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IRREVERSIBLE THERMAL EFFECT IN MULTILAYER DIELECTRIC OPTICAL FILTERS

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Abstract: The article deals with irreversible changes of the optical properties of multilayer interferometric films of ZnS and cryolite. Structural studies by electron microscopy show polycristalline structure which changes during heating-cooling cycle. It is suggested in a qulitative analysis that irreversible change of the optical properties comes from irreversibility of the structural changes.

1. Introduction

Thermal changes of thin film interferometric filters of Fabry-Perot (F-P) type deposited in vacuum were considered in the articles of Peršin et al[1,2], and those treated under atmospheric conditions in the articles of Gruyters et al.[3] More complex experiments and investigation of both kind of influences, supported with electron microscopy studies of the optical thin films, were performed by Pulker[4] and his collaborators. Irreversible shift of the transmition peak due to the heating-cooling cycle in these experiments has been observed[1,2,3]. Although the reasons of changes of the optical properties originate from the changes of refraction index, detailed knowledge of the process is not yet completed.

A lot of experimental data for the optical thin films, even of the same material, are in a disagreement in the number of cases known in literature. Neverthe-

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less, the physical description which determines optical changes of thin films under their thermal treatment from the change of the film thickness although phenomenological in nature and evident at the first sight — seems not to be perfectly valid.

On the basis of Pulker's results$^{4)}$ and our own experiments we have suggested in this paper that the irreversible optical changes of thin optical films and those structural must be strongly connected.

2. *Experimental procedure*

The interferometric filters which we have studied were formed in the evaporator at the vacuum pressure of $5 \cdot 10^{-6}$ mmHg on the glass substrate of the temperature of 25°C.

Two types of filters were formed from ZnS and cryolite (Na_3AlF_6) layers of $\lambda_0/4$ optical thickness, with the ZnS as a spacer in both filters. Measurement of thickness has been perfomed by optical method, usual in those kind of experiments.

Deposited filters were of the following configurations:

I. HL HL HL HL 32H LH LH LH LH,

II. HL HL HL HL 64H LH LH LH LH,

where H represents $\lambda_0/4$ ZnS layer of high refractive index, and L represents the cryolite layer of low refractive index but of the same optical thickness ($\lambda_0/4$).

Filters were exposed to the atmospheric influences for 30 days and then, carefully studied. Fig. 1 shows schematic block diagram of the equipment used for the testing and the thermal treatment of the filters. Filters under investigation have been heated by using IR light source of 500 W, mounted in the focal plane of the lens L_1. The interference pattern has been projected on the slit of Jarrel Asch (3) monochromator by means of high precision lens L_1. The interference filters were situated at the centre of the slit.

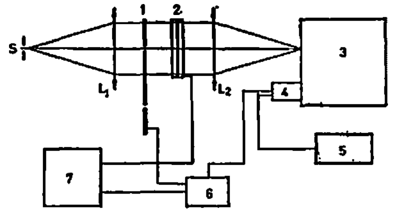

Fig. 1. Schematic block diagram of the experimental apparatus.

Signal processing tehnique consisted from an RCA 7102 type photomultiplier and PAR lock-in amplifier which connected with mechanical choper served to increase signal-to noise ratio. Dual channel strip chart recorder HP 7102A simultaneously recorded the amplified signal and the temperature of the filter.

3. *Results and discussion*

We have exposed optical filters of ZnS and cryolite to the adsorption of atmospheric gases and to thermal treatment after that. Optical thickness of these filters were 40.000 Å (noted as the filter I), and 81.000 Å (noted as the filter II).

Using described equipment, the first step in our experiments, was to find spectral characteristic of transmission of both filters at room temperature. Obtained results can be seen on Figs. 2 and 3. From these diagrams a number of spectral maxima whose number increases with increasing of the spacer thickness, can be seen.

