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NITROGEN LASER BEAM INTERACTION WITH COPPER SURFACE

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The ultraviolet and visible spectra of plasmas produced by N_2-laser radiation focused onto a copper target in air and in vacuum have been recorded photographically. The nitrogen laser beam ($\lambda = 337$ nm) had a maximum energy density of 1.1 J/cm^2, the pulse duration was 6 ns, and the repetition rate 0.2 Hz. The measured electron temperature was 15000 K ($\pm30\%$) in air and 13000 K ($\pm50\%$) in vacuum and the electron densities were 6.5×10^{17} cm^{-3} ($\pm60\%$) and 3.0×10^{17} cm^{-3} ($\pm60\%$), respectively. The irradiated surface in air and in vacuum was studied employing a metallographic microscope. In vacuum, the droplets were created and expulsed at the crater edges. Their formation is explained by the hydrodynamical model. They were formed in a time interval which is about two times shorter than the duration of the laser pulse. In air, droplets were also formed. The weight loss from the Cu-crater in vacuum was about 0.3×10^{-4} μmole/pulse, in air it was about three times less.

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1. Introduction

The use of pulsed UV lasers in material processing such as thin-film deposition, surface cleaning, surface etching, etc., has attracted great interest. Experiments are focused on the studies of the emitted particles, plasma generation and surface damage (e.g., Refs. 1 to 6). Laser ablation of copper in an atmosphere has been studied (Ref. 7 and references therein) at a rather high fluency (10 - 1000 J/cm^2). Laser ablation of copper in vacuum at very low fluency (less than 1 J/cm^2) has also been investigated, e.g., by Gill at al. [7], Jordan at al. [8] and Kools and Dieleman [9]. In this paper, we describe the plasma parameters and the surface damage of Cu targets irradiated by a N_2-laser at a rather low fluency, in vacuum and in air.

2. Experimental setup

The nitrogen laser, emitting pulses of 6 ns duration with a maximum energy density of 1.1 J/cm^2 [10,11] has been used in the experiments. The target surface was almost perpendicular to the beam axis. During irradiation, the target was in vacuum at a base pressure of 0.1 mbar or in air at atmospheric pressure. The laser radiation was focused onto the Cu surface to achieve an average energy density of 0.8 J/cm^2 per pulse. The laser beam profile was not uniform and showed an irregular spatial distribution with two hot spots [11].

The method of time-integrated spectroscopy was applied [11]. A single prism quartz spectrograph (Model Q-24, C. Zeiss-Jena, Germany) with a spectral resolution better than 0.01 nm at 300 nm was used. The spectral region from 240 nm to 500 nm was investigated using an entrance slit of a width of 15 μm. The optical axis of the spectrograph was parallel to the target surface and perpendicular to the laser beam axis. It was aligned to a height of 0.1 mm above the target surface. Some 30 laser pulses were necessary to produce a satisfactory spectrum on the film. The surface damage was studied with an optical metallographic microscope (Leitz "Aristomet").

3. Results

3.1. Electron density and electron temperature of the Cu-plasma

The spectra of the copper plasma produced in vacuum ($p = 0.1$ mbar) and in air (normal pressure) were deduced from the photographic records. Spectral lines were studied in detail by scanning the film in a densitometer with a narrow and short slit, selecting the part corresponding to the maximum of intensity of plasma radiation. Relative line intensities provided data for the derivation of the electron temperature under the assumption of LTE (see for example Ref. 12 or 13). The Cu line pairs which were analysed are given in Table 1. The transition probabilities for these lines were taken from Ref. 14 and they are listed in Table 2.

The mean value of the derived electron temperature is 15000 K ($\pm$30%) in air and 13000 K ($\pm$50%) in vacuum. The broadening of the spectral lines is primarily due to Stark broadening [11]. Figure 1 illustrates this effect for the Cu I 465.1 nm line. The measured full-width-at-half-maximum (FWHM) is 0.5 nm. That line, the Cu I 458.7 nm and 454.0

nm lines, and the Cu II 254.4 nm line were also used for electron density determination [13]. The Stark broadening parameters are given in Table 3. The obtained electron densities were 6.5×10^{17} cm^{-3} (±60%) in air and 3.0×10^{17} cm^{-3} (±60%) in vacuum.

TABLE 1. Cu line pairs in air and vacuum.

