FORMATION OF SPUTTERED SEMICONDUCTOR CLUSTERS

R. Heinrich and A. Wucher

Fachbereich Physik, Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, FRG

1. Introduction
Bombardment of solid surfaces by energetic particles causes the release of atomic and molecular species. While ionic molecules are a rather common observation, e.g. in secondary ion mass spectrometry [1], the detection of neutral atoms and clusters is much more difficult. A laser beam with a high laser power density can serve as an efficient post-ionization medium, but fragmentation of clusters as a consequence of multiple photon absorption often precludes their detection. In fact, non resonant multiphoton ionization of many clusters containing more than a few atoms with laser pulses in the nanosecond range seems to be virtually impossible. On the other hand, it has been shown in a number of recent investigations, that ionization by the absorption of only one single photon allows the efficient detection of sputtered metallic clusters with relatively low fragmentation rates [2,3,4]. The key to success in these cases is the availability of intense UV or even VUV radiation with a photon energy in excess of the highest ionization potential. In our previous experiments, we have used an F₂ laser operating at a wavelength of 157 nm (hv = 7.9 eV) in order to detect Agₙ, Alₙ, Taₙ, and Nbₙ clusters sputtered from the respective metallic samples [5]. In the present work, we try to extend this type of investigations to clusters which are formed during sputtering of a semiconductor surface. Although it has been shown that mass spectra of Siₙ or Geₙ cluster beams may be fragmentation dominated even under single photon ionization conditions [6], we will demonstrate that efficient photoionization of both germanium atoms and clusters is possible and can even be saturated at moderate laser power densities, without the indication of significant fragmentation. This allows the determination of the relative yields of sputtered clusters from the measured data without prior knowledge of the photoionization cross sections.

2. Experimental
A detailed description of the apparatus used in this study has been given previously [2,7,8]. In brief, the <111> surface of a Germanium single crystal is bombarded under 45° with 5 keV argon ions. Prior to each experiment, the sample was irradiated for a time interval which is long enough to completely amorphize the surface [9]. During the mass spectrometry experiment, the Ar⁺ beam is operated in a pulsed mode. During the ion pulse, the sample was kept at a negative potential in order to prevent positively charged ionic species from leaving the surface. Sputtered neutral particles which are ejected from the surface are ionized by a pulsed laser beam directed closely above and parallel to the sample surface. The photoions created this way are extracted
toward a reflectron-type time-of-flight mass spectrometer (TOF-MS) by an electric field of approximately 215 V/mm which is switched on shortly (~50 ns) after the laser pulse.

The ionizing laser employed in the present experiments is a conventional excimer laser (Lambda Physik model LPX 120i) operated with F₂/He, which produces pulses of about 4 mJ energy and about 20 ns duration at a wavelength of 157 nm. The output beam was coupled into the ultrahigh vacuum (UHV) chamber housing the TOF experiment by a CaF₂ window and a 200 mm focal length CaF₂ lens. The beam line as well as all optical elements were contained in a flow box which was flushed with dry nitrogen to transport the VUV radiation. In order to study the laser intensity dependence of the photoion signals, the pulse energy could be reduced in a controlled fashion by a stack of two variable dielectric attenuators located in front of the lens, the resulting laser intensity was monitored in vacuo by a home made photoelectric detector described elsewhere /10/.

The laser was fired about 20 ns after the end of the primary ion pulse. The primary ion pulse length τ was chosen to be long enough (5 µs) to ensure that a further increase of τ did not increase the measured signals. Hence, particles of all emission velocities are present in the ionization volume and the measured signal represents the total number density of the corresponding sputtered neutral species integrated over its entire velocity distribution. Furthermore, the laser beam was shaped to a cross section of 1.7 × 0.6 mm² in directions along and perpendicular to the sample surface, respectively, and positioned at a distance of 0.7 mm above the surface. Under these conditions, the spatial extension of the laser beam is comparable to the volume accepted by the TOF-MS, and transport of particles into and out of the ionization volume during the laser pulse can be neglected.