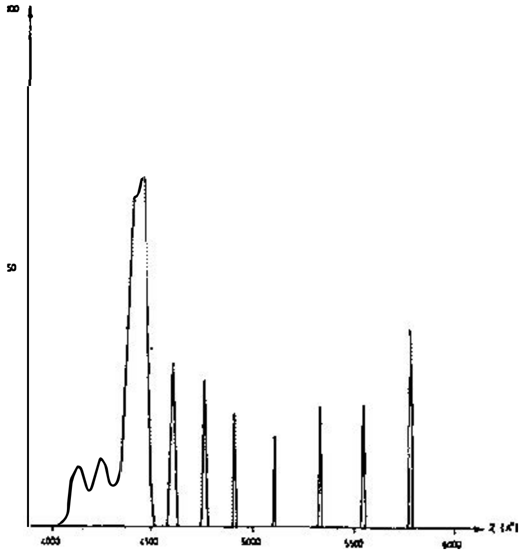

Fig. 2. Transmission spectral characteristic of the filters with the spacer of 40.000 Å.

In the next step, we have investigated the change of transmitivity of the filters in the heating-cooling cycle. Temperature dependence of transmission intensity in that cycle was studied at the wavelength of 4776 Å for the filter I, and of 5984 Å for the filter II. Corresponding results can be seen on the Figs. 4 and 5.

Transmission intensity measurements have been done near the maximum of transmission curve, permitting the detection of the shift of transmission peak. The shift of the transmission peak can be found from the relation

$$\Delta \lambda = \frac{1}{\left(\frac{\Delta I_{tr}}{d\lambda}\right)_{\lambda_0}} \Delta I_{tr}, \tag{1}$$

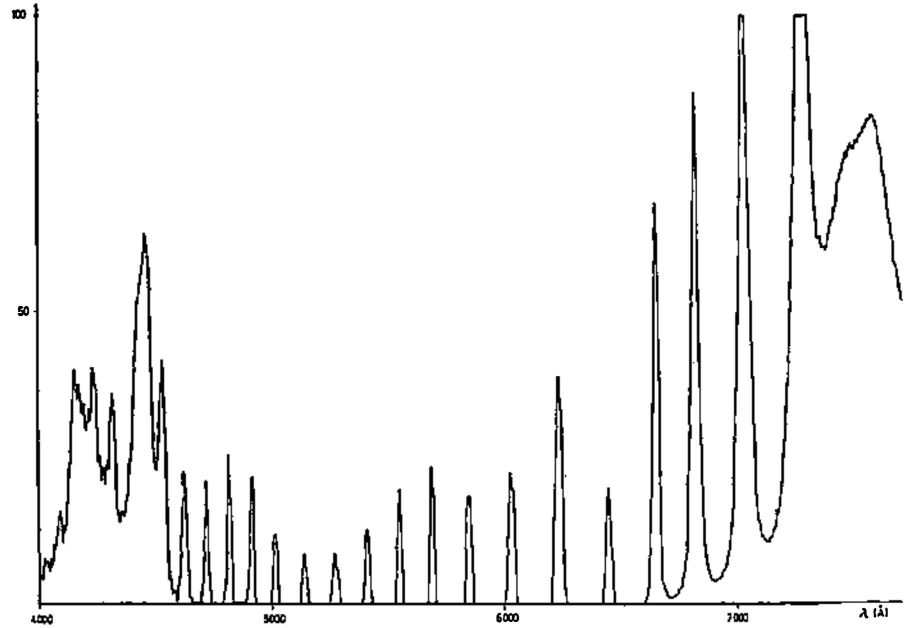

Fig. 3. Transmission spectral characteristic of the filters with the spacer of 81.600 Å.

where ΔI_{tr} represents the change of transmission intensity, and $\frac{dI_{tr}}{d\lambda}$ the rate of change of intensity at the wavelength λ_0; both changes can be determined from experimental results. Thus, the shift of transmission peak can be found as a parametric function of temperature. However, relation (1) is valid in relatively small range of temperatures, where $\frac{dI}{d\lambda} = \text{const}$, and gives the result that relative value of transmission intesity decreases in the heating process. This kind of behaviour leads to the conclusion that the transmission peak shifts towards the larger wavelengths.

Our experimental results, as well as the results reported in literature$^{3)}$ show irreversible change of transmission intensity under thermal treatement of filters in the repeated heating-cooling cycle, and are presented on Figs. 6 and 7 for the filters I. and II. Widely used explanation of these results on the basis of the change of refraction index, or the optical thickness (nd_0), seem not to be satisfactory.

Obviously, optical changes must depend at the structural changes of the filters, which come into play during the process of their thermal treatement.

In this paper we suggest that irreversible optical changes are connected with irreversible structural changes — the qualitative explanation of which points at the three possible causes, which we shall now discuss in detail.

