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ON FABRICATION OF LARGE FORMAT OPTOELECTRONIC ELEMENTS

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We discuss different methods for synthesis and analysis of large format optical elements with predetermined reflectance or/and transmittance characteristics. Chemical vapor deposition, electron beam evaporation and ion beam sputter deposition are well-established techniques for production of optical coatings and multilayers. There are some intrinsic limitations for the quality of such elements, i.e. position of source, target and substrate. Holographic techniques are an alternative to "classical" optical elements fabrication. We compare different methods for analysis of the optical response of large "classical" and holographic elements (Abélès characteristic matrix and Lorenz – Mie theory) as well as some possible applications, related to solar concentrators and holographic Fabry – Perrot elements.

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1. Introduction

Fabrication of large format optical elements demands expensive and very sophisticated equipment. Common practice is to use multilayer structures obtained by thermal evaporation in vacuum. Electron beam evaporation is used as well but it has the disadvantage of relatively low energy of particles impinging on the substrate. Sputter processes offer much higher energy. The ion beam sputter deposition as well as chemical vapor deposition have several advantages but substrate size and location arise problems. The optical performance of optical elements obtained by any of the above methods is limited by the microstructure of the films and the quality of the substrate surface [1]. Holographic techniques are an alternative to such "classical" optical elements fabrication. Holographic elements are periodic structures obtained by the help of interference patterns formed by mutually coherent beams. A hologram is a record of that pattern in a photosensitive material via modulation of the complex refractive index or the physical thickness of the material.

Here, we report investigations on improving the sensitivity of one of the best materials for holographic recording – dichromated gelatin, as well as methods for analysis of the optical response of optical elements and results related to applications concerning solar concentrators and large format holographic Fabry – Perrot etalons.

2. Hologram generation

Dichromated gelatin (DCG) is almost the ideal material for holographic storage: it has high diffraction efficiency (DE), high spatial resolution and low light scattering [2]. DCG intrinsic spectral sensitivity is from UV to the blue-green radiation. The refractive index modulation capacity is one of the largest among holographic materials, which is due to cross linking of gelatin molecules by Cr^{3+} ions obtained from photoreduction of Cr^{6+}. Induced modulation can be as high as 0.15. As the physical thickness of the DCG layers is usually 7-20 micrometers, the hologram DE reaches easily

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90 - 98%. Besides the values of DE, of prime interest for many applications is the spectral position of the DE maximum λ_{max} and the DE band halfwidth $\Delta\lambda$.

We have studied different organic dyes, which enlarge the spectral sensitivity of DCG layers. Triphenylmethane (TPM) and thiasine (TA) dyes are most appropriate as DCG sensitizers to red light recording: they are water soluble, photoreducible, have absorption bands in the red (600 - 700 nm), and they are compatible with $Cr_2O_7^{2-}$ ions. TPM is more compatible with the dichromate but the layers have lower photosensitivity. TA is recognized as excellent red light sensitizer [3-5] and two representatives from that group are used in our experiments: methylene green (MG) and toluidine blue (TB). In Fig. 1, we show their spectral characteristics. We found that TB has better sensitizing capabilities although MG has NO_2 in its molecule, which allows greater concentrations in the sensitizing solution. The results reported below are obtained with TB dye. We have improved the low solubility of the TB by increasing the pH of the solutions, thus preserving the number of more photosensitive $Cr_2O_7^{2-}$ ions in comparison to CrO_4^{2-} ions.

