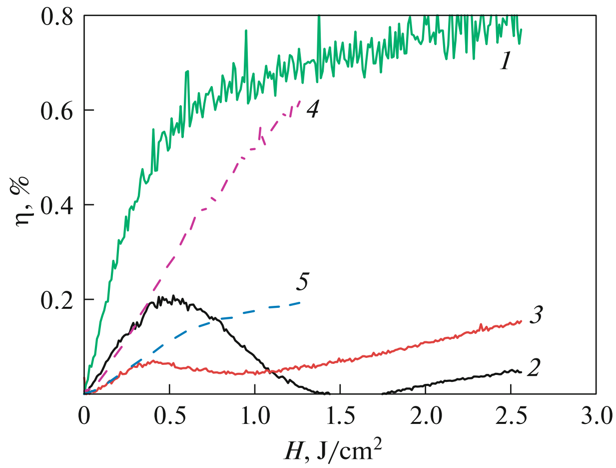

Fig. 1. Variations of the diffraction efficiency with exposure for holographic diffraction gratings inscribed into the $Cu–As_2Se_3$ structure under different conditions: (*2*, *5*) without corona discharge, (*1*, *4*) using negative corona discharge (U = −7 kV), and (*3*) using positive corona discharge (U = +7 kV). The thickness of SCG layer is (*1*, *2*, *3*) 0.27 and (*4*, *5*) 0.11 μm.

Figure 2 shows transmission spectra for freshly prepared samples of the metal–As_2Se_3 structures before (curves *1*, *3*, *5*) and after (curves *2*, *4*, *6*) being irradiated in the absence of corona discharge. Spectra *1* and *2* were recorded for samples with an As_2Se_3 layer thickness of 0.11 μm, spectra *3* and *4* are for samples with a 0.27-μm-thick As_2Se_3 layer, and spectra *5* and *6* are for samples with a 1-μm-thick As_2Se_3 layer. Transmission spectra for an $Al–As_2Se_3$ structure recorded before (curve *5*) and after (curve *6*) irradiation are shown in the same figure (Fig. 2) for comparison. For this sample, the thickness of As_2Se_3 layer was 1 μm, and the Al layer with a thickness of a few tens of nanometers was characterized by a transmission coefficient of around 50% at a wavelength λ = 0.63 μm. It is known for $Cu–As_2Se_3$ structures, that light induces diffusion of Cu ions from the copper layer into the SCG layer, whereas photodiffusion of Al ions into the SCG layer does not occur in $Al–As_2Se_3$ structures. Irradiating the $Al–As_2Se_3$ structure with actinic light induces only (photo)structural transformations leading to photodarkening of the material, as can be appreciated from Fig. 2 (compare curves *5* and *6*). It can be seen in the same figure that, in contrast to the $Al–As_2Se_3$ structure, irradiating the $Cu–As_2Se_3$ structure makes it more transparent in the region of weak absorption due to thinning of the copper layer. The maxima in curves *3* and *4* (thickness of As_2Se_3 layer is 0.27 μm) are due to light interference in thin films.

The effect that irradiation conditions have on spectral distribution of photoinduced changes in transmission spectra $\Delta T(\lambda) = T(\lambda) - T_0(\lambda)$ of the $Cu–As_2Se_3$ structure can be appreciated from the family of curves

