

## Fully absorbing one-dimensional photonic crystal

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Received November 9, 2021

Revised January 2, 2022

Accepted April 9, 2022

We investigated the resonant absorption capacity of a one-dimensional photonic crystal, the relationship between the resonant frequency and the width of its absorption band, and the composition and thickness of the layers forming it. Frequency oscillations of radiation reflection from 2.5-layer semimetal-dielectric-metal film structures caused by interference on the film thickness were studied. We measured the infrared reflection spectra of Bi<sub>87</sub>Sb<sub>13</sub> film samples on mirror-smooth substrates with a reflective metal (Al, Ti) layer and a dielectric layer MgF<sub>2</sub> + LiF or SiO<sub>2</sub> + Si<sub>3</sub>N<sub>4</sub>). We have developed samples that absorb up to 99.5% of radiation at maximum and integrally up to 60% of resonant thermal radiation. The composition of structures for interfacing with silicon technologies and constructing matrices of sensitive bolometric receivers has been optimized. We have proposed the implementation of active selective thermal imaging systems with matching the source and receiver of radiation simultaneously in frequency and frequency band. The analogy of the absorbing properties of film structures and the properties of human eye cells was shown.

**Keywords:** bismuth, film, IR, interference, eye color sensitivity.

DOI: 10.21883/EOS.2022.08.54765.2907-22

## Introduction

The development of the long-range infrared (terahertz) range of electromagnetic radiation is a priority for physics. The main drawback of modern terahertz technology is the lack of simple and affordable solutions. This work is devoted to the construction of thin-film resonance radiation absorbing structures, which can be very useful for the creation of effective receivers, sources or IR filters and terahertz radiation with a given absorption band.

Let's consider the absorption of a thin film with thickness of  $d_1$  comparable to the wave length film substance with refractive values  $n_1$  and absorption  $k_1$  ( $n_1 - 1 \gg k_1$ ) on an almost fully reflective metal mirror surface. Let a wave with a length of  $\lambda$  fall on the film normally to surface

$$E = \exp(2\pi i x / \lambda), \quad (1)$$

with the wave amplitude, for simplicity, being equal to 1. Reflection and transmission coefficients (by amplitude) at the boundary between free space and infinite medium [1]

$$r_1 \approx (n_1 - 1) / (n_1 + 1), \quad t_1 = \sqrt{1 - r_1^2}. \quad (2)$$

Let a wave with an amplitude of  $a$  spread from the edge to the depth of the film, a wave with an amplitude of  $b$  come from the depth of the film to the edge, and a wave with an amplitude of  $r$  be reflected from the edge. Then

$$a = t_1 - b r_1, \quad r = r_1 + b t_1,$$

$$b = a \exp(4\pi i n_1 d_1 / \lambda) \exp(-4\pi k_1 d_1 / \lambda) = a \alpha. \quad (3)$$

The absorption resonance in the film corresponds to the condition when the wave that has passed through the film comes out in antiphase with the reflected one —

$$\exp(4\pi i n_1 d_1 / \lambda) = -1, \quad d_1 = (-1 + 2N)\lambda / (4n_1), \quad (4)$$

where  $N$  — is the maximum absorption number.

Let's find, at what  $n_1$  and  $k_1$  in the first maximum absorption, all power will be absorbed in the film. From (3)

$$r = (r_1 + \alpha) / (1 + r_1 \alpha). \quad (5)$$

Since  $r = 0$ , then

$$r_1 = \exp(-\pi k_1 / n_1), \quad k_1 \approx (n_1 / \pi) \ln((n_1 + 1) / (n_1 - 1)). \quad (6)$$

With large  $n_1$   $k_1$  decreases and rapidly approaches  $2/\pi \approx 0.6366$ .  $n_1 - 1 = k_1$  with  $k_1 \approx 0.7267$ .

It is difficult to find the material for the absorbing film. Dielectrics typically have low absorption ( $k_1 \ll 1$ ). Metals — both large  $n_1$  and  $k_1$  [1]. Conductors with low conductivity suit better. However, as a rule, they are alloys, whose composition is difficult to control, forming thin films therefrom. Bismuth semimetal is the most promising of the pure substances. It forms thin films with predictable characteristics [2–4]. In this case, as shown in one of our recent works [5], its refraction index in the IR range is about 9.5, while the absorption index is 1.2. Even with bismuth, the absorption rate is too high.

