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Photoinduced diffraction grating in AgCl–Ag film on surface of silicone gel composition SYLGARD-184

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To extract and record scintillations, application of thin silver diffraction grating (DG) on fiber surface has been proposed, the fiber being based on gel composition SYLGARD-184. Such a grating has been formed in photosensitive composite AgCl–Ag film which was thermally deposited on the fiber surface in vacuum. This method has been shown to be suitable for making a film with required waveguide properties and photosensitivity. After irradiation with linearly polarized laser beam and after fixing removal of AgCl, a DG of Ag nanoparticles was obtained. Using diffraction from the DG, refractive index of the optical fiber has been measured. It has been shown that high dose of radiation exposure does not result in changes of properties of the sample obtained.

Keywords: photosensitive film; laser irradiation; diffraction grating; silicone gel composition; ionizing radiation.

Для вывода и регистрации сцинтилляций предлагается применить тонкую серебряную дифракционную решетку (ДР) на поверхности дополнительного световода, полученного на основе гель-композиции SYLGARD-184. Такая решетка сформирована в фоточувствительной композитной пленке AgCl–Ag, нанесенной на поверхность световода методом термического вакуумного напыления. Показано, что этот метод пригоден для приготовления пленки, обладающей необходимыми фоточувствительными и волноводными свойствами. При облучении линейно поляризованным лазерным пучком и после фиксирующего удаления AgCl получена ДР, состоящая из наночастиц Ag. По дифракции от ДР измерен показатель преломления световода. Показано, что высокая доза радиационного облучения не приводит к изменениям свойств полученного образца.

Фотоіндуковані дифракційні гратки у плівках AgCl–Ag на поверхні силіконової гель-композиції SYLGARD-184. *Л.О.Агєєв, М.З.Галунов, В.М.Резнікова, Є.Д.Маковецький, Н.Л.Караваєва, А.В.Креч.*

Для виведення та реєстрації сцинтиляцій пропонується застосувати тонку срібну дифракційну гратку (ДГ) на поверхні додаткового світловода, отриманого на основі гель-композиції SYLGARD-184. Таку гратку сформовано у фоточутливій композитній плівці AgCl–Ag, що нанесена на поверхню світловода методом термічного вакуумного напилення. Показано, що цей метод є придатним для приготування плівки, яка має необхідні фоточутливі та хвилеводні властивості. При опромінюванні лінійно поляризованим лазерним пучком і після видалення AgCl, що фіксує, отримано ДГ, що складається з наночастинок Ag. По дифракції від ДГ виміряно показник заломлення світловода. Показано, що висока доза радіаційного опромінювання не призводить до змін властивостей отриманого зразка.

1.Introduction

Currently, much attention is paid to development of scintillators resistant to high doses of ionizing radiation [1]. Recently, it was discovered that gel compositions prepared on basis of silicone gel composition SYLGARD-184 have this property [2]. The gel composition retains its characteristics at radiation doses up to 170 Mrad. However, disadvantages of the composition are its high plasticity and high volume extinction coefficient for scintillation, which prevents scintillation from registering through the ends of plane-parallel sample. So there is need of a system for collecting and displaying radiation scintillation in a planar direction using a fiber with low scattering factor. This can be done using a diffraction grating (DG) deposited to the surface of optical fiber transparent to scintillation and set in optical contact with the scintillator.

The purpose of this research is preparation of gratings from Ag nanoparticles on gel composition surface using a photosensitive thin polycrystalline film of AgCl–Ag [3] and radiation resistance test of the obtained sample.

2. Experimental

2.1. Preparation of substrate, and vacuum deposition of films

Photosensitive AgCl–Ag film is usually made by alternating thermal vacuum deposition of chemically pure AgCl and Ag from a flat molybdenum evaporator on the mirror surface of the substrate [3, 4].

In this experiment for the first time substrate was prepared from a gel composition SYLGARD-184 in the form of practically plane-parallel disk of 25 mm in diameter and 5 mm in thickness with mirror surfaces. To prepare the substrate, components of the gel composition were mixed at proportions specified by manufacturer [5], thoroughly mixed and poured into a fiber-shaped container. Then the samples remained in the shaping container till completion of polymerization (from 24 to 48 hours, depending on the polymerization conditions). Then the samples were extracted from the container and were fully ready for deposition of films on them.

