Diffraction efficiency growth of nano-scale holographic recording produced in a corona discharge

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Abstract. The nano-scale holographic gratings were recorded in 29 nm and 56 nm thick As2S3 films. The chalcogenide layers were deposited on a transparent chromium electrode with thickness 10 nm, produced on a glass substrate. Both chromium and chalcogenide films were deposited in one vacuum cycle by e-beam and thermal evaporation, respectively. The diode 532 nm diode laser was used as a light source in the present holographic experiments. The total internal reflection arrangement (Stetson-Nassenstein) was used in holographic recordings. The reference beam was totally reflected from the air-As2S3 boundary surface by an input glass prism. The object beam was normally incident on the recording medium. The corona charging was performed by a needle fixed at the distance of 1 cm from the holographic recording medium by applying a – 5 kV voltage. The diffraction efficiency increased from 9 to 30 times when the corona discharge was applied during the holographic recording, in comparison to the uncharged recording. The possible reason of the observed effect is discussed on the basis of the Franz-Keldysh effect and Moss rule.

1. Introduction
The holographic grating measuring methods are very useful for the rapidly developing field of nanoscience and nanotechnology. During the past years we have performed a series of experiments connected with holographic recording in nano-sized As2S3 films [1-4]. The results of these studies have demonstrated the possibilities of the total internal reflection holographic technique for grating and image recording in As2S3 with different nano-scale thicknesses. The main disadvantage of this recording is the low diffraction efficiency value, so the researchers are looking for different methods for resolving this problem. The application of strong electric field seems to be most promising in this direction. Recently, Nastas et al. [5-6] have reported diffraction efficiency enhancement of a holographic grating recorded in 1.0 μm and 0.3 μm thick film using corona discharge. Up to 3 times diffraction efficiency increase has achieved by 8 kV electric field applying [5-6]. Investigations are now being carried out to increase the diffraction efficiency by applying the electric field in nano-scale
recording. In a recently published paper [7] spatial frequencies influence of the diffraction efficiency of holographic recording in As₂S₃ films with thicknesses of 29 nm, 15 nm and 10 nm has been presented. The authors found that the optimal thickness for low (310 mm⁻¹) and high (2700 mm⁻¹) spatial frequencies was about 30 nm.

In the present paper we reported the results obtained from the investigation of electric charge influence on the diffraction efficiency of holographic gratings recorded in 29 nm and 56 nm thick chalcogenide As₂S₃ film. This study is continuation of investigations reported earlier in [7].

2. Theoretical background

2.1. Holographic recording in nano-sized thin films

In the holographic scheme the plane object wave normally falls at the recording medium. The second reference wave (the evanescent wave) is created by total internal reflection (TIR).

The TIR of s-polarized plane wave with amplitude \( a_0 \) takes place at the prism-air interface in the case when the thickness of the registration medium is \( d << \lambda \) (\( \lambda \) is the laser wavelength in the air) [8]. When the incident angle is \( \varphi_i > \varphi_c \) (\( \varphi_c \) is the critical angle) we have

\[
\sin \varphi_c = 1 / n_1
\]

(1)

where \( n_1 \) is the refractive index of the glass prism.

The evanescent wave amplitude is

\[
a_e = \frac{2a_0n_1\cos \varphi_c}{(n_1^2 - 1)\frac{\lambda}{2\pi n_1}} \exp \left(-\frac{z}{z_0}\right)
\]

(2)

where the penetration depth is defined by

\[
z_0 = \frac{\lambda}{2\pi n_1\left(\sin^2 \varphi_i - \sin^2 \varphi_c\right)\frac{\pi}{\lambda}}
\]

(3)

The plane wave amplitude is

\[
a_p = a_0 \exp \left(\frac{2\pi}{\lambda} n_1 z\right)
\]

(4)

In the case when \( \frac{2\pi n_1 z}{\lambda} << 1 \), \( \frac{z}{z_0} << \left(\sin^2 \varphi - \sin^2 \varphi_c\right)\frac{\pi}{\lambda} \), \( \exp \left(-\frac{z}{z_0}\right) \approx 1 \), the interference term, obtained after simple trigonometric transformations, is

\[
I_{op} = 8 \frac{a_0a_e \cos \varphi_i}{(n_1^2 - 1)^\frac{1}{2}} \cos^2 \left(\frac{\pi n_1 x \sin \varphi_c}{\lambda}\right)
\]

(5)

The grating step along x-axis is

\[\Lambda = 1 / n_1 \sin \varphi_i\]

(6)

2.2. Electric field influence on the diffraction efficiency

The Klein parameter \( Q \) [9] is low in the case of holographic recording in very thin photosensitive films. This parameter is used to distinguish thick (volume) from thin (plane) holographic grating and is defined as

\[
Q = \frac{2\pi \lambda d}{n\Lambda^2}
\]

(7)

where \( n \) is the refractive index of the recording medium; \( \lambda \) is the wavelength of the laser, using in recording; \( d \) is the thickness of the film; \( \Lambda \) is the diffraction grating’s step.
The calculations for recording with 532 nm wavelength in 60 nm thick As$_2$S$_3$ film ($n = 2.41$) gives $Q - 0.5$, when grating step is 400 nm, corresponding to spatial frequency of 2500 mm$^{-1}$. This defined the grating as very thin. In spite of the low $Q$ value, the coupled-wave theory, developed by H. Kogelnik [10] is accurate in the case of the thin grating diffraction efficiency, illuminated at Bragg – angle condition, when only one diffraction order is observed. This is thoroughly investigated in [11] for the low modulation condition, that is our case of nano-sized holographic recording.