By using electron microscopy studies the polycrystalline structure of our ZnS films has been observed. Naturally, crystal grains vary in shape as well as in size with the main diameter (between 10^2 — 10^3 Å) which is in very good agreement with Pulker's data. The individual crystals exhibit shapes ranging from almost spherical or irregulary amorphous to rather definite polyedra, such as stright--sided fragments of cubes, octaedra and prisms. Pulker,[4] and Pulker and Zaminer[5] have reported prismatic, and even more cylindrical form of crystallites obeserved by electron microscopy. We shall discuss the structure in detail, because it is in our opinion the reason of anomalous changes of the optical properties of thin films under their thermal treatement. It is assumed that the most important type of crystallites is prismatic, which can be taken as cylindrical in an idealised model, and which has really been observed at the cross section micrograph of ZnS films[4].

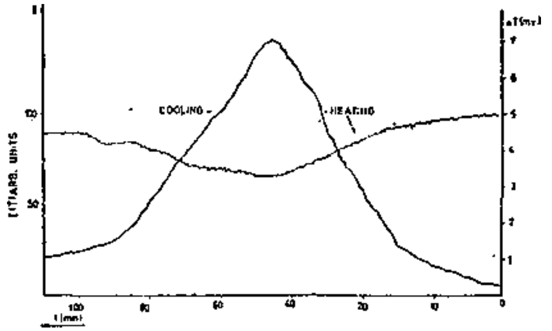

Fig. 4. Dependence of transmission intensity temperature function of the filter I during the heating-cooling cycle.

Our experiments have shown that crystalline diameter dramatically changes with temperature, namely, that heating and cooling cycle leads to the increasing of grain diameter.

Evidently, this process will strongly influence on the optical as well as on the other physical properties, which depend on packing density, grain radius as well as water concentration adsorbed in the pores of polycrystallic structure of thin films. Looking at the problem from that point of view, a great disagreement in the experimental results of various authors, relating to the optical properties of thin films obtained in vacuum and atmosphere conditions — can be easily understood.

Evidently, optical changes are irreversible, as well as the structural changes are. Careful analysis of the structural characteristics shows three possible processes taking place in the same time:

- release of water from porous structure of ZnS,
- fusing of grains into larger grains, and
- starting of stress induced diffusion.

The first process is well known to occur and was frequently reported in literature[3], so we shall not discuss it.

The second process leads directly to the change of the packing density[4].

Defining the packing density q as the volume V of the number z of crystals per unit volume, one has

$$q = z \cdot V,$$

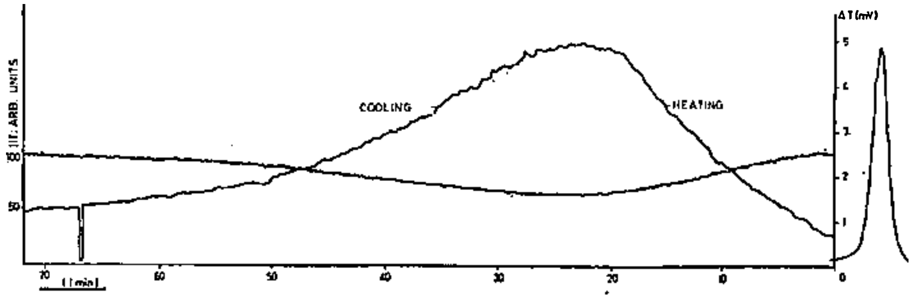

Fig. 5. Dependence of transmission intensity temperature function of the filter II during the heating-cooling cycle.

the number of the crystals per unit volume is then

$$z = \frac{q}{V}.$$

The surface 0, of that z crystailites per unit volume is

$$0 = z \cdot 2r = \frac{2q}{r},$$

where r is the grain radius.

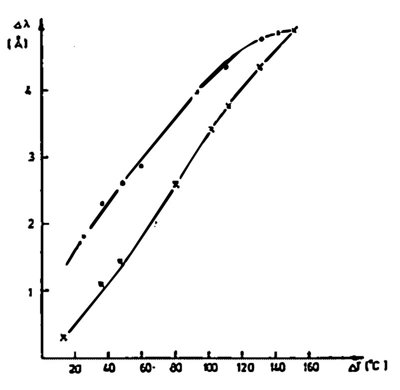

Fig. 6. Temperature dependence of the shift of transmission intensity of the filter I.

