Electron stimulated desorption of negative and positive hydrogen ions from hydrogenated silicon surfaces

A. Hoffman and M. Petravić*
Chemistry Department and The Solid State Institute, Technion, Haifa 32000, Israel
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Electron-stimulated desorption of negative and positive hydrogen ions from hydrogenated amorphous silicon (*a*-Si:H) surfaces has been studied as a function of incident electron energy. Well-defined thresholds for emitted ions are observed at electron energies close to Si core-level binding energies, suggesting that the core-level electronic transitions are most likely responsible for emission of both negative and positive hydrogen ions. In addition to thresholds, the negative-ion yield, studied from both *a*-Si:H and hydrogenated SiO_2 surfaces, exhibits some resonantlike features, indicating that some other, multistep channels for negative-ion desorption may also be activated. It has been also suggested that negative-ion formation may follow emission of secondary electrons.

The desorption of ions by low-energy electron bombardment, known as electron stimulated desorption (ESD), represents a useful tool for characterization and modification of solid surfaces.[1] Several models have been proposed for ESD from ionic and covalent surfaces. Although these differ in detail, all models consider primary electronic excitations, the relaxation of which results in the breaking of chemical bonds and desorption of neutral and ionic species from the surface.[1,2] For electron energies below about 30 eV, ion desorption is initiated predominantly by valence-band excitations. Valence-band ionization, which results directly in positive-ion formation has been studied in the most detail.[1,3] However, negative ions can also be observed in the low-energy regime and they originate from more complex processes involving unoccupied electronic states via electron attachment.[4]

It now appears that, in many cases, the valence excitation mechanism plays a minor role in the desorption of positive ions, as a growing number of experiments show dominant thresholds at much higher energies related to the excitation of core levels.[5] Only very recently have desorbing negative ions been attributed to core-level excitation processes, possibly involving the formation of excited molecular complexes and/or charge-exchange processes.[6–9]

In this paper, we report on ESD of negative and positive hydrogen ions from the surface of a hydrogenated amorphous silicon sample (*a*-Si:H). Onsets observed in the positive-ion yield were related to the core-level binding energies of substrate atoms. For negative ions, resonantlike features were observed, in addition to thresholds, suggesting that the desorption of hydrogen ions may occur via several different, multistep channels.

The *a*-Si:H films were prepared by the glow discharge technique in a system described previously.[10] A film of thickness of about 1500 Å was deposited on Si substrate at 230 °C and 0.2 Torr using silane. The deposition rate was 1.5 Å/sec. The absolute hydrogen concentration in the film of 21 ± 2 at % was determined by the elastic recoil analysis (ERA), using 2-MeV helium ions. Figure 1 shows the number of counts, recorded by a Si detector, as a function of proton energy, together with the corresponding H concentration as a function of depth. For the ERA simulation, we used a general purpose nuclear reaction analysis program described in Ref. 11.

All ESD experiments were performed in a quadrupole-type ion microprobe (Riber MIQ 256) equipped with an electron source (Riber CER 306 Auger and electron-energy-electron-diffraction grazing angle electron gun) under conditions described in a previous publication.[7] The base pressure during analysis was in the low 10^{-10} Torr range. In the 100-eV range, typical electron currents of 1–10 μA, focused to a spot of $\sim$1 mm^2, can be routinely achieved.[12] The quadrupole count rate for each ion was maximized separately and taken from the peak in the energy distribution by biasing the sample holder to typically $+/-15$ V for positive and negative ions, respectively.

