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Silicon clusters produced by femtosecond laser ablation: Non-thermal emission and gas-phase condensation

Alexander V. Bulgakov*
Institute of Thermophysics, Prospect Lavrentyev 1, 630090 Novosibirsk, Russia

Igor Ozerov† and Wladimir Marine‡
CRMC-N, UPR 7251 CNRS, Université de la Méditerranée,
Faculté des Sciences de Luminy, Case 901, 13288 Marseille, Cedex 9, France

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Neutral silicon clusters Si$_n$ (up to $n = 7$) and their cations Si$_n^+$ (up to $n = 10$) have been produced by femtosecond laser ablation of bulk silicon in vacuum and investigated using time-of-flight mass spectrometry. Two populations of the Si$_n^+$ clusters with different velocity and abundance distributions in the ablation plume have been clearly distinguished. Possible mechanisms of cluster formation (Coulomb explosion, gas-phase condensation, phase explosion) are discussed.

PACS: 52.38.MF; 61.46.+w; 79.20.Ds

Femtosecond laser ablation is a rapidly developing technique offering new possibilities in various applications. The fundamental mechanisms that lead to material removal are, however, still poorly understood. The interaction of fs laser pulses with silicon is an example of a complex interplay of thermal and ultrafast, non-thermal processes involved to ablation [1, 2, 3]. Studies of composition and expansion dynamics of the laser-induced plume can provide a considerable insight into the ablation mechanisms. Several recent experiments on this subject [2, 4, 5, 6] were mainly devoted to the atomic component of the plume though an observation of small silicon clusters was also mentioned [2]. Little is known about silicon cluster formation under ablation with short laser pulses. With ns pulses, low-fluence desorption of Si dimers [7] and small neutral Si$_n$ clusters [8] were observed. Desorption of small clusters from both crystalline and nanostructured Si surfaces was induced by using high-energy (6.4 eV) photons [9]. Multiple-charged cluster ions were formed in ps-laser stimulated field evaporation [10]. Recently we reported the first results on the observation of neutral and cationic clusters under femtosecond laser ablation of silicon [11]. In this work, we analyze mechanisms of clusters formation based on measurements of the abundance and velocity distributions.

I. EXPERIMENT

The experiments were performed with Si[100] surface under ultrahigh vacuum conditions ($\sim 10^{-10}$ mbar). The Si target was irradiated at a 45 ° incidence angle using a Ti:sapphire laser (Mai-Tai coupled with a TSA amplifier, Spectra Physics, 80 fs pulse duration, 10 Hz repetition rate, up to 30 mJ energy per pulse) operating at 800 nm. A part of the laser beam was selected by an aperture to provide a nearly uniform intensity distribution over the irradiated spot. The target was rotated/translated during measurements to avoid considerable cratering. Some experiments were performed with the fixed target in order to investigate the effect of accumulation of laser pulses at the same spot. The fluence on the target was varied in the range 80-800 mJ/cm^2.

The abundance distributions of neutral and positively charged particles in the laser-ablation plume were studied using a reflectron time-of-flight mass spectrometer. The neutral particles were analyzed using electron impact ionization (110 eV) and a plasma suppressor [12]. At a distance of 11 cm from the target, the ablated or post-ionized ions were sampled parallel to the plume axis by a 500 V repeller pulse at a time delay t_d in respect to the laser pulse. Mass spectra were averaged over 300 laser shots with the rotated target and over 5 shots with the fixed target.

II. RESULTS AND DISCUSSION

Monatomic Si$^+$ ions and Si atoms are the most abundant particles in the plume throughout the laser fluence range studied. The ion signal appears at a threshold fluence $F_{th} \approx 100$ mJ/cm^2 [11] for the etched Si surface irradiated previously with a fairly large number of laser pulses. Efficient emission of both neutral silicon clusters Si$_n$ (up to $n = 7$) and their cations Si$_n^+$ (up to $n = 10$) has been observed for $F > F_{th}$. The cluster abundance distributions are found to be essentially different for the fresh and etched ablated surfaces. Figure 1 shows a typical evolution of cation mass spectra with increasing the number N of laser pulses applied to the same spot. The spectra were obtained at time delay t_d, corresponding to a maximum average yield of clusters. With the fresh surface, the relatively large Si$_n^+$ clusters ($n > 3$) are observed in high abundance with the "magic" number at n

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[*] Fax: +7 3832 343480, Tel.: +7 3832 391045; Electronic address: bulgakov@itp.nsc.ru

[†] Electronic address: ozerov@crmcn.univ-mrs.fr

[‡] Electronic address: marine@crmcn.univ-mrs.fr

= 6 (Fig. 1a). In addition, doubly charged cluster ions are present in the plume among which Si_5^{2+} is particularly abundant (note that Si_5^{2+} was observed earlier as a magic cluster in the field evaporation experiment [10]). The monatomic Si^+ peak is relatively weak under these conditions.

