



# Mass and energy distribution of negatively and positively charged small cluster ions sputtered from GaAs(100) by 150 keV Ar<sup>+</sup> bombardment



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## ABSTRACT

Mass and energy distribution of positively and negatively charged small Ga<sub>x</sub>As<sub>y</sub> cluster ions consisting of up to six atoms sputtered from a GaAs(100) surface after 150 keV Ar<sup>+</sup> ion bombardment are reported. Positively charged ions contain a larger fraction of Ga atoms while negatively charged ions are rich in As. Measured energy distributions display a maximum at low kinetic energies of a few eV followed by a steep decrease with increasing energy which is more pronounced for larger ions.

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## 1. Introduction

Ion bombardment of solid targets results in the emission of sputtered atoms, ions and polyatomic species. Sputtering has wide-spread applications, e.g., in plasma-chemical etching processes and for the deposition of functional films [1,2]. The sputtering process is well understood and described within the collision cascade model [3,4]. Many sputtering experiments have been carried out with metals and metal alloys. In this communication we report new results of an experimental investigation of sputtering from a gallium arsenide (GaAs) surface by 150 keV Ar<sup>+</sup> ion bombardment. Gallium arsenide is an important semiconductor with applications in microelectronics and it is used to manufacture devices like light-emitting diodes, laser diodes, and solar cells [5–7].

In order to increase the understanding on sputtering and ionization processes occurring on the surface, a pure GaAs(100) surface was bombarded by 150 keV Ar<sup>+</sup> ions and the mass and energy distribution of sputtered ion species was recorded. Even though plenty of energetic ion bombardment experiments have been done on metal surfaces [8,9], detailed observations employing semiconductor surfaces are still lacking [10–15].

The energy distribution of the sputtered particle carries important information about the interaction phenomena and its ionisation. A theoretical model for the energy of ejected particles was

developed by Thompson [16,17]. Accordingly, the energy distribution of sputtered atoms is given by,

$$\frac{dN(E)}{dE} \propto \frac{E \cos \theta}{(E + E_b)^p} \quad (1)$$

where  $N(E)$  is the number of sputtered particles with kinetic energy  $E$ ,  $E_b$  is the surface binding energy,  $\theta$  is the emission angle with respect to the surface normal, and  $p \approx 3$ . The predicted energy distribution has a maximum at  $E_{\max} \approx E_b/2$  and asymptotically drops off with  $E^{-2}$  [16–18]. For sputtering of clusters composed of  $n$  atoms a narrower energy dependence with  $p \approx 3n$  has been discussed [18,19]. A statistical model for the energy distribution of sputtered clusters was derived by Können et al. [20].

Previous measurements at low bombarding energies of a few keV have shown that a significant fraction (up to about 4 %) of the sputtered Ga atoms is ionised [21]. Much smaller fractions are observed for As<sup>+</sup>, Ga<sup>−</sup>, and As<sup>−</sup> ions [14]. In general, sputtered species are in their neutral ground state, in a neutral excited state, or in an ionized state which can be positively or negatively charged. When leaving the surface, the ejected species continue for a while to interact with the surface which may involve interaction with delocalized valence electrons and/or localized core electrons [22]. Electronic friction and electron promotion processes may contribute to the exchange of electrons. Other mechanisms that are frequently discussed in this respect are resonance ionisation, resonance neutralisation, and Auger-type processes [23–25]. Within the resonance tunneling model, the escape probability  $P$  to survive in its initial charge state is derived as [24]

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$$P = \exp(-v_0/v_\perp) \quad (2)$$

where  $v$  is the velocity of the ejected ion,  $v_\perp = v \cos \theta$  is the velocity component with respect to the surface normal, and  $v_0 = A/a$  is a constant that depends on the transition rate  $A$  and the reciprocal mean interaction distance  $a$ . Experiments investigating the survival of excited states in front of solid surfaces yield typical values of  $v_0 \approx 10^4 - 10^5$  m/s [25–27] which appears reasonable if  $A \approx 10^{14} - 10^{15}$ /s and  $a \approx 1 \text{ \AA}^{-1} = 10^{10}$ /m is assumed. A more thorough derivation of the ionisation probabilities  $P^+$  and  $P^-$  of positively and negatively charged ions, respectively, and the dependency on the work function  $\Phi$  yields [28–32]