Now consider how to modify the absorption capacity of the film structure by adding another layer to it. According to the standard logic, a layer of dielectric (with a thickness of  $d_2$ ) with small  $n_2$  and  $k_2$  must be added to the

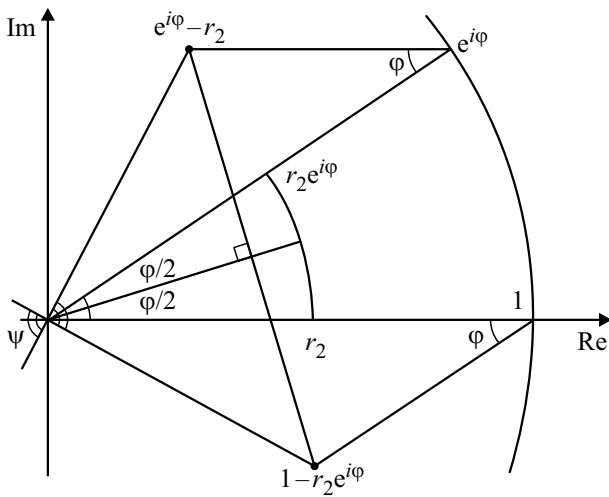


Figure 1. Phase factor definition.

layer of bad conductor with excessively big  $n_1$  and  $k_1$ . For simplicity, let us put  $n_1 \gg n_2$  and  $k_2 = 0$  and let us consider the structure of semimetal–dielectric–metal. Then, given (1)–(3), (5), the reflection ratio from the structure is

$$r = (r_1 + \alpha\beta)/(1 + r_1\alpha\beta), \tag{7}$$

where

$$\beta = (\exp(i\varphi) - r_2)/(1 - r_2 \exp(i\varphi)),$$

$$\varphi = 4\pi n_2 d_2/\lambda, \quad r_2 \approx (n_1 - n_2)/(n_1 + n_2). \tag{8}$$

As there is no absorption in dielectric, then  $\beta$  is just a phase factor of  $|\beta| = 1$ ,

$$\beta = \exp(i\psi). \tag{9}$$

Fig. 1 demonstrates how to estimate the value of angle  $\psi$ . The modular numerator and denominator of fractions, the quotient of which is  $\beta$  (8), are deposited on complex plane. The angle  $\psi$  is the phase shift between this numerator and denominator. It's easy to see that

$$\tan\left(\frac{\psi}{2}\right) = \frac{(\exp(i\varphi) - r_2 - 1 + r_2 \exp(i\varphi))}{(\exp(i\varphi) - r_2 + 1 - r_2 \exp(i\varphi))}$$

$$= \frac{(1 + r_2)(\exp(i\varphi) - 1)}{(1 - r_2)(\exp(i\varphi) + 1)} = \frac{n_1}{n_2} \tan\left(\frac{\varphi}{2}\right). \tag{10}$$

In the range from 0 to  $\pi$  the angle  $\psi$  increases monotonously depending on  $\varphi$ . By increasing the thickness of the layer, we only add the phase shift of the wave. Absorption resonance condition (see (4)):

$$\exp(i\psi + 4\pi n_1 d_1/\lambda) = -1,$$

$$d_1 = (-1 - \psi/\pi + 2N)\lambda/(4n_1). \tag{11}$$

Thickness corresponds to the first interferometric absorption maximum

$$d_1 = (1 - \psi/\pi)\lambda/(4n_1). \tag{12}$$

A set of pairs of layers thicknesses correspond to the resonance. Increasing the one compensates decreasing of the other one. Absorption index corresponds to full absorption in the structure