Film deposition was conducted in a vacuum post VUP-5. A substrate was placed in a vacuum chamber at a distance of 15 cm from the evaporator. The evaporator had been loaded with 10 mg of AgCl which was completely evaporated by gradually raising the temperature of the evaporator through AgCl melting point $T_{melt} = 455$°C to $T \approx 900 \div 1000$°C. Thickness of the polycrystalline layer deposited on the substrate was 25 nm. Then, after air repressuring and pumping out again, deposition of 5 mg of Ag was conducted (from $T_{melt} = 961$°C to $T \approx 2000$°C) which delivers surface granular layer of AgCl with thickness of Ag of approximately 8 nm (Fig. 1). Approximate thicknesses of the film were estimated by weight of the vaporized substances for both layers of AgCl–Ag composition [4]. Duration of deposition was 3 min for AgCl and 0.25 min for Ag. Parameters of deposition conditions are important because on the one hand they affect sensitivity of AgCl–Ag composition, and at the same time they can provide a negative impact on condition of the substrate surface (violation of its smoothness) because of radiation heating from evaporator, and because of damage to the surface during film deposition process.

Damage to the sample surface is revealed through appearance of light scattering. Scattering has not been observed after preparation, and the sample was subjected to further studies.

2.2. Photosensitivity and waveguide properties of AgCl–Ag

A photosensitive AgCl–Ag thin-film composition has properties of an asymmetric dielectric waveguide [6] due to presence of a transparent dielectric layer of AgCl on a transparent substrate which refractive index n_S is smaller than n of AgCl. Interference of an incident light beam with waveguide modes scattered in the sample results in a variety of structures created from silver within this composition.

Direct photosensitivity of AgCl–Ag to intense light exposure is associated with excitation of localized plasmons [7, 8] in small Ag particles (Fig. 1), with photoelectric effect on these particles and subsequent ion transfer of Ag mass to the acting field minima [3, 4]. Irradiation with continuous linearly polarized laser beam with wavelength λ and polarization direction $\mathbf{E}_0$ results in generation of a diffraction grating (DG). A typical micrograph of DG is shown in Fig. 2. Photographs in Fig. 1,2 were obtained with transmission electron microscope JSM-840 after special fixing processing of AgCl–Ag film [4]. When observing DG with a laser beam during DG formation, diffraction beams 6 and 7 appear to be stretched along direction parallel to $\mathbf{E}_0$, and their angular positions on screens 8 and 9 depend on the

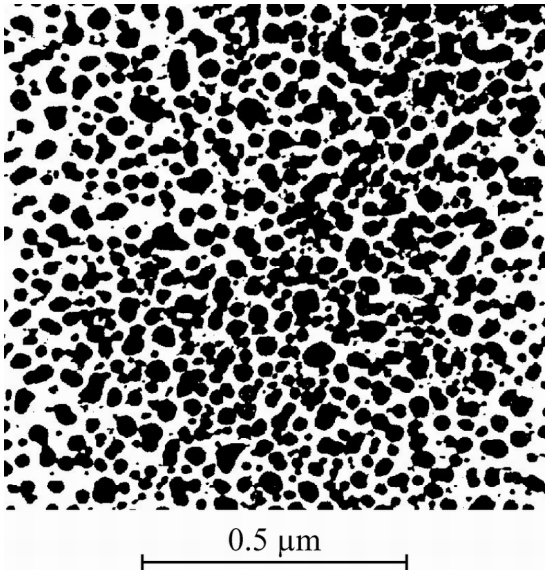


Fig. 1. Microphotograph of Ag film at AgCl surface after preparation of AgCl–Ag film.

incidence angle φ (Fig. 3). Besides diffraction, there are small-angle scattering fringes 4 and 5, the angular position of which is permanently connected with the incident beam 1 and reflected beam 2.

As a rule, development of DG is associated with excitation of TE_m-type waveguide modes [3, 6]. The propagation constant β of the mode is $\beta = k \cdot n \cdot \sin\theta$ where $k = 2\pi/\lambda$. In geometrical optics approximation, θ is the angle of incidence on film boundaries for a mode-shaping wave propagating inside the film in a zigzag manner. Instead of β, we use the effective refractive index $n_{ef} = n \cdot \sin\theta$. Film thickness h changing, the value of n_{ef} ranges within

$$n_S \le n_{ef} < n, \tag{1}$$

where $n_{ef} \to n$ at $h \to \infty$. The characteristic equation for guided TE_m-modes of the film can be written as

$$h = \frac{\lambda}{2\pi\sqrt{n^2 - n_{ef}^2}} \times \left(\arctan\sqrt{\frac{n_{ef}^2 - 1}{n^2 - n_{ef}^2}} + \arctan\sqrt{\frac{n_{ef}^2 - n_S^2}{n^2 - n_{ef}^2}} + m\pi \right). \tag{2}$$

For each mode with index m there is a minimum thickness h_m (cutoff thickness) for the mode to exist. Cutoff condition is determined by (2) at second arc tangent equaling zero due to $n_{ef} = n_S$, and the cutoff thicknesses are

