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SILICON SURFACE IRRADIATED BY NITROGEN LASER RADIATION

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This paper is dedicated to Professor A. Bonefačić on the occasion of his 70th birthday

Monocrystalline silicon target was irradiated with a nitrogen laser beam ($\lambda = 337$ nm, maximum energy density 1.1 J/cm^2, pulse duration 6 ns and repetition rate 0.2 Hz). The plasma formed at the silicon surface was observed spetroscopically in air ($n_e = 3 \times 10^{18}$ cm^{-3}, T_e = 18 500 K) and in vacuum ($n_e = 6.5 \times 10^{17}$ cm^{-3}, T_e = 16 000 K). The irradiated surface in vacuum was studied by a metallographic microscope. Droplets were created at crater edges. Their formation is explained by the hydrodynamical sputtering model.

1. Introduction

The laser ablation processes are nowadays very frequently used. They include both practical applications such as thin-film deposition, surface cleaning, surface etching, production of nanophase materials, etc., as well as more fundamental investigations, such as damage of solid surfaces, surface ablation processes and plasma generation induced by laser irradiation [1-5]. In this paper, the plasma parameters and the surface damage of a monocrystalinne silicon target ablated with a N_2 laser radiation are desribed.

2. Experimental setup

An N_2-laser, emitting pulses of 6 ns duration with a maximum energy density of 1.1 J/cm^2 and a mean power density of 150 MW/cm^2, and wavelength of 337 nm, was used. The laser repetition rate was 0.2 Hz. This type of N_2-laser has been described previously in detail by Cubbedo [6] and Rebhan et al [7].

The time-integrated spectroscopic investigation was applied. The laser radiation was focused onto the target surface by a quartz lens of a focal length of 160 mm. A monocrystalline silicon wafer was used as the target material. The target was placed inside a small vacuum chamber evacuated by a rotation pump, or it was in air at normal pressure.

The target surface was almost perpendicular to the beam axis. The produced plasma was imaged onto the entrance slit of a single prism quartz spectrograph (Model Q-24, C. Zeiss-Jena, Germany). The observed spectral range was from 240 nm to 550 nm. The high-speed Ilford HP-5 film was used for the recording. The slit width was set at 25 μm. Some 20 laser pulses were necessary to produce a satisfactory spectrum on the film. A tungsten filament lamp was employed as the intensity standard. A C. Zeiss-Jena Schnellphotometer II was used for the densitometric work. The surface damage of the target was studied with an optical metallographic microscope (Leitz "Aristomet").

3. Results

3.1. Electron density and electron temperature of Si-plasma

The spectra of silicon plasma produced in vacuum at 0.07 mbar and in air at normal pressure were deduced from photographic recording. Individual line profiles were measured with the help of a narrow and short densitometer slit on the part of the spectrum that corresponds to the most intensive plasma radiation.

In dense the laser-produced plasmas, Stark broadening is the dominant broadening mechanism [8,9], and the electron density can be deduced from the measured full width at half-maximum (FWHM) of a line [10-12]. The Stark broadening parameters were taken from the literature [11,12]. The estimated electron densities were 6.5×10^{17} cm^{-3} and 3×10^{18} cm^{-3} for plasmas produced in vacuum and in air, respectively. The temperatures were estimated from the relative intensities of two silicon lines of successive stages. The electron temperatures in plasma were 16000 K in vacuum and 18500 K in air. The parameters of spectral lines used for the derivation of plasma electron temperature and density are given in the Table 1.

TABLE 1. The parameters of the spectral lines used for the determination of the plasma electron density (from Ref. 10,11) and temperature (from Ref. 12). λ is the wavelength of the laser beam, w Stark broadening parameter (full width at half-maximum) at nominal electron density of 1×10^{16} cm^3 and temperature of 20000 K, g_k the statistical weight, E_k the energy of the upper state and A_{ik} is the transition probability of the line in question.

Line	λ (nm)	w (nm)	E_k (eV)	g_k	A_{ki} (10^8s^{-1})	Ref.
Si I	288.16	0.74×10^{-3}	5.08	3	1.89±0.50	[11]
Si I	390.55	1.46×10^{-3}	5.08	3	0.118±0.03	[11]
Si II	413.10	3.16×10^{-3}	12.84	8	1.42±0.35	[10]

3.2. Surface damage of the target and droplet formation

The laser beam energy density on target was not uniform over the cross-section of the focal spot. It was extensively investigated earlier [8,9]. The consequences of this non-uniformity are various damage patterns observed on the target surface. We concentrate here on the ablation craters on the parts of silicon surface that were irradiated most intensively by the laser beam. The ablation craters cut deeply into the target material and show presence of droplets that seem to be ejected from the edge of the damaged target area. We measured the size of individual droplets on the micrographs. Diameters of individual droplets are in the range of 0.5 – 4 μm, with the mean value of about 1.8 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. Fig. 1. shows one such ablation crater in detail.

To explain the formation of droplets, we used the model of hydrodynamical sputtering developed by Kelly and Rottenberg [14]. They postulated that surface asperities are somehow formed and, once present, are accelerated away from the liquid substrate. The separation of asperities from the surface will be opposed (for an ideal spherical shape of the droplets) by a force $f = -8\pi r\gamma$, where γ is the liquid silicon surface energy. For a Si-surface, $\gamma = 0.73$ J/m ^{2} [14,15]. r is the mean droplet radius, in our case 0.9 μm. In our experiment the force equals 2.2×10^{-5} N. When droplets are ejected, total droplet momentum away from the substrate exceeds the product $f\Delta t$, i.e.

