Functional Materials 11, No.3 (2004)

Polymer-crystalline structures of cutoff type with homogeneous layers of high refraction index

A.I.Belayeva, S.N.Kolomiets

National Technical University "Kharkiv Polytechnical Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

Effect of design parameters on characteristics of cutoff and band polymer-crystalline systems with layers thickness divisible by $\lambda/4$ has been studied in detail. The polymer-germanium systems have been shown to be of the greatest practical interest. A method has been developed to smooth the secondary extremes in the transparence band of a quarter-wave polymer-germanium cutoff filter by introduction of additional interference layers made of polyethylene. The possibility to form a band type spectral characteristic has been shown in experiment for polymer-germanium systems in far IR spectral region.

Детально исследовано влияние конструктивных параметров на характеристики отрезающих и полосовых полимер-кристаллических систем со слоями кратными $\lambda/4$. Показано, что наибольший практический интерес представляют системы полимер-германий. Разработан метод сглаживания вторичных экстремумов в полосе прозрачности четвертьволнового отрезающего фильтра полимер-германий добавлением дополнительных интерференционных слоев из полиэтилена. Экспериментально показана возможность формирования спектральной характеристики полосового типа на системах полимер-германий в далекой ИК области спектра.

A heightened interest in investigation in long-wavelength infrared (IR) spectral region being observed today is due first of all to wide possibilities of such studies in improving understanding of structure for a wide class of natural and synthetic objects (such as gases, liquids, solids, plasma, astrophysical complexes). The progress in those fields is defined to a great extent by advances in perfection of spectral methods, including the development of long-wavelength range filters that are obligatory elements of many instruments such as spectrophotometers with diffraction gratings and Fourier spectrometers. Simplified spectral analyzers using such filters are developed, too.

Polymer-crystalline systems are among multilayer systems of promise as long-wavelength range filters. In those systems, polymer films play a ternary part being interference layers with a low refraction index (L layers), supports for high-refraction layers (H layers), and joining glues to provide the optical contact in the multilayer structure. In this work, effect of design parameters on characteristics of cutoff and band polymer-crystalline systems with layers thickness divisible by $\lambda/4$ has been studied in detail.

The most important design parameters defining the spectral characteristics of cutoff type multilayer interference structures (MIS) include the refraction indices (RI) of interference layers and the general number of the layers [1]. As low-refracting materials, polymer films of polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) were used having RIs similar to one another and amounting $n \approx 1.5$ within a wide spectral range including both long-wavelength and short-wavelength regions [2]. As high-refracting materials, KRS-5, LiF, and Ge were used. KRS-5 was employed in the spectral range $\lambda < 60$ μm. In the $\lambda = 30$ to 50 μm, the KRS-5 RI shows some dispersion but the change is still small within 40 to 50 μm region, so that the mean n value for KRS-5 in the wavelength interval 40 to 50 μm can be assumed to be of about 2.2.

For LiF, there is a somewhat different situation. In short-wavelength spectral region, LiF has a low RI $n \approx 1.35$ ($\lambda = 2$ μm) and can be used in combination with high-refracting materials. For the wavelength range of 35 to 40 μm (it is just the spectral range where LiF is used in combination with polymer films), the RI of LiF is high being about 3. The third high-refracting material used here is the semiconductor Ge. Some modifications of that material are used successfully within a wide range of IR spectrum [1]. Germanium has the highest RI among the three materials mentioned ($n \approx 4$ at $\lambda = 100$ to 300 μm) and is sufficiently transparent in the long-wavelength IR region ($\lambda > 100$ μm).

Thus, in combination with polymer films, the RI ratio of H and L layers varies from about 1.47 (for polymer-KRS-5 couple) to about 2.67 (for polymer-Ge couple). In the polymer-crystalline systems, there are no massive substrates. Let the structures of $(HL)^mH$, $(LH)^mL$, and $(HL)^m$ be considered. Such structures are sets of alternating quarter-wave low-refracting and high-refracting layers. The increasing RI ratio of the materials used is known to result in a broadened high-refraction band of an interference mirror as well as in an increased steepness of the cutoff edge of an interference filter, the number of layers being the same.

