

## Resonantlike desorption of negative ions by core-level excitation under electron bombardment

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Electron-stimulated desorption of positive and negative hydrogen ions from hydrogenated GaAs surfaces has been studied as a function of impact electron energy. Well-defined peaks in the negative ion yield are observed at incident electron energies close to Ga and As core-level binding energies, suggesting that resonantlike core-level electronic transitions involving matrix atoms are most likely responsible for such behavior. We propose that the formation and subsequent breakup of superexcited molecular complexes containing a core hole can lead directly to the ejection of negative ions.

It is well known that both positive and negative ions can be induced to desorb from surfaces under electron bombardment by a process called electron-stimulated desorption (ESD).<sup>1,2</sup> Below about 30 eV, mostly valence-band electronic excitations initiate ion desorption.<sup>1,3</sup> Valence-band ionization which results directly in positive ion formation has been studied in most detail. Negative ions can also occur as a result of valence-band excitations. In this case, desorption originates from more complex processes involving antibonding levels and dissociation of substrate-surface molecular complexes<sup>4</sup> or charge exchange between the surface and an outgoing neutral or positive ion.<sup>5</sup>

In addition to ion desorption stimulated by valence-band excitations at low electron energies, ESD has been observed at much higher bombardment energies.<sup>1,2</sup> In these cases, sharp onsets in positive-ion desorption yield have often been found to correlate with excitations of core levels. Such behavior has been explained in terms of core-level ionization and subsequent interatomic Auger decay involving substrate atoms and adsorbates.<sup>6</sup> Only very recently have desorbing negative ions been attributed to core-level excitation processes, possibly resulting from charge-exchange processes<sup>7-9</sup> and/or involving the formation of excited substrate-adsorbate complexes.<sup>7,10</sup>

In this paper, we present an observation of strong resonantlike behavior in negative-ion ESD spectra at electron energies corresponding to core-level excitation of substrate atoms. Furthermore, comparison of the predominant resonance behavior in negative-ion yields with the threshold behavior for positive ions suggests that ion desorption occurs via distinctly different multistep processes in each case.

In this study, both positive and negative hydrogen ion yields were measured as a function of primary electron-beam energy from (100) GaAs samples previously exposed to a hydrogen plasma, below its visible part, for 10 min at 380 °C. Secondary ion mass spectrometry (SIMS) measurements confirmed that plasma exposure had enriched the surface region with both hydrogen and oxygen. From elastic recoil analysis using 2.5-MeV He ions, a hydrogen concentration in the near surface region of about 7–8 at. % was

estimated. The ESD experiments were performed in a quadrupole-type ion microprobe (Riber MIQ 256). The base pressure in the analysis chamber was  $2 \times 10^{-10}$  Torr and increased by a factor of 2–3 during electron bombardment. The electron beam, which can be focused to a spot of area less than 1 mm<sup>2</sup>, impacts at about 45° with respect to the sample surface normal. Electron energy was varied from 5 to 500 eV and both negative and positive ions at  $m/e=1$  (representing hydrogen) were collected by a high sensitivity SIMS quadrupole analyzer. A bias of 30 V (negative for

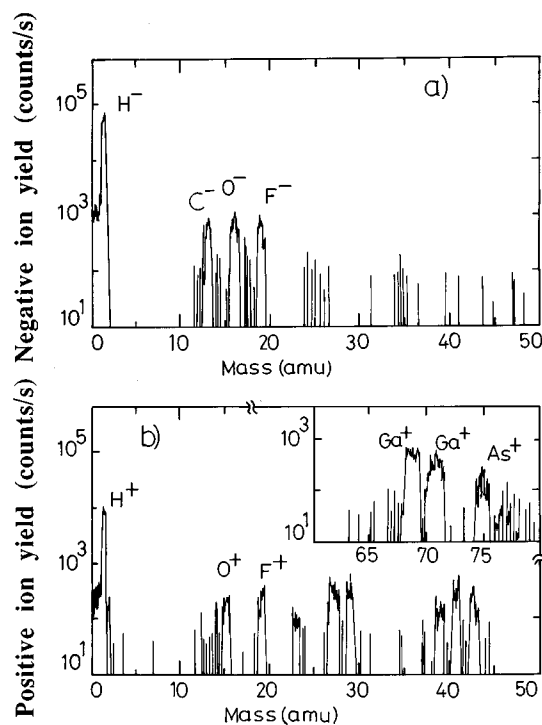


FIG. 1. (a) ESD negative-ion mass spectrum from hydrogenated GaAs, obtained by 300-eV electron bombardment; (b) positive-ion mass spectrum from the same sample under 400-eV electron bombardment. The inset shows Ga<sup>+</sup> peaks at 69 and 71 amu and As<sup>+</sup> peak at 75 amu.

