

# Vacuum Ultraviolet Single Photon Versus Femtosecond Multiphoton Ionization of Sputtered Germanium Clusters

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Neutral atoms and clusters desorbed from a solid germanium surface by ion bombardment are detected by laser postionization and time-of-flight mass spectrometry. Two different photoionization schemes are compared which are generally believed to be candidates for the 'soft' ionization of polyatomic species without significant photon induced fragmentation. First, a single photon ionization process is employed using an F<sub>2</sub> laser as an intense VUV source with a photon energy in excess of all relevant ionization potentials. It is shown that the available laser pulse energy is sufficient to saturate the ionization of Ge atoms and all detected Ge<sub>n</sub> clusters. The resulting mass spectra are compared to those obtained with a non-resonant multiphoton ionization process using a high intensity laser delivering pulses of 250 femtoseconds duration at a wavelength of 267 nm. Also in this case, the ionization process can apparently be driven into saturation. The mass spectra measured under these conditions are found to be almost identical to those obtained using single photon ionization. We take this as an indication that the results obtained with both postionization techniques closely reflect the true cluster sputtering yields and, in particular, are not dominated by photon induced fragmentation. © 1998 John Wiley & Sons, Ltd.

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If a solid is bombarded with energetic particles, surface atoms as well as agglomerates of several atoms are released into the gas phase. Specifically, the formation of clusters have been of considerable interest in sputtering physics over the past three decades.<sup>1</sup> Unfortunately, the large majority of sputtered material leaves the surface as neutral particles and must therefore be ionized prior to mass analysis and detection. Electron impact ionization, which has been successfully employed to detect sputtered neutral atoms and a number of small molecules,<sup>2–4</sup> has turned out to be too inefficient to detect larger species. So far, the only technique which is capable of detecting larger clusters among the flux of sputtered neutral particles is laser photoionization. Here, however, photon induced fragmentation processes often present a severe problem with respect to the quantitative interpretation of acquired mass spectra. Due to very fast internal conversion and dissociation processes from the intermediate electronic state, multiphoton ionization of sputtered clusters larger than dimers with nanosecond laser pulses seems to be extremely difficult if not impossible. On the other hand, single photon ionization (SPI) circumvents this problem. In this case, metal<sup>5–11</sup> and semiconductor clusters<sup>12</sup> containing up to some 30 atoms have been detected.

The question still remains as to the extent the results of such experiments are influenced by photofragmentation. It is therefore highly desirable to compare the data acquired

with this method to those obtained with a fundamentally different, alternative ionization mechanism. A suitable candidate for such a method is the ultrashort pulse multiphoton ionization (MPI) using intense femtosecond lasers. The idea is that if the optical pumping rates are faster than typical conversion or dissociation rates, it can be expected that polyatomic species may be efficiently ionized without significant intermediate state fragmentation. This strategy has been applied successfully to detect neutral clusters sputtered from Ag and In surfaces.<sup>13</sup>

Here we compare mass spectra of neutral atoms and clusters which are sputtered from the same surface, mass analyzed and detected under otherwise identical or comparable conditions and ionized either by MPI with subpicosecond pulses or single photon ionization (SPI) schemes. Due to the fundamentally different nature of the two processes, such an investigation may shed light on the possible role of photofragmentation in this type of experiment. We have chosen Ge as the sample material, since it is known that the surface of semiconductors like Si and Ge is completely amorphized under ion bombardment,<sup>14</sup> ensuring a well-characterized surface state.