When the number of laser shots increases, the mass spectrum is significantly modified (Fig. 1b,c). The Si_n^+ ($n > 3$) and Si_5^{2+} clusters are observed in lower abundance (the latter almost disappears at $N > 100$) while the concentration of the smaller species (n = 1-3) increases progressively with N. After ~40 laser shots, Si^+ ion is totally dominant in the plume (this is not seen in Fig. 1 since the Si^+ signal is maximized at shorter time delays). The cluster distribution exhibits an odd-even alternation with preferred formation of even-numbered Si_n^+ clusters. Further increase in the number of laser pulses results in further decrease of the relative yield of the cationic clusters. After few hundreds of laser shots the signal saturates and the abundance distribution becomes rather smooth with peak intensities monotonously decreasing with cluster size (Fig. 1c).

Typical mass spectra for neutral Si_n clusters obtained with the fresh and etched ablated surfaces are shown in Fig. 2. The effect of the number of accumulated laser pulses is not so strong in this case though the same tendency of decreasing in the relative yield for Si_n clusters ($n > 4$) is obvious. The odd-even alternation in the cluster distribution is also observed at low N values (Fig. 2a) but it is less pronounced than for cationic clusters.

The observed effect of the number of applied laser pulses on particle emission suggests an accumulation of the laser-induced damage on the Si surface. Indeed, with an optical microscope we observed clearly shaped spots at the surface for very low fluences down to approximately 150 mJ/cm^2 (for multi-pulse conditions with ~1000 laser shots per spot). We can thus conclude that the damage threshold is approximately equal to the ion desorption threshold for silicon under these conditions. The low-fluence damage (modification) of Si surfaces with ultrashort laser pulses was observed earlier and attributed to amorphization of silicon [13, 14]. The effect of laser pulse accumulation on the damage threshold (the incubation effect) was also revealed. The multi-pulse damage threshold determined in [14] is well consistent with that evaluated here. Similar incubation effect in silicon was observed recently with ns laser pulses [8, 15]. The precise nature of the incubation effect is not clear (it can be, e.g., due to chemical modification, mechanical stress, defect accumulation [14, 15]) and needs further investigation.

Variation of the time delay t_d allowed the analysis of particle velocity distributions and the characterization of the temporal evolution of the plume composition. The measurements were perfermed with the etched Si surface when no signal change with the number of laser pulses occurred. Figure 3 shows the time-of-flight (TOF) distributions of several cationic particles for different laser fluences. The distributions for Si^+ ions are maximized at ~9 μs time delay that corresponds to ~12 km/s ion velocity. Increase in fluence results just in a broadening of the distributions with little or no shift towards higher velocities. At the same time, the yield of Si^+ ions increases strongly with fluence as $\sim F^n$ with $n \approx 7.5$ [11].

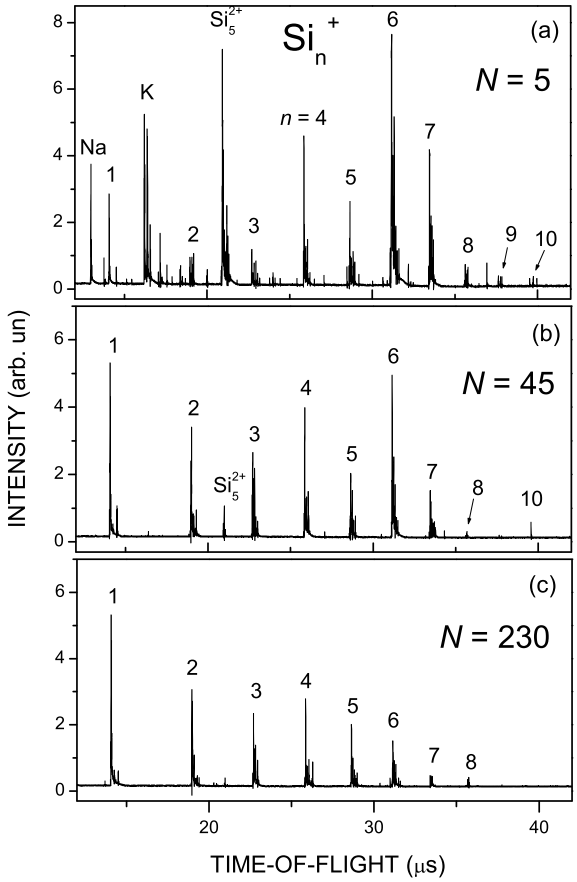

FIG. 1: Mass spectra of cationic silicon clusters produced at laser fluence F = 350 mJ/cm^2 with different number N of laser pulses applied. Time delay t_d = 32 μs