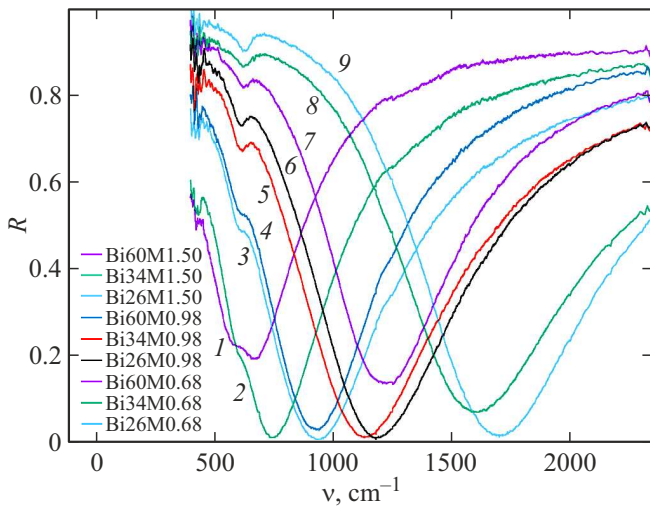
$$k_1 \approx (n_1/(\pi - \psi)) \ln((n_1 + 1)/(n_1 - 1)) \approx 2/(\pi - \psi). \tag{13}$$

Thus, at a given radiation wavelength, by changing the thickness of the second layer  $d_2$ , one can choose the values of relation of  $d_2/\lambda$  and  $\psi$  (8), (10), which correspond to full absorption (to the value  $k_1$ ). The single value of the thickness  $d_1$  of the first layer (12) corresponds to the thickness of the second layer. At this wavelength, there is a single pair of layers thicknesses of a semimetal–dielectric–metal structure, for which the absorption will be complete in the first maximum of absorption.

### Experiment

It is better to take a semimetal with a refraction index of  $k_1$  as close as possible to  $2/\pi$  as an upper (main absorbing) layer. So we took not just a bismuth, but bismuth with added antimony. If it is necessary to increase rather than reduce the concentration of charge carriers, bismuth is alloyed by tin or tellurium impurities [6,7]. As it is known [8], bismuth and antimony form a series of solid solutions with any component content. Atoms of bismuth and antimony freely replace each other without destroying the crystal structure. The addition of antimony reduces the overlap of the valence and conductivity bands.  $\text{Bi}_{1-x}\text{Sb}_x$  composites exhibit semiconductor properties. At room temperature, the minimum conductivity of the composite is observed when the atomic fraction of antimony is 13%. Approximately at this content, refraction index should be minimal as well. Therefore, we used the composition of  $\text{Bi}_{87}\text{Sb}_{13}$  to prepare the top layer of the structure.

The films were formed by vacuum thermal spraying of a mixture of particularly pure ( $10^{-5}$ ) bismuth and antimony in high vacuum from a tungsten container to a substrate heated up to  $110^\circ\text{C}$ . To be sure, bismuth and antimony have close saturated vapor pressures at the spray temperature ( $700\text{--}800^\circ\text{C}$ ). Therefore, the content of the components is uniform throughout the film volume.  $\text{Bi}_{1-x}\text{Sb}_x$  composites have a layered crystalline structure [4–9], just like the bismuth itself. The atoms in the layers are connected much stronger than the layers between each other. The mirror-smooth substrate on which sputtering was made has a guiding effect on the growth of bismuth crystals. The crystal layers grow parallel to the substrate surface. At the temperature used, the crystallites are oriented not only perpendicular to the plane of the substrate, but also in the plane of the substrate [4,10]. The long-range order extends not only to the area of the individual crystallite, but also to the scale of the whole film, while the individual crystallites are interconnected by doubling which is characteristic of bismuth.



**Figure 2.** The reflection spectra of  $\text{Bi}_{87}\text{Sb}_{13} - (\text{MgF}_2 + \text{LiF}) - \text{Al}$  structures: 1 —  $\text{Bi}_{60}\text{M}_{1.50}$ , 2 —  $\text{Bi}_{34}\text{M}_{1.50}$ , 3 —  $\text{Bi}_{26}\text{M}_{1.50}$ , 4 —  $\text{Bi}_{60}\text{M}_{0.98}$ , 5 —  $\text{Bi}_{34}\text{M}_{0.98}$ , 6 —  $\text{Bi}_{26}\text{M}_{0.98}$ , 7 —  $\text{Bi}_{60}\text{M}_{0.68}$ , 8 —  $\text{Bi}_{34}\text{M}_{0.68}$ , 9 —  $\text{Bi}_{26}\text{M}_{0.68}$ .