## EXPERIMENTAL

The present experiments have been carried out in two different laboratories. The experimental arrangements used at both sites have been described in detail<sup>5,13,15</sup> and only a brief description of the features essential for this work will be given here. A sketch of the setup is given in Fig. 1. A Ge(111) surface is bombarded at 45° with respect to the surface normal. The primary ions are generated in two different sources. In the first setup (hereafter referred to as

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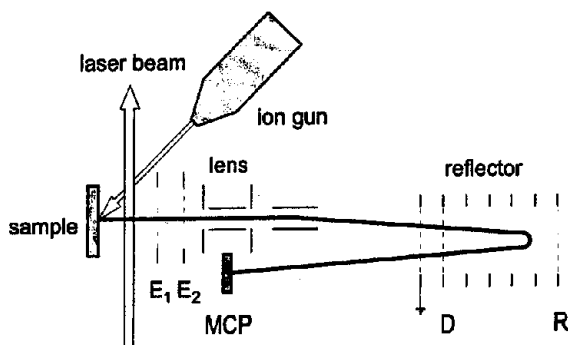


Figure 1. Schematic setup of laser postionization time-of-flight SNMS systems used in the present work.

setup I), a Finkelstein-type rare gas ion source is used which delivers  $\text{Ar}^+$  ions of 5 keV with a D.C. beam current of 5  $\mu\text{A}$ . The second setup (setup II) is equipped with a liquid metal ion gun delivering  $\text{Ga}^+$  ions of 25 keV with a D.C. beam current of 80 nA. Both ion sources are operated in a pulsed mode at a pulse length of about 1  $\mu\text{s}$ . Neutral particles which are sputtered from the sample surface are ionized by a pulsed laser beam directed closely above the parallel to the surface. The laser pulse is triggered approximately 100 ns after the end of the primary ion pulse. Together with the relatively long ion pulse duration, this configuration ensures that sputtered particles of all emission velocities intersect the laser pulse. The photoions created in this way are extracted into a reflectron time-of-flight (TOF) mass spectrometer operated at a mass resolution of  $m/\Delta m = 500$  (setup I) or  $m/\Delta m = 1500$  (setup II) and detected by a Chevron stack of microchannel plates. Due to the large dynamic range spanned by the signals of sputtered atoms and larger clusters, special care was taken to avoid channel plate saturation effects by taking mass spectra at different gain settings. This is particularly important for setup I due to the larger primary ion current.

The ionization laser employed in setup I is a conventional

excimer laser (Lambda Physik model LPX 120i) operated with a  $\text{F}_2/\text{He}$  gas fill. Under optimized conditions, this laser produces 4 mJ pulses of about 20 ns duration at a wavelength of 157 nm. The corresponding photon energy of 7.9 eV exceeds the ionization potential of Ge atoms and, hence, enables SPI of Ge atoms and  $\text{Ge}_n$  clusters. The output beam is transported in dry  $\text{N}_2$  and coupled into the ultrahigh vacuum (UHV) chamber housing the TOF experiment by a  $\text{CaF}_2$  window and a 200 mm focal length  $\text{CaF}_2$  lens. The laser beam is shaped to a cross section of  $1.7 \times 0.6 \text{ mm}^2$  in directions along and perpendicular to the sample surface, respectively, and positioned at a distance of 0.7 mm above the surface. In order to study the laser intensity dependence of the photoion signals, the pulse energy could be reduced by a stack of two variable dielectric attenuators located in front of the lens.

The femtosecond laser system used in setup II was manufactured by Clark MXR and has been described in detail elsewhere.<sup>13,15</sup> In short, a Ti:sapphire oscillator pumped by an argon ion laser delivers pulses of 50 fs at a wavelength of 800 nm, which are stretched and fed into a regenerative amplifier and four-pass post amplifier pumped by two frequency doubled high repetition Nd:YAG lasers. After recompression, the system delivers pulses of 3.5 mJ and 100 fs at 800 nm, which are then frequency tripled in BBO crystals to yield UV pulses of 450  $\mu\text{J}$  and 250 fs at 267 nm. The laser beam is focused into the UHV chamber by a 300 mm focal length  $\text{CaF}_2$  lens and a  $\text{MgF}_2$  window. The resulting focal beam dimension is 50  $\mu\text{m}$  in diameter. By retracting the lens, however, the beam diameter in the interaction region is shaped to 200  $\mu\text{m}$  full width at half maximum (FWHM) and positioned at a distance of 1 mm above the surface. For laser power density studies, the pulse energy could be reduced using polarizing filters.