Cu line pairs in air					Cu line pairs in vacuum				
I	515.3 nm	and	I	427.5 nm	II	254.4 nm	and	I	324.7 nm
II	254.4 nm	and	I	282.4 nm	II	268.9 nm	and	I	324.7 nm
II	249.0 nm	and	I	249.2 nm	II	249.0 nm	and	I	249.2 nm
I	515.3 nm	and	I	510.6 nm					

TABLE 2. Transition Probabilities of Cu I *and* Cu II *(Ref. 14).*

Line	λ (nm)	E_k(eV)	g_k	$A_{ki}(10^8 s^{-1})$	Acc.
Cu I	249.2	4.97	4	0.0311	B
Cu I	282.4	5.78	6	0.078	C
Cu I	324.7	3.82	4	1.39	B
Cu I	427.5	7.74	8	0.345	C
Cu I	510.6	3.82	4	0.020	C
Cu I	515.3	6.19	4	0.60	C
Cu II	249.0	8.23	5	0.015	D
Cu II	254.4	13.39	7	1.1	D
Cu II	268.9	13.39	7	0.41	D

B 10%; C 25%; D 50%

TABLE 3. Stark widths of Cu.

Line	λ (nm)	T(K)	n_0 $(10^{17} cm^{-3})$	w (nm)	Ref.
Cu I	454.0	10000	1.0	0.180	15
		20000	1.0	0.088	
Cu I	458.7	10000	1.0	0.140	15
		20000	1.0	0.076	
Cu I	465.1	10000	1.0	0.087	15
		20000	1.0	0.058	
Cu II	254.4	24000	1.0	0.014	16

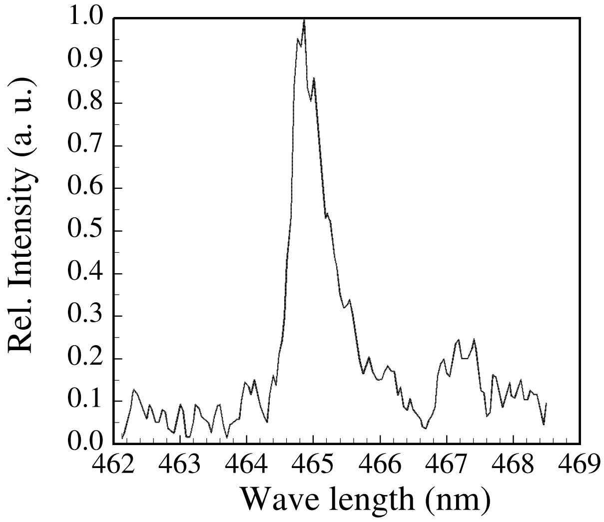


Fig. 1. Cu *I line 465.1* nm *in* Cu *plasma in air.*

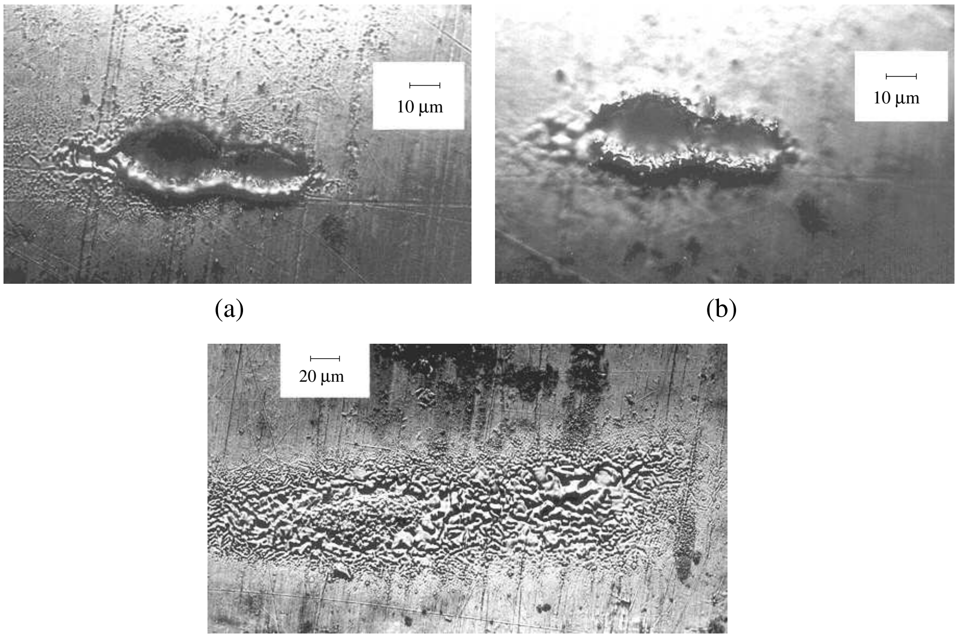
Our experimental electron temperature in vacuum is in agreement with the temperature derived from the model of Ref. 8. However, the result for the electron density in vacuum is higher than what we measured by means of our spectroscopic equipment. The discrepancy is probably due to the fact that our N_2 laser had a low average energy per pulse of about 8 mJ, and the model of Ref. 8 is valid for a range of 100 mJ - 10 J.

