

## Ir transparency of thin bismuth films

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The infrared transmission and reflection spectra of a series of samples of bismuth films of different thicknesses on identical single-crystal silicon substrates were measured. Transmission and reflection oscillations caused by interference on the film thickness are investigated. Properties of Si-plates are estimated. Refractive index and absorption index of bismuth are calculated.

**Keywords:** bismuth, film, IR, interference.

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### Introduction

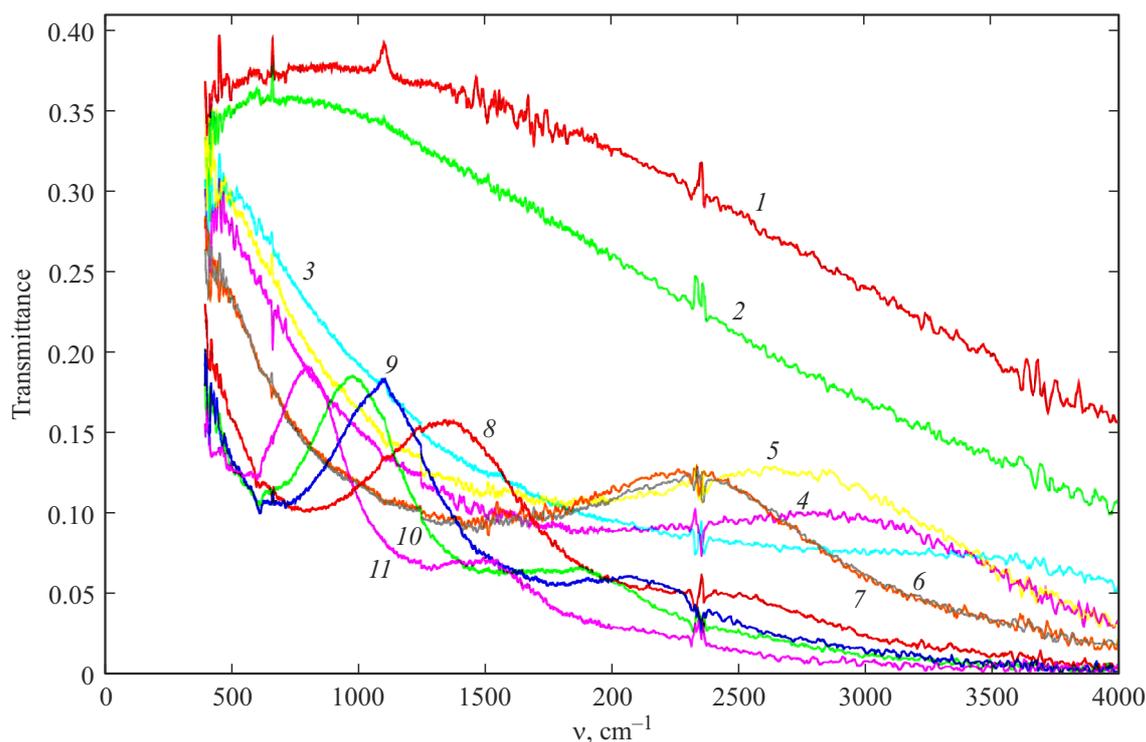
The properties of bismuth have always been of interest to the academic community. First, it is the heaviest stable substance. This alone is sufficient to lend it an extremely low thermal capacity and a large interatomic distance in the lattice. Second, it is largely inert chemically and belongs to a rare type of substances that are found in nature in their pure form. Oxidation of its surface may be performed intentionally to visualize crystalline defects [1]. Third, bismuth, antimony, and graphite are the only elementary substances to feature a strongly anisotropic layered crystal structure [2,3]. Notably, the structures of antimony and bismuth are so close that their atoms substitute each other with almost no distortion. These substances form a series of solid solutions with arbitrary component fractions and a common crystal structure. Fourth, bismuth and graphite are the only elementary substances belonging to the class of semimetals. Taken together, the third and the fourth remarks place bismuth and  $\text{Bi}_{1-x}\text{Sb}_x$  structures in the class of  $\text{glq}$  topological insulators. "In recent years, the examination of properties of such insulators and graphene has become a hot research topic [2,4]. We will not dwell on these properties here. Bear in mind only that the differences in behavior of structures are smoothed down at room (high) temperature (i.e., the temperature at which bismuth and its properties are examined in the present study) [5,6]. Another fact of importance for the fabrication of such structures should be noted. Fifth, the sputtering temperatures of bismuth and antimony corresponding to a saturated vapor pressure of approximately 0.1 Torr are very close. Therefore, when a mixture of these substances is subjected to vacuum thermal sputtering, components of the obtained structures are distributed uniformly throughout their entire volume.