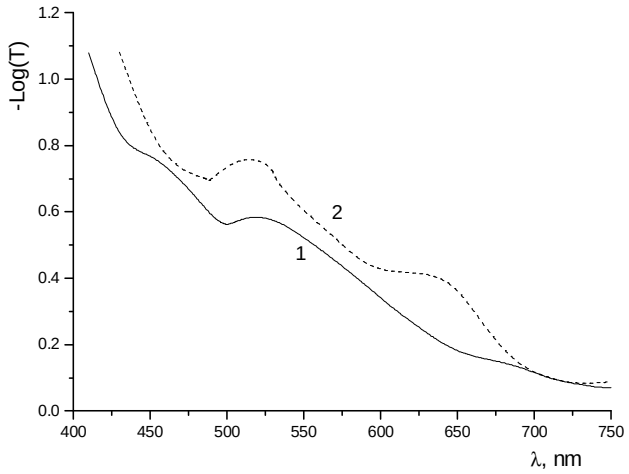

Fig. 1. Absorption spectra of methylene green (1) and toluidine blue (2).

We have used two methods for obtaining DCG photosensitive layers – by direct wet coating of naked glass substrates 25 × 25 cm large, and by bathing gelatin coated glass plates in an dichromate / dye sensitizer solution. The recepie for direct coating is: gelatin: 30 ÷ 40 g/l, $(NH_4)_2Cr_2O_7$: 2 ÷ 5 g/l, $H_2PtCl_6.6H_2O$: 0.002 ÷ 0.005 g/l, dimethylformamid 20 ÷ 30 g/l and NH_4OH is added to correct pH up to 8 ÷ 8.5. The bath solution of the gelatin layers is 0.1 ÷ 0.5 g/l TB, $(NH_4)_2Cr_2O_7$: 10 ÷ 50 g/l, $H_2PtCl_6.6H_2O$: 0 ÷ 0.002 g/l, dimethylformamid: 0 ÷ 30 g/l, pH: 8.5 ÷ 9.5, t = 20°C, bathing time: 10 ÷ 30 min.

We add $H_2PtCl_6.6H_2O$ in order to attack the NH_2 groups of the gelatin which leads to a better dubbing of the layers. The dimethylformamid acts as electron donor that impedes the spontaneous dark reduction of Cr^{6+} ions. In that way the speed of the photosensitive layers is increased and the holograms have greater refractive index modulation. DE of reflection holograms recorded in a standard Denisjuk (recording wavelenghth = 647 nm). In Fig. 2, the performance of DCG layers obtained by direct coating is compared to that of bathed layers. The exposure and hologram processing procedures being the same, we obtain higher DE at longer wavelengths and larger halfwidth $\Delta\lambda$ for the bathed layers. We assume that the sensitizing process of the bathed DCG is better but this is at the expense of more complicated technological control. The time for the bathing is of crucial importance in order not to have a gradient in the dye concentration in the bulk of the layer.

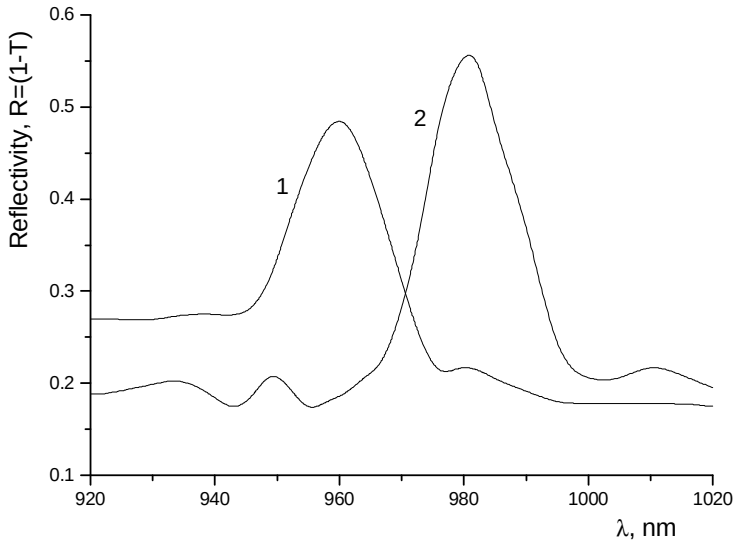

Fig. 2. Reflection spectra of holographic mirrors recorded in Tol Bl DCG layers: (1) coated; (2) bathed.