## RESULTS AND DISCUSSION

Mass spectra of neutral Ge atoms and  $\text{Ge}_n$  clusters sputtered from a Ge surface by 5 keV  $\text{Ar}^+$  (setup I) and 25 keV  $\text{Ga}^+$

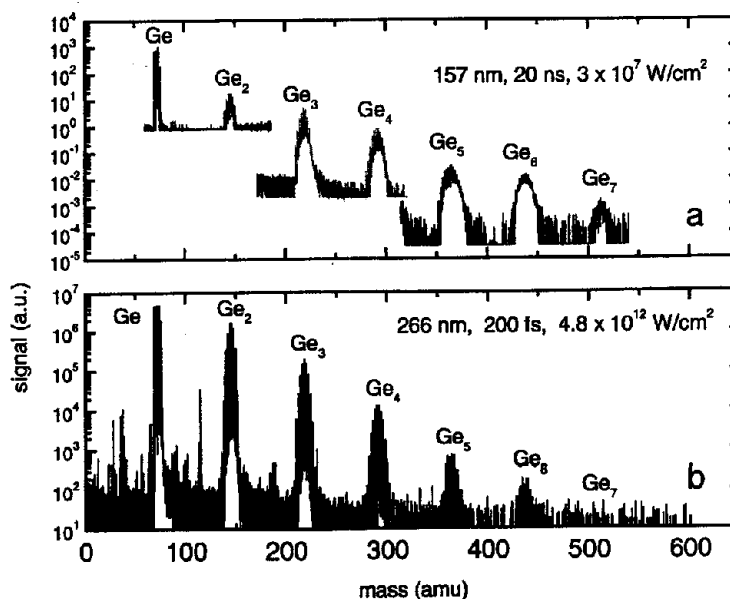
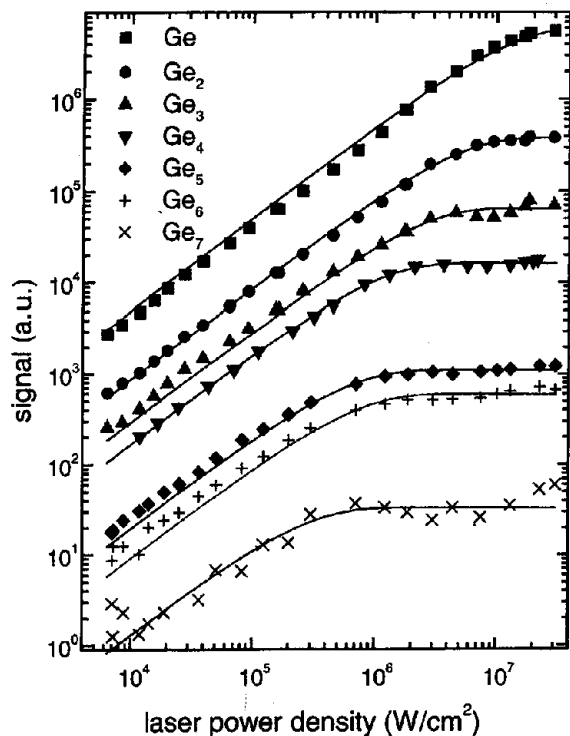