Single crystals of bismuth are easy to grow. Even when grinding a solidified boule, one may find crystals up to a centimeter in size with natural faceting. Bismuth crystals have a layered structure. The interatomic distance

within a layer is significantly shorter than the distance to atoms of a neighboring layer. The structural anisotropy of bismuth exercises a decisive influence on the growth of its crystals. The growth of layers parallel to the surface on which this process unfolds is energetically favorable. The growth surface exerts an orienting effect, and adhesion to the surface is weak. Any significant surface irregularities induce a catastrophic disturbance of adhesion. Bismuth films on such surfaces degrade with time, bismuth exfoliates and flakes off. The stability of films may be regarded as a surface quality criterion. A bismuth film often cracks simply at sharp irregularities. Therefore, we, for example, advise depositing contact pads not below, but on top of bismuth. Naturally, it is crucial to maintain surface cleanliness. Freshly cleaved mica still remains a popular choice of a fairly easy-to-obtain substrate for sputtering [1,5–7]. We have utilized stored single-crystal silicon that was prepared properly in a clean room.

The adhesion of bismuth films to the surface is enhanced greatly when a substrate is heated to approximately 110°C [7]. This effect is noticeable for different types of substrates: mica, silicon, silicon with an oxynitride coating, and polyimide. As was demonstrated in [6,7], the effect is attributable to a change in the structure of a film itself, which, in the case of a room-temperature substrate, consists of randomly oriented crystallites. If a substrate is heated, crystallites are relatively oriented and coupled by twinning, which is typical of bismuth. The size of crystallites may be increased by annealing films in vacuum. However, the effects related to crystallite size become significant only at low temperatures, when this size is comparable to the mean free path of carriers. Therefore, we did not perform annealing. Thus, samples prepared by vacuum thermal sputtering of high-purity ( $10^{-5}$ ) bismuth from a tungsten boat onto a substrate heated to 110°C were used in measurements.

Plasma absorption of electromagnetic radiation by free carriers [8] is observed in bismuth. Its maximum cor-



**Figure 1.** Transmission spectra of bismuth films with a thickness of 1 — 23, 2 — 46, 3 — 92, 4 — 115, 5 — 138, 6 — 194, 7 — 200, 8 — 300, 9 — 345, 10 — 400, and 11 — 600 nm on a silicon substrate.

responds to a reciprocal wavelength of approximately  $400\text{ cm}^{-1}$ . However, it should be noted that films differ from a bulk sample in that the surface plays an important role in them. At a carrier density of about  $10^{-4}$  of the number of atoms, one of each 300 atoms is an outer one in a film with a thickness of 200 nm. The tensorial effect is also anomalously intense in bismuth. Therefore, only a qualitative agreement between our results and the experimental data for bulk bismuth samples is to be expected. Specifically, the same smooth monotonic growth of the refractive index and smooth monotonic reduction of the absorbance with increasing frequency are expected. The values should correspond roughly to the far high-frequency „tail“ of plasma absorption.