3.2. Surface damage of Cu target

Due to the nonuniformity of the laser beam profile, two damage spots were created on the target surface. The central part of the smaller spot belongs to a maximum energy density of 1.1 J/cm^2 and the center of the second spot was created with an energy density about 0.5 J/cm^2 [11]. Going from the center towards the rim of the spots, the energy density decreased. The plasma was created in the central parts.

a) Irradiation of Cu-surface in vacuum. Figures 2a, b and c show the damage spots after 30 pulses in vacuum. Figure 2a shows the crater area of higher intensity. Figure 2b shows the "crown" of the crater. The ablation crater in vacuum cuts deeply into the target material (8 μm after 30 pulses with a surface spot size about 1.8×10^{-5} cm^2). It shows the presence of droplets that seem to be ejected from the edge of the damaged target area. Diameters of individual droplets are in the range of 0.8 to 1.8 μm with the mean value of about 1.0 μm. It is possible that smaller droplets are present but they were not detected due to the limited resolution of the optical microscope we used.

To explain the formation of droplets, we used the model of hydrodynamical sputtering developed by Kelly and Rottenberg [17].



(a) (b) (c)

Fig. 2. a) The ablation crater in vacuum after 30 laser pulses in the area of the higher intensity. Droplets scattered around the crater are seen. b) The "crown" of the ablation crater shown in a). c) The damage spot in vacuum after 30 laser pulses in the area of the lower intensity laser beam.

When the droplets are ejected, the droplet momentum exceeds the product $f\Delta t$, where f is the surface tension of Cu and t is time, i.e.

$$\frac{4r^3\pi}{3}\rho_l\frac{\Delta L}{\Delta t} > 8\pi r\gamma\Delta t\,. \tag{1}$$

The density of the liquid is $\rho_l = 7900$ kgm^{-3}, r is the mean droplet radius, the surface tension is $f = 8\pi r\gamma = 1.6\times10^{-5}$ N, the surface energy of the liquid $\gamma = 1.30$ Jm^{-2} [17], and

$$\Delta L = 2r\alpha\Delta T + 2r\frac{\rho_s-\rho_l}{3\rho_l}\,. \tag{2}$$

ρ_s is the density of the solid. The linear thermal expansion of the liquid is $\alpha\Delta T = 0.038$ [17], and the linear expansion due to melting $(\rho_s-\rho_l)/(3\rho_l) = 0.014$ for Cu [17]. In our case $L = 0{,}05$ μm. In order to satisfy the expression (1), Δt should be about 2.5 ns. Furthermore, we have

$$\Delta t = \tau - t_m\,, \tag{3}$$

where τ is the duration of the laser pulse and t_m is the time at which the temperature T reaches the melting temperature $T_m = 1356$ K. Also, we have

$$\Delta t = \tau \left(1 - \frac{T_m^2}{\widetilde{T}^2} \right) , \tag{4}$$

where $\widetilde{T}$ is the maximum temperature. Taking into account Eqs. (3) and (4), t_m is about 3.5 ns and $\widetilde{T}$ about 2100 K.

Figure 2c shows the damage at the second spot also after a 30 pulse irradiation in vacuum. The maximum depth of the damage is about 2 μm. The melt solidification due to surface cooling is observed.

b) Irradiation of Cu-surface in air at atmospheric pressure. In that case the damage is not as deep as in vacuum. The first smaller spot (Fig. 3a) has a crater of a the depth of 2.5 μm after 30 pulses and the depth of the second spot could not be measured by means of our optical microscope (Fig. 3b). However, at the boundary regions, Cu-oxides are observed (Fig. 3b). Around both spots, hums are seen. We suppose that the hums are created by sodification of molten surface deformed by capillary waves.

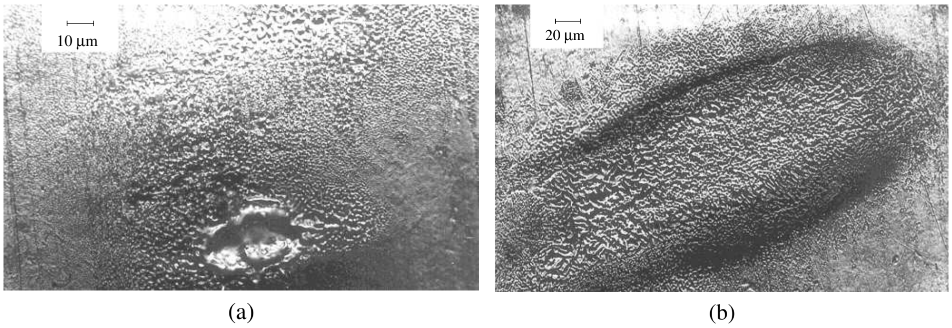


Fig. 3. a) The ablation crater made in air after 30 laser pulses in the area of higher intensity. b) The damage spot made in air after 30 laser pulses in the area of the lower intensity laser beam.

