Mechanoluminescence of composite layer applied on polymer surface excited by short acoustic pulses in water

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Abstract. A composite mechanoluminescent layer has been produced on the surface of polymethylmethacrylate by liquid-phase embedding of SrAl₂O₄:(Eu²⁺, Dy³⁺) phosphor microparticles into the polymethylmethacrylate surface layer. The photoluminescence and mechanoluminescence of the obtained layer have been investigated. The mechanoluminescence was excited by the short acoustic pulses. A possible mechanism of mechanoluminescence excitation is under discussion. The produced composite layer is shown to exhibit high efficiency of “mechano-optical” transformation.

1. Introduction
The mechanoluminescent materials offering the ability to effectively transform mechanical actions to an optical signal are of great interest for producing mechano-optical converters, sensor elements and detecting devices [1–7]. In combination with the elements of optoelectronics and semiconductor electronics, they can be used in production of the smart systems for measurements, control and management in robotics and in aircraft and space technology [8–10]. The best known material of this kind is ZnS:Mn²⁺. A variety of materials have been synthesized thus far, which are capable of effective transforming external mechanical action to optical radiation. The materials have been obtained whose mechanoluminescence overlaps nearly the whole of the visible wavelength range. The materials are also known that effectively luminesce in the near IR region. As a rule, these are the fine-dispersed powder-like dielectric or semiconductor materials doped with luminescent additives. The investigations of the mechanism and ways of mechanoluminescence excitation in different materials are pursued in order to improve the efficiency of mechano-optical transformation.

2. Materials and experimental procedure
This paper presents a study of photo- and mechanoluminescence of a composite layer produced from the polymer material polymethylmethacrylate and the fine-dispersed powder (the mean size of powder particles ≈65 μm) of the phosphor SrAl₂O₄:(Eu²⁺, Dy³⁺). The excitation of photoluminescence was realized by a group of lasers with different wavelengths. Mechanoluminescence was excited by the...
short acoustic pulses. The mechanoluminescent powder was produced by high-temperature sintering of the oxides $\text{Al}_2\text{O}_3$, $\text{Eu}_2\text{O}_3$, $\text{Dy}_2\text{O}_3$, $\text{SrCO}_3$.

Figure 1. The photographs of the composite layer on the polymethylmethacrylate surface taken by the scanning electron microscope: (a) – the layer surface; (b) – the layer spall.

The composite mechanoluminescent layer sensitive to mechanical action (sensor layer) of the thickness of $\Delta h \approx 200 \mu m$ was formed directly in the surface layer of the polymethylmethacrylate plate that is transparent in the visible region.

Figure 2 presents a scheme of the experimental setup for the investigation of the kinetics of mechanoluminescence excited by the short laser pulses in water. A metal (stainless steel) plate 100 μm thick was glued to the composite layer surface. It is important that the metal plate should have a good acoustic contact with the surface of the composite material. The laser pulse ($W_{\text{pulse}} \approx 10 \text{ mJ}$, $\tau_{\text{pulse}} \approx 7 \text{ ns}$, $\lambda = 532 \text{ nm}$) was focused on the surface of the stainless-steel plate to a spot of the diameter $d = 0.5 - 2.0 \text{ mm}$.

Figure 2. The scheme of the experimental setup: 1 – metal plate, 2 – composite layer on the surface of polymethylmethacrylate plate, 3 – substrate of polymethylmethacrylate, 4 – photomultiplier, 5 – laser pulse.

The laser pulse gave rise to an acoustic impulse emerging from the zone of laser pulse action on the plate. When propagating through the metal plate the acoustic impulse reached the contacting to it
mechanoluminescent layer and initiated the mechanoluminescence signal. The signal was registered on the photomultiplier 4.

3. Results and discussion
Figure 3 illustrates the signal of mechanoluminescence excited by the acoustic impulse emerging under the laser pulse action on the metal plate.