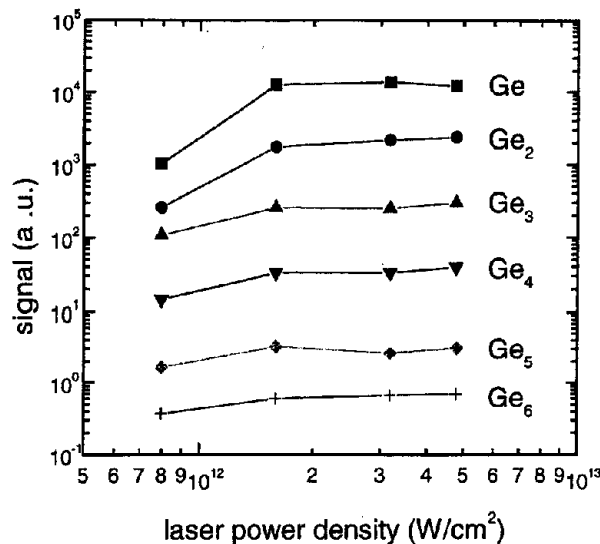
Figure 2. Mass spectra of neutral atoms and clusters sputtered from a completely amorphized germanium surface by (a) 5 keV  $\text{Ar}^+$  ions (setup I) and (b) 25 keV  $\text{Ga}^+$  ions (setup II).



**Figure 3.** Laser peak power density dependence of the integrated signals of sputtered neutral Ge atoms and  $\text{Ge}_n$  clusters positioned with the VUV laser at 157 nm and 20 ns pulse duration.

ions (setup II) are shown in Fig. 2. Both spectra refer to conditions where the surface (initially the (111) oriented plane of a single crystal) was pre-bombarded with an ion dose large enough to completely amorphize the surface.<sup>14</sup> The apparent widths of the cluster peak groups reflect the fact that Ge has 5 natural isotopes at masses between 70 and 76 amu. The number of isotopomers for a given cluster size  $n$ , therefore, greatly increases with increasing  $n$ , with the corresponding mass peaks spanning a range of  $6n$  amu. It is clearly seen that the mass resolution of both systems is sufficient to resolve all individual peaks of each observed cluster group. The spectrum displayed in Fig. 2(a) was taken with the nanosecond VUV laser at a power density of  $3 \times 10^7 \text{ W/cm}^2$ . The different baselines in these spectra arise from deliberate variation of the microchannel plate voltage in order to avoid gain saturation effects. The spectrum of Fig. 2(b), on the other hand, has been obtained with the femtosecond laser system at  $\lambda = 267 \text{ nm}$  and a power density of  $5 \times 10^{12} \text{ W/cm}^2$ . In this case, the complete spectrum was taken with one MCP gain setting and, hence, the signal recorded for Ge atoms is largely saturated. The signal observed at  $m/z$  113 and 115 is due to a small indium contamination of the surface and the peak group below  $m/z$  50 is due to doubly charged ions.

From Fig. 2 it is apparent that both positionization mechanisms employed here are capable of efficiently ionizing sputtered neutral Ge atoms and clusters to sizes of 7 atoms. In order to quantitatively interpret the measured data, it is necessary to investigate the dependence of the measured signals on the laser intensity. The results for the VUV laser system ( $\lambda = 157 \text{ nm}$ ) are shown in Fig. 3. The absolute values of the peak power density  $P_L$  were calculated by assuming rectangular spatial and temporal beam profiles



**Figure 4.** Laser peak power density dependence of the integrated signals of sputtered neutral Ge atoms and  $\text{Ge}_n$  clusters positioned with the high intensity laser at 267 nm and 250 fs pulse duration.

with widths corresponding to the respective FWHM values. It is seen that in the regime of low laser intensity all signals are linearly dependent on  $P_L$ , a behavior which is expected due to the single photon absorption process leading to the ionization of the particles. At  $P_L$  levels between  $10^6$  and  $10^7 \text{ W/cm}^2$ , the photoionization process is apparently driven into saturation, and all signals except for that of the monomers reach a constant saturation plateau. In fact, the solid lines in Fig. 3 represent least square fits of the theoretically expected saturation behavior