In contrast to Si^+ ions, the cluster TOF distributions are found to be strongly fluence-dependent. At low fluence, near the threshold value, the TOF distribution for Si_2^+ is rather narrow, single-peaked, and maximized at $t_d \cong 18$ μs (Fig. 3a), that is the most probable velocity is approximately two times lower than that of Si^+. This means that these plume particles have nearly the same momentum. At 400 mJ/cm^2, the distribution for Si_2^+ is still single-peaked but a noticeable shift towards higher time delays is observed (the maximum occurs at ~25 μs, the corresponding velocity is ~ 4.4 km/s). The fast Si_2^+ dimers are still present in this ablation regime but their distribution is masked by slower ions. With further

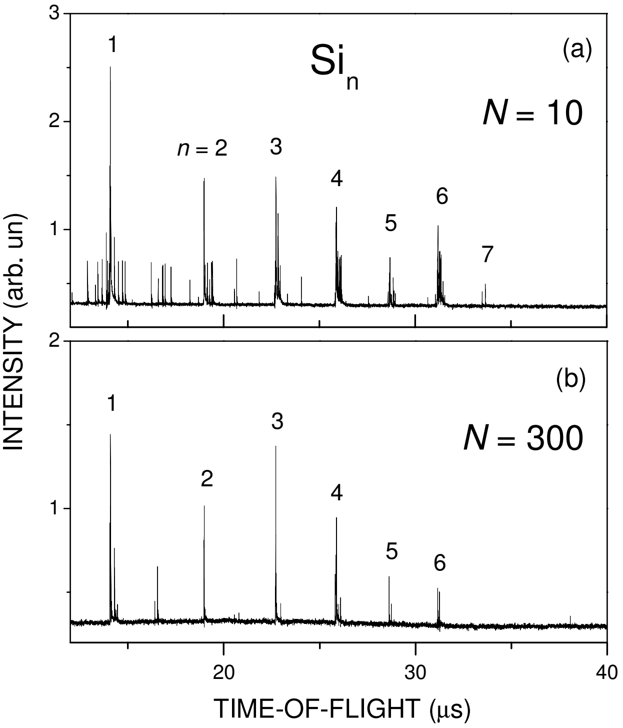

FIG. 2: Mass spectra of neutral silicon clusters produced at $F = 350$ mJ/cm^2 and detected at $t_d = 32$ μs with relatively fresh (a) and etched (b) surfaces.

increase in laser fluence, the second, even slower, population of Si_2^+ appears in the plume. At 550 mJ/cm^2 this slow population dominates (Fig. 3c). The first faster peak in the distribution is still present, well separated from the second peak, and is still maximized at ~25 μs.

The evolution of TOF distributions for larger Si_n^+ clusters is qualitatively similar to that for Si_2^+ as illustrated in Fig. 3 for the S_6^+ cation. At a threshold fluence of around 450 mJ/cm^2, the distributions are transformed from single-peaked to double-peaked. The second (slow) cluster population becomes rapidly dominat with further increase in fluence. The most probable velocity of the second population decreases slightly with cluster size from 2.5 km/s for Si_2^+ to 2 km/s for Si_6^+. The abundance distribution for this slow cluster population exhibits a pronounced odd-even alternation with dominance of the Si_6^+ peak and similar to that observed at shorter delay times with relatively fresh surface (Fig. 1a). It is thus remarkably different from the falling smooth distribution for faster clusters (Fig. 1c).

Based on the obtained results, we can address the fundamental question on cluster formation mechanism under different irradiation regimes. At very low laser fluence, from the ion appearance threshold F_{th} up to $\sim 2F_{th}$, Si^+ and Si_2^+ ions are likely produced by an impulsive Coulomb explosion (CE) from a charged surface. Two observations support the CE mechanism [11, 16], namely, (a) the momentum scaling for the particles under low fluence regimes and (b) decrease of velocity for Si_2^+ ions when fluence is increased beyond $\sim 2F_{th}$, that is a behavior opposite to thermal desorption. The slower Si_n^+ clusters (which overshadow the CE ions in the (2-4)F_{th} fluence range and form the fast cluster population at higher fluences) can be interpreted as "plasma ions", i.e., ions formed in the ionized vapor plume by collision-induced condensation. The velocities of these "plasma ions" decrease only slightly with cluster size and scale by a law intermediate between constant kinetic energy and constant velocity that implies the gas-phase condensation mechanism rather than direct ejection of the clusters [12].

