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KINETICS OF LASER-INDUCED THERMAL EMISSION OF POROUS CARBON MATERIALS: DEPENDENCE ON LASER WAVELENGTH

For the porous carbon material excited by the first and second harmonics of a neodymium laser, the shape of pulsed signals of laser-induced thermal emission is investigated. It is found that the duration of thermal emission pulses significantly depends on the wavelength of the laser excitation, which is caused by the differences in the depth of penetration of laser radiation into the surface layer. The mentioned effect is actual, if the penetration depth of laser radiation exceeds the length of thermal diffusion in the studied material for a time of the order of the laser pulse duration. The computer modeling is carried out for the processes of pulsed laser heating and formation of thermal emission signal. The simulation results showed satisfactory agreement with the measurement results.

K e y w o r d s: laser-induced thermal emission, kinetics, porous carbon.

1. Introduction

In various applications of lasers, thermal radiation that occurs during a local heating of irradiated objects attracts the attention of researchers as a source of information about the properties of the irradiated material and about the processes of its interaction with laser radiation [1–10]. In the case of the laser heating of microparticles or surface layers of light-absorbing materials, an important tool is the study of the kinetics of growth and decay of thermal emission under the pulsed laser excitation [11–17]. Usually, for the excitation of laser-induced thermal emission (LITE) of surface layers of light-absorbing materials, laser pulses of a nanosecond duration are used, which leads to the emission of thermal radiation pulses with the duration of the order of $10^{-8}...10^{-7}$ s in different media. As a rule, the leading edge of LITE pulses is significantly shorter than the duration of laser excitation pulses, which is due to the strongly non-linear dependence of the exitance of the heated surface on its temperature (according to Planck's formula). As for the trailing edge of LITE pulses, the decay of thermal radiation is determined by the kinetics of temperature of the surface of the emitting object (a microparticle or the surface layer of the irradiated material), which, in turn, depends on the thermal characteristics of the material, as well as on the depth of laser radiation penetration into the material. In this context, it is worth mentioning the extraordinary LITE decay kinetics of carbon materials, in which two components with characteristic decay times of the order of 10^{-8} s and 10^{-7} s can be distinguished [11, 12]. As shown in [11], the "slow" component in the LITE decay is observed, when the depth of penetration of laser radiation into the irradiated material exceeds the distance over which heat can spread in

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Ц и т у в а н н я: Зеленський С.Є., Колесник О.С., Ящук В.П. Кінетика індукованого лазером теплового випромінювання поруватих вуглецевих матеріалів: залежність від довжини хвилі лазера. *Укр. фіз. журн.* **69**, № 3, 143 (2024).

this material during the time of the order of the laser pulse duration.

The above-mentioned condition for the occurrence of a "slow" component in the LITE decay was formulated in [11] on the basis of a computer modeling of the processes of heating and cooling of surface layers of materials under the pulsed laser irradiation. In further works [12, 14] devoted to the study of the kinetics of LITE of surface layers of carbon materials, the influence of surface roughness on the "slow" emission decay kinetics was analyzed, as well as the role of air in the formation of LITE signals of porous materials. In addition, an improved calculation procedure was introduced in [14] with the account for the temperature dependence of the coefficients of thermal conductivity and heat capacity of the irradiated material and air. Following [11, 12, 14], this work continues the analysis of the LITE decay kinetics of a porous carbon material, in particular, the experimental studies were carried out which additionally substantiate the above-mentioned condition for the occurrence of a "slow" component in the LITE decay. The idea of the experiments is that the depth of penetration of laser radiation into the irradiated material can be varied by changing the wavelength of laser radiation; at the same time, the thermal characteristics of the material, which determine the length of temperature propagation, remain unchanged.

2. Methods

Similarly to previous works [11, 12, 14], this work uses a Q-switched neodymium laser (pulse duration $\tau_{\text{i}} = 20$ ns) and a detection system for pulsed thermal emission in the spectral interval 430 ± 20 nm using a high-speed photomultiplier H1949-51 (rise time 1.3 ns) and a digital oscilloscope with the bandwidth of 250 MHz.