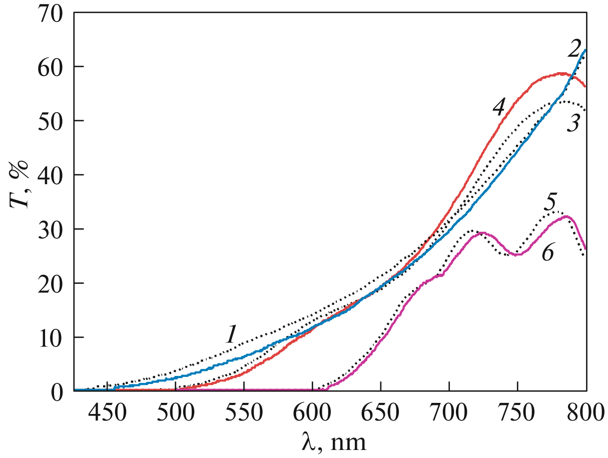

Fig. 2 Transmission spectra for (*1*–*4*) Cu–As_2Se_3 and (*5*, *6*) Al–As_2Se_3 structures recorded (*1*, *3*, *5*) before and (*2*, *4*, *6*) after being irradiated. The thickness of As_2Se_3 layer is (*1*, *2*) 0.11, (*3*, *4*) 0.27, and (*5*, *6*) 1 μm.

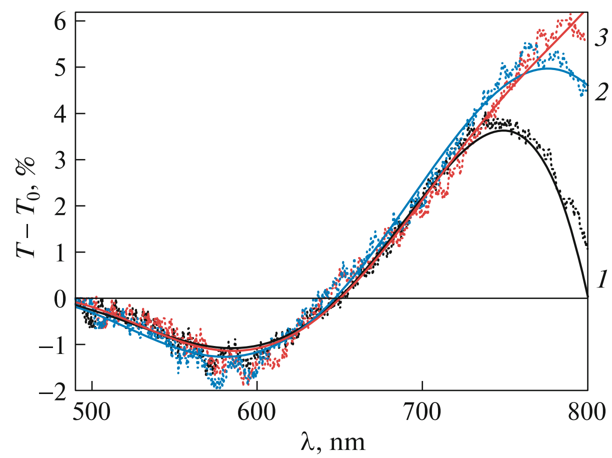

Fig. 3. Spectral dependences of photoinduced variation of transmission for the Cu–As_2Se_3 structure having a thickness of the SCG layer of 0.27 μm; the structure was optically irradiated while being exposed to the electric field of corona discharge induced by applying voltages *U* of (*1*) –7, (*2*) 0, and (*3*) +7 kV.

shown in Figs. 3 and 4 for samples having a 0.27- and 0.11-μm-thick As_2Se_3 layer, respectively. Here, $T_0(\lambda)$ and $T(\lambda)$ are the transmissions of the structure under study before and after irradiation, respectively. In each of these figures, curves *2* correspond to the cases when samples were irradiated but not exposed to corona discharge (i.e., conventional irradiation was used), and curves *1* correspond to the samples that were irradiated while exposed to a negative corona discharge ($V = -7$ kV). Curve *3* in Fig. 3 is for the sample that was irradiated while exposed to a positive corona discharge (+7 kV).

The spectral region in which $T(\lambda) < T_0(\lambda)$ corresponds to the irradiation-induced photodarkening of Cu–As_2Se_3 structure, and the spectral region in which $T(\lambda) > T_0(\lambda)$ corresponds to irradiation-induced transparency of the sample. Curves *1*–*3* of Fig. 3 nearly coincide in the short-wavelength spectral region where the absorption is high. These results tell us that corona discharge does not affect photodarkening of the Cu–As_2Se_3 structure, despite the fact that it affects the Cu ion photodiffusion into the As_2Se_3 layer. At the same time, the corona discharge had a marked effect on light-induced transparency of the Cu–As_2Se_3 structure that was observed in the long-wavelength region where the absorption is weak. The positive electric field of corona discharge enhanced the effect of light-induced transparency (compare curves *3* and *2* in Fig. 3), while the negative field had a weakening effect (compare curves *1* and *2* in Fig. 3).

The weaker effect of light-induced transparency observed for the Cu–As_2Se_3 structure irradiated while exposed to the field of a negative corona discharge was also observed in the case of a thinner As_2Se_3 layer (Fig. 4). The Cu–As_2Se_3 structure with an SCG layer 0.11 μm in thickness (Fig. 4) differs in that, when it is irradiated while exposed to a negative corona discharge, the position of the minimum (corresponds to the greatest photodarkening) exhibits a marked shift toward the long-wavelength region compared to the case in which corona discharge was not used (compare curves *1* and *2* in Fig. 4). Meanwhile, the negative corona discharge enhances photodarkening of the Cu–As_2Se_3 structure.