$$S(P_L) = S_{\text{sat}}[1 - \exp(-\sigma P_L / h\nu \Delta t)] \quad (1)$$

to the measured data. In Eqn (1),  $\sigma$  denotes the single photon absorption cross section,  $h$  is Planck's constant,  $\nu$  is the laser frequency and  $\Delta t$  is the laser pulse duration. It is seen that all measured data are very well approximated by Eqn (1), and therefore even the monomer signal can be easily extrapolated towards complete saturation. The saturated signals  $S_{\text{sat}}$  can be taken as representative of the number density of the respective neutral particles within the ionization volume. Of particular note is that the cluster signals do not turn over at large laser intensities, indicating that *multiphoton* fragmentation processes are absent in the laser intensity regime explored here.

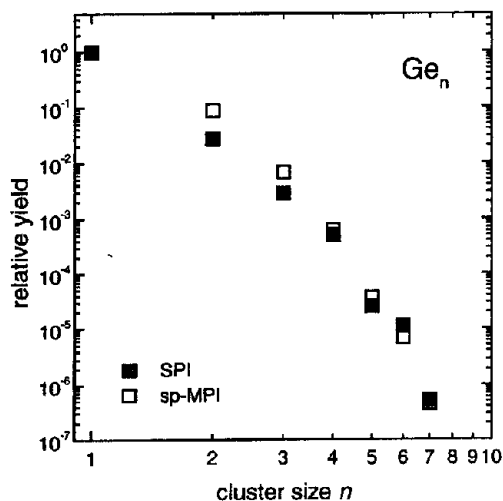
Results of a parallel study using the femtosecond laser system are shown in Fig. 4. At lower laser intensity, the signals of Ge atoms and  $\text{Ge}_2$  dimers fall rapidly with decreasing  $P_L$ . In order to discuss this behavior, it is of interest to estimate the Keldysh parameter<sup>16</sup>

$$\gamma = I / 2U_p \quad (2)$$

with  $I$  being the ionization potential of the particle and

$$U_p = \varepsilon^2 e_0^2 / 4\omega^2 m_e \quad (3)$$

the ponderomotive potential induced by the laser field of strength  $\varepsilon$  and angular frequency  $\omega$ . The constants  $e_0$  and  $m_e$  denote the electron charge and mass, respectively. For  $P_L$  below  $10^{13} \text{ W/cm}^2$ ,  $\gamma$  is large compared to unity ( $\gamma > 10$ ) and the multiphoton ionization process should obey the usual  $P_L^n$  behavior where  $n$  is the minimum number of



**Figure 5.** Relative yield distribution of neutral atoms and clusters sputtered from an amorphized germanium surface vs. the cluster size  $n$ . Closed symbols refer to single photon postionization with the VUV laser, open symbols refer to femtosecond multiphoton postionization.

photons needed for ionization. The slope indicated in Fig. 4 corresponds to  $P_L^{3.6}$  instead of  $P_L^2$  which would be expected if two 267 nm photons are needed to ionize Ge atoms and dimers. At present we are unclear as to the origin of this discrepancy.<sup>17</sup> Moreover, it is technically difficult to reduce  $P_L$  over more than one order of magnitude, and the low intensity regime could not be explored in further detail. For the present purpose, however, it is sufficient to recognize that at laser power densities above  $2 \times 10^{12}$  W/cm<sup>2</sup>, saturation of the ionization process is clearly reached, and the signals measured under these conditions can therefore be directly compared to those measured with the VUV laser. The resulting distribution of relative cluster yields, i.e. cluster sputtering yields normalized to that of the monomers, as determined with both postionization techniques under saturation ionization conditions is shown in Fig. 5. In order to convert from the number density to sputtered flux, the saturated signals have been corrected by the cluster size dependence of the average inverse emission velocity which has been determined elsewhere to vary as  $n^{-1.2}$ .<sup>12</sup>

From the data presented in Fig. 5 it is evident that the cluster yield distributions determined with both postionization methods are very similar. In view of the large range spanned by the relative cluster yields, together with the fact that two fundamentally different postionization mechanisms are used to detect the sputtered neutral particles, we consider this surprisingly good agreement. Interestingly, the yields of dimers and trimers obtained with the sp-MPI process are slightly higher than those determined with SPI. To the best of our knowledge, there are three possible reasons for this finding.