The substrates, on which the radiation absorbers were formed, were mirrored smooth plates of polished single crystal silicon. Each of them was dusted with a reflective layer of pure aluminum. In the first submitted series of measurements (Fig. 2), magnesium fluoride  $\text{MgF}_2$  was chosen as the main material of the second dielectric layer. It is a chemically inert transparent optical material with well-studied properties. In the range of reciprocal wavelengths  $\nu$  from 1000 to 4000  $\text{cm}^{-1}$  its refractive index rises from 1.2 to 1.37 [11], according to the approximating formula  $n_2 \approx 1.38 - 380^2/(\nu - 120)^2$ . It has a low spray temperature ( $\sim 1000^\circ\text{C}$ ) and is convenient for preparing films of a given thickness. In order to render the film amorphous and thus homogeneous in thickness, lithium fluoride  $\text{LiF}$  (20%) was sprayed together with magnesium fluoride (80%), having approximately the same spray temperature and similar optical characteristics. Metal fluorides mix perfectly like oxides to form fluoride glass.

Measurements of infrared spectra in the  $\nu$  range from 400 to 4000  $\text{cm}^{-1}$  ( $2.5 - 25 \mu\text{m}$ ) were performed using a direct-action Shimadzu IR460 spectrometer. A special insert included in the instrument kit was used. 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.

In the final stage of these measurements, a series of nine specimens were made with the thickness of „bismuth“ being 26, 34 and 60 nm and the thickness of „magnesium fluoride“ being 0.68, 0.98 and 1.50  $\mu\text{m}$ . At every step of the preparation, the quality of the films could be easily controlled visually thanks to the excellent mirroring.

Radiation dissipation is negligible and the sum of reflection and absorption is 1.

It can be seen that the measurement results agree quite well with the theoretical assumptions. For five of the samples presented, the resonance absorption is between 98.3 and 99.5%. The reciprocal wavelength of resonance absorption ranges from 730 to 1700  $\text{cm}^{-1}$ . Resonance absorption curves have a smooth repetitive shape from measurement to measurement due to the fact that both  $\text{Bi}_{87}\text{Sb}_{13}$ , and  $(\text{MgF}_2 + \text{LiF})$  optical characteristics change monotonically without cutting features. Only at the edge of the spectrometer range at 650  $\text{cm}^{-1}$  is the absorption line of magnesium fluoride which at the film thickness of 0.68  $\mu\text{m}$  is about 10%. The absorption properties of structures are necessarily due to their structure.

Let's analyze in detail the characteristics of 26/1.50, 26/0.98, 26/0.68 structures, resonance absorption of which is closest to 1 (99.5, 98.8 and 98.3%). Their resonant reciprocal wavelengths are 935, 1180 and 1700  $\text{cm}^{-1}$ . At the same time, the refractive index of magnesium fluoride is 1.16, 1.25 and 1.32. Accordingly, the dielectric thickness causes a phase shift of  $\varphi = 2.04, 1.81$  and 1.92 rad. The dielectric layer (as per (10), putting  $\langle n_1 \rangle = 6.6$ ) adds a phase shift of  $\psi = 2.93, 2.85$  and 2.86 rad. Then refractive index of  $\text{Bi}_{87}\text{Sb}_{13} - n_1 \approx 7.0, 7.7$  and 5.0 can be estimated from (12). The resulting refractive index is slightly lower than we expected. This is probably because a significant fraction of the power is absorbed in „magnesium fluoride“, rather than in „bismuth“. The significant measurement error is also caused by the low accuracy ( $\sim 5\%$ ), with which we know the thickness of the layers of structures.

Despite significant quantitative differences, we obtained full qualitative consistency of the experimental results with theoretical predictions. You can also clearly see a continuous set of pairs of layers thicknesses corresponding to the absorption resonance and a single pair of thicknesses corresponding to full absorption. The simplicity and readability of the formation principles made it relatively easy to select such pairs of thicknesses and build a fully absorbing single-dimension photon crystal.