According the coupled wave theory, the diffraction efficiency ($\eta$) is

$$\eta = \sin^2 \frac{\pi \Delta n d}{\lambda \cos \theta} \approx \left( \frac{\pi \Delta n d}{\lambda \cos \theta} \right)^2$$  \hspace{1cm} (8)$$

where $\Delta n$ is the refractive index change (modulation), $\theta$ is the Bragg angle value, in the present case – the angle of incidence.

In order to calculate the refractive index change in corona discharge condition, one has to estimate the additional refractive index change under the applied high electric field $F$ . For this purpose we shall use in the first place the connection between refractive index of semiconductors and energy gap ($E_g$) [12] and after that 1-D Franz-Keldysh effect [13]. The empirical Moss rule is defined as

$$n^4 E_g = 77$$  \hspace{1cm} (9)$$

We should mention that for As$_2$S$_3$ we have $n = 2.42$ for 532 nm (our measurements) according to [14] $n = 2.41$ and $E_g$ is 2.32 eV [15]. The condition (9) in this case is satisfied very well – the difference is less than 1.5%. After some mathematical manipulation, we have

$$4 \frac{\Delta n}{n} = - \frac{\Delta E_g}{E_g}$$  \hspace{1cm} (10)$$

According to 1-D Franz-Keldysh effect, the parallel energy gap shift is [13]

$$-\Delta E_g = \frac{3}{2} \left( \frac{e h F}{m^*} \right)^{\frac{2}{3}}$$  \hspace{1cm} (11)$$

where $m^*$ is the effective electron mass; $e$ is the electron charge; $F$ is the electric field intensity; $h$ is the reduced Planck constant.

By using relations (8), (10) and (11), for the diffraction efficiency when electric field $F$ is applied we have

$$\eta_F = \frac{9}{64} \frac{\pi^2 d^2 n^2}{\lambda^2 \cos^2 \theta E_g^2} \left[ \frac{(e h F)^2}{m^*} \right]^{\frac{1}{3}} = 1.39 \frac{d^2 n^2}{\lambda^2 \cos^2 \theta E_g^2} \left[ \frac{(e h F)^2}{m^*} \right]^{\frac{1}{3}}$$  \hspace{1cm} (12)$$

3. Experimental

3.1. Sample preparation

The samples were prepared in one vacuum cycle ($P \sim 10^{-3} \text{ Pa}$) used thin film’s deposition system Leybold Haraeus A 702 Q. Firstly, thin transparent electrode from chromium with 10 nm thickness was deposited on suitably cleaned glass substrates by electron beam evaporation. The deposition rate was 0.2 nm/s. The transmission coefficient of the electrode in the spectral range 400 nm – 1500 nm was between 70 % and 80 % and the electrical resistivity was $\rho = 2 \text{ m\Omega cm}$. Subsequently the investigated samples – thin layers from high purity As$_2$S$_3$ with thickness 29 nm and 56 nm were deposited on the chromium electrode by thermal evaporation.

Optical transmission and reflection measurement in the spectral range 400 nm – 1500 nm were carried out using UV – VIS – NIR spectrophotometer (Cary 05E, Varian, Australia).
3.2. Holographic recording
The high spatial frequency grating is recorded in the Stetson-Nassenstein regime, using the holographic setup presented in figure 1.

Figure 1. Holographic set-up for total internal reflection grating recording:
1 – recording laser, 532 nm; 2 – beam splitter; 3b – total internal reflecting beam; 3a – normally incident beam; 4a,b – mirrors; 5 – prism; 6 – matching liquid; 7 – chromium electrode; 8 – recording medium; 9 – power meter; 10 – monitoring He-Ne laser, 632.8 nm; 11 – corona electrode (needle); 12 - high voltage supply

The reference beam (3b) is totally reflected from the chalcogenide film – air interface at the 54° incidence angle. The object beam (3a) is incident normally on the chalcogenide film. The total laser beam intensity is 10 mW/cm². The grating’s step $\Lambda$ is 0.376 $\mu$m and the corresponding spatial frequency is 2660 mm⁻¹. A low intensity He-Ne laser (10) is employed as a read-out beam to monitor the build-up dynamics of the gratings during the holographic recording.

The holographic recording in chalcogenide As₂S₃ films was carried out simultaneously with their charging in a negative corona field. The corona charging was performed by the needle (11) fixed at a distance of 1 cm from the sample, applying a voltage of $–5$ kV (12).

