「様式３」

Project No.： 2075

Laser-Induced Incandescence of Porous Carbon Materials

［１］Organization
Project Leader：
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Representative at RIE：
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Participants：
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［２］Research Progress

According to the research plan of the project, the following scientific activities were performed at Taras Shevchenko National University of Kyiv and at Research Institute of Electronics, Shizuoka University.

In continuation of the previous project No.2006, pulsed laser heating of structured surfaces was investigated both theoretically and experimentally. The experiments revealed unexpected similarity in the properties of laser-induced thermal emission decay of different samples of carbon materials. The appropriate computer simulations showed that laser-induced thermal emission of rough surfaces is primarily formed at peaks of the surface relief. Besides, the experiments revealed that thermal diffusivity of carbon which forms the surface relief peaks is extremely low (the appropriate values are typical for heat-insulating materials, and this was also an unexpected result).

Concerning the effect of surface roughness on the decay of thermal emission of rough surface layers, an important parameter is the ratio of the laser penetration depth (Δ) to the temperature diffusion length (δ). In other words, it is important whether the temperature wave has time to travel out of the heat release region under the laser irradiation. Here two different cases should be considered. If δ exceeds Δ, the presence of surface roughness can significantly increase the local surface temperature. However, in this case the emission decay time is relatively short and is difficult to be measured with the use of Q-switched laser pulses. In another case, when Δ exceeds δ, the emission decay curves contain slow components with the emission decay time dependent on the ratio Δ/δ. In this case, if the surface relief height is of the order of the laser radiation penetration depth, the surface roughness can increase the emission decay time by tens of percent.

Besides the above-mentioned, the activities included discussions concerning the project's progress and results (via e-mail and on the meetings in Kyiv and Hamamatsu).

The participants of the project actively collaborated in organizing the 20th Intern. Young Scientists Conference "Optics & High Technology Material Science" SPO 2019 held at the Faculty of Physics of Taras Shevchenko National University of Kyiv 26-29 Oct. 2019: Prof. S. Zelensky was the member of the Program Committee, Prof. T. Aoki was the member of the International Committee, Prof. T. Aoki and Dr. K. Zelenska were the members of the Organizing Committee of SPO-2019.

［３］Results

(３－１) Research results

For excitation of thermal emission, a Q-switched YAG:Nd^{3+} laser was used similarly to the previous project No.2006. Thermal emission pulses were detected by a photomultiplier tube H1949-51 (rise time 1.3 ns) through a band-selective glass filter SS-4 (transmittance window 400–500 nm) with digital oscilloscopes TDS-2022B (bandwidth 200 MHz) and MSO-4104 (1 GHz).

For laser-induced thermal emission of rough surfaces, the computer simulations predict size dependence of emission decay kinetics in the micrometer and sub-micrometer range of surface roughness. That is why the experiments were made with the samples which have surface structural elements of various sizes and shapes. The following carbon samples were used: (1) carbon electrode for spectroscopy applications; (2) porous carbon (charcoal) samples made of walnut shells; (3) oak wood charcoal; (4) pharmaceutical activated carbon pellets; (5) dried China ink (carbon black); (6) dried black gouache paint.

Typical examples of SEM images of the studied surfaces are given in Fig.1. As is seen from the figure, the samples are porous and have sophisticated surface structure with a lot of micron- and submicron-sized structural elements.

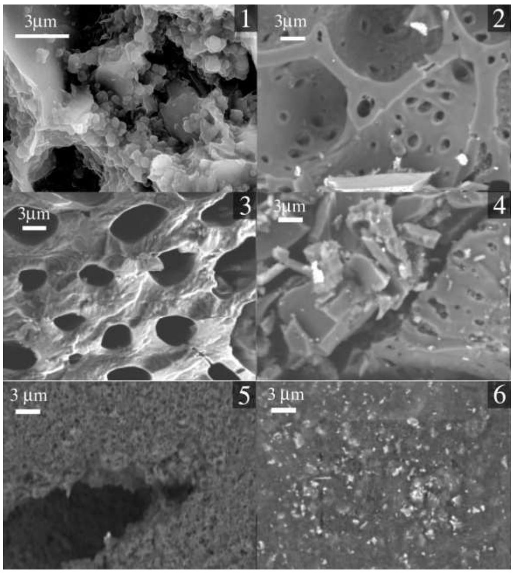

Fig.1. Typical SEM images of the sample surfaces: (1) carbon electrode; (2) walnut charcoal; (3) oak wood charcoal; (4) activated carbon pellet; (5) China ink; (6) black gouache paint.