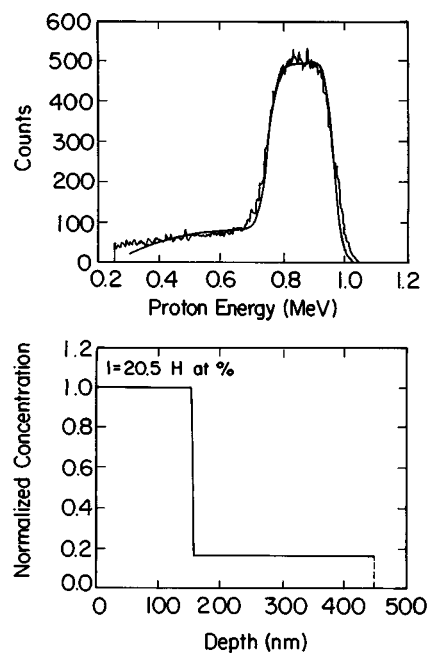

FIG. 1. ERA spectrum for intrinsic *a*-Si:H film on silicon and the corresponding, derived H concentration vs depth profile.

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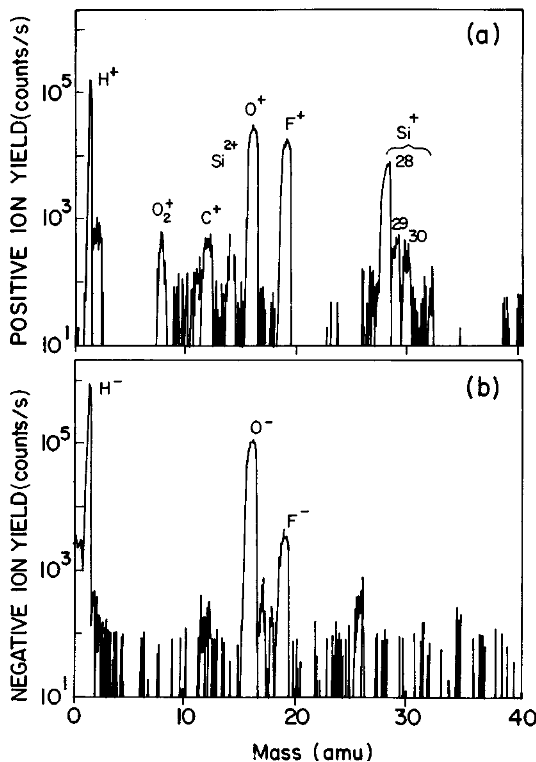

FIG. 2. (a) ESD positive-ion mass spectrum from a-Si:H, obtained by 400-eV electron bombardment; (b) negative-ion mass spectrum from the same sample under 500-eV electron bombardment.

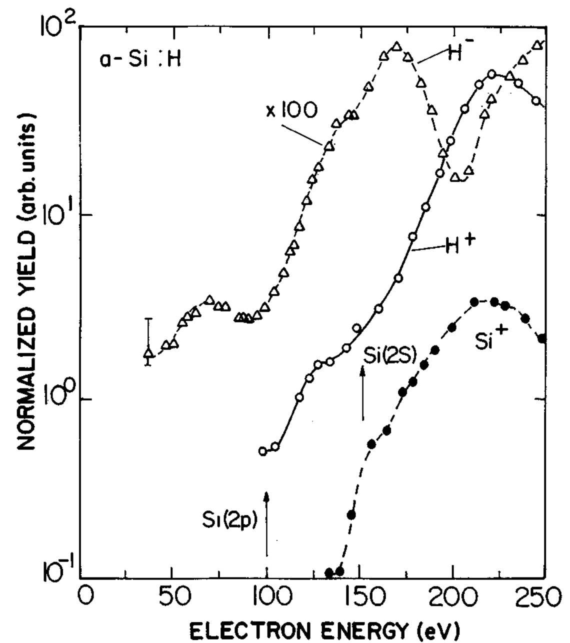

FIG. 3. Desorption yields of Si^+, H^+, and H^- from a-Si:H, as a function of electron-beam energy. Binding energies of Si $2p$ and $2s$ core levels are indicated by arrows.