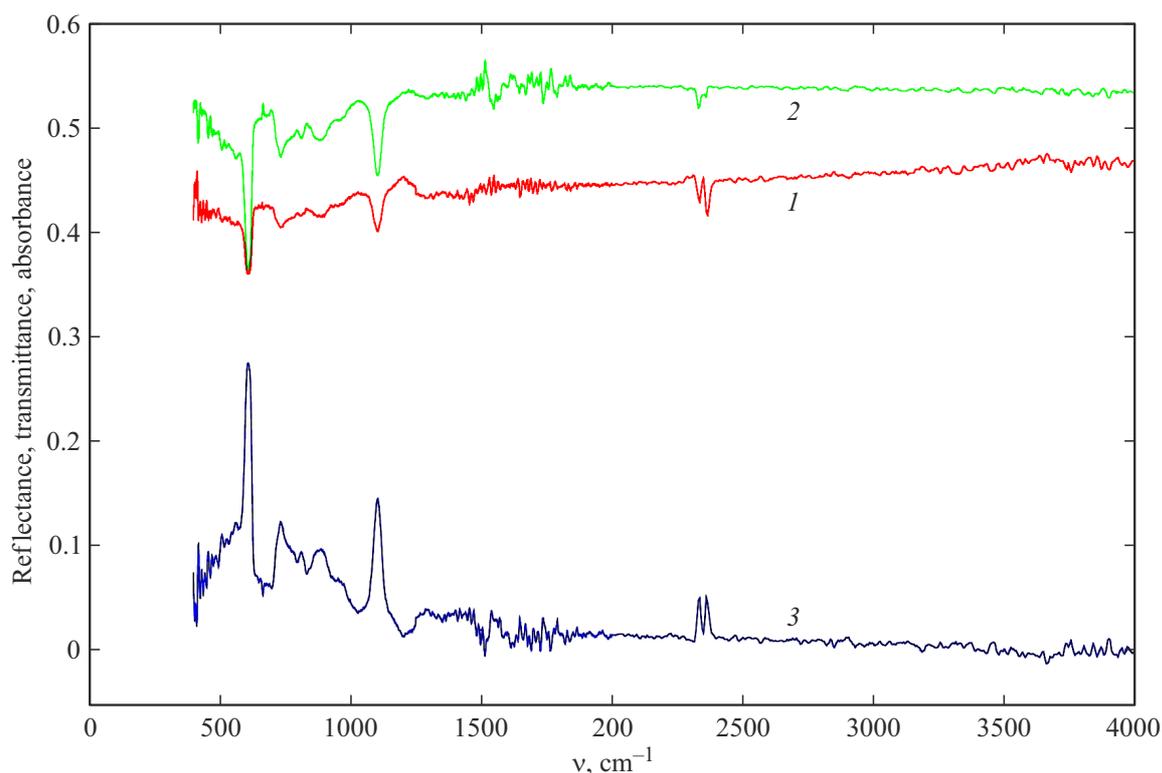
### Transmission spectra of samples

Silicon, which transmits infrared radiation well, was chosen as a substrate material [9]. Plane-parallel plates of single-crystal undoped silicon (with phosphorus being the primary residual impurity) polished from both sides with a thickness of 0.4 mm and a resistance of  $4.5\ \Omega/\text{sq}$  were used. Bismuth films with a thickness of 23–600 nm were sputtered onto them. The samples reflect visible light like mirrors with negligible distortion. Their scattering may be neglected. Measurements of infrared spectra in the  $400\text{--}4000\text{ cm}^{-1}$  ( $2.5\text{--}25\ \mu\text{m}$ ) range were performed using a direct-action Shimadzu IR460 spectrometer. Two spectra without and with a sample positioned transverse to the radiation beam

in front of the receiver window were measured successively in each case. To plot a spectrum, the results of the second measurement were divided pointwise by the results of the first one. The measured transmission spectra of samples are presented in Fig. 1.

It is easy to see that the spectra are shaped primarily not by the substrates, but by the properties of films. Transmittance oscillations, which are attributable to interference on the film thickness, are seen clearly. The oscillation frequency is, with a fine degree of accuracy, inversely proportional to the film thickness. This is indicative, on the one hand, of the lack of any substantial dependence of the optical parameters of bismuth on the film thickness and, on the other hand, of fine reproducibility of the obtained results. Since the transmittance decreases considerably as the film thickness grows, bismuth features a significantly high absorbance. The features related to spectrometer operation (specifically, the characteristic bump at  $2350\text{ cm}^{-1}$  due to an automatic change of optics) are also apparent.

The transmittance maxima (reflectance minima) form when a wave reflected off the second film interface arrives in antiphase with the wave reflected off the first interface. It follows from the analysis of positions of transmittance maxima and minima that the upper two spectra (with a film thickness of 23 and 46 nm) feature only the zeroth transmittance maximum, and even the first transmittance minimum is outside of the operating range of the spectrometer. The next three spectra (with a film thickness of 92, 115, and 138 nm) probably reveal the zeroth transmittance maximum,



**Figure 2.** Reflection (1), transmission (2), and absorption (3) spectra of a silicon substrate.

and the first transmittance maximum and the first minimum between them are already visible. The next two spectra (194 and 200 nm) feature the first maximum and the first and the second minima. In the remaining four spectra (300, 345, 400, and 600 nm), at least the first three transmittance maxima are distinguishable.