Samples of porous carbon (tablets of pharmaceutical activated carbon) were used for measurements after the preliminary heating at a temperature of 150 °C for 15 min. Measurements were performed at room temperature.

It is known [18] that the characteristics of pulsed LITE signals (amplitude, duration) are changed significantly during the irradiation with the first 10...15 pulses of the laser. In order to avoid the influence of these changes, in this work, the measurements were performed after the pre-irradiation of each sample with approximately 20 laser pulses with a power density of about 30 MW cm^{-2}.

Oscillograms were measured in two series under the excitation by laser radiation with a wavelength of $\lambda_1 = 1064$ nm and $\lambda_2 = 532$ nm (the first and second harmonics of neodymium laser radiation). At the measurements the intensity of the laser radiation was selected so that the amplitude of LITE signals was equal under excitation both at λ_1 and λ_2. Under such conditions, if the cross-sections of the laser beams on λ_1 and λ_2 are equal, both series of oscillograms will correspond to the same maximal temperature of the surface layer during the laser irradiation. Accordingly, to ensure the uniformity of the cross-sectional areas of 1064 and 532 nm laser beams, both beams were passed through the same aperture (with the diameter of 0.5 mm, which is approximately half the diameter of both used laser beams). During the measurements, the locations of the laser beams, of the sample under study, and of the recording equipment remained unchanged; the power supply voltage of the photomultiplier was stabilized.

As for the computer simulation of the laser excitation of thermal radiation, the method described in [14] was used. The method is based on the classical parabolic equation of heat conduction with the function of heat sources in the form $\alpha F(z,t)$, where α is the absorption coefficient at the wavelength of laser radiation, F is the intensity of laser radiation as a function of coordinate z along the laser beam and a function of time (here, the dependence of the laser intensity on z is described by Bouguer's law with the absorption coefficient α, and the dependence on time is given by the Gaussian function with the width τ_{i}).

As in previous works, for calculations of LITE signals $I(t)$ in a narrow spectral interval, we used Planck's formula for the energy density of blackbody thermal radiation ρ_λ with the substitution of the calculated temperature of the sample surface $T(z=0,t)$

$$I(t) = \text{const}\, \rho_\lambda (T(z=0,t)).$$

3. Results and Discussion

In the formation of thermal emission signals of the surface layers of light-absorbing materials under the pulsed laser excitation, the main physical characteristics of the material are the coefficient of thermal conductivity κ (W m^{-1} K^{-1}), the heat capacity C_p (J m^{-3} K^{-1}), and the absorption coefficient

α (m^{-1}) at the wavelength of laser radiation. It is also important to account for the behavior of the mentioned characteristics with temperature in the interval from the initial sample temperature T_0 to the maximal value T_{max}, which is reached during the laser irradiation on the surface of the sample. In the case considered in this work, the interval of temperature change is approximately 300...3000 K. It is known [19, 20] that the coefficient of thermal conductivity and the heat capacity of carbon change significantly in the specified temperature interval. For example, the coefficient of thermal conductivity of carbon decreases by about an order upon heating [20]. In addition, as shown in [14], the presence of air above the surface and inside the pores of the porous carbon material can significantly affect the formation of LITE signals. The mentioned circumstances radically affect the results of a computer modeling of the processes of laser heating of surface layers of porous carbon materials.

As for the absorption coefficient α, which is present in the heat conduction equation as a parameter of the heat source function, to our knowledge, there is lack of information on its temperature dependence in the literature. In this paper, $\alpha = \text{const}$ is assumed.

The behavior of the coefficient of thermal conductivity and of the heat capacity of porous carbon during the laser heating was analyzed in work [14]. At temperatures of 2000...3000 K, which are relevant for the observation of LITE in the visible light range, the distance over which the temperature wave propagates during the time of the order of the laser pulse duration can be estimated as $\delta \approx \sqrt{\kappa \tau_i / C_p} \approx 60$ nm. On the other hand, the penetration depth of the laser radiation into the material can be estimated as $\Delta = 1/\alpha$.