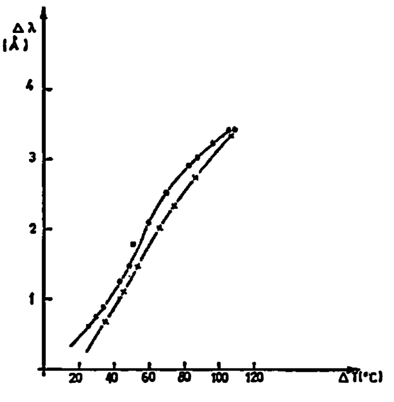

Fig. 7. Temperature dependence of the shift of transmission intensity of the filter II.

Evidently, the film thickness d_0 depends on the grain number N and its radius r

$$d_0 = f(N, r).$$

Obviously, resonant wavelength of Fabry-Perot filter, defined by relation[1)]

$$\lambda_0 = \frac{n_0 d_0}{2k},$$

will strongly depend on the number of crystals making a film of thickness d_0. This is supposed by shematic illustration given on Fig. 8a. Passing of light through the film means the passing through the lot of grains and the pores betwen them. It means that the light beam refracts twice on every grain laying on it's path, leading to the conclusion that the optical path obtained from the structural analysis is quite different from the pure geometrical one. Since the geometrical analysis does not take into account a film structure and its temperature dependence, one can not expect a serious agreement between theory and experiment. By increasing of temperature the number of grains decreases, but their dimension increases; although dimension of the film does not change it s internal structure changes significantly, Fig. 8b. The optical path through the grain, Fig. 8c will depend on temperature.

Henceforth, the film thickness d_0 appears to be a temperature functional

$$d_0 = f[N(T); r(T)]$$

and of more conplicated dependence, than it can be thought at the first sight.

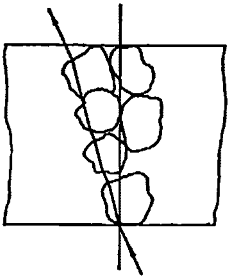

Fig. 8a. Grain structure of thin film (cross section).

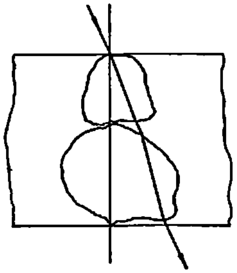

Fig. 8b. Grain strucuture of the same film at the higher temperature.

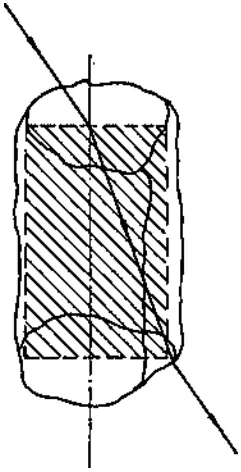

Fig. 8c. Cross section of the irregular grain and passage of light through it. (shematic).

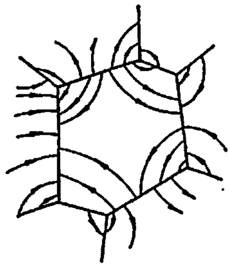

Fig. 9. Shematic representation of the stress induced diffusion in the grain.

Finally, the third mentioned process of stress induceed difusion can be easily started by heating and cooling cycle.

It is well known that the stress developed in the process of deposition of dielectric materials like ZnS, MgF_2, cryolite, could easily relax by initiating diffusion process which could be described in terms of the effective viscosity proportional to the square of linear grain dimension (Herring[6]). Shematic presentation of autodifusion process in polycrystalline structure is shown on Fig. 9. Result is the change of the grain shape, which can take effect on the optical properties, but more experimental work is needed to elucidate this problem.

References

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IREVERZIBILAN TERMIČKI EFEKT U VIŠESLOJNIM DIELEKTRIČNIM OPTIČKIM FILTRIMA

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Sadržaj

U članku su tretirane ireverzibilne promjene optičkih svojstava višeslojnih interferometrijskih filtera od ZnS i kriolita. Strukturne studije pomoću elektronske mikroskopije pokazale su polikristaliničnu strukturu, koja se mijenja u ciklusu grijanja i hlađenja. Dana je kvalitativna analiza ovih promjena i sugerirano da optičke promjene proizilaze iz ireverzibilnih strukturnih svojstava filma.