The processing of the exposed holograms (equivalent to development of classical AgX materials) is done in H_2O and isopropanol (i-Pr) baths with increasing concentrations. We use three baths with 0, 50 and 100% i-Pr concentrations. Temperatures of all baths are 20 ˚C. Thermal treatment (baking) after baths is done at 75 ˚C for 150 min. Such a processing gives additional degrees of freedom for the manipulation of the central diffraction maximum and its width. By lowering the temperature of the heat treatment λ_{max} shifts to longer wavelengths (Fig. 3). Although the holograms have the same modulation of the refractive index, some unwanted reaction of COOH gelatin groups in the non-exposed parts of the hologram leads to lower signal to noise ratio and lower DE (curve 3, Fig. 3).

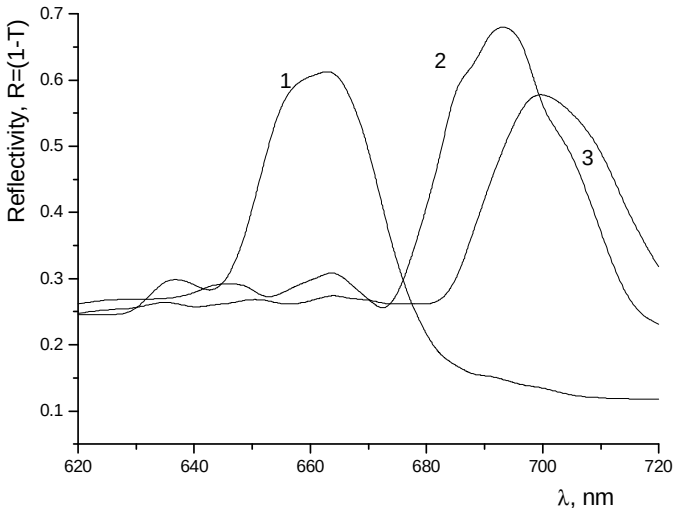

Fig. 3. Reflection spectra of holographic mirrors recorded in Tol Bl DCG layers: (1) standard development, backed 180′ at 75 °C after development, (2) standard development, backed 60′ at 60 °C, (3) dichromate pre-bath, backed 60′ at 60 °C.

The treatment described above is often referred as “mild” processing, opposed to a different “drastic” processing, which consists in the following: the exposed DCG layers are bathed in H_2O and

then put in boiling 100% I-Pr. Then holograms are intensively dried in hot air of low humidity. Hologram modulation is substantially increased but this is accompanied with milky appearance in places where the exposure is not sufficiently high. The "mild" processing results in photoinduced changes of DCG pemittivity, whose dependence on exposure energy can be described by a function with exponential saturation. In other words, the hologram refractive index spatial distribution can be represented by a continuos smooth function. For the "drastic" regime, the wave front transformations by the hologram are generated by a number of voids in the homogeneous gelatin matrix. This difference in the hologram performance needs a different mathematical approach to DE analysis of the holograms.

3. DCG holographic structures: analysis and applications

There are numerous approximate and exact mathematical tools available for the analysis of DCG holograms obtained with the "mild" processing. One of the most powerful method is the rigorous multi-wave coupled waves approach developed by Moharam and Gaylord [6]. It is applied for both reflection and transmission holographic optical elements. The algorithm is clear and the only problems present concern computing power and time. It is worth mentioning that the optical performance of unslanted reflection structures (holographic mirrors) can be analyzed by a modified characteristic matrix (Abeles) approach. It gives exact solution of the Maxwell equations and boundary effects and second field derivatives are taken into account [7]. This method is flexible and computer "economic." More, it enlightens the inner connection between thin film multilayer structures and reflection holograms.