$$P^+ = \frac{2}{\pi} \exp[-(I - \Phi)/\epsilon_0^+] \quad \text{and} \quad P^- = \frac{2}{\pi} \exp[-(\Phi - A)/\epsilon_0^-] \quad (3)$$

where  $I$  is the ionisation energy,  $A$  is the electron affinity,  $\epsilon_0 = h\gamma v_\perp / C_1 \pi$  depends on  $v_\perp$ ,  $h$  is Planck's constant,  $\gamma$  is a reciprocal interaction distance, and  $C_1$  is a constant which is determined by the position in front of the surface where the effective energy difference is taken [28]. Eq. (3) predicts a velocity-dependent ionisation fraction which is in qualitative agreement with Eq. (2) and an exponential scaling of the ion yield with work function  $\phi$ . Such an exponential work function dependency was verified during sputtering of Si by  $\text{Cs}^+$  ion irradiation [15,33–37]. A different model assuming a short-lived electron–hole plasma with a temperature  $T_e$  which develops during the collision cascade yields similar expressions but with a velocity-independent  $\epsilon_0 = kT_e$ , where  $k$  is the Boltzmann constant [36,37].

In this paper we present new results for the sputtering of positively and negatively charged  $\text{Ga}_x\text{As}_y$  ions with  $n = x + y$  up to 6 by 150 keV  $\text{Ar}^+$  bombardment of a GaAs(100) surface. Mass and energy distributions of sputtered ions are reported. The results provide new insights into the sputtering of ions and the ion–surface interaction.

## 2. Experiment

The experimental details have been described previously [19]. Energetic  $\text{Ar}^+$  ions are produced in a cold Penning ion source and accelerated by a 400 kV ion accelerator. The ion beam enters the target chamber through a 3 mm (diameter) entrance orifice. The experimental chamber is maintained at a base pressure of  $8 \times 10^{-9}$  mbar. The target consists of a chemically clean and polished GaAs(100) sample which is bombarded by 150 keV  $\text{Ar}^+$  ions. It can be rotated in such a way that the angle of ion incidence can be changed [38,39]. In the present study, the ion beam hits the target at  $22.5^\circ$  with respect to the target surface normal (Fig. 1). A commercial electrostatic secondary neutral (SNMS) quadrupole mass spectrometer (HIDEN EQS) with a mass range up to 510 amu has been employed for detection of ionized species [40–42]. The mass spectrometer is equipped with an electrostatic energy analysis and operated in the pulse counting mode. The built-in energy filter is a  $45^\circ$  sector field electrostatic energy analyzer with a radius of 7.5 cm; it has an energy range of up to 100 eV per charge unit and an energy resolution of 0.25 eV (FWHM). The analyser is positioned at  $45^\circ$  with respect to the ion beam and  $30^\circ$  out of the target plane. The target is kept unbiased during the experiment and the ion beam current is maintained constant at about 2  $\mu\text{A}$  during the experiment. Singly charged positive and negative sputtered ions are observed and analysed using the EQS detector. The experiments were carried out at room temperature.

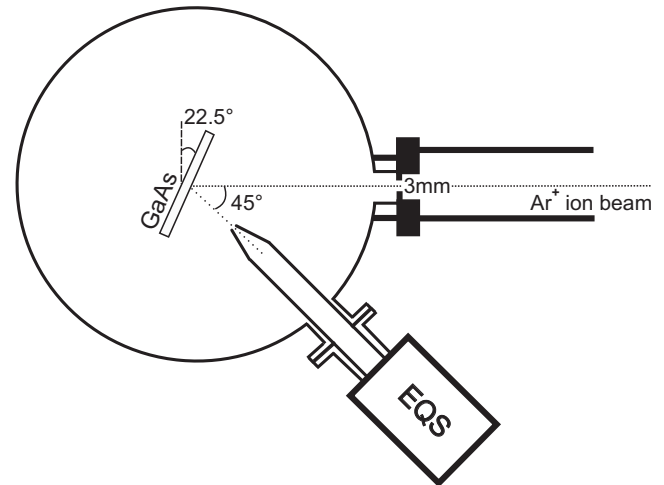


Fig. 1. Experimental set-up (schematic).