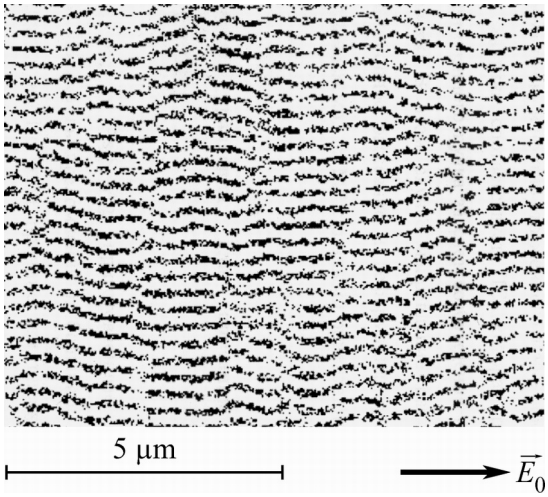
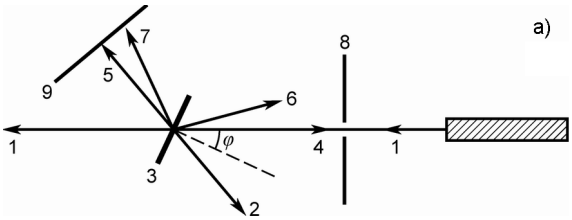


Fig. 2. Microphotograph of diffraction grating created from Ag particles on substrate surface.



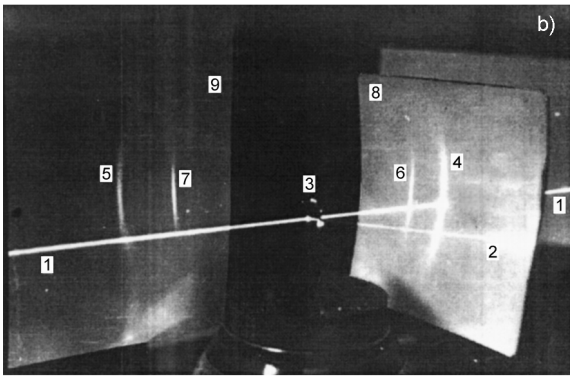


Fig. 3. Observations of diffraction and anisotropic scattering from diffraction grating: a) scheme, top view: b) photograph of the actual scheme; *1* — S-polarized laser beam; *2* — reflected beam; *3* — the sample; *4,5* — scattering beams: the counter beam and the beam opposite to the reflected one; *6,7* — diffraction beams in reflected and transmitted light; *8,9* — observation screens.

$$h_m = \frac{\lambda}{2\pi\sqrt{n^2 - n_{ef}^2}} \cdot \left(\arctan\sqrt{\frac{n_{ef}^2 - 1}{n^2 - n_{ef}^2}} + m\pi \right). \tag{3}$$

Generation of DG in AgCl–Ag under action of a laser beam begins with action of seed mode on the film due to Rayleigh scattering of the beam by small scattering centers and due to interference of the beam

and the modes. Photosensitivity leads to accumulation of Ag particles in the minima of interference. Further DG development goes by mechanism of positive feedback: the DG amplifies the mode, interference contrast increases and the DG continues to grow until it reaches saturation stage. During photostructural transformations leading to Ag mass transfer, optical constants of AgCl–Ag composition change over the exposure. At a stage close to saturation, when almost all the silver was transferred to the minima of interference, the absorption coefficient for λ of the acting beam tends to zero, and the refractive index becomes n — refractive index of AgCl. This circumstance just allows us to describe the development of DG to a saturation stage on the basis of waveguide properties of only a transparent AgCl layer, without considering any absorbing impurities of Ag [9].

Distinction of DG, which develops in the film, from a perfect grating is determined by the fact that DG consists of a set of micrograting (MG), each one of them developing at excitation of modes on an individual scattering center (Fig. 2). At oblique incidence of the inducing beam with the component $k_x = k\sin\varphi$ on the film plane, moduli of MG wave vectors ($K = 2\pi/d$ where d is MG period) and modes β are related by the following condition at S-polarization of the beam ($\mathbf{E}_0$ is perpendicular to the plane of incidence) [4]:

$$K_{\pm} = \beta \pm k_x. \qquad (4)$$

At saturation in DG development, it is K_--micrograting that have an advantage, and as follows from (4), their period is equal to

$$d = \frac{\lambda}{n_{ef} - \sin\varphi}. \qquad (5)$$

DG in reflection provides diffraction of "−1" order, which, by selecting a desired angle of incidence φ_a, allows to fulfill the autocollimation condition (beam diffraction is directed strictly towards incident beam, $\varphi_a = -\varphi$). At autocollimation, DG period is equal to

$$d = \frac{\lambda}{2 \cdot \sin\varphi}. \qquad (6)$$

From (5) and (6), the formula for measuring n_{ef} is obtained:

