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A hybrid metal polymer based on polymethyl methacrylate with embedded metal nanoparticles

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A study was made of a hybrid metal-polymer material consisting of polymethyl methacrylate (PMMA) and nanoparticles distributed throughout its volume, silver, gold, copper or aluminum. The effective permittivity and absorption cross section are calculated, and the processes of temperature relaxation are modeled. It has been shown that mixtures of PMMA with silver, copper, aluminum, or gold nanoparticles can be used as an active medium in optoacoustic ultrasound generators.

Keywords: hybrid material, ultrasound generator, nanoparticle, polymethyl methacrylat.

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1. Introduction

Optoacoustic generation of ultrasound occurs due to expansion and subsequent compression of the active medium of the transducer, accompanying the absorption of the laser pulse or their periodic sequence [1,2]. After energy deposition of the light pulse, heating and thermal expansion occur, which is followed by thermal relaxation and contraction. These expansion-compression cycles can generate the mechanical wave on ultrasonic frequencies. The Russian history of optoacoustic research takes its rise in 70s years of the twentieth century with the research of the research team of L.M. Lyamshev and K.A. Naugolnykh [3,4]. The key to the high efficiency of optoacoustic conversion is the competent selection of materials for the active medium of the generator. Firstly, strong laser radiation absorption is necessary, secondly, high coefficient of thermal expansion, and thirdly, sufficient heat diffusivity for adequate heat removal and overheating avoidance [5].

In the first optoacoustic generators, metal layers were used as active medium, since they made it possible to achieve significant heating due to the absorption of laser pulses and fast temperature relaxation, which makes it possible to achieve high operating frequencies, but the energy conversion efficiency was low due to low values of thermal expansion coefficients [6]. In real practice, frequencies of 2−19 MHz are used in medical non-invasive diagnostics and industrial defectoscopy, so increasing the efficiency of the device in this frequency range is a more critical task than expanding the range itself. The use of hybrid materials in the design of optoacoustic generator that properly combines the physical properties of different materials can lead to an increase in the efficiency of energy conversion. Such materials have already found a use in some areas of photonics: as light-emitting materials [7,8], in solar panels [9], to control terahertz radiation [10,11].

The organosilicon material polydimethylsiloxane (PMDS) [12,13] has the highest coefficient of thermal expansion, while polydimethylsiloxane is a heat insulator and does not allow adequate thermal relaxation at high frequencies. For efficient light absorption, the layer of metal [14] or metal nanoparticles [15] is added to the polydimethylsiloxane layer. Devices with such active media have already been implemented in practice [16].

As an alternative to polydimethylsiloxane, as hybrid metal polymer matrix, polymethylmethacrylate (PMMA) can be used. Its heat diffusivity ($0.2\,\mathrm{mm^2/s}$) is almost twice that of polydimethylsiloxane (PMDS) ($0.11\,\mathrm{mm^2/s}$), while the thermal expansion coefficient is three times less ($9\cdot10^{-5}\,\mathrm{K^{-1}}$ for PMMA versus $30\cdot10^{-5}\,\mathrm{K^{-1}}$ for PMDS). It is shown that optoacoustic generators with PMDS cannot adequately operate at frequencies > 10 MHz. Nevertheless, frequencies up to 30 MHz are in demand in defectoscopy and medicine. The range 10−30 MHz can be occupied by active media based on PMMA. The purpose of this work is to study the properties of hybrid metal-polymers based on polymethylmethacrylate (which is a common photoresist and for which many technological processes have been developed) and nanoparticles of silver, gold, copper, and aluminum.

2. Results and discussion

To develop a model of an optoacoustic generator with a metal polymer as active medium, it is necessary to know its refraction and absorption indices. In this case, the effective optical characteristics can be calculated using the Maxwell–Garnet formula:

$$\varepsilon_{\text{mix}} = \varepsilon_{\text{PDMS}} \left[1 - \frac{3f(\varepsilon_{\text{PDMS}} - \varepsilon_{\text{Ag}})}{2\varepsilon_{\text{PDMS}} + \varepsilon_{\text{Ag}} + f \cdot (\varepsilon_{\text{PDMS}} - \varepsilon_{\text{Ag}})} \right], \quad (1)$$

where $\varepsilon_{\text{PMMA}}$ is the permittivity of polydimethylmethacrylate and a ε_{Met} is the permittivity of metal. Using this formula, the spectra of the real and imaginary parts of the effective permittivity were calculated, which are shown in Fig. 1. The data on permittivities of metals are taken from experimental works [17–19].