## 3. Results

### 3.1. Mass distribution

Measured mass distributions of positively and negatively charged  $\text{Ga}_x\text{As}_y$  ions sputtered by 150 keV  $\text{Ar}^+$  ion bombardment are displayed in Figs. 2 and 3. GaAs is composed of two stable  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  isotopes with mass numbers  $m = 69$  ( $a = 30.05\%$ ) and  $m = 71$  ( $b = 19.95\%$ ), respectively, and one  $^{75}\text{As}$  isotope with mass number  $m = 75$  ( $c = 50\%$ ), where  $a$ ,  $b$ , and  $c$  are relative abundances (Table 1). The mass spectrum of positively charged monomers shows two peaks at mass numbers  $m = 69$  and  $71$  which correspond to  $^{69}\text{Ga}^+$  and  $^{71}\text{Ga}^+$  ions. By contrast, the mass spectrum of negatively charged monomers is dominated by a single major peak at mass number  $m = 75$  corresponding to  $^{75}\text{As}^-$  ions. The mass spectrum of positively charged dimers with two atoms is composed of  $\text{Ga}_2^+$  ions at  $m = 138$ ,  $140$  and  $142$  while the mass spectrum of negatively charged dimers is dominated by  $\text{GaAs}^-$  ions at  $m = 144$  and  $146$  and  $\text{As}_2^-$  ions at  $m = 150$ . The mass spectrum of positively charged trimers with three atoms is dominated by  $\text{Ga}_3^+$  ( $m = 207$ ,  $209$ ,  $211$ ,  $213$ ) and  $\text{Ga}_2\text{As}^+$  ( $m = 213$ ,  $215$ ,  $217$ ) ions. Mass spectra of negatively charged trimers display pronounced peaks of  $\text{Ga}_2\text{As}^-$  ( $m = 213$ ,  $215$ ,  $217$ ),  $\text{GaAs}_2^-$  ( $m = 219$  and  $221$ ), and  $\text{As}_3^-$  ( $m = 225$ ) ions.

The main peaks in the mass spectra of positively or negatively charged  $\text{Ga}_x\text{As}_y$  ions with four atoms ( $x + y = 4$ ) are positively charged  $\text{Ga}_4^+$  ions at  $m = 276$ ,  $278$ , and  $280$ ,  $\text{Ga}_3\text{As}^+$  or  $\text{Ga}_3\text{As}^-$  ions at  $m = 282$ ,  $284$ , and  $286$ ,  $\text{Ga}_2\text{As}_2^+$  or  $\text{Ga}_2\text{As}_2^-$  ions at  $m = 288$ ,  $290$ , and  $292$ , and negatively charged  $\text{GaAs}_3^-$  ions at  $294$  and  $296$  (Table A1). Neither  $\text{As}_4^+$  nor  $\text{As}_4^-$  ions have been detected (Fig. 3).

Mass spectra of positively or negatively charged cluster ions with five atoms ( $x + y = 5$ ) are dominated by  $\text{Ga}_4\text{As}^+$  ions at  $m = 351$ ,  $353$ ,  $355$ , and  $357$  or  $\text{Ga}_3\text{As}_2^-$  ions at  $m = 357$ ,  $359$ ,  $361$ , and  $363$ , respectively (Table A1). Positively charged  $\text{Ga}_2\text{As}_3^+$  ions appear at  $m = 363$  and  $365$ . Lastly, the mass spectra of positively or negatively charged cluster ions with six atoms ( $x + y = 6$ ) are largely composed of positively or negatively charged  $\text{Ga}_5\text{As}$  ions in the mass number range  $m = 420$ – $430$ , positively or negatively charged  $\text{Ga}_4\text{As}_2$  ions at mass numbers  $m = 426$ – $434$ , and negatively charged  $\text{Ga}_3\text{As}_3^-$  ions at  $m = 434$ ,  $436$ , and  $438$  (Table A2). There is some evidence for the appearance of negatively charged  $\text{GaAs}_5^-$  ions at  $m = 444$  and  $446$ . Mass spectra of negatively charged  $\text{Ga}_x\text{As}_y^-$  clusters with five and, in particular, six atoms should be considered with care due to their low statistical significance (Fig. 3).

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