These results can be explained qualitatively by considering the Cu–As_2Se_3 structure as consisting of sev-

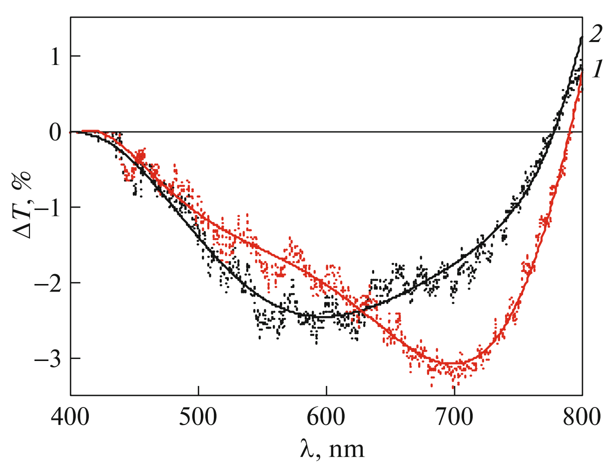

Fig. 4. Spectral dependences of photoinduced variation of transmission for the Cu–As_2Se_3 structure having a thickness of the SCG layer of 0.11 μm; the structure was optically irradiated while being exposed to the electric field of corona discharge induced by applying voltages *U* of (*1*) –7 and (*2*) 0 kV.

eral layers, each contributing to the net absorption of light. That being so, the structure before irradiation consists of a metal layer and a pure (undoped) As_2Se_3 layer, whereas, in the irradiated structure, a region of the As_2Se_3 layer adjacent to the metal electrode becomes doped with Cu ions. Put differently, the initially homogeneous As_2Se_3 layer separates into two sublayers as a result of copper ion photodiffusion. The thickness of layers constituting the structure, and therefore their absorption, change differently as a result of light-induced diffusion of copper ions into the As_2Se_3 layer. It is this circumstance that underlies the effect that the irradiation conditions for the Cu–As_2Se_3 structure have on its transmission spectra.

SCG films doped with Ag ions were shown to undergo photodarkening in the short-wavelength region [14]. Similarly, photodoping of the As_2Se_3 sublayer with Cu causes the absorption edge of this layer, and therefore that of the whole Cu–As_2Se_3 structure, to redshift. At the same time, the photodiffusion of Cu ions from the underlying electrode leads to its thinning, thereby rendering it and the whole structure more transparent. The lessening of absorption of light with a longer wavelength is not so pronounced in the doped sublayer compared to the undoped As_2Se_3 sublayer, let alone the nonirradiated As_2Se_3 layer. This can explain the behavior of spectral dependences of photoinduced transmission $\Delta T(\lambda)$ in the initial part of the region, where it starts falling. It seems that the increase seen in spectra at longer wavelengths is caused by the fact that, as the absorption by the doped As_2Se_3 layer diminishes further, the decrease in absorption by the underlying metallic layer, due to its thinning, makes a marked contribution to the photoinduced changes in the Cu–As_2Se_3 structure transmission. Thus, the photoinduced increase in absorption by the As_2Se_3 layer and the decrease in absorption by the metallic layer, in combination, lead to the emergence of a minimum on the spectral dependence of photoinduced transmission $\Delta T(\lambda)$.

The decrease in absorption by the As_2Se_3 layer, inclusive of its doped sublayer, leads to a decrease in absorption by the Cu layer determining the transmission of Cu–As_2Se_3 structure in the long-wavelength region. This gives rise to the effect of light-induced transparency of the Cu–As_2Se_3 structure in the indicated spectral region.