For simulations of laser heating of rough surface layers, a micron-sized cylindrical element with a truncated-cone peak was used (see Fig.2). Characters A, B, C, D, and M in Fig.2 denote points on the irradiated surface where the surface temperature and exitance are analyzed.

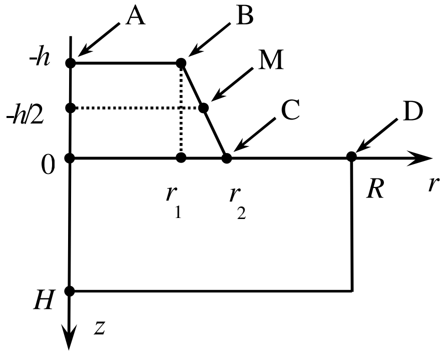

Fig.2. Surface layer element.

The procedure of calculations was described in the previous report No.2006 (2018–2019).

In the experiments, the photomultiplier's photocurrent is proportional to the thermal radiation power which can be calculated as

$$I_\sigma(t) = \iint_\sigma \varepsilon \, dS \ ,$$

where σ is the area of the sample surface which emits thermal radiation.

The total emitted energy of thermal radiation (within the interval Δλ) was calculated:

$$E_\sigma = \int_{-\infty}^{\infty} I_\sigma \, dt \ .$$

Typical examples of calculated surface distribution of maximal laser-induced temperature and exitance are given in Fig.3 for h=200 nm.

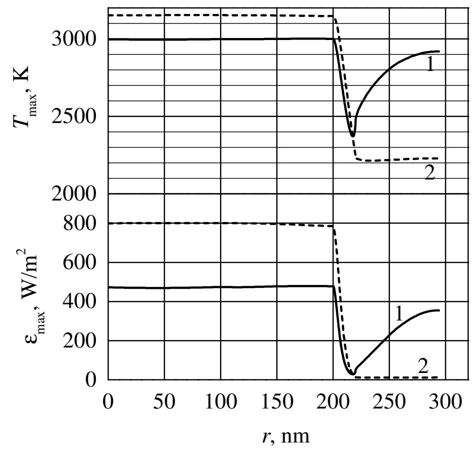

Fig.3. Maximal surface temperature T_{max} and exitance ε_{max} as functions of coordinate r for Δ/δ=7.5 (1) and 0.5 (2).

As is seen from Fig.3, under the pulsed laser irradiation, peaks and valleys on rough surfaces can be heated to significantly different temperatures. As a result, the integral characteristics of surface emission are complicated functions of the surface roughness and require thorough analysis.

Fig.4 demonstrates the effect of a peak height, h, on the emitted pulse energy of laser-induced thermal radiation of rough surfaces. Thermal radiation energies emitted from peaks and valleys are denoted E_1 and E_2, respectively. As is seen from Fig.4, E_1 considerably exceeds E_2 in a wide range of h for both $\Delta>\delta$ and $\Delta<\delta$. Hence we can conclude that the observed laser-induced thermal radiation is mainly emitted by peaks of the surface relief.

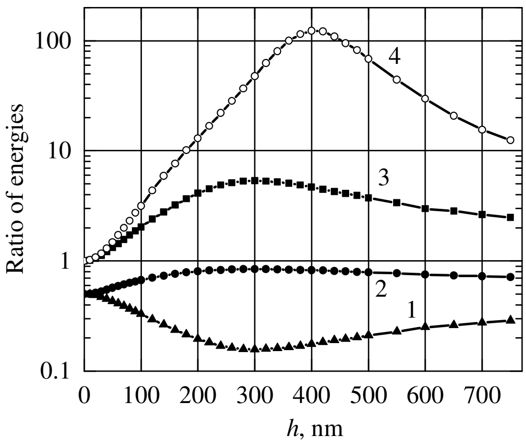

Fig.4. Calculated ratios of emitted energy for peaks, E_1, and valleys, E_2, as functions of peak height: $E_2/(E_1+E_2)$ (curve 1), $E_1/(E_1+E_2)$ (2), and E_1/E_2 (3,4) for Δ/δ=0.5 (4) and Δ/δ=7.5 (curves 1–3).

Fig.5 demonstrates the effect of h on the maximal surface temperature T_{max} under the laser irradiation. Notation A–D in Fig.5 corresponds to Fig.2. As is seen from Fig.5(a), in case of $\Delta>\delta$ the maximal temperature on the top of the peak (points A and B) is almost independent of h; hence, the excess of E_1 over E_2 (curve 3 in Fig.4) is caused by the decrease of temperature in points C and D (Fig.5(a)). Concerning the case of $\Delta<\delta$, as is seen from Fig.5(b), T_{max} increases by approximately 250 K when h is close to the value of δ=200 nm; hence, E_1/E_2 in Fig.4, curve 4, is much larger than unity. (Here it should be noted that the surface exitance strongly depends on temperature: for example, ε increases by a factor of 2 when the surface temperature increases from 3000 K to 3200 K.)