It follows from the obtained data that films with a thickness of approximately 200 nm, which reveal transmittance oscillations clearly but still have a limited absorbance, provide the greatest amount of data for further studies. However, one should first determine the substrate properties and their influence on the sample data.

## Measurements of substrate properties

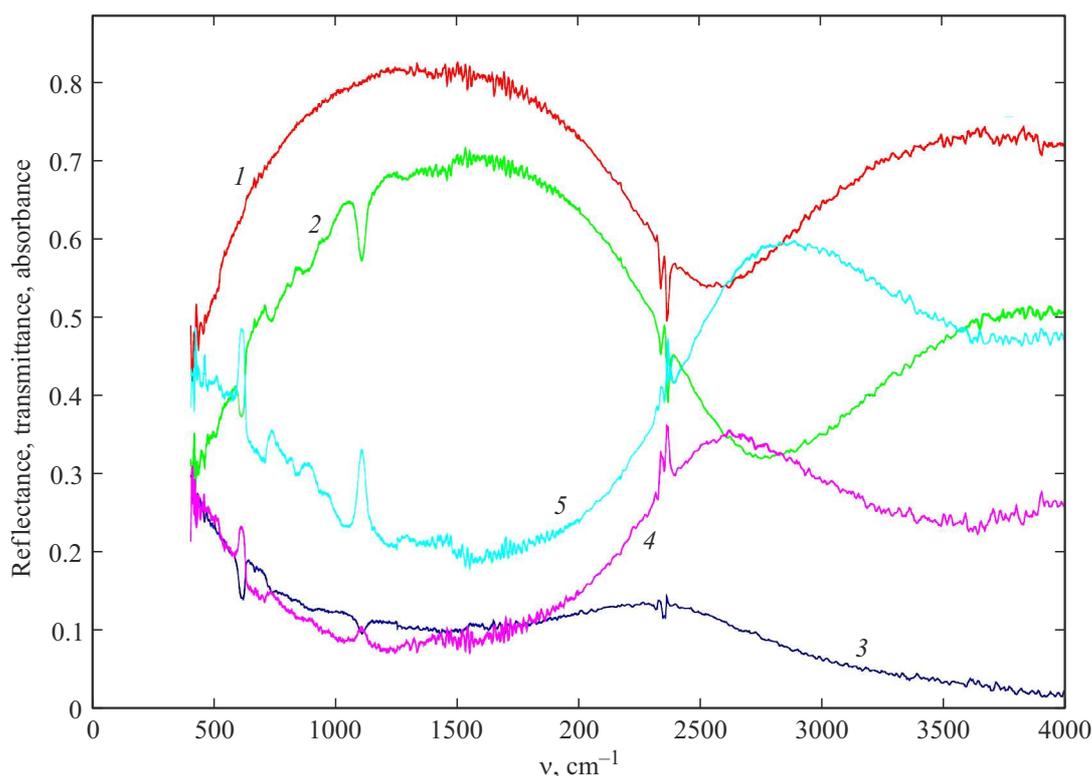
The transmission and reflection spectra of the substrate (Fig. 2), which is a single-crystal undoped silicon disk with a diameter of 100 mm and a thickness of 0.40 mm polished to mirror reflection in the visible range, were measured. A special inset provided with the instrument was used to measure the reflection spectra. The sample and the substituting mirror with a reflective gold coating were aligned so as to maximize the signal from the receiver. To plot a reflection spectrum, the measured data for reflection from the sample were divided pointwise by the results of measurements with the mirror. It should be noted that the accuracy of these measurements (1–2%) is significantly lower than the one for the transmittance measurements.

Silicon is highly transparent. Two intense absorption lines at 600 and 1100  $\text{cm}^{-1}$  are visible. The absorbance does not exceed 2% in the 1500–4000  $\text{cm}^{-1}$  range and varies from 2 to 10% in the 400–1500  $\text{cm}^{-1}$  range (with the exception of the lines mentioned above). The jump at 2350  $\text{cm}^{-1}$  is induced by a change of spectrometer optics. Transmittance  $T_s$  varies only weakly (from 0.54 to 0.535) in the 1500–4000  $\text{cm}^{-1}$  range. Reflectance  $R_s$  increases slightly more significantly (from 0.45 to 0.465). The observed peaks demonstrate that the effect of absorbance on transmittance is approximately two times greater than its effect on reflectance.