4. Results and discussion
The optical constants (refractive index $n$ and extinction coefficient $k$) and thickness $d$ of the thin films were calculated using transmittance and reflectance measurements and applying the triple method proposed by Konstantinov and Panayotov [16]. This method operated with three spectrophotometric measurements – $(T, R_f, R_m)$ or $(T, R_b, R_m)$, where $T$ is the transmission, $R_f$, $R_b$ and $R_m$ – the reflections from the front and back side of the BK-7 substrate, and from the film deposited on Si – wafer substrate, respectively. The physically corrected solution for $d$ is isolated from the condition $d = f(\lambda) = const$. Further, for a more precise estimation of refractive index (to an accuracy better than ± 0.05) and extinction coefficient, double $(T, R_f)$ and $(T, R_b)$ methods developed by Abeles and Theye were applied [17, 18].

The refractive indices of the As₂S₃ film with thickness 29 nm and 56 nm are presented in figure 2. The refractive index values are considerably different for the two films with different thicknesses. The above results are in agreement with previous reports, which claim the existence of a critical value for $d$, below which optical constants are thickness dependent [19]. It is seen that refractive indices of both layers increase after light exposition, which is a typical effect for the arsenic sulphide films. The observed refractive index change of $\Delta n$ was about 0.15 for $\lambda = 532$ nm and it could be related with the photodarkening phenomena due to formation of localized electronic states in the tails of the condition and valance bands [20].

The diffraction efficiency dependences on the exposure for both 29 nm and 56 nm As₂S₃ films with and without corona charging are illustrated in figure 3.

The maximum value of diffraction efficiency for charged samples with thickness 29 nm is reached at exposure 250 mJ/cm², while for these with thickness 56 nm - at about 550 mJ/cm². This is due to
the fact that thicker samples require more exposition energy to reach maximum value and then to achieves saturation.

The experimental results clearly demonstrate that the corona charging during the holographic recording increases the diffraction efficiency of about one order of magnitude for 56 nm and 30 times for 29 nm thick As$_2$S$_3$ film. The possible reasons for the observed effect could be the following:

1. Additional refractive index modulation due to the Franz-Keldysh effect.
2. Diffusion of chromium oxide ions, having high refractive index, into chalcogenide film.

In our experiments, the average surface potential value measured by the vibrating electrode method is about 70 V. From equation (8) the refractive index change (modulation) without electric field is

$$\Delta n_0 = \sqrt{\eta_\lambda \cos \theta / \pi d}$$

For holographic recording in 29 nm and 56 nm As$_2$S$_3$ films $\Delta n_0$ are respectively 0.05 and 0.03. The refractive index change when electric field $F$ is applied is

$$\Delta n_F = \frac{3}{8} \frac{n}{E_s} \left( \frac{e h F}{m^*} \right)^{\frac{1}{3}}$$

In our calculations we have $n = 2.42$ for 29 nm thick film; $E_s = 2.32$; $F = 1.3 \times 10^9$ V.m$^{-1}$ and $F = 2.4 \times 10^9$ V.m$^{-1}$ for 56 nm and 29 nm respectively. According to Kolomiets [21] $m^* = 7.5 m_o$ ($m_o$ is a free electron mass). The obtained diffraction efficiency ratio is

$$(\eta_F / \eta_0)_d = (\Delta n_F / \Delta n_0)^2$$
The calculated value of the ratio \( \left( \frac{\eta_F}{\eta_0} \right)_{d} \) for film with thickness 56 nm is about 11, which is in satisfactory agreement with the experimentally obtained value 9. For 29 nm thick film, however, the calculated ratio is nearly the same \( \sim 12 \), when the experiment gives 30. Evidently, there is additional refractive index modulation related with chromium oxide ions diffusion. To elucidate this effect, the Auger Electron Spectroscopy (AES) analysis is performed with the analyzer energy resolution about 0.3 %. Auger analysis is carried out using 75 nA, 3 keV electron beam with a diameter 10 \( \mu \)m, directed normally to the surface. The CrO peak is clearly detected. The refractive index of CrO is 2.71 [22], so the corresponding modulation is 0.19. Thus
\[
\left( \frac{\eta_F}{\eta_0} \right)_{29 \text{nm}} = \left( \Delta n_{\text{CrO}} / \Delta n_0 \right)^2 = \left( \frac{0.19}{0.005} \right)^2 = 28
\]
This result is in good agreement with the experiment.

5. Conclusion
This study shows that the corona discharge method is a promising tool for diffraction efficiency enhancement of nano-scale holographic recording and it is suitable for variety application of holographic technique in nano-optics. Significant increasing of the diffraction efficiency in the order of 10 \( \sim 30 \) times was observed when corona discharge was applied during the holographic recording. The possible reason of the observed effect is that the additional refractive index modulation could be due to the Franz-Keldysh effect and chromium oxide ions diffusion.

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