For laser radiation wavelengths $\lambda_1 = 1064$ nm and $\lambda_2 = 532$ nm, we estimate the corresponding values of carbon absorption coefficients α_1 and α_2 using the resource [21]: $\alpha_1 = 1.81 \times 10^7$ m^{-1}, $\alpha_2 = 2.45 \times 10^7$ m^{-1}, which leads to the following estimates (with regard for the porosity of the material 74% [14]) $\Delta_1 \approx 213$ nm and $\Delta_2 \approx 157$ nm.

Thus, the above-given estimates indicate that the relation $\Delta > \delta$ is realized, and the "slow" component can be observed in the LITE decay. The calculated temperature distributions under the surface of the sample are shown in Fig. 1 for the above two values of the absorption coefficients α_1 and α_2. The graphs shown in Fig. 1 correspond to the moment of time,

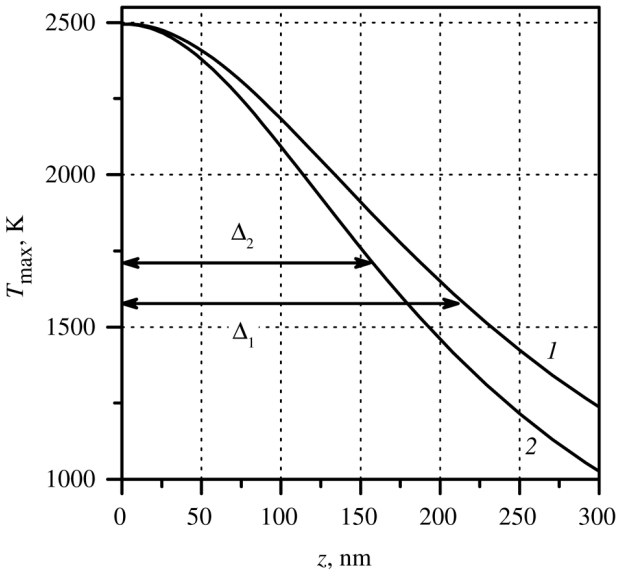

Fig. 1. Dependence of the maximal temperature on the depth below the surface of the sample heated by laser pulses with a wavelength of $\lambda_1 = 1064$ nm (curve *1*) and $\lambda_2 = 532$ nm (curve *2*)

when the surface temperature (and, accordingly, the LITE signal) reach their maximal values. Therefore, these graphs $T_{max}(z)$ can be considered as the initial temperature distributions that will determine the LITE decay.

Calculated oscillograms of LITE signals under the excitation at laser wavelengths of 1064 and 532 nm are shown in Fig. 2. Both curves correspond to the same value of maximal surface temperature of 2500 K, which approximately corresponds to the experimental conditions. As can be seen from Fig. 2, the pulses of LITE excited by laser radiation with $\lambda_1 = 1064$ nm (curve *1*) and $\lambda_2 = 532$ nm (curve *2*) differ significantly by the duration of trailing edge.

It is also worth paying attention to the following circumstance. In Fig. 2, the moment $t = 0$ corresponds to the position of the maximum of the laser pulse. As can be seen from Fig. 2, the maximum of the pulse of thermal emission is shifted relative to the maximum of the laser pulse by the order of the duration of the laser pulse, which is a characteristic feature of LITE in the studied objects.

To compare the results of calculations with the results of experiments, it seems appropriate to consider such a parameter as the duration of LITE pulse τ_{01} measured at a level of 0.1 of the maximal value of the