The spectra of the imaginary and real parts of the refraction index for hybrid metal-polymers from a PMMA matrix with silver, gold, aluminum, and copper nanoparticles are shown in Fig. 1. For simulation, the radius of nanoparticles was chosen to be 50 nm and density per unit volume 20%. It can be seen that aluminum differs from other metals in higher values of the imaginary part of the permittivity, which suggests the higher order of light scattering in the material.

To evaluate the ability of hybrid material to absorb, the dependences for cross sections of metal nanosphere absorption for various integrated metals, were plotted.

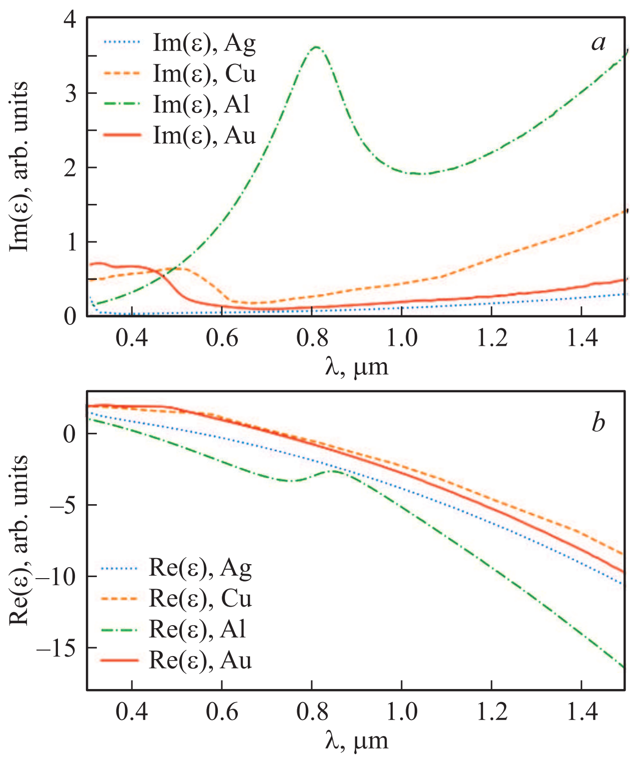

Figure 1. Spectra of the real (*a*) and imaginary (*b*) parts of the effective permittivity for hybrid materials based on PMMA and metal nanoparticles with volume fraction of 20%. (A color version of the figure is provided in the online version of the article).