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

where

$$\Delta L = 2r\alpha\Delta T + 2r\left(\frac{\rho_s-\rho_l}{3\rho_s}\right) \tag{2}$$

Here $\alpha\Delta T$ is the linear thermal expansion of the liquid [13-15], $\Delta T = \hat{T} - T_m$, where $\hat{T}$ is the maximum temperature, and T_m is the melting temperature of silicon (1685 K).

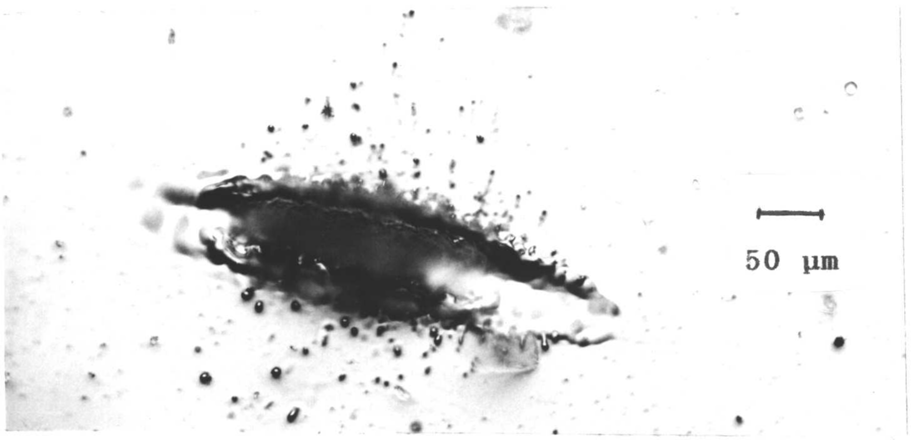

Fig. 1. The ablation crater produced in the area of highest intensity of the laser beam. 100 laser pulses were applied to produce this crater. The rim of the crater is elevated above the target surface and shows signs of extensive melting. Note many droplets scattered around the crater.

$$\frac{\rho_s - \rho_l}{3\rho_s} \tag{3}$$

is the linear expansion due to melting and for Si it equals $-\ 0.032$ [14]; ρ_s is the density of the solid and ρ_l is the density of the liquid. The whole length $2r+\Delta L$ in our case equals 2.61 μm. Furthermore, in Eq. (1) we have $\Delta t = \tau - t_m$, where τ is the duration of the laser pulse and t_m is the time at which the temperature T equals T_m. Also, from Ref. 13

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

In order to satisfy the expression (1) and taking into account Eq. (4), t_m should be less than 2.7 ns and $\hat{T}$ less than 2100 K.

4. Discussion and conclusion

The central part of the target surface that was irradiated by the laser beam was heavily ablated and deep craters were formed. During the short laser pulses, the plasma formed and the of silicon droplet were ejected. The spectroscopic analysis was carried out assuming that a local thermodynamic equilibrium (LTE) formed and that the plasma was optically thin. According to the criterion given in Ref. 9, LTE is satisfied for electron densities higher than 8×10^{15} cm^{-3} at the electron temperature of 16 000 K or higher, and for an energy difference of less than 4 eV between upper and lower level of a transition in question. This validates our assumption of LTE. We observed that the temperatures and densities are higher in air than in vacuum. In agreement with Matthias [17] and Strupp [4], the threshold for surface damage and plasma formation is higher in vacuum than in air. Under vacuum, higher power densities are required to produce the plasma and the related effects because a sufficient density of evaporated neutral atoms must be created to generate a gas load near the surface.

The measured values of the electron temperature and electron density in vacuum are in good agreement with the measurements of Blanco, Botho and Campos with a Nd:YAG laser (1.064 μm, 10 ns, 280 mJ) [18]. They derived the plasma parameters from Si II lines. They obtained for the plasma a temperature of about $2 \times 10^4 K$ and an electron density of 1×10^{17}cm^{-3}.

From the irradiance distribution of the laser beam [8], it was observed that the surface temperature decreased toward the edges of the crater. At the edges, the temperature is still sufficient for the expulsion of the droplets, contrary to the results of a similar experiment by Kelly and Rottenberg [14]. They carried out the experiment with about 1.5 times higher power density (laser beam of a wavelength of 248 nm, FWHM of the pulses of 12 ns). It is possible that droplets did form during their experiment, but were evaporated by the laser beam before they could recondense onto the target surface. Such a possibility was studied recently by Prishivalko, Astafieva and Leiko [19]. Namely, the time when the temperature equals the melting temperature was short compared to the laser pulse duration. For example, in our experiment, that time (t_m) was shorter by a factor of two compared to the duration of the laser pulse.

The droplets which were observed on target surface near the crater were pulled to the target by the backward plasma flux which is generated during the laser pulse. This is in agreement with the results of Brailovsky, Gaponov and Lushin [20] obtained in an experiment with a brass target.

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POVRŠINA SILICIJA OZRAČENA DUŠIKOVIM LASERSKIM ZRAČENJEM

Monokristalni silicij se ozračivao snopom iz dušikovog lasera ($\lambda = 337$ nm, maksimalna snaga 1.1 J/cm^2, trajanje pulsa 6 ns i frekvencija 0.2 Hz). Plazma nastala na površini silicija se promatrala spektroskopski u zraku ($n_e = 3 \times 10^{18}$ cm^{-3}, $T_e = 18500$ K) i u vakuumu ($n_e = 6{,}5 \times 10^{17}$ cm^{-3}, $T_e = 16000$ K). Površina ozračena u vakuumu se proučavala pomoću metalografskog mikroskopa. Opazile su se kapljice oko ruba udubine na siliciju. Nastajanje kapljica se tumači hidrodinamičkim modelom.