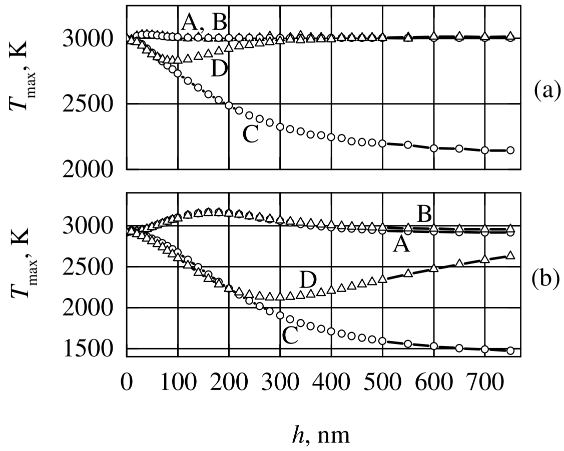

Fig.5. Maximal temperature in points A, B, C, D as a function of peak height h for Δ/δ=7.5 (a) and Δ/δ=0.5 (b).

Typical examples of calculated time history of exitance are given in Fig.6. Here the square laser pulse is located between t=–10 ns and t=10 ns.

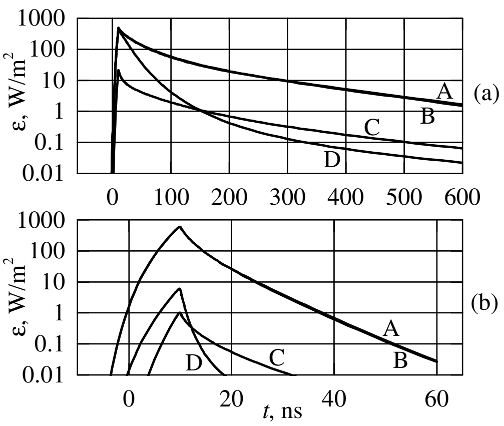

Fig.6. Calculated time history of ε in points A, B, C, D for Δ/δ=7.5 (a) and 0.5 (b). h=300 nm.

As is seen from Fig.6(b), on condition $\Delta<\delta$ the decay time of laser-induced thermal emission is of the order of ten nanoseconds. As far as in the experiments the laser generates bell-shaped pulses, the calculated decay time of laser-induced thermal emission (Fig.6(b)) is of the order of trailing edge of the laser pulse; hence, we do not analyze the decay of thermal emission in case of $\Delta<\delta$.

In case of $\Delta>\delta$, as is seen from Fig.6(a), the decay curves are much longer, and approximation of these curves with a double-exponent function

$$f=A_1\times\exp(-t/\tau_1)+A_2\times\exp(-t/\tau_2)$$

gives the values of time constants τ_1 and τ_2 of the order of

10^{-8} s and 10^{-7} s respectively.

In this project, various carbon samples made of materials with different thermal characteristics were used. For example, thermal conductivity of carbon rods was estimated approximately as $\kappa \approx 50$ W/m K, whereas charcoals typically have $\kappa \approx 0.084$ W/m K. However, despite the mentioned differences, all of the samples demonstrated similar kinetics of decay of laser-induced thermal emission. The measured values of τ_2 of different carbon samples are given in Table 1. As is seen from the table, surface layers of different carbon materials have close values of τ_2.

Table 1. Thermal emission decay time τ_2 of carbon materials under irradiation by a sequence of ten laser pulses.

Material	τ_2, ns
Carbon electrode	132±7
Pharmaceutical activated carbon pellet	123±9
Oak wood charcoal	167±12
Walnut shell charcoal	118±4
Dried China ink	122±3
Dried black gouache	132±4

As is seen from Fig.4, in a wide range of h, laser-induced thermal emission of peaks on rough surfaces exceeds the emission of valleys; hence, it can be concluded that the observed kinetics of thermal emission reflects the properties of the material which forms the surface relief, and these properties can be different as compared with the bulk material. That is why, with taking into account the data presented in the table, we conclude that the investigated surface layers of different carbon materials have close values of thermal diffusivity.

Consider the effect of surface roughness on the value of τ_2. The total emitted power $I_\sigma(t)$ was calculated as a function of time, and the calculated values of τ_2 are presented in Fig.7 as functions of h for Δ=333 nm, δ=67 nm (curve 1) and δ=45 nm (curve 2).