The relief hums are assumed to be half-balls with a radius of $R = \lambda_m/5$, where λ_m is the wavelength. In our case $\lambda_m = 2.5\ \mu$m. Near the small crater, and also inside the bigger damage spot, the hums are joined in irregular half-cylinders.

4. Discussion and conclusion

The N_2 laser pulse used in our experiment had a low average fluency, of about 0.8 J/cm^2, but its average power density at the target surface was rather high, about 130 MW/cm^2. In both investigations (plasma and target damage), the data show different results in vacuum and in air. The surrounding gas has a strong influence on the processes in the copper target and on the expansion of the plume. In the presence of air, thermal processes in the target are spread far over the surface but in vacuum the damage is almost entirely concentrated to the irradiated area. In that case, the central parts of the damage spots were pushed into a metastable region of the thermodynamic diagram, where the thermal conductivity $k \to 0$ and specific heat $C_p \to \infty$ (Ref. 18 and references therein.) The depth of the crater is deeper than in air. Using the simple theory of hydrodynamical sputtering [17], we tried to explain the formation of droplets in vacuum. Sufficiently high temperature for the formation is reached in a time which is shorter by approximately a factor of 2 than the duration of the laser pulse. The droplets were pulled to the target by the backward plasma flux which is generated during the laser pulse, as was observed in the experiment with a brass target [19]. In the experiment in air, the droplets were formed and in the vicinity of irradiated spots and relief hums are observed. If the plasma is produced in the surrounding gas, i.e. in air, the thermal turbulent conversion of air supports the thermal conduction over target surface. In the irradiated spots, the hums are irregular half-cylinders. We assume that the Rayleigh-Taylor instability appeared [19].

The obtained electron temperature in air is a little higher than in vacuum, but the electron density is larger by a factor of 2 in vacuum. This means that the atmospheric pressure of the surrounding gas prevents free expansion of the plasma.

The laser ablation experiments [20, 21] have shown that the plume propagation in a high background gas can lead to a limited emission of the ablated materials. The analysis of microscope pictures allowed the calculation of the weight loss from the Cu-craters. In vacuum and for 3 pulses, the weight loss is about 1×10^{-3} μmole, and at atmospheric pressure in air it is about 3 times less, because the absorbed laser energy is partly used for the heating of the surrounding copper surface. Mele at al. [22] determined the experimental weight losses per pulse for Al and Cu surfaces for high fluencies (2-7 J/cm^2) using a KrF laser (248 nm, 18 ns FWHM). In our experiment, the fluency was approximately at the threshold and the obtained weight loss of the copper target in vacuum of 1.4×10^{-3} μg/pulse is consistent with the results of Ref. 22.

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DJELOVANJE SNOPA DUŠIKOVOG LASERA NA POVRŠINU BAKRA

Snopom iz N_2-lasera, fokusiranim na površinu bakra u zraku i vakuumu, proizvodila se plazma. Ultraljubičast se i vidljiv spektar plazme snimao na film pomoću kvarcnog spektrografa. Impulsi iz lasera ($\lambda = 337$ nm) imali su najveću gustoću energije od 1.1 J/cm^2, trajanje 6 ns i učestalost 0.2 Hz. Izmjerile su se elektronske temperature od 15000 K ($\pm 30\%$) u zraku i 13000 K ($\pm 50\%$) u vakuumu, a elektronske gustoće bile su 6.5×10^{17} cm^{-3} ($\pm 60\%$) odnosno 3.0×10^{17} cm^{-3} ($\pm 60\%$). Pomoću metalografskog mikroskopa proučavale su se površine ozračene u zraku i vakuumu. U vakuumu su oko rubova kratera nastajale kapljice u vremenu oko pola trajanja laserskog impulsa, i one su padale oko kratera. Njihovo se stvaranje objašnjava hidrodinamičkim modelom. I prilikom ozračivanja u zraku izbacivale su se kapljice. Izbačena masa iz kratera u bakru je u vakuumu iznosila oko 0.3×10^{-4} μmola/impulsu, a oko trećinu toga u zraku.

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