Fig. 1 presents the spectral characteristic of a quarter-wave KRS-5-PE system with $\lambda_0 = 45$ μm consisting of seven bilayer PE-KRS-5 components fused together. The cutoff edge steepness $\chi \approx 0.9$. At smaller number of layers, the KRS-5-PE system exhibit a considerable residual transmission in the high reflection region; that is why those cannot be used to define the cutoff edge of an interference filter. For LiF-PE couple, the residual transmission in the 11-layer system is less than 5 %. The cutoff edge steepness is $\chi \approx 0.85$. For Ge-PE systems, a high cutoff edge steepness $\chi \approx 0.85$ within the region of $\lambda > 110$ μm is attained already in a 7-layer system, the residual transmission in the high reflection region is <1 %. Thus, an RI increase of the H material in a polymer-crystalline structure allows to attain high values of the cutoff edge steepness at smaller general number of layers. Thus, there is a qualitative consistence with the MIS formation regularities [1]. As the RI ratio of H and L layers increases, the high reflection band of a polymer-crystalline filter becomes broadened. For Ge-polymer system, $\Delta\lambda/\lambda_0 \approx 0.5$ at the level of $0.1T_{max}$, that is of great importance for the practical applications because it is much easier to provide the cutoff of background short-wavelength radiation.

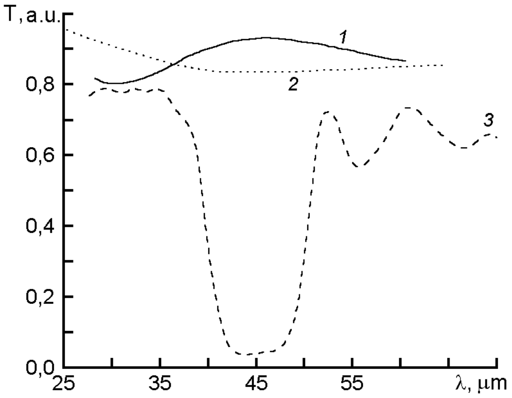

Fig. 1. Transmission of a bilayered KRS-5-PE interference component (*1*), about 7 μm thick PE film (*2*) and a 14-layered KRS-5-PE interference system (*3*) in the spectral range near 45 μm.

The steep cutoff edge in the polymer-crystalline filters is more difficult to attain in experiment as the Δn of the materials used increases. For example, while it is rather easy to provide a PE-KRS-5 cutoff filter with $\chi \approx 0.9$ (to that end, it is sufficient to prepare a 14- or 15-layered system), it is essentially impossible to obtain $\chi \approx 0.9$ for the PE-Ge couple, although already 7-layered system provides $\chi \approx 0.85$. Such results can be explained by that the requirements to local microscale homogeneity of the optical thickness of the layers increase considerably as the RI of the H layer rises. When germanium is used, even minute local inhomogeneities effect considerably the multiray interference conditions. A local inhomogeneity in the optical thickness of the H layers may arise due to the high-refracting coatings are deposited on a rough substrate surface.

The known data on the metal coating deposition onto rough substrates [3] show that the surface of the layer may be smoothed in the course of its growing. When a MIS is formed by sequential deposition of the H and L layers onto a massive substrate in a single technologic cycle, even if the substrate is rough, the interface roughness may be reduced during application of each next layer (of course provided that the required technological regimen are met). Thus, the number of rough interfaces between high-refracting and low-refracting layers will be limited and will no increase in essence at increasing total number of layers.

When multilayer polymer-crystalline interference structures are prepared, each high-refracting layer is deposited onto a substrate, so the increasing total number of layers results inevitably in an increased number of rough interfaces. As the RI of the layer material rises, the introduced error should also rise, thus resulting in considerable deviations when germanium is combined with polymers. It is to note that as the wavelength increases, the deviations in the MIS optical characteristics due to the surface roughness become smaller, since the wavelength ratio to the inhomogeneity size increases. As a result, it is much easier to prepare polymer-crystalline interference structures for the $\lambda > 100$ μm spectral region than for $\lambda < 100$ μm one.