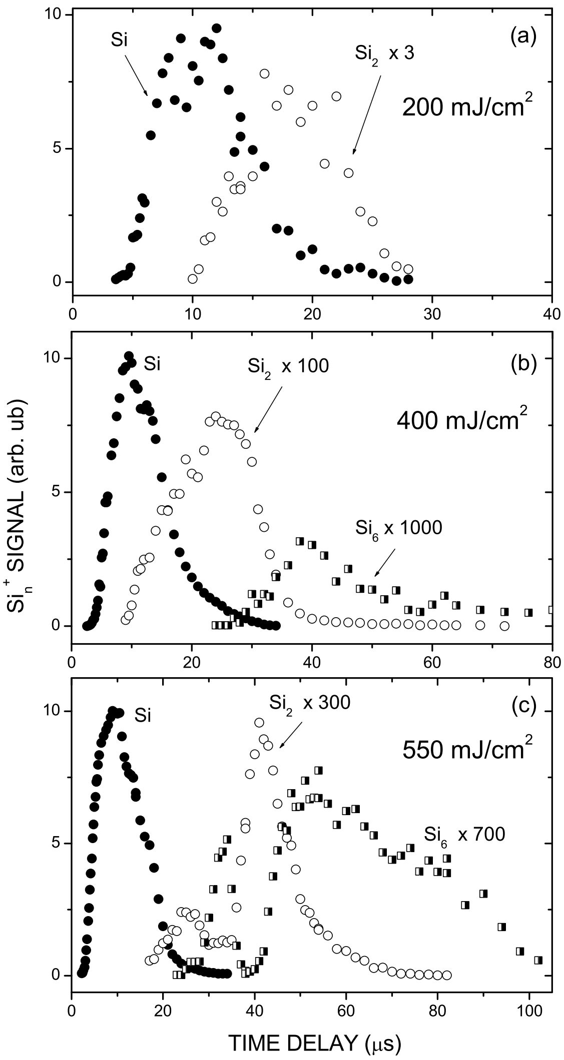

FIG. 3: TOF distributions for Si^+, Si_2^+ and Si_6^+ cations at three laser fluences.

Of particular interest is the origin of very slow cluster ions observed at high fluences ($F > 4.5F_{th}$) as the second population in the TOF distributions (Fig. 3c). The evident separation of this population from the first one indicate that another mechanism is likely responsible for its formation. We suggest that the slow ions are due to phase explosion (PE) from the Si surface melted via an ultrafast, non-thermal process which was recently found for semiconductors under fs-laser irradiation [1, 2, 3]. The fast excitation of a dense electron-hole plasma causes destabilization of the lattice, and the semiconductor melts in a time less than 1ps. The non-thermal melting occurs at fluences fairly higher than needed for purely thermal melting process. The melted surface, even if its temperature is far below the thermodynamic critical temperature, inevitably enters the region of metastable states with the subsequent phase explosion as one of probable stabilization mechanisms [17]. The overheated liquid can decay into the gas phase without formation of the critical vapor nucleus [17] so the ejection of small clusters is quite possible. More work is needed to be certain about the origin of the cluster ions under these conditions but some observations support the PE mechanism. The amount of material released under the PE is macroscopic and the ejected particles undergo many collisions within the plume during their expansion into vacuum. As a result, the most stable clusters survive predominantly in the plume thus resulting in abundance distributions with magic numbers. Numerous previous investigations indicate special stability of Si_4^+, Si_7^+, and particularly Si_6^+ [18]. This is well correlated with the observed abundance distributions of the slow ions (similar to that shown in Fig. 1a). In addition, the observed weak size dependence of cluster velocities for the second population (Fig. 3c) correlate with recent simulations of short-pulse laser ablation [19] where nearly the same flow velocities were obtained for clusters of different size ejected via the PE mechanism.

III. CONCLUSIONS

We have observed efficient emission of both neutral and cationic silicon clusters under femtosecond laser ablation of silicon in vacuum. Cluster abundance and velocity distributions are found to depend strongly on laser fluence and the number of laser pulses applied. The obtained results provide clear evidence that different cluster formation mechanisms (Coulomb explosion, gas-phase condensation, phase explosion) are involved. Further work aimed at clarifying the contributions of these mechanisms for various ablation conditions is currently under way.

Acknowledgments

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