In accordance with [11], in the regime of developed laser evaporation, when $I_{\text{las.}} > I_{\text{th}}$, the vapor pressure in the laser exposure zone can be estimated with the following expressions:

$$p_s(T) \approx p_0 \exp \left( \frac{q_1}{T_{\text{ev}}} \right) \exp \left[ - \frac{q_1}{T(I_{\text{las.}})} \right]$$

(1)

$$I_{\text{th}} \approx \frac{q \rho}{\alpha_{\text{abs}} \sqrt{\tau}}$$

(2)

where $p_0$ - external pressure; $T_{\text{ev}}$ - boiling temperature of the material; $q_1$ - evaporation heat per atom of the target material; $I_{\text{las.}}$ - laser radiation power density; $I_{\text{th}}$ - threshold of developed evaporation; $q$ - specific heat of evaporation; $\alpha_{\text{abs}}$ - laser radiation absorption coefficient; $\rho$ - density of the target material; $\chi$ - thermal conductivity of the target material; $\tau$ - laser pulse duration.

Figure 3. The mechanoluminescence signal of the composite layer excited by an acoustic impulse emerging under the laser pulse action on the metal plate: 1 – laser pulse; 2 – mechanoluminescence signal.

The action of the acoustic impulse causes the deformation of the polycrystalline microparticles of the phosphor containing a great many grains. In the polycrystalline materials the deformation mainly results from intergranular sliding at the cost of the movement of the grain-boundary dislocations. It is known [12] that in the vicinity of dislocations high enough stresses $\sigma(r, \theta)$ exist which can bring about curving (displacement) of the bands and levels of the impurities and defects.

$$\sigma(r, \theta) = \frac{1+\nu}{3\pi(1-\nu)} G b \frac{\sin \theta}{r}$$

(3)

where $\nu$ - is Poisson ratio, $b$ - is Burgers vector, $G$ - is elastic modulus, $r$ - is the distance from the dislocation core.

In the stress field of dislocations the energy levels of traps are shifted to the conduction band:

$$E \approx E_d + \frac{\Delta V}{\nu}$$

(4)

$$\Delta V \approx \beta \sigma$$

(5)

where $E_d$ is the position of a trap level far from the dislocation, $\Delta V/V$ - is a relative variation of the volume in the vicinity of dislocation, $\theta$, $\beta$ - are the constant coefficients.
As the result, the energetic distance $\Delta E$ - between the trapping levels and the conduction band bottom will reduce:

$$\Delta E = E_c - E \leq kT \quad (6)$$

At the same time, the probability of tunnel transitions of the electrons from the occupied trapping levels into the conduction band will grow sharply. Further, nonradiative capture of the electrons by the Eu$^{3+}$ ions from the conduction band comes about, which results in the appearance of excited Eu$^{2+*}$ ($\text{Eu}^{3+}\rightarrow\text{Eu}^{2+*}$). Mechanoluminescence is conditioned by the radiative transitions of the Eu$^{2+*}$ ions.

4. Conclusion

A composite mechanoluminescent layer exhibiting high effectiveness of mechano-optical transformation has been produced in the surface layer of the transparent in the visible region solid material polymethylmethacrylate. The kinetics of mechanoluminescence of the composite layer excited by the short acoustic pulses in water have been studied. A scheme of the electron levels of the luminescent centre Eu$^{2+}$ and “traps” in the phosphor SrAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ has been suggested that agrees with the observed photoluminescence lines. It has been shown that the obtained mechanoluminescent layer possesses high sensitivity to pulsed acoustic and dynamic mechanical actions and can be used as a sensor element in registration and visualization of acoustic and mechanical impacts.

Acknowledgment

The work has been supported by the Ministry of science and higher education within the framework of “production of new nanomaterials and nanostructures for solving the actual problems of micro- and nanoelectronics and nanophotonics”; by the Russian Foundation for Basic Research, Project №16-29-14003 ofi_m in part of “investigation of deformation-stimulated optical generation of nanomicroparticles of phosphor in a polymer matrix”.

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