It is expedient to draw some practical conclusions from the above consideration. First of all, it is unnecessary to increase excessively the layer number, but it is to proceed from specific requirements to the spectral characteristics of a filter to be prepared. For the polymer-germanium couples, the cutoff edge steepness values of $\chi \approx 0.85$ at $\lambda \approx 100$ μm are attained in 7-layered systems. Such systems are effective elementary components to define the χ values for filters in long-wavelength IR region. In some cases, when the cutoff edge must not to be very steep, even a 3-layered Ge-polymer-Ge system where the residual transmission in the high reflection region is $T < 2$ % can be used successfully to solve practical problems.

Of highest practical interest are shortwave cutoff filters, i.e., the systems having a high transmission in the long-wavelength region and a low one in the short-wavelength range. In multilayer structures consisting of alternating high-refracting and low-refracting quarter-wave layers, there are secondary extremes in the high transparence region. The spacing of those extremes depends on the total number of layers in the system and on the RI values of the substrate and the second boundary medium [4]. The extreme depth is defined by the RI relationship between the substrate material and H and L layers. To smooth the secondary extremes in the long-wavelength region, the $\lambda/8$ layers of high-refracting materials are used. To improve the smoothing, more sophisticated methods are employed, e.g., a series of layers with RI different from those of the H and L layers are included in MIS [5].

In a polymer-crystalline cutoff filter, there is no substrate, therefore, if the layer thickness deviations are insignificant, the secondary extreme depth depends on the RI ratio (n_H/n_L) of the materials used. When the PE-KRS-5 combination is used, the attenuation in the transparence region due to the secondary extremes does not exceed 10 % in practice. As the n_H/n_L increases, the extreme depth rises, so that for the polymer-Ge system, there are valleys in the operating range exceeding 30 or 40 %. This is inadmissible in practical applications. It is to note that in far IR region, those extremes occupy a rather wide spectral region due to large λ values. Therefore, to improve the transparence within several (even at least one) minima is of interest. As it is just the polymer-Ge interference structures that exhibit the optimal characteristics in far IR range, let the potentialities of the secondary extreme smoothing be considered taking just those systems as examples.

The studies have shown that in a polymer-Ge cutoff filter, the secondary extremes can be smoothed by adding framing PE layers to the MIS. Even a 3-layer Ge-polymer-Ge system can be used in some cases as an elementary interference filter defining the cutoff edge. In the 3-layered system, one transmission minimum occupies a range of about $2\lambda_0$ where λ_0 is the wavelength for which the H and L layers are quarter-wave ones. An improved transmission in the operating range for the above system can be attained by adding two framing PE films having the optical thickness $\lambda^*/4$ where λ^* is the wavelength corresponding to the minimal transmission (see Fig. 2). Such framing can be added after the 3-layered system is prepared and its spectral characteristic is recorded. The framing PE films with a thickness different from $\lambda^*/4$ smooth also in part the spectral characteristic, but as small deviation from $\lambda^*/4$ as for example 10 % causes a considerable drop of the cutoff edge slope.

In a 7-layered polymer-Ge interference system, several deep extremes exist within

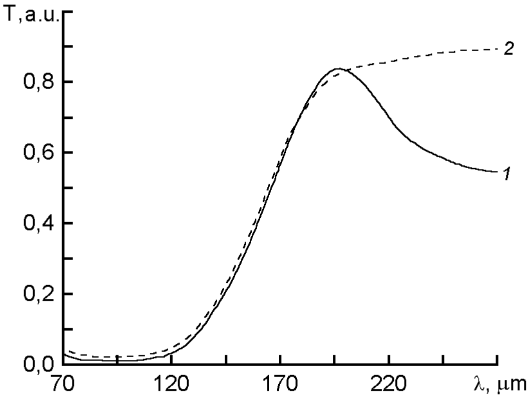

Fig. 2. Transmission of a 3-layered Ge-PE-Ge interference system in the spectral range near 90 μm (*1*) and of the same system provided by framing PE layers of $\lambda^*/4$ thickness (*2*).