3. Results and discussion

Fig. 1 shows a mass spectrum of sputtered neutral germanium clusters taken at a peak laser power density of about 3×10⁷ W/cm² where the ionization of all clusters is largely saturated (see below). It is seen that the signal detected for germanium atoms by far dominates the measured spectrum. For a quantitative interpretation of the measured signals it is important to study their dependence on the peak power density \( P_L \) of the ionizing laser. Fig. 2 shows the laser intensity dependence of the measured total signals (i.e. the signal integrated over the entire isotopic mass distribution of a certain cluster size). In the regime of low \( P_L \), all signals rise linearly with increasing \( P_L \), as is expected for a single photon absorption process. For higher laser power densities the signals reach a constant level, which indicates that the ionization process is saturated and all sputtered neutral particles interacting with the laser are post-ionized. In fact, the
measured signal can be fitted to the theoretically expected saturation behavior of the photoionization process according to

$$S(\lambda) = S_{\text{sat}}[1 - \exp(-\sigma_\lambda \frac{\rho}{n_\lambda} \Delta t)]$$  \quad (1)

where $\sigma_\lambda$ denotes the single photon ionization (SPI) cross-section and $\Delta t$ is the duration of the laser pulse. The resulting fitting curves obtained under the assumption of Eq. (1) with $\sigma_\lambda$ and the saturated signals $S_{\text{sat}}$ taken as fitting parameters are displayed as lines in Fig. 2. It should be noted that the observed agreement is not trivial, since the measurement of the saturation behavior of post-ionization processes is often corrupted by a volume effects, i.e. a laser intensity dependent variation of the effective ionization volume. As discussed in detail in ref. [2], these effects are minimized here by approximately matching the spatial laser beam profile to the restricted acceptance volume of the mass spectrometer. The values of $S_{\text{sat}}$ obtained from the fits in Fig. 2 can be used to determine the relative yields of sputtered clusters, i.e. the yields normalized to that of emitted single atoms. In the conversion it is important to note that the measured signals represent the number density of the sputtered particles within the ionization volume rather than their flux. The signals must therefore be further corrected by the mean inverse velocity of the sputtered neutral particles, which in turn can be determined from a measurement of the emission velocity distribution. A corresponding investigation of sputtered germanium clusters [11] reveals the relation

$$\left< v^{-1} \right> \propto n^{1.2}$$

Fig. 3 shows the resulting yield distribution, which can be described by a power law as a function of the cluster size. Similar power law dependencies of the relative cluster yields were also found for a number of metals like silver, aluminum, niobium, tantalum [2], copper [3] and indium [4].

A few words are in order regarding the possible role of photon induced fragmentation processes which may falsify the data depicted in fig. 3. In principle, fragmentation cannot a priori be neglected. The occurrence of multiphoton processes, in which the sputtered neutral cluster absorbs more than one photon, would clearly manifest in a decay of the measured signals towards high laser power densities. From fig. 2, it is apparent that these processes are absent in the present case. Fragmentation by absorption of a single photon, on the other hand, cannot be identified here, since it does not alter the measured laser intensity dependence. For this reason, the data depicted in fig. 3 must be regarded as lower limits to the true cluster yields.

The linear laser intensity dependence of all measured signals which is observed in the regime of low $P_\lambda$, provides further evidence, that the measured mass spectra are
not dominated by fragmentation. This finding is important, since it is in marked contrast to mass spectra measured on a supersonic Germanium cluster beam with virtually the same technique, laser and photon energy [6], where no regime of laser intensity could be found in which the measured mass spectrum was independent of \( P_L \). This difference is due to the fact that our clusters are generated by sputtering, where the number of clusters larger than a given cluster size \( n \) is always negligible compared to that of \( \text{Ge}_n \). Hence, even if all larger clusters \( \text{Ge}_{m-n} \) would be fragmented by the laser beam, the resulting contribution to the signal of \( \text{Ge}_n \) would be negligibly small. It is of note that these conditions are fundamentally different from those in a supersonic beam, where the mean cluster size can be very large.

4. Conclusion

We have studied the formation of neutral germanium clusters during sputtering of an amorphous germanium surface by laser post-ionization. By choosing a laser wavelength in the VUV spectral region, it was ensured that all sputtered species (germanium atoms and all germanium clusters) are ionized by a single photon absorption process. It is shown that under these conditions the ionization efficiency of all investigated species can be saturated. From the acquired data, it is possible to extract the relative yield of sputtered germanium clusters. As a result, we obtain a power law distribution describing the dependence of the yield on the cluster size, which is very similar to those found in investigations of metal clusters.

References