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Evidence of a nonthermal mechanism for ejection of ions and neutrals during excimer laser ablation of Ge

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Resonance ionization spectroscopy combined with time of flight mass spectrometry is used to analyze the ejection of ions and neutrals from the surface of a Ge target irradiated with ultraviolet XeCl excimer laser pulses. The ejection of ions and neutrals has been observed to occur at temperatures well below the melting point of the target and, therefore, through a nonthermal mechanism that may be dominant for fluences below the threshold for visible plasma formation. Within this regime, the velocities of the ejected neutrals in the ground state are in the order of 3×10^4 cm/s.

The successful application of laser ablation to the deposition of a great variety of materials¹⁻⁶ has generated an intensive interest in the understanding of the fundamental mechanisms of the ablation process itself. Most of the recently proposed models⁷⁻¹¹ assume that the initial mechanism for the ejection of ions and neutrals is thermal in nature.⁵ However, a limited number of papers providing evidence of ion ejection during laser ablation of solid targets with fluences well below the melting threshold have appeared in the last few years.¹²⁻¹⁴

This work describes the observation of ions and neutrals ejection from a Ge solid target irradiated with ultraviolet (UV) XeCl excimer laser pulses. A combination of time of flight mass spectrometry (TOFMS)¹⁵⁻¹⁹ with resonance ionization spectroscopy (RIS)²⁰⁻²² provides a unique tool for analyzing the ejection of ions and ground state neutrals as a function of the laser fluence with isotope selectivity.

The experimental setup combines a XeCl laser ($\lambda = 308$ nm, pulse length = 28 ns) used for Ge target (CERAC, 99.999%) ablation with a frequency doubled pulsed dye laser used for RIS (pulse length = 30 ns). The ablation experiments are carried out in a vacuum system (1×10^{-5} Torr) with a reflectron type TOF mass spectrometer equipped with a channel plate ion detector and a geometry similar to one reported elsewhere.¹⁸ The ablating beam is tophat-shaped and is free of hot spots, as determined by use of a thermosensitive paper. It is focused onto the target to a size of 0.5 mm^2 by means of a spherical lens and at an angle of incidence of 45° . The ablating fluence was in the $50\text{--}800 \text{ mJ/cm}^2$ range, and the fluence values are determined within 15%. The ionization laser beam (≈ 0.1 mm in diameter) is parallel to the target and intersects the path of the ablated species. Its energy is in all cases 5 mJ. Both the delay between the two laser pulses and the distance of the dye laser beam to the target can be varied during the experiment. The detection of the ejected neutrals is performed by tuning the dye laser at the wavelength corresponding to the resonant two photon ioniza-

tion of ground state Ge ($4p^2\ ^3P_{J=0}$) through the intermediate state $5s\ ^3P_{J=1}^0$, $\lambda = 265.2 \text{ nm}$.²³ For each isotope mass, two different peaks, separated by the time delay between the ablation and the ionization pulses, are observed in the TOFM spectrum. The first peak corresponds to the nascent ions created in the ablation process, whereas the second one corresponds to the post ionized neutrals. No difference was observed in the nascent ion signal intensity when the ionization laser beam was blocked. These results were obtained by averaging the signal along 16 or more laser shots with the errors in both ions and neutrals signals estimated to be lower than 7%.

Figure 1 shows the TOFMS signal corresponding to $^{74}\text{Ge}^+$ ions as a function of the ablation laser fluence. The behavior of the other isotopes ($^{70}\text{Ge}^+$, $^{72}\text{Ge}^+$, $^{73}\text{Ge}^+$, and $^{76}\text{Ge}^+$) is similar, the data of $^{74}\text{Ge}^+$ is shown alone for the sake of clarity. The fluence threshold for ejected ion detection is as low as $\approx 80 \text{ mJ/cm}^2$, and the ion signal is an increasing quadratic function of fluence. For fluences above $\approx 600 \text{ mJ/cm}^2$, the peaks of the TOFM spectrum, corresponding to ions of different mass overlap and form a broad single peak probably due to space charge effects.

The melting threshold of bulk crystalline Ge at 248 nm, $E_m(248 \text{ nm})$, has been experimentally determined to be 320 mJ/cm^2 .²⁴ A very reasonable estimation of $E_m(308 \text{ nm})$ can be made, assuming that E_m is proportional to $(1-R)\tau^{1/2}$,²⁵ R being the reflectivity of the material, and τ the pulse length, and using the reflectivities of Ge at 248 and 308 nm.²⁶ Such estimation provides a value of $E_m(308 \text{ nm}) = 310$ or 250 mJ/cm^2 if the differences in the pulse length are neglected. Even if small differences between the thermal conductivity of our target with respect to that of a single crystalline material are considered, the threshold fluence experimentally observed (80 mJ/cm^2) for ion ejection is well below the target melting threshold. Similar results for the ejection of ions from single crystalline Ge upon irradiation at 193 and 248 nm, with fluences well below the melting threshold, have been reported elsewhere.^{12,13} In addition, the threshold observed for visible plasma forma-

FIG. 1. TOFMS signal associated with $^{74}\text{Ge}^+$ ejected ions as a function of the ablation laser fluence at the target site. The behavior of the other isotopes is entirely similar.

FIG. 2. TOFMS signal associated with ^{74}Ge ejected ground state neutrals as a function of the ablation laser fluence at the target site. The delay between the ablation and the RIS pulses is $15\ \mu\text{s}$, and the distance between the RIS beam and the target surface is $0.33\ \text{cm}$. The behavior of the other isotopes is entirely similar.

tion is, in our case, $\approx 650\ \text{mJ}/\text{cm}^2$. If we assume that this value is close to the fluence necessary for reaching the boiling point of Ge ($3100\ \text{K}$), the temperature rise associated when irradiating with a $80\ \text{mJ}/\text{cm}^2$ pulse has to be lower than $350\ \text{K}$. Since the melting temperature of Ge is $1210\ \text{K}$, the ion ejection observed at the threshold fluence has to be a low temperature phenomenon.