The silicon disk is so thick that the resolution of the used IR spectrometer is not sufficient to reveal reflectance and transmittance oscillations over thickness. Therefore, when calculating reflection off the substrate, we sum the powers of radiation reflected off the first and the second interfaces instead of radiation amplitudes and consider the phase of a wave reflected off the second interface to be random (equiprobable). The low absorbance value allows one to estimate relatively easily and accurately refractive index  $n_s$  of silicon.

Let us assume that the incident wave has an intensity of 1, the air–silicon interface reflectance is  $r_s$ , the intensity of the wave propagating from the first interface to the second one is  $a$ , and the intensity of the wave propagating from the second interface to the first one is  $b$ . Then,

$$T_s = -(1 - r_s)a; \quad R_s = r_s + (1 - r_s)b;$$



**Figure 3.** Reflection (1,2), transmission (3), and absorption (4,5) spectra of a bismuth film with a thickness of  $0.2\mu\text{m}$  on a silicon substrate measured with radiation incident from the film side (1,3,4) and the substrate side (2,3,5).

$$a = 1 - r_s + r_s b; \quad b = r_s a.$$

Excluding  $a$  and  $b$ , we find

$$r_s = (1 - T_s)/(1 + T_s); \quad r_s = R_s(2 - R_s).$$

Since [10]

$$r_s = (n_s - 1)^2/(n_s + 1)^2; \quad n_s = (1 + \sqrt{r_s})/(1 - \sqrt{r_s}),$$

relying on the more accurate data on transmittance, which varies from 0.54 to 0.535 in the  $1500\text{--}4000\text{ cm}^{-1}$  ( $6.7\text{--}2.5\mu\text{m}$ ) range, we find that  $r_s$  increases from 0.299 to 0.303, while  $n_s$  increases from 3.41 to 3.45 in the same range. According to different estimates, the refraction index of silicon in this range varies from 3.42 to  $3.44\mu\text{m}$  [9]. This agrees well with our results. The absorbance of silicon remains below  $10^{-3}$  within the entire range.

### Calculation of the refraction index and the absorbance of bismuth

The reflection spectra with radiation incident onto the plate from the bismuth side and from the silicon side were measured additionally for a bismuth film with a thickness of 200 nm, and the absorption spectra were calculated (Fig. 3). Since the transmittance values are, in accordance with the Fermat principle, almost equal in these cases, only one transmittance curve is shown in Fig. 3.

Oscillations due to the interference of waves reflected off the near and far interfaces are seen clearly in the reflection, transmission, and absorption spectra of a film with thickness  $d = 0.2\mu\text{m}$ . The reflectance with radiation incident from the bismuth side is higher than the one measured with incidence from the silicon side. Oscillations provide an opportunity to estimate the refraction index of bismuth. Oscillations of reflection off the substrate are indistinguishable. Therefore, it is more convenient to examine the case of incidence from the bismuth side. The reflection off the substrate then does not produce an additional phase shift. The first reflectance maximum ( $\nu_1 = 1400\text{ cm}^{-1}$ ,  $R_{1b} = 0.82$ ) corresponds to a film with a thickness of a quarter ( $\delta$ ) of the wavelength; the second maximum ( $\nu_3 = 3700\text{ cm}^{-1}$ ,  $R_{3b} = 0.73$ ), to a film thickness of three fourths of the wavelength; the minimum between them ( $\nu_2 = 2600\text{ cm}^{-1}$ ,  $R_{2b} = 0.54$ ), to a film thickness of a half of the wavelength. The refraction index of bismuth is  $n \approx \delta/(d\nu)$ .