The electric field of corona discharge affects the photodiffusion of Cu ions into the As_2Se_3 layer. The pulling electric field created as a result inscribing a holographic pattern into the thin-film Cu–As_2Se_3 structure by subjecting it to irradiation, and, simultaneously, a negative corona discharge enhances the diffusion of positively charged copper ions, whereas the field created during inscribing using positive corona discharge has an inhibiting effect on the Cu ion diffusion. Therefore, in contrast to the conventional irradiation method, the use of negative corona discharge gives rise to a doped As_2Se_3 sublayer exhibiting a stronger absorption and a copper layer exhibiting a better transmission. Conversely, the use of a positive corona discharge gives rise to a to doped As_2Se_3 sublayer with a lesser absorption and a copper layer with lesser transmission. Compared to the conventional irradiation method (curves *1*, *2* in Fig. 3), the lessening of the effect of photoinduced transparency observed when a negative corona discharge was used can be explained by the fact that the increase in absorption by the doped As_2Se_3 sublayer proved to be higher than the increase in the copper layer transmission. Similarly, the enhancement of photoinduced transparency observed when the positive corona discharge was used (curves *2*, *3* in Fig. 3) can be explained by the fact that the decrease in absorption occurs mainly due to the doped As_2Se_3 sublayer, which is not the case if conventional irradiation is used.

Looking at the experimental results from this perspective, we can conclude that the effect of the use of corona discharge has on the optical properties of Cu–As_2Se_3 structure when the latter is irradiated consists mainly in alteration of the As_2Se_3 layer transmission.

A noticeable absorption in the short-wavelength spectral region was also observed for the undoped As_2Se_3 layer. In this case, the effect of corona discharge on the net transmission of doped and undoped As_2Se_3 sublayers was weaker than in the long-wavelength range. This may explain why we did not see the effect of corona discharge on photodarkening of a Cu–As_2Se_3 structure with a thicker As_2Se_3 layer (Fig. 3). We anticipate that the corona discharge will have a greater effect on the transmission of Cu–As_2Se_3 structure with a thinner As_2Se_3 layer. This was confirmed in our studies of transmission spectra of the Cu–As_2Se_3 structure having a 0.11-μm-thick As_2Se_3 layer (Fig. 4).

We note that studying the spectra of photoinduced variation of transmission $\Delta T(\lambda)$ enabled us to identify the contribution of phase-amplitude holographic diffraction gratings to the absolute value for the diffraction efficiency of amplitude component. As can be seen from the presented spectra, the change in diffraction efficiency due to corona discharge, as measured in transmitted light (0.63 μm), occurred due only to phase modulation of light flux.

CONCLUSIONS

1. Using corona discharge during inscription into Cu–As_2Se_3 structures leads to enhanced holographic sensitivity of the resulting structure and improved diffraction efficiency of inscribed holographic diffraction gratings, compared to diffraction gratings inscribed

without using corona discharge. With a positive corona discharge, the effect is reversed.

2. Irradiation of the thin-film $Cu-As_2Se_3$ structure with actinic light led to changes in its transmission spectrum. Photodarkening was observed in the sort-wavelength region of the visible spectrum, where the absorption is strong; while the effect of light-induced transparency was observed in the long-wavelength region, where the absorption is weak.

3. The spectra of photoinduced transmission variation $\Delta T(\lambda)$ feature a minimum, due possibly to the opposing effects that (i) the decrease in the As_2Se_3 layer transmission due to photodoping by copper ions and (ii) the increase in copper layer absorption due to its thinning have on the transmission of As_2Se_3 structure.

4. Compared to irradiation alone, combining irradiation and positive corona discharge leads to enhanced transmission in the long-wavelength region of the visible spectrum, whereas with negative corona discharge we observed a decrease in the transmission.

5. Changes in the diffraction efficiency caused by the use of corona discharge, as measured in transmitted light ($\lambda = 0.63$ μm), occur due only to phase modulation of light flux.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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