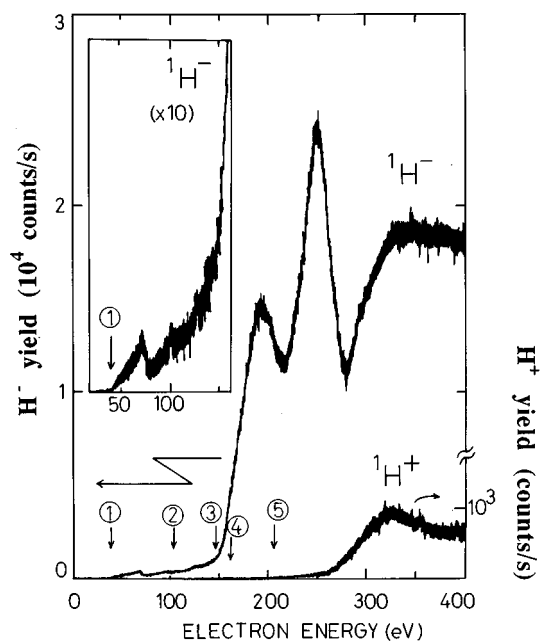


FIG. 2. Desorption yields of  $\text{H}^-$  and  $\text{H}^+$  from hydrogenated GaAs as a function of electron-beam energy. Binding energies of some arsenic and gallium core levels (with respect to the Fermi level) are indicated by arrows: (1) As 3d, (2) Ga 3p, (3) As 3p, (4) Ga 3s, and (5) As 3s. Inset shows the low-energy region on an expanded scale.

negative ions and positive for positive ions) was applied to the sample holder to obtain improved sensitivity and dynamic range for emitted secondary ions. In the field-free experiments, only the high-intensity structure is observed in the ESD spectra. Biasing is a standard method for enhancing sensitivity and is regularly used to extract energy thresholds in ESD.<sup>7–11</sup> The electron gun and optics used for electron bombardments (Riber CER 306 Auger and low-energy electron diffraction grazing angle electron gun) were not useful at electron energies below about 40 eV as a result of very small currents in the nA range.<sup>12</sup> In the 100-eV range, however, typical currents of 1–10  $\mu\text{A}$  into a spot size of a few  $\text{mm}^2$  can be routinely achieved.

Figure 1 shows typical ESD mass spectra from hydrogenated GaAs. The negative-ion spectrum in Fig. 1(a), taken for 300-eV electrons, is dominated by  $\text{H}^-$  and  $\text{O}^-$  signals, but  $\text{C}^-$  and  $\text{F}^-$  were also observed. For the positive-ion spectrum in Fig. 1(b), where the incident electron energy was 400 eV,  $\text{H}^+$ ,  $\text{O}^+$ , and  $\text{F}^+$  signals were found. It is also interesting to note that both  $\text{Ga}^+$  (two isotopes) and  $\text{As}^+$  ions were observed in the mass spectrum [inset in Fig. 1(b)].

ESD yields for  $\text{H}^-$  and  $\text{H}^+$  are shown in Fig. 2 as a function of electron-beam energy. The energy scale has been corrected for the applied bias voltage and the work function of the W filament ( $\sim 5$  eV) of the gun. At electron energies above 300 eV, both  $\text{H}^-$  and  $\text{H}^+$  yields rise to a plateau or broad maximum, indicative of threshold behavior previously observed in other systems.<sup>7–11</sup> The negative-ion spectrum exhibits interesting structure at electron energies less than about 300 eV, where well-defined peaks in yield are observed. Such strong structural features at high incident electron energies have not previously been observed, although

TABLE I. Comparison of core-level binding energies with respect to Fermi level (Ref. 14) with leading edges of all observed peaks in yield for negative hydrogen ions. The electron level numbers correspond to the peak numbers in Fig. 2.

Electron level	Binding energy (eV)	Leading edge energy (eV)
(1) As 3d	43–46	45
(2) Ga 3p	105–108	115
(3) As 3p	143–148	145
(4) Ga 3s	160	155
(5) As 3s	207	210

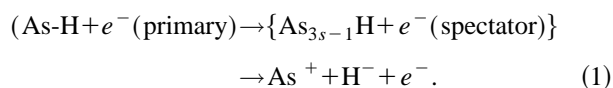
some less pronounced structures have been found in ESD of  $\text{H}^-$  from amorphous hydrogenated silicon ( $a\text{-Si:H}$ ).<sup>13</sup>

As indicated in Fig. 1, our GaAs surface has oxygen, carbon, and fluorine present, in addition to hydrogen and matrix atoms Ga and As. However, when we consider the correlation of our observed yield increases with core-level energies of these elements, our data appear to indicate a strong role for the matrix atoms As and Ga. For example, the onset of the peaks appears to correlate well with core-level binding energies of As and/or Ga (labeled by arrows in Fig. 2). Indeed, the leading edge of the three strongest  $\text{H}^-$  peaks in Fig. 2 correlate best with As-related core levels (see Table I), namely, As 3d at 43 eV, As 3p at 143 eV, and As 3s at 207 eV.<sup>14</sup> Therefore, we speculate that such correlations in Fig. 2 imply that  $\text{H}^-$  desorption arises primarily from excitation and breakup of As-H bonding complexes. This is interesting since Auger electron spectroscopy and x-ray photoelectron spectroscopy measurements indicated that the topmost layers were close to stoichiometric (1 Ga:1 As). This could imply preferential bonding of H to As or, alternatively, different total cross sections for resonant desorption of  $\text{H}^-$  from As-H and Ga-H bonding sites.