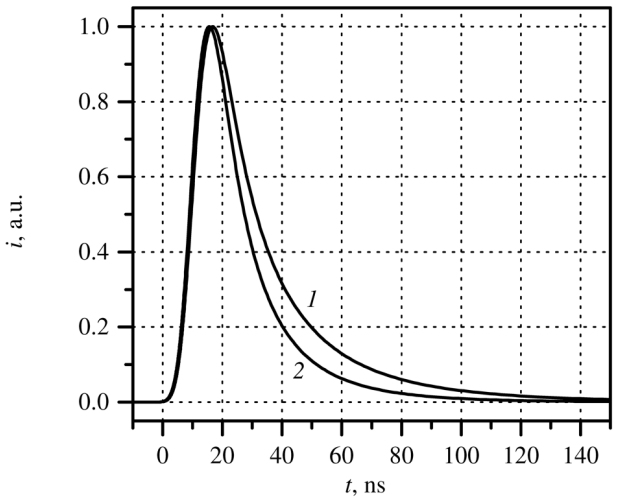

Fig. 2. Calculated oscillograms of LITE at a wavelength of 430 nm under excitation by laser pulses with wavelengths $\lambda_1 =$ $= 1064$ nm (curve *1*) and $\lambda_2 = 532$ nm (curve *2*)

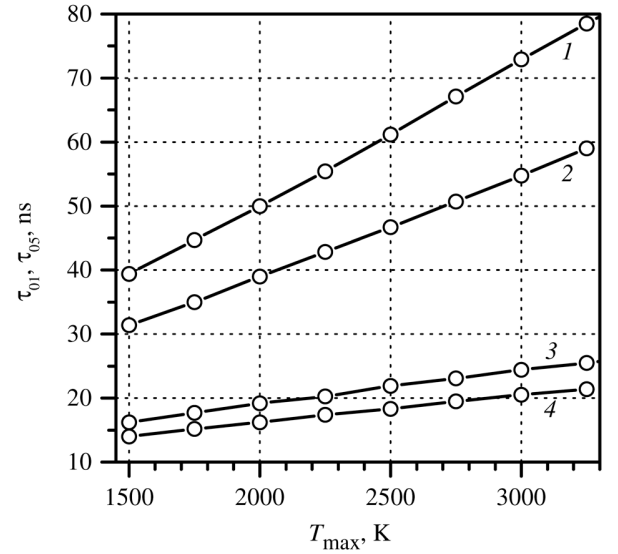

Fig. 3. Calculated values of the duration of thermal emission pulses at a wavelength of 430 nm at a level of 0.1 (curves *1*, *2*) and 0.5 (curves *3*, *4*) for different values of the maximal surface temperature under the excitation by laser radiation with a wavelength of λ_1=1064 nm (curves *1*, *3*) and $\lambda_2 = 532$ nm (curves *2*, *4*)

signal. The introduced parameter τ_{01} will allow us to account for the features of the emission pulses caused by the presence of the "slow" decay component.

The results of calculations of the duration of LITE pulses are shown in Fig. 3. For comparison, Fig. 3

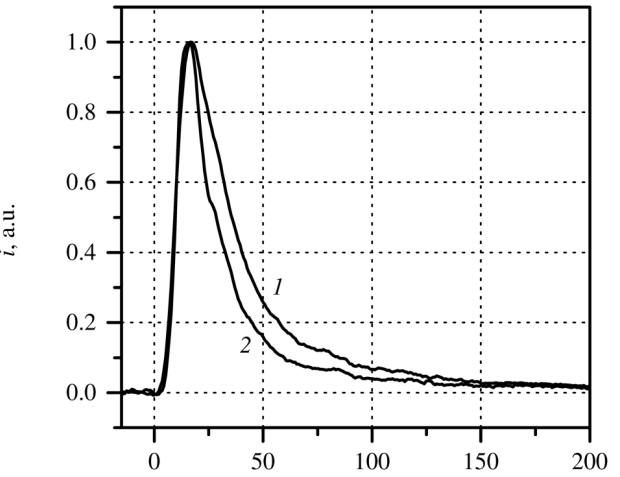

Fig. 4. Typical oscillograms of LITE signals of porous carbon material under the excitation by laser radiation with wavelengths $\lambda_1 = 1064$ nm (curve *1*) and $\lambda_2 = 532$ nm (curve *2*)

shows the calculated data not only for the emission pulse duration τ_{01}, but also for τ_{05} at a level of 0.5 of the maximum. As can be seen from the figure, for τ_{01} the changes caused by the variation of the laser excitation wavelength are significantly stronger than for τ_{05}. Thus, the change of the laser wavelength from 532 nm to 1064 nm leads to the increase of τ_{01} by 25...33%, while τ_{05} increases by 16...19%.