Let's note another very important feature of the obtained structures. When the thickness of the upper layer of structure is small and the phase shift in the dielectric layer  $\psi$  is close to  $2\pi$ , according to (8), (10), the phase incursion in the entire structure changes very slowly depending on the radiation wavelength. As a result, our structures have an exceptionally wide area of high absorption. For example, for a 26/1.50 structure, the lower and upper boundary of the absorption band are 600 and 1400  $\text{cm}^{-1}$ . The width of the structure absorption spectrum is comparable to that of the black body. At 300 K, the maximum spectral density of the black body radiation corresponds to a reciprocal wavelength of about 590  $\text{cm}^{-1}$ , while the lower and upper boundary of the emitted band is 240 and 1130  $\text{cm}^{-1}$ . The ratio of the band width to the reciprocal wavelength at the maximum value of the black body radiation temperature is independent and is about 1.5. The

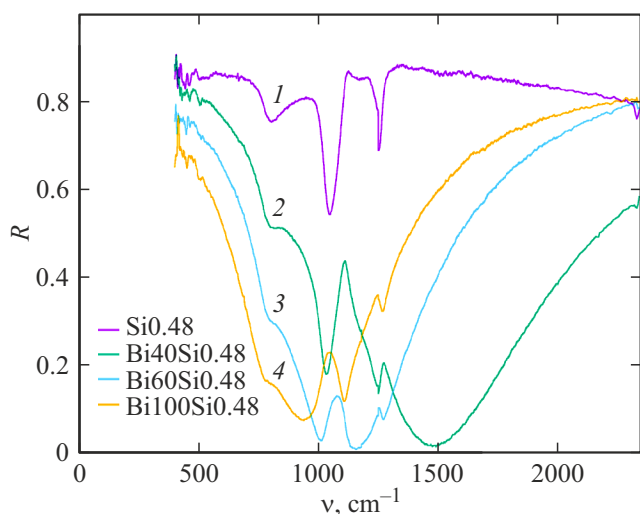
same parameter for 26/1.50 structure is 0.85. It corresponds to a resonance radiation temperature of 475 K. The integral absorption coefficient of the resonance thermal radiation structure is 56%. With such a large absorption of the semimetal–dielectric–metal structure, it is very promising to work as bolometric detectors of thermal radiation.

According to the Kirchhoff's law, for thermal radiation, the absorption ratio of a body's surface is equal to its luminosity. Accordingly, the same effective radiation-absorbing structures can simultaneously serve as equally effective radiators. The structures are suitable for constructing active thermal imaging systems with the agreement of the radiator and receiver simultaneously on the resonance frequency and frequency band. Add that the electrical resistance of  $\text{Bi}_{87}\text{Sb}_{13}$  changes significantly with temperature. The thermal ratio of resistance of  $\text{Bi}_{87}\text{Sb}_{13}$  film  $d(\ln(R_e))/d(T) = -0.0045 \text{ K}^{-1}$  [12] measured by us at temperatures from  $-20$  to  $+20^\circ\text{C}$ . The top layer of the structure can also immediately serve as a thermoresistor, recording the absorbed power.

In bolometric receivers, thermal isolation of the receiving element from the environment is necessary for the sensitive detection of the incident radiation. In our case, the film structure has to be separated from the substrate into which the heat goes.

There is a technology of forming film windows on a single crystal silicon plate. Several layers of oxide or silicon nitride with a specified thickness are applied consecutively to the surface of the plate. Then, a matrix of rectangular open spaces is formed on the reverse side in accordance with the orientation of the single crystal according to standard technology. After that, silicon is removed and a matrix of through rectangular thin-film windows is obtained by directed etching through these places.

We modelled the structure and measured its reflection. First, a protective layer of 70 nm thick silicon nitride was



**Figure 3.** The reflection spectra of  $\text{Bi}_{87}\text{Sb}_{13}$  —  $(\text{SiO}_2 + \text{Si}_3\text{N}_4)$ —Ti structures: 1 —  $\text{Si}_{0.48}$ , 2 —  $\text{Bi}_{40}\text{Si}_{0.48}$ , 3 —  $\text{Bi}_{60}\text{Si}_{0.48}$ , 4 —  $\text{Bi}_{100}\text{Si}_{0.48}$ .