The "drastic" chemical treatment of DCG hologram leads to the presence of cracks inside the gelatin matrix. The concentration of voids follows the light interference pattern, being zero at intensity maxima. The hologram scatters light rather than diffracts it. In order to analyze the performance of such structures we propose to apply methods developed by the theory of light scattering by particles. These methods are applied to inhomogeneous thin films structures, too [8]. If the voids are small compared to the reconstruction wavelength, the concept of effective refractive index is meaningful, at least as far as transmittance and reflectance are concerned:

$$N / N' = 1 + (I\, c / k^3)\, (\mathbf{X} \cdot \mathbf{e}_x)_q \qquad (1)$$

where N is the effective refractive index of the hologram; N' – the refractive index of gelatin; k – the wavenumber; **X** is the complex vector scattering amplitude defined by the complex scattering matrix S, which relates the scattering field E_s with the incident field E_i by $E_s = S*E_i$; $\mathbf{e}_x$ is the unit vector of observation at angle q; i = sqrt(-1); c is the concentration of voids. The effective N should not be interpreted too literally, i.e. small light attenuation, described by the imaginary part of N, may be wholly the result of scattering, although the medium hosting the voids (gelatin) is not dissipative. The size parameters and the geometrical characteristics of the voids is of importance. We assume that they are spheroids, because they are a special case of ellipsoids covering the range from disks through spheres and prolate / oblate spheroids to needlelike forms. Disk-shaped cracks (oblate spheroids) are more likely to be present in reflection holograms. Highly aspherical voids (prolate spheroids with high aspect ratio, or needles) are obvious candidates for transmission holograms. Once the complex effective refractive index is estimated, the calculation of hologram DE is straightforward by any approximate or rigorous approaches [9].

Hologram diffraction efficiency close to the theoretical maximum can be achieved in 7 – 10 μm thin layers.

As far as applications are concerned, holographic structures have the unique property that one optical element can simultaneously perform several functions, namely reflect, focus and filter light beams.

Large format (about 1 × 1 m^2) holograms acting as solar concentrator have being manufactured [10]. Inexpensive DCG optical elements are produced by means of replications by the help of a master hologram. The photosensitive layer is 10 ± 0.4 μm thick. DE is higher than 75%; losses and noise are less than 1%. Collection and concentration of solar radiation is provided over a bandwidth as large as 600 nm. The unique feature of holographic recording offers a simultaneous action of 2 and

more holograms by means of multiple exposure holograms. Such elements are used in solar chemistry for photoreactors, where the blue (useful) part of the spectrum is focused in the reactor and the red (unwanted) radiation is dispersed. Holographic lenses 200×500 mm concentrate light of 420 ± 25 nm in a spot of 10 mm.

The high reflectance and wavelength selectivity of DCG holographic mirrors open a new way for production of Fabry – Perrot etalons [11]. A glass substrate is coated on both sides with DCG. Reflecting structures are generated by one and the same exposure. The 'mirrors' quality depends mainly on the quality of the recording wave front, which easily is better than $\lambda/10$. More important is that performance of the holographic etalon is less sensitive to the surface quality of the substrate. Etalons with very thick (several centimeters) or very thin (few millimeters) base and aperture of more than 10 cm of diameter can be manufactured at a low cost.

5. Conclusions

We have discussed some of the advantages of the holographic approach to the synthesis of large format optical and optoelectronic elements. Dichromated gelatin (with actinic or sensitized spectral sensitivity) is an excellent candidate for this type of optical structures. Sensitizers of the thiasine group have proved to be very efficient in tuning the stop band of DCG holograms. In our experiments we have observed many indirect clues (width of reflection stop band, lack of side lobe maxima, etc.) that the intimate mechanism of DCG recording is related to formation of nanoscale voids. Although this idea has been discussed for quite a long time, here we have presented a quantitative approach for evaluation of DCG hologram performance, based on the theory of light scattering from nanoparticles. Large format optical elements find many applications because they are inexpensive and efficient. Besides, the unslanted reflection holograms can perform as one-dimensional photonic crystals, so they can be used as model structures for the needs of the emerging nanotechnologies.

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