First, the signal of Ge atoms could be underestimated with sp-MPI, for instance due to incomplete saturation of the ionization process or to differences between the effective ionization volume for atoms and clusters. While the former appears unlikely in view of the data presented in Fig. 4 the latter could in principle, be, possible due to the fact that a focused laser beam was employed in the femtosecond experiment. If the photoionization cross section of atoms were significantly smaller than that of dimers and larger clusters, one could indeed expect a smaller effective ioniza-

tion volume for the atoms. However, the data in Fig. 4 suggest that this is not the case, since dimers and monomers approach saturation at comparable laser intensities.

The second possible reason is that the dimer and trimer yields are underestimated in the SPI experiment. Since the ionization process is clearly saturated (cf. Fig. 3), this would mean that the measured signals must be reduced by photo-fragmentation effects. As mentioned above, multiphoton fragmentation, where the photoionized particle absorbs additional photons and fragments, would have to show up in the data of Fig. 3 and, hence, can be ruled out. The only possible loss mechanism would therefore be fragmentation by single photon absorption, a process which follows the same laser intensity dependence as the SPI process and therefore cannot be safely ruled out. However, the magnitude of the observed effect would require the fragmentation cross section to be at least 3 times as large as the SPI cross section, a result that would be unexpected.

A third possible reason is given by the fact that we have used different projectile species and energies in both experiments. In a number of studies performed mostly for clean metal surfaces, it has been shown that the yield distribution of sputtered clusters is generally correlated with the total sputtering yield  $Y_{tot}$  of the sample.<sup>11</sup> This correlation works in such a way that the relative contribution of larger clusters increases with increasing  $Y_{tot}$ . In some cases, similar trends have been found for the relative dimer yield.<sup>2,18</sup> Therefore, if the sputter yield of Ge differs greatly between bombardments by different projectiles, differences in the relative dimer yield may be expected. There are no experimental data available for the sputter yield of Ge under bombardment by 25 keV Ga<sup>+</sup> ions. Using the TRIM sputter simulation code,<sup>19</sup> we estimate  $Y_{tot}$  are 6.4 and 3.7 atoms/ion for 25 keV Ga<sup>+</sup> and 5 keV Ar<sup>+</sup> primary ions, respectively. In our previous work, we have measured the cluster yield distribution as well as the total sputter yields of two different Ge surfaces [(100) and (111)], each in the single crystalline and amorphized surface state, under 5 keV Ar<sup>+</sup> bombardment.<sup>12</sup> In these experiments, the measured values of  $Y_{tot}$  varied between 3.5 and 6.8 atoms/ion depending on the surface state and orientation, but no significant differences were found for the cluster yield distribution. On the basis of these data, then, we do not expect large variations of the cluster yield distribution for 25 keV Ga<sup>+</sup> and 5 keV Ar<sup>+</sup> bombardment.

## CONCLUSION

It is demonstrated that sputtered neutral Ge atoms and clusters can be efficiently ionized both by SPI using nanosecond VUV laser pulses and by MPI using subpicosecond UV pulses. The goal of the present work is to judge the reliability of the resulting mass spectra with respect to photon induced fragmentation influences by comparing the results obtained with these two fundamentally different postionization techniques. It is found that the cluster yield distributions determined with both methods are similar. More specifically, all relative cluster yields agree within a factor of two or less, the only exception being the dimers where the deviation amounts to a factor of less than four. This result appears to be very encouraging, since it provides strong indication that the mass spectra measured with both postionization techniques closely represent the true neutral particle densities within the ionization region and, in particular, are not dominated by fragmentation.

## Acknowledgement

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