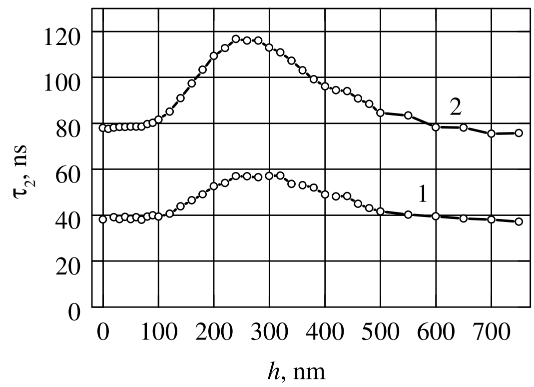

Fig.7. Calculated values of thermal emission decay time τ_2 as functions of h for Δ/δ=5 (curve 1) and 7.5 (2).

As is seen from Fig.7, if h is comparable with Δ, the emission decay time τ_2 is increased by a factor of approximately 1.5 as compared with flat surfaces. This circumstance should be taken into account in the estimation of material's thermal diffusivity with the use of procedure described in the previous project No.2006. For example, for surface layers of carbon rods, the estimates of thermal diffusivity and thermal conductivity should be increased up to the values of 2×10^{-8} m^2/s and 0.08 W/m K respectively.

Concerning the above-given estimate of thermal conductivity of carbon 0.08 W/m K, the following considerations should be taken into account. The mentioned estimate is much smaller than typical values accepted in the literature. However, it is known that thermal conductivity of carbon demonstrate significant variations; sometimes thermal conductivity of graphite at high temperature is extremely small or tends to decrease significantly due to the loosening of graphite structure. Besides, it is known that thermal characteristics of carbon materials are strongly dependent on the material's structure and on the type and concentration of defects. With taking into account the above mentioned we conclude that the observed close values of τ_2 of different carbon samples can be a consequence of similar thermal properties of rough and structured surface layers which contain a lot of structural imperfections and defects.

Concerning the effect of moisture on the kinetics of laser-induced thermal emission decay, the experiments revealed significant shortening of the decay time of slow component, as is shown in Fig.8.

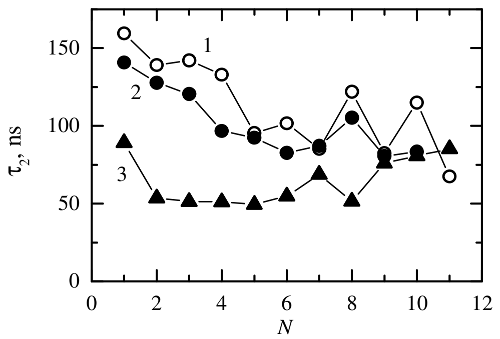

Fig.8. Laser-induced thermal emission lifetime as a function of laser irradiation dose for dry (1) and wet (2,3) activated carbon pellets for $\Delta m/m$=0.15 (2) and 0.95 (3), where m is the dry pellet mass, and Δm is the mass of water absorbed by the pellet.

Thus we can conclude that the presence of moisture in porous carbon surface layer leads to the significant decrease of laser-induced thermal emission (as is shown in the previous project No.2006), and also to the decrease of the emission decay time (as is shown in Fig.8).

［4］Achievements (List of Publications)

（１） S. Zelensky, T. Aoki, Decay Kinetics of Thermal Radiation Emitted by Surface Layers of Carbon Materials under Pulsed Laser Excitation// Opt. Spectr. **127**(5) 931–937 (2019). doi: 10.1134/S0030400X19110298.

（２） V. Karpovych, O. Tkach, K. Zelenska, S. Zelensky, T. Aoki, Laser-Induced Thermal Emission of Rough Carbon Surfaces // Journal of Laser Applications **32**, 012010 (2020); https://doi.org/10.2351/1.5131189.

（３） V. Karpovych, O. Tkach, K. Zelenska, S. Zelensky, T. Aoki, Decay of Laser-Induced Thermal Emission of Rough Carbon Surfaces // The 20th International Young Scientists Conference Optics and High Technology Material Science SPO-2019, Kyiv, Ukraine. p.169.

Travelling Report （Mention each travel by CRP budget.）

Name:	Serge Zelensky
Affiliation:	Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
Period of time:	02.10.2019 – 25.10.2019
Destination:	Research Institute of Electronics, Shizuoka University
Purpose:	Study of kinetics of laser-induced incandescence of rough surfaces of porous carbon materials containing liquid fillers. Participation in scientific meetings at Research Institute of Electronics, Shizuoka University during the period of stay.
Name of receiver:	Prof. Toru Aoki

S. Zelensky
13.03.2020