$$n_{ef} = 3\sin\varphi. \qquad (7)$$

Formula (7) makes it possible to measure the effective refractive index of the mode which excitation helps developing the DG, and in the case of boundary TE_0-mode, when $n_{ef} = n_S$, we get a method of measuring the refractive index of dielectric substrate. Conducting measurements with a goniometer with accuracy of 0.1° and setting angles manually, we get refractive index measurement error of approximately ±0.003. Note that expression (7) allows to measure n_S dispersion in all visible spectrum (at irradiation by intense S-polarized laser beams with different wavelengths λ) and requires exact autocollimation angle setting only. Experience shows that in many cases measurements can be performed on a very small area when focusing the beam.

AgCl–Ag composition is reversible, and its structure changes under changing conditions of irradiation by intense light. In addition, AgCl is decomposed by an electron beam. Therefore, observation of diffraction of laser beams and microscopic or electron microscopic observations are performed after fixing the DG, i.e. removing AgCl in hyposulphite solution [4]. It is important for silver-formed DG to be localized on the substrate surface in order to remain unchanged after fixing.

2.3. Forming of DG and measuring refractive index of the substrate

We have studied the case when DG is developing due to excitation of boundary TE_0-mode ($m = 0$, $n_{ef} = n_S$) which is the boundary one between discrete modes of the film and almost continuous spectrum of substrate modes. For $\lambda = 650$ nm, $n = 2.06$ (AgCl) and $n_S \approx 1.4$ (substrate) from (3) we obtain thickness of the cutoff TE_0-mode ≈ 27 nm which is slightly larger than the thickness $h_0 \approx 25$ nm of the prepared AgCl film in the sample. For an asymmetric waveguide, when a thin film of AgCl is on thick (nearly semi-infinite) substrate, and provided $h \le h_0$, DG development is determined by TE_0-mode only [6].

The sample was irradiated by a linearly polarized beam from continuous semiconductor laser ($\lambda = 650$ nm, $P = 25$ mW). In one case, the beam fell along the normal to AgCl–Ag film. The irradiated area on the film had a size of 2 by 3 mm. In another case, irradiation was conducted by S-polarized beam, and size of the irradiated area depended on the angle of incidence. The incidence angle φ was selected correspondingly to the autocollimation angle φ_a for

diffraction in reflection ($\varphi_a = -\varphi$). The exposure time was $t \approx 30 \div 40$ min and corresponded to saturation in the development of DG.

When the sample is irradiated by a normally incident laser beam, diffraction from DG is not visible on screens 8 and 9 (Fig. 3) because $d < \lambda$. After irradiation, the sample was fixed, reinstalled on the goniometer, and diffraction was observed at the angle of autocollimation, which was equal to $\varphi_a = 44.6°$. As follows from (5, 6), DG period is equal to $d = \lambda / n_S = 262.6$ nm and $n_S = 2\sin\varphi_a = 1.405$.

To measure n_S and d in the case of irradiation by S-polarized beam, it is not necessary to fix the obtained DG to preserve it under laser beam with modified angle of incidence. After completion of the exposure, diffraction is immediately observed on screen 8 (Fig. 3) if autocollimation angle is properly selected, in this case the value is $\varphi_a = 27.9°$. According to formula (7), this angle gives the same value $n_S = 1.405$ as in the case of normal incidence. But DG period is different in this case. Its value $d = 693.7$ nm is given by (5).

2.4. Resistance to radiation

Fixed sample with DG obtained was subjected to irradiation by electrons with energy of 9.1–9.4 eV and by photons of deceleration emission from KIPT qaccelerator to a dose of approximately 170 Mrad (exposure rate of 1500 Mrad/h). After the irradiation there were no observed changes of the sample (e.g. a change in transparency or possible staining of the substrate, disappearance of diffraction from the area where DG were formed). Measurements of DG period d gave the same result as before irradiation. Note that diffraction from the DG provides a picture which is the Fourier transform of the DG structure. Possible changes in the structure would be reproduced in the diffraction pattern inevitably. However, in the experiment no changes were observed in shape, intensity or angular position of the diffraction reflection, which indicates that there were no changes in structure of the DG after exposing to high doses of radiation.

3. Conclusions

Experiment on preparation of diffraction grating of Ag particles on the surface of gel composition SYLGARD-184 gave positive results. There was shown the possibility of preparing composite photosensitive AgCl–Ag film by thermal vacuum deposition while not damaging smoothness of the gel composition surface; the known method for forming DG by polarized laser beam and then fixing the DG was verified; it was shown that diffraction measurements make it possible to measure the refractive index of the fiber obtained; high radiation resistance of the prepared sample has been proved.

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