The ESD data are summarized in the next few figures. Typical positive- and negative-ion mass spectra from the a-Si:H surface are shown in Fig. 2. In the positive spectrum [Fig. 2(a), 400-eV electron bombardment], in addition to hydrogen ions (1 amu) and three silicon isotopes (28, 29, and 30 amu, respectively), we have observed some anion-related peaks, such as O^+ and C^+, multiply charged ions, such as Si^{2+} and O^{2+}, and the ever present F^+. The negative spectrum [Fig. 2(b)] obtained by 500-eV electron bombardment, is dominated by H^-, O^-, and F^- peaks at 1, 16, and 19 amu, respectively. Oxygen peaks are more likely related to the native oxide at the surface, while carbon and fluorine represent the most common contaminants on semiconductor surfaces.

Figure 3 shows representative Si^+, H^+, and H^- desorption curves as a function of bombarding electron energy in the 20–250-eV range. The energy scale was corrected for both the bias voltage and the work function of the W filament (~5 eV) of the electron gun, while the ion yield was normalized by the electron current measured on the sample holder.[12] Both H^+ and H^- curve exhibit thresholds at ~95 and ~145 eV. The 145-eV threshold is followed by maxima at 170 and 220 eV for negative and positive ions, respectively. There is an additional threshold for negative ions at about 200 eV. The negative-ion curve also exhibits two resonantlike features following the thresholds at 31 and 145 eV and peaking at about 70 and 170 eV, respectively. No positive-ion signal was detected below 100 eV, due to the low ion yields and/or limitations of the source used for electron bombardment.[12]

The thresholds in H^+ are most likely related to the Si $2p$ (~100 eV) and Si $2s$ (~150 eV) core-level binding energy. Such threshold behavior is indicative of a desorption mechanism involving Auger decay of a core hole in a covalent Si-H bond. This process may lead to a localized two-hole ($2h$) final state in the bonding orbital and desorption of H^+ via unscreened hole-hole repulsion.[14] We note here that our H^+ data (Fig. 3) are in good agreement with the total ESD cross section reported in Ref. 13, for deuterium on Si(111) surface.

A close similarity between H^+ and Si^+ desorption curves (see Fig. 3) points to another desorption channel, which may account for ESD of both H^+ and Si^+. As reported previously for SiO_2 surfaces,[7,16] the electron bombardment can produce excited Si atoms, carrying $2p$ ($2s$) holes. In the case of a-Si:H, it is likely that some excited Si atoms carry H atom with them and are emitted as $(SiH)^+$ complexes. An Auger deexcitation of Si holes in vacuum produces $(SiH)^{2+}$ molecules, which will readily dissociate to Si^+ and H^+. This mechanism has previously been proposed to explain the emission of H^+ from a-Si:H under noble-gas-ion bombardment.[15] Our data on H^+ and Si^+, shown in Fig. 3, are consistent with such a picture. We would like to point out here that the lowest threshold for Si^+ occurs at ~135 eV, delayed from the Si $2p$ threshold by ~35 eV. This is consistent with the measurements on SiO_2,[7,16] for which similar shifts were explained in terms of some additional, multielectron excitations leading to delayed onsets in Si^+.[16]

Turning now to desorption of H^-, we note that thresholds at ~95 and ~145 eV suggest that the core-level ionization on Si site also plays an important role in H^- desorption. As an Auger process produces, in general, two holes in the bonding orbital, it cannot by itself account for the direct formation of negative ions. However, the charge state of a particle leaving the surface may well be quite different from the charge state immediately after the relaxation process.[9] Core hole relaxation process may be responsible for breaking

the Si-H bond, while the outgoing neutral and positively charged H atoms may capture electrons in the surface region and desorb as negative ions. This process assumes that the ejected particles remain in the surface region long enough (i.e., to have low kinetic energies) to be able to recapture electrons. It also requires an environment rich in low-energy secondary electrons. As the secondary electron emission for most materials consists mostly of low-energy (0–10 eV) electrons and exhibits maximum for electron bombardment in the 100–300 eV range, one expects the most efficient charge transfer, i.e., the highest negative-ion yield, in the 100–300-eV range. This is consistent with our results for H^- shown in Fig. 3.