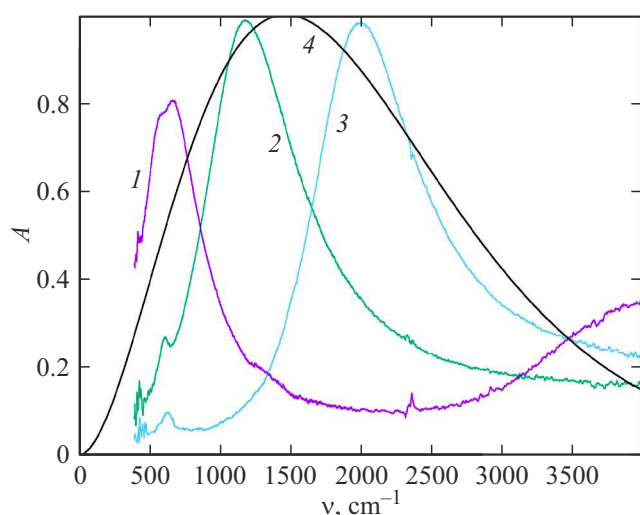
applied to the plate. Then a layer of 80 nm thick titanium was applied by magnetron spraying, thick enough to reflect infrared radiation almost completely. Then once again a layer of silicon nitride with a thickness of 70 nm was applied. After that, a layer of polysilicon was applied, which in a wet oxygen medium oxidized to silicon oxide  $\text{SiO}_2$ . Layer thickness — 340 nm. Then once again a layer of silicon nitride with a thickness of 70 nm was applied. The total thickness of the nitride-oxide film is  $0.48 \mu\text{m}$ . Then, using the technology described above,  $\text{Bi}_{87}\text{Sb}_{13}$  layers with the thickness of 40, 60 and 100 nm. were applied to the plate. Reflection spectra of nitride oxide film on titanium and three 2.5-layer structures are presented in Fig. 3.

As with structures with magnesium fluoride, the samples have good mirror reflection. The dispersion of radiation samples can be neglected. Unlike  $(\text{MgF}_2 + \text{LiF})$ , dielectric  $(\text{SiO}_2 + \text{Si}_3\text{N}_4)$  has approximately twice the refractive ratio and three to four times the absorption ratio. There are three strong absorption lines at  $800$ ,  $1050$  and  $1250 \text{ cm}^{-1}$ . But even for the strongest of them the absorption in the film reaches only 43%. The average absorption over the spectrometer range is 16%. The maximum absorption in 2.5-layer structures is close to 1, and for structures with  $\text{Bi}_{87}\text{Sb}_{13}$  40, 60 and 100 nm makes 98.4, 99.1, and 92.5% for structures with reciprocal wavelengths of 1480, 1160 and  $940 \text{ cm}^{-1}$  respectively. Absorption resonance in the structure is superimposed on absorption in the dielectric, which complicates the measurement. However, it can be said that the structures correspond to a resonant radiation temperature of about 680, 560 and 480 K and an integral absorption coefficient of 58, 56 and 54%. Despite the visible absorption of radiation in the dielectric layer, structures are equally effective for selective broadband thermal imaging. The composition of the dielectric layer fully corresponds to the composition of the layers from which the windows on silicon plates are formed.

The developed 2.5-layer structures have high mechanical strength, very high chemical inertness. After three years of indoor storage, the 26/1.50 structure absorption spectrum remained unchanged, with a resonance absorption coefficient of 99.5%.