The results of experiments confirm the calculated predictions regarding an increase in the duration of the emission pulse when changing the laser excitation wavelength from 532 nm to 1064 nm. Typical experimental oscillograms are shown in Fig. 4. The oscillograms in Fig. 4 correspond to the maximal temperature of the sample surface of approximately 2500 K. (In order to estimate $T_{\max}$, the common two-frequency technique was used in the experiment: the amplitudes of LITE signals were measured at two wavelengths of 430 and 570 nm, with preliminary calibration of the recording equipment using a tungsten incandescent lamp and an optical pyrometer.)

The experimentally measured and calculated values of the duration of LITE pulses at levels of 0.1 and 0.5 for $T_{\max} = 2500$ K are shown in Table. As is seen from the table, the results of calculations are in satisfactory agreement with the results of experiments, although there is a tendency to underestimate the results in the calculations. Among the possible reasons for such an underestimation, it is worth noting the inaccuracy of determining the thermal and optical characteristics

Calculated and experimental duration of LITE pulses of porous carbon material at a wavelength of 430 nm under excitation by laser radiation with a wavelength of $\lambda_1 = 1064$ nm and $\lambda_2 = 532$ nm

$\lambda_{1,2}$, nm	τ_{01}, ns		τ_{05}, ns	
	Calc.	Exp.	Calc.	Exp.
1064	61.2	79.8	21.9	26.9
532	46.6	54	18.3	19.4

of the material under study, including the errors of the approximation of their temperature dependences in a wide temperature range, and imperfection of the methodology for modeling the thermal and optical characteristics of porous materials. It can also be assumed that the results of calculations are affected by the fact that the applied model does not consider the contributions of the radiation of deep layers of the material to the integral LITE signal. Regarding the last assumption, it requires a separate study which is beyond the scope of this work.

4. Conclusions

To conclude, it should be emphasized that, in this work, we obtained the direct experimental evidence of the influence of the wavelength (or of the penetration depth) of laser radiation on the characteristics of LITE of the surface layer of porous carbon material, in particular, on the duration of the trailing edge of the emission pulse. The computer modeling shows that the duration of the trailing edge of a LITE pulse significantly depends on the initial temperature distribution under the surface of the sample, which, in turn, depends on the absorption coefficient of the laser radiation.

In addition, it should also be emphasized that the results obtained in the work give an additional substantiation of the conclusions obtained in previous works [11, 12] regarding the condition for the occurrence of "slow" component of the LITE decay: the length of thermal diffusion during the laser heating shall be less than the penetration depth of the laser radiation into the material.

Finally, the satisfactory consistency of the results of calculations with the results of experiments testifies to the benefit of the model used in the calculations and confirms the correctness of its approximations.

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КІНЕТИКА ІНДУКОВАНОГО ЛАЗЕРОМ ТЕПЛОВОГО ВИПРОМІНЮВАННЯ ПОРУВАТИХ ВУГЛЕЦЕВИХ МАТЕРІАЛІВ: ЗАЛЕЖНІСТЬ ВІД ДОВЖИНИ ХВИЛІ ЛАЗЕРА

Досліджено форму імпульсних сигналів індукованого лазером теплового випромінювання поруватого вуглецевого матеріалу при збудженні першою та другою гармоніками неодимового лазера. Виявлено, що тривалість імпульсів теплового випромінювання суттєво залежить від довжини хвилі лазерного збудження, що зумовлено відмінностями глибини проникнення лазерного випромінювання у поверхневий шар. Зазначений ефект є актуальним за умови, якщо у досліджуваному матеріалі глибина проникнення лазерного випромінювання перевищує довжину теплової дифузії за час порядку тривалості лазерного імпульсу. Проведено комп'ютерне моделювання процесів імпульсного лазерного нагрівання і формування сигналу теплового випромінювання. Результати моделювання показали задовільне узгодження з результатами вимірювань.

Ключові слова: індуковане лазером теплове випромінювання, кінетика, поруватий вуглець.