Additional support for the existence of a nonthermal mechanism for species ejection can be obtained from the analysis of the ejection of ground state neutrals. For fluences between the ejection and the visible plasma formation thresholds—low fluence regime—the TOFMS signal of ions (Fig. 1) increases significantly, whereas that of neutrals remains fairly constant (Fig. 2). For instance, the TOFMS signal of $^{74}\text{Ge}^+$ increases by a factor of ≈ 10 , while the TOFMS signal of ^{74}Ge increases only by a factor of ≈ 2 in that interval. If the mechanism of emission of both ions and neutrals were thermal ($1/T$ dependence), the strong difference observed between the emission of ions and neutrals would not be expected. The difference can be due to the fact that ions and neutrals are ejected through a nonthermal mechanism whose efficiency as a function of fluence is higher for the former than for the latter. Recent experiments on UV laser ablation of Ge at much higher fluences, in which ions are observed to be present in the plasma several tens of nanoseconds before neutrals,²⁷ might provide further support to the existence of two different mechanisms for the ejection of ions and neutrals. An abrupt increase in the TOFMS signal of neutrals is evident in Fig. 2 between 550 and $650\ \text{mJ}/\text{cm}^2$, this could be interpreted as a change in the predominant mechanism for neutral ejection at higher fluences. The absence of any special feature in Figs. 1 and 2 for fluences around the expected melting threshold (200 – $300\ \text{mJ}/\text{cm}^2$) can be explained¹³ by the extremely low vapor pressure of Ge at the melting point ($7 \times 10^{-7}\ \text{Torr}$).

The existence of a nonthermal ejection mechanism can also be analyzed by the determination of the most probable velocity of the ejected species, with the assumption that such velocity is related to the target surface temperature.

This was done by measuring the evolution of the TOFMS signal of the two photon ionized neutrals as a function of the distance of the dye laser beam to the target for a given delay between the ablation and the dye laser pulses.^{15,17} The efficiency of ion extraction of the apparatus is not substantially altered since the dye beam is moved over a distance ($\approx 3\ \text{mm}$), which is much smaller than that between the repeller plate (target) and the grid ($\approx 37\ \text{mm}$).

The data corresponding to ^{74}Ge are shown in Fig. 3. It can be deduced that the most probable velocity of the ejected ground state neutrals in the direction normal to the target surface is in the order of $(3.3 \pm 0.4) \times 10^4\ \text{cm/s}$. The same result is obtained for the other Ge isotopes and also when changing the fluence below the visible plasma formation threshold ($650\ \text{mJ}/\text{cm}^2$) or the delay between the ablation and the ionization pulses.

The features of the experimentally observed velocity distribution functions in laser ablation experiments have been, in general, explained by considering a thermal emission mechanism and introducing different effects on the

FIG. 3. TOFMS signal associated with ground state ^{74}Ge ($\square$) ejected neutrals vs distance of the ionization beam to the target. The delay between the ablation and the RIS pulses is $5.13\ \mu\text{s}$, and the ablation fluence is $450\ \text{mJ}/\text{cm}^2$. The dashed line is a guide to the eye.

behavior of the generated plasma:⁵ collisional effects in the near surface region, adiabatic expansion, and isothermal expansion followed by adiabatic expansion. These are the “Knudsen layer,”^{8–10} the “supersonic expansion,”^{7,28} and the “isothermal expansion”¹¹ models, respectively.

In the case of the Knudsen layer model, the relationship between the most probable velocity observed for the emitted particles (V_p) and the surface temperature (T_s) is given by $T_s = (1/k)(MV_p^2/2)(1/2.52)$,⁸ where k is the Boltzmann constant, M is the particle mass, and it is assumed that the particles are detected with a density sensitive detector, such as laser induced fluorescence or RIS. In our case, for a most probable velocity of $(3.3 \pm 0.4) \times 10^4$ cm/s, the model leads to a surface temperature of 190 ± 50 K, which is too low, since the energy density used (450 mJ/cm²) is above the melting threshold. The use of the isothermal expansion model¹¹ typically provides drift velocities of the plasma species higher than 10^5 cm/s, at least one order of magnitude higher than the ones we observed. Finally, the supersonic expansion model^{7,28} predicts maximum particle velocity scaling as $v_m = [2/(\gamma - 1)](\gamma k T_i / M)^{1/2}$,²⁹ where T_i is the temperature before expansion (surface temperature), γ ($= 1.67$) is the ratio of specific heats, M is the isotope mass, and k is the Boltzmann constant. From Fig. 3 it can be deduced that the velocity of the fastest emitted particles is in the $7\text{--}8 \times 10^4$ to 10^5 cm/s interval which provides surface temperature values, in the former formula ranging from 300 to 620 K, which are again too low.

The previous analysis also supports a nonthermal mechanism for species ejection. Among the different nonthermal mechanisms for particle emission proposed in the literature, the one proposed by Helvajian and co-workers, ejection through plasmon interactions,¹⁴ also leads to particle velocities that are at least one order of magnitude higher than the ones observed in our case. The similarity of our results with those reported by Chen and co-workers in Ref. 12, and later explained by Wu³⁰ on the basis of ejection through interaction of atoms in defect sites with energetic holes, makes this latter model more likely.

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