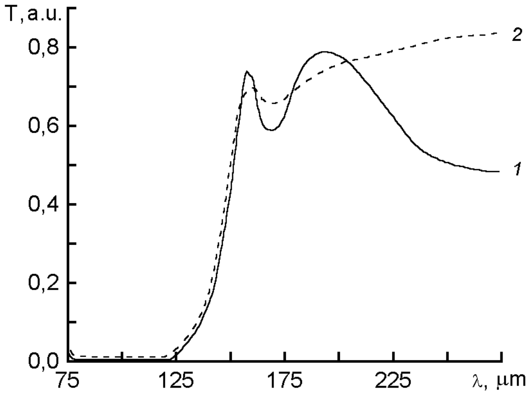

Fig. 3. Transmission of a non-optimized (HL)H polymer-Ge system (*1*) and of an optimized one (*2*).

the operating spectral region. Those can be also smoothed effectively by adding the framing PE layers. Those films should have the optical thickness of $\lambda^{**}/4$ where λ^{**} is the wavelength of the second transmission minimum, reading from the high-reflection band (Fig. 3). The additional framing PE layers in the 7-layered polymer-Ge interference system make it possible to obtain a cutoff filter for the far IR region with the transmission of 70 to 80 % in the operating range. The cutoff edge steepness is about 0.85, thus, these systems are of promise for practical applications.

The physical mechanism of the extreme smoothing in the spectral characteristic of a multilayer interference filter due to framing PE films is associated with the "clarification" of the system. A MIS in the high transmission region can be presented as a single layer with the equivalent RI, n_{eq}, that can be calculated [6] as

$$n_{eq}^2 = \frac{(N+1)n_H + (N-1)n_L}{(N+1)n_L + (N-1)n_H} n_H n_L, \qquad (1)$$

where N is the number of layers in the system. At $N \to \infty$, $n_{eq}^2 = n_H n_L$. As the n_H and n_L values for Ge and PE in the far IR ($\lambda \approx 100$ μm) are 4 and 1.5 [2], respectively, we obtain $n_{eq}^{(3)} = 2.8$ and $n_{eq}^{(7)} = 2.6$ for 3- and 7-layered Ge-PE systems, respectively. It is known from the antireflecting practice that the optimum results in reduced reflection loss for a surface with the RI value n are attained when coating films with RI $n_{ar} = \sqrt{n}$ are used. In our case, the films with $n_{eq}^{(3)} = 1.67$ and $n_{eq}^{(7)} = 1.62$ should be used to attain the best results. It is known, however, that a considerable reduction of reflection can be provided also at RI values close to the optimum ones; this is the case of additional PE layers in the polymer-Ge systems.

It is to note in particular that the proposed method of the secondary extreme smoothing by additional framing PE layers can be used also to correct the whole spectral characteristic of a polymer-crystalline cutoff filter. The MIS are very sensitive to deviations in the layer thickness. In this case (especially when materials with considerably differing RI values are used) the valleys in the transparence region become more pronounced and the spectral positions of the secondary maxima may change, too. By adding the framing PE layers performed taking into account the actual arrangement of the transmission minima (that can be determined precisely as the spectral characteristic of the prepared quarter-wave system is recorded), the error can be corrected (partially compensated), thus reducing rejects in manufacture of the interference components. This simplifies significantly the preparation process of a polymer-crystalline cutoff filter, since it is not necessary to study in detail the structure features of PE films in order to provide reliable welding. Even if the elastic strain threshold is exceeded and the optical thickness of the PE layer is changed due to that fact, the error introduced can be compensated in part at the next preparation stage of the cutoff filter.

The most important spectral characteristics of a band interference filter include the maximum transmission in the transparence band, the transmission in the background region within the short-wavelength and long-wavelength ranges adjacent to the transparence band. As to the background, of greatest interest is the width of suppression bands and the residual transmission in those bands of an elementary interference system defining the spectral position of the transmission band. As the simplest band type structures, considered are symmetrical polymer-crystalline structures consisting of alternating quarter-wave H and L layers separated by $\lambda/2$ divisible high-refracting or low-refracting layers.