Thus, we find that  $n_1 \approx 8.9$ ,  $n_2 \approx 9.6$ , and  $n_3 \approx 10.1$ . The refraction index of bismuth varies weakly within the operating range of the spectrometer. In a qualitative agreement with the trends observed in bulk bismuth samples, the index increases smoothly and monotonically with radiation frequency [8]. Its mean value is  $\langle n \rangle \approx 9.5$ . When the radiation frequency increases by a factor of 3 (from  $1300$  to  $3900\text{ cm}^{-1}$ ), the transmittance decreases by approximately the same factor. Therefore, it can be said that

the absorbance also varies only weakly. It may be estimated by analyzing the attenuation of reflectance oscillations. In the high-frequency limit, oscillations are lacking, and the reflectance tends to

$$\langle R_b \rangle = (\langle n \rangle - 1)^2 / (\langle n \rangle + 1)^2 \approx 0.655.$$

Comparing the deviations from the mean value for films of a quarter ( $R_{1b} - \langle R_b \rangle = 0.165$ ) and three fourths of the wavelength ( $R_{3b} - \langle R_b \rangle = 0.075$ ), we find that radiation is attenuated by a factor of 2.2 in propagating over an additional wavelength. Therefore, the absorbance of bismuth

$$\langle k \rangle \approx \langle n \rangle \ln 2.2 / (2\pi) = 1.2.$$

More accurate values of the absorbance of bismuth may be determined with the use of transmittance  $T$  and reflectance  $R$  values of the sample. It is more convenient in this case to consider incidence from the silicon side. Let us assume that the refraction index of silicon is  $n_k = 3.42$  and the reflectance and transmittance are as follows. At the air–silicon interface:

$$r_k = (n_k - 1)^2 / (n_k + 1)^2 = 0.300; \quad t_k = 1 - r_k = 0.700,$$

at the silicon–bismuth interface:

$$r_u = ((n - n_k)^2 + \langle k \rangle^2) / ((n + n_k)^2 + \langle k \rangle^2); \quad t_u = 1 - r_u,$$

at the bismuth–air interface:

$$r = ((n - 1)^2 + \langle k \rangle^2) / ((n + 1)^2 + \langle k \rangle^2); \quad t_u = 1 - r.$$

The following is then true [10] for the intensities of waves  $A$  and  $B$  propagating in silicon in forward and backward directions, respectively:

$$B = (R - r_k) / t_k; \quad A = 1 + B - R.$$

The intensity of wave  $C$  propagating in bismuth in the forward direction is

$$C = (A + r_u B - 2\sqrt{r_u AB}) / t_u.$$

The transmittance of the sample is

$$T = tC \exp(-4\pi k d v).$$

The following is derived from the results of measurement of the reflectance and transmittance at  $v_1 - v_3$ :  $R_{1k} = 0.700$ ,  $T_1 = 0.102$ ,  $R_{2k} = 0.353$ ,  $T_2 = 0.112$ ,  $R_{3k} = 0.502$ ,  $T_3 = 0.033$ . Thus, we find that the absorbance of bismuth at the corresponding reciprocal wavelength is  $k_1 = 1.25$ ,  $k_2 = 1.07$ ,  $k_3 = 1.7$ . Owing to the smallness of transmittance  $T_3$ , the accuracy of the obtained  $k_3$  value is low (40%). As was expected,  $k_2$  is lower than  $k_1$  [8]. In order to perform even more accurate measurements of the refraction index and the absorbance of bismuth, one needs to take into account the phase shift produced when a wave passes through the interface of two media. Owing to this phase shift, the zeroth transmittance maximum is seen clearly, e.g., in the spectra of films with a thickness of 23 and 46 nm.

## Conclusion

The accuracy of measurement of the film thickness, which was determined using an LEF-3M-1 laser ellipsometer, is the lowest ( $\sim 5\%$ ). The accuracy of the determined absolute values of the refraction index and the absorbance of bismuth (except for  $k_3$ ) is approximately the same. Their ratio  $k/n$  is known with a higher accuracy (1–3%).

Bismuth features very rare optical properties. Even in our observations, an absorbance of 60% was measured for a 0.2- $\mu\text{m}$ -thick film. Bismuth films are easy to fabricate with reproducible properties. In view of the fact that bismuth is highly chemically inert and has a very low thermal capacity and a considerable thermal resistance coefficient ( $4.5 \cdot 10^{-3} \text{ K}^{-1}$  [11]), bismuth films appear to be highly promising materials for radiation absorption and the fabrication of sensing elements of bolometric IR, THz, and microwave receivers. The use of interference in films allows one to construct devices with unique optical characteristics, which are crucial to exploration of these bands of the electromagnetic spectrum.

## Conflict of interest

The authors declare that they have no conflict of interest.

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