## Conclusion

Thus, the principles of the construction of a resonantly fully absorbing electromagnetic radiation 2.5-layer thin-film structure of a semimetal–dielectric–metal are theoretically substantiated and confirmed in practice. It is explained how to form structures with a wide range of absorption. There are 7 structures with resonant reciprocal wavelength from  $730$  to  $1700 \text{ cm}^{-1}$ , at maximum absorbing at least 98.3% of radiation and having an integral absorption coefficient of resonance thermal radiation from 55 to 60%. The structure of the system of active infrared imaging, consistent in frequency and frequency band, has been described. The compatibility on one substrate (in one chip) of the matrix of



**Figure 4.** Structure absorption spectra (on Al): 1 — Bi60M1.50, 2 — Bi26M0.98, 3 — Bi26M0.52, 4 — the black body radiation spectrum with a temperature of 750 K.

sensitive bolometric receivers with absorbing structures and elements of amplification and processing of the received signal has been confirmed.

Semimetal–dielectric–metal structures have at once the set of properties necessary for effective thermal reception-transfer — wide band and full resonance absorption, alignment of luminosity and absorption, wide angle of view, high thermal coefficient of electrical resistance of the top layer insulated from the substrate, low thickness and heat capacity of the unit area of the structure. According to our estimates, due to this combination, it is possible to create non-refrigerated systems of selective active thermal imaging in the range of radiation wavelengths from 10 and at least  $80\ \mu\text{m}$ . We believe that the relative simplicity, reliability and durability of the structure, ease of use and low cost of the proposed devices will be useful for the development of the long infrared (terahertz) range. We hope that the devices built on the basis of the described structures will find technical application.

## Biophysics Application

The results obtained in the article can be used for a possible explanation of the nature of eye color sensitivity. We believe that it is most likely that each color-sensitive cell acts as a microbolometer, reacting to the absorbed power due to its temperature change. The film structure on the surface of the cell, similar to the one described above, has a spectral selective absorption. To substantiate this claim, we cite a number of known facts and a range of physical and logical arguments.

There are two vision systems in the eye — day and night ones, and for each of them there are appropriate cells — „cones“ and „rods“. At night the illumination is small, so the vision is optimized for the maximum sensitivity

that chemical radiation detection gives. The photochemical reaction is characterized by the red border and broadband reception at all higher frequencies. Night vision is therefore black and white. Note that the substances responsible for spectral selective absorption have not yet been detected. We believe that such substances do not exist. By contrast, illumination during the day is high. You have to limit the area of the pupil to avoid burning the retina. Therefore, in daytime, sensitivity can be sacrificed to extend the dynamic range, faster performance, and spectral selectivity. Of course, recording the thermal effect of light is repeatedly less sensitive, but in the presence of night vision sensitivity is not so necessary.

The speed of the bolometer determines its cooling rate. The temperature relaxation time, which is about 0.1 s, is quite consistent with an object of micron sizes in a water medium.

The surface of the cell is a film. Therefore, constructing a resonantly absorbing film structure in terms of evolution is not an impossible task. All you need is a series of mutations that first fixes high surface absorption at the heat sensitivity of the cell. This is already an obvious evolutionary advantage due to high performance. Then another series of mutations, fixing the direction of radiation reception and spectral selectivity. Fig. 4 illustrates the analogy of the absorption properties of film structures and properties of color-sensitive eye cells.

The absorption spectra of three layers of structures, identical in composition and differing only in the thickness of layers, are presented. At 750 K radiation temperature, this set of spectroscopically selective absorbers provides approximately the same three-color vision as the eye in the visible range (6000 K). For the first structure, the first and second absorption maxima are simultaneously visible. The latter ensures the closure of the „color circle“. In the absence of variance, the frequency of the second absorption maximum (4) is three times the frequency of the first, corresponding to the beginning and end of the visible range.

And finally, a few words about „cones“. To form a wave with the same amplitude and opposite phase wave reflected from the outer boundary of the structure (fulfillment of the resonance absorption condition), our structures have a third reflective metal layer. However, it is known that living organisms do not synthesize metals. The organic resonance film absorbing structure should be a complete internal reflection from the optically less dense deep layer. Then, to meet the resonance absorption condition, light must fall on the film at a certain sufficiently large angle. The best shape for the absorbing surface is a cone with an axis along the direction of the incident light. This is the shape the „cones“ have. It is optimal for directed spectrally selective resonance absorption. In addition, it provides great heat dissipation and correspondingly high performance.

## Conflict of interest

The authors declare that they have no conflict of interest.

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