We would like to point out here that the electron-beam current in our gun changes continuously with the electron energy.<sup>12</sup> While this change does not affect the threshold behavior and the general shape of desorption curves, it does contribute to higher ion yields at higher impact energies. As the electron current increases for a factor of  $\sim 10$  when the electron energy changes from 70 to 200 eV and for an additional factor of  $\sim 1.7$  when the energy changes from 200 to 250 eV, the intensities of  $\text{H}^-$  peaks at  $\sim 180$  and 250 eV are, in fact, the same, and they are only about ten times higher than the intensity at the 70-eV peak.

Such strong resonantlike behavior as illustrated in Fig. 2 has not previously been observed for core-level excitation and negative-ion desorption under electron bombardment. We offer the following speculative explanation for this behavior, using the As 3s core-level excitation as an example. The first step in the desorption process is core-level excitation of the 3s level of As bonded to H which is stimulated by a primary electron impact of just sufficient energy to induce excitation. Under such conditions, a core hole is created, but the excited core electron may not have sufficient energy to escape from the atom. Rather, it could be trapped as a “spectator” within an empty (Rydberg) state above the Fermi level. Alternatively, if the incident electron loses almost all of its energy in exciting a core-level process, it can then have

a high probability for resonantlike capture by the excited molecule's potential well in a manner analogous to ESD at low electron energies.<sup>4</sup> As a result, a superexcited molecular complex  $(As_{3s-1}H+e^-)^*$  may be formed. During dissociation of this excited complex, the "spectator" electron (which may be either the excited core electron or the captured incident electron) may attach itself to the electronegative component of the complex to create a negative desorbing ion ( $H^-$ ). This process assumes that the lifetime of the excited complex is sufficiently long to permit electron attachment. Such a multistep sequence may be written as follows:



The appearance of  $As^+$  ions in the ESD spectra [Fig. 1(b)] is also consistent with this process. Other peaks from Fig. 2 can similarly be explained in terms of the dissociation of appropriate excited complexes formed initially by specific core-level excitation of either As or Ga. Another desorption channel, which would account for the sharpness of resonantlike features, is also possible: both the incident electron and the excited core electron may simultaneously participate in the desorption process, i.e., they may both be trapped in a quasibound state of the excited molecular complex. During dissociation of this complex, one of the "spectator" electrons may attach itself to the hydrogen atom to create a negative desorbing ion.

A similar mechanism to that described by relation (1) has recently been proposed to explain  $O^-$  formation during photon-induced fragmentation of gas-phase  $SO_2$  molecules.<sup>15</sup> In the previous reports of negative-ion desorption (threshold behavior) resulting from core-level excitation processes in solids, a charge-exchange process between desorbing positive ions and the surface was suggested as a likely mechanism for  $O^-$  desorption from  $SiO_2$  (Refs. 7 and 8) and

$Y_xBa_{1-x}Cu_yO_{1-y}$  superconductors<sup>9</sup> and  $H^-$  desorption from  $\alpha$ -Si:H.<sup>13</sup> At incident electron energies higher than core-level energies, the probability for capture of the incident electron or the excited electron is much lower. In this case, there are no spectator electrons available for attachment to an electronegative adsorbate species and the probability of negative-ion formation, directly upon dissociation, is expected to be low. Consequently, the dissociation of an excited molecular complex formed at a well-defined incident electron energy is a process entirely consistent with the resonantlike behavior shown in Fig. 2.

The data displayed in Fig. 2 clearly suggest two dominant core-level processes which initiate desorption of hydrogen ions from GaAs. Negative-ion ejection below 300 eV is dominated by resonantlike behavior, whereas positive-ion ejection and negative-ion ejection above 300 eV are predominantly of threshold behavior. In this latter case we suggest, consistent with previous reports,<sup>7-10</sup> that the negative-ion emission is dominated by charge-exchange process involving electron capture at the surface by desorbing positive ions and neutrals.

In conclusion, we have demonstrated that ESD of negative adsorbate ions can originate from strong resonantlike core-level excitation processes involving substrate-adsorbate molecular complexes. Furthermore, our data clearly indicate that there are several multistep channels for positive- and negative-ion desorption, all of which can be initiated by core-level excitation and/or ionization of a substrate atom bonded to an adsorbate atom. Consequently, positive or negative ESD yield curves can be rich in structure, indicative of the onset of particular core-level excitation process initiated by electron impact. The ultimate desorption yield depends on the primary electron energy, availability of secondary electrons, interaction/decay cross sections, and lifetimes of intermediate states.

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