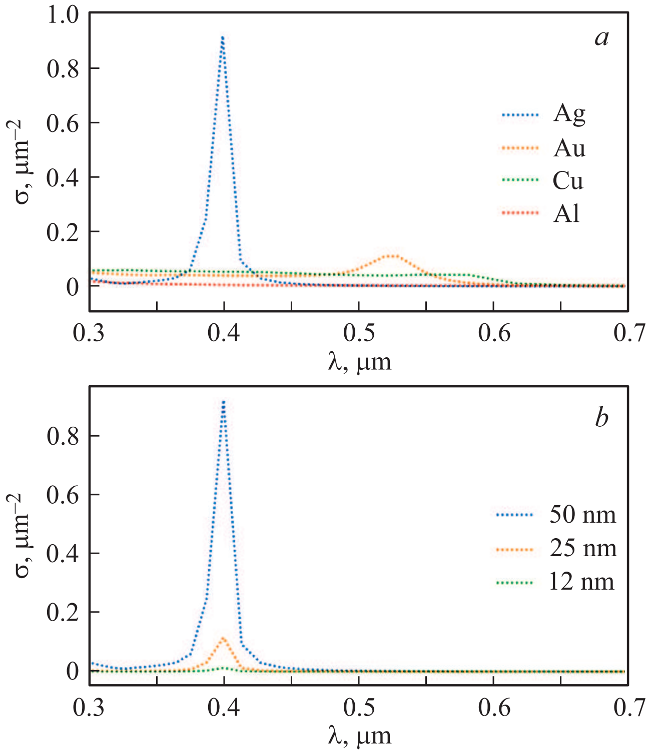

Figure 2. Cross-section for scattering on the metal nanoparticle in the volume of polymethylmethacrylate. *a* is radius of nanoparticles 50 nm, nanoparticles of silver, copper, aluminum, gold; *b* are silver nanoparticles of different radii.

The absorption cross sections of silver, gold, copper, and aluminum nanospheres with radius of 50ńm in PMMA matrix were calculated in the Comsol Multiphysics 5.5 environment and are shown in Fig. 2, *a*. It can be seen that the largest absorption cross section is achieved for the silver nanosphere at wavelength of ~ 400 nm. Fig. 2, *b* shows the absorption cross sections as a function of wavelength for silver nanoparticles of different radii.

Besides the optical characteristics of the hybrid metal polymer, its thermodynamic characteristics are also important. To estimate the cooling rates, 3D-simulating of the hybrid material was performed in the Comsol Multiphysics 5.5 environment. PMMA sample with metal particles embedded in it with radius of 50 nm was placed in the following conditions: temperature of metal nanoparticles is 375 K, temperature of the PMMA matrix and the environment (air and quartz glass substrate) is 293 K. The quartz glass substrate was chosen from the considerations that it is convenient to place the active medium of the optoacoustic converter directly on the end of the optical fiber [20]. Fig. 3 shows the dependences of the average temperature of nanoparticles on time in the process of temperature relaxation. It can be seen that during the time period corresponding to the frequencies ~ 10 MHz (10^{-7} s), the silver, gold, and aluminum nanoparticles have time to cool down to 340 K, while the copper ones cool

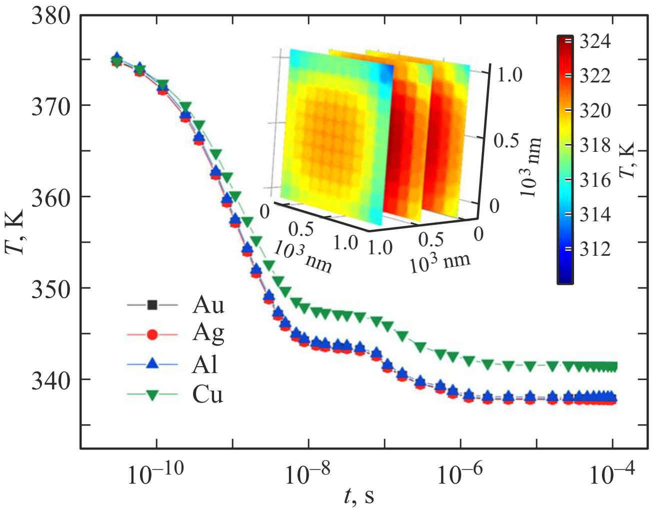

Figure 3. Dependence of the average temperature of silver, copper, aluminum, and gold nanoparticles during free-cooling. Radius of nanoparticles is 50 nm, their volume concentration is 20%, initial temperature of nanoparticles is 375 K, initial temperature of PMMA and environment is 293 K. The insert shows the structure of the computational model and the temperature distribution in it 0.001s after the start of cooling.

noticeably more slowly. The temperature 375 K is close to the critical temperature for PMMA, however, the potential operating temperature range is sufficient for the operation of the optoacoustic generator. The insert shows the structure of the computational model and the temperature distribution in it 0.001s after the start of cooling.

3. Conclusion

Taking into account the above results of simulating the optical and thermophysical properties of hybrid metal-polymers, it can be concluded that polymers based on a PMMA matrix and metal nanoparticles can be used as alternative to hybrid materials based on polydimethylsiloxane. The combination of PMMA with silver nanoparticles seems to be the most advanced.

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Conflict of interest

The authors declare that they have no conflict of interest.

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