Only systems where germanium is used as the high-refracting material are of practical interest as band filters. Due to high RI ratio of H and L layers, even a 3-layer Ge-polymer-Ge system where the quarter-wave Ga layers act as mirrors is suitable to be an elementary one defining the spectral position of the transmission band. The spectral characteristic of a 3-layer Ge-PTFE-Ge in the $\lambda \approx 120$ μm range is presented in Fig. 4. In the transparence band maximum, the transmission of that system is about 75 %, the half-width $\Delta\lambda/\lambda_0 = 0.1\lambda_0$. Even in a 3-layer Ge-polymer-Ge system, suppression bands are formed in short-wavelength and long-wavelength ranges adjacent to the transparence band that are sufficient to combine it with cutoff systems. The short-wavelength band is about $0.3\lambda_0$ wide, the long-wavelength one, about $0.2\lambda_0$, the residual transmission is about 5 %. The framing mirror thickness deviations from $\lambda_0/4$ cause an increased residual transmission in the suppression bands and a reduced transparence maximum in the transparence band.

A combination of short-wavelength and long-wavelength cutoff filters may be an alternative of good prospects in formation of the band type spectral characteristic within the long-wavelength IR region. In this case, considerably advantages can be attained as compared to systems containing central layers divisible by $\lambda/2$. First, in this case, the suppression bands in both short-wavelength and long-wavelength bands adjacent to the transparence one are broadened. Second, it is possible to vary in a smooth manner the transparence band half-width within wide limits. This alternative makes it possible to prepare both narrow-band and wide-band systems.

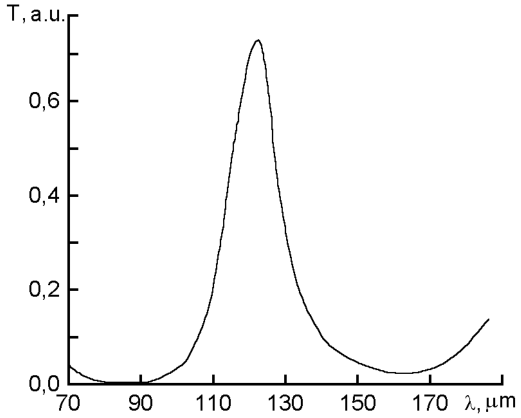

Fig. 4. Transmission of a Ge-PTFE-Ge band filter.

Thus, the dependence of optical properties on design parameters has been studied in experiment for cutoff type quarter-wave polymer-crystalline structures. The polymer-Ge systems have been shown to be of the greatest practical interest. A method has been developed to smooth the secondary extremes in the transparence band of a cutoff type quarter-wave polymer-Ge filter by adding PE interference layers. The possibility to provide a band type spectral characteristic in the far IR region has been demonstrated in experiment on the polymer-Ge systems.

References

1. A.I.Belayeva, V.A.Sirenko, Cryogenic Multilayer Coatings, Naukova Dumka, Kiev (1991) [in Russian].
2. V.M.Zolotaryov, V.N.Morozov, E.V.Smirnova, Optical Constants of Natural and Technical Media: A Reference Book, Khimia, Leningrad (1984) [in Russian].
3. J.R.McNeil, L.J.Wei, G.A.Al-Jamaily et al., *Appl. Opt.*, **24**, 480 (1985).
4. I.N.Shklyarevsky, V.I.Khramtsova, *Optika i Spektr.*, **45**, 570 (1978).
5. I.N.Shklyarevsky, V.I.Khramtsova, *Optika i Spektr.*, **58**, 1359 (1985).
6. Sh.A.Furman, Thin-Wall Optical Coatings, Mashinostroenie, Leningrad (1977) [in Russian].

Полімер-кристалічні структури відрізаючого типу з однорідними шарами високого показника заломлення

А.І.Бєляєва, С.М.Коломієць

Детально досліджено вплив конструктивних параметрів на характеристики відрізаючих і смугових полімер-кристалічних систем із шарами кратними $\lambda/4$. Показано, що найбільший практичний інтерес представляють системи полімер-германій. Розроблено метод згладжування вторинних экстремумів у смузі прозорості чвертьхвильового відрізаючого фільтра полімер-германій додаванням додаткових інтерференційних шарів з поліетилену. Експериментально показано можливість формування спектральної характеристики смугового типу на системах полімер-германій в далекій ІЧ області спектра.