On the other hand, resonantlike features in the H^- desorption curve (see Fig. 3) indicate that some more complex processes can be active in ESD of negative ions, possibly involving formation and subsequent breakup of superexciting molecular complexes containing a core hole.[6,8]

We have also examined desorption of H^- from a hydrogenated SiO_2 surface.[17] Figure 4 shows the H^- yield from SiO_2 as a function of electron energy. We note a close similarity with the H^- desorption curve from a-Si:H, shown in Fig. 3. The lowest thresholds in the H^- yield from SiO_2 (Fig. 4) occur in the 20–30-eV region, corresponding to the O $2s$ core-level excitations. This indicates, once again, that the relaxation of core holes, followed by some charge-transfer processes in the near surface region, may account for the negative-ion desorption. At the same time, a threshold of ~23 eV is expected from a localized two-hole state in the Si-H bonding orbital: approximately 14 eV is required to create two holes in the Si-H bond, while hole-hole repulsion contributes an additional 9 eV.[18] However, as mentioned above, this process may account for the bond breaking and the direct formation of positive ions, while the charge state of the emitted particle depends on the particle's kinetics and the probability of the charge-transfer processes.

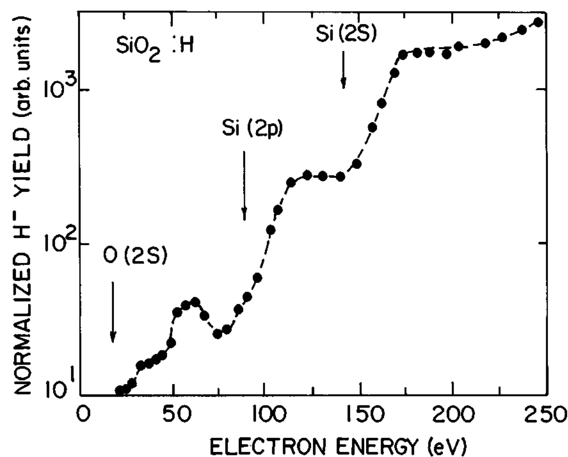

FIG. 4. H^- desorption yield from a hydrogenated SiO_2 surface, as a function of electron energy. Binding energies of some Si and O core levels are indicated by arrows.

In conclusion, we have examined desorption of negative and positive hydrogen ions from a-Si:H surfaces for electron energies in the 0–250-eV range. Desorption yields display distinctive thresholds at energies related to core-level excitations of Si atoms. We have argued that the ESD of both negative and positive hydrogen ions is mediated by core-level ionization of substrate atoms, possibly involving relaxation through charge-transfer processes and, in the case of negative ions, charge exchange in the near surface region.

*Permanent address: Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra Australian Capital Territory 0200, Australia.

[1] For review, see, for example, R. D. Ramsier and J. T. Yates, Jr., Surf. Sci. Rep. **12**, 243 (1991).

[2] P. Avouris and R. E. Walkup, Annu. Rev. Phys. Chem. **40**, 173 (1989).

[3] D. Menzel and R. Gomer, J. Chem. Phys. **41**, 3311 (1964); P. A. Redhead, Can. J. Phys. **42**, 886 (1964).

[4] L. Sanche, Phys. Rev. Lett. **53**, 1638 (1984); H. Sambe, D. E. Ramaker, L. Parenteau, and L. Sanche, *ibid.* **59**, 236 (1987); **59**, 505 (1987).

[5] R. A. Baragiola and T. E. Madey, in *Interaction of Charged Particles with Solids and Surfaces*, Vol. 271 of *NATO Advanced Study Institute, Series B: Physics*, edited by A. Gras-Marti (Plenum, New York, 1991), p. 31.

[6] A.-M. Lanzillotto, T. E. Madey, and R. A. Baragiola, Phys. Rev. Lett. **67**, 222 (1991).

[7] M. Petravić, Phys. Rev. B **48**, 2627 (1993).

[8] M. Petravić and J. S. Williams, J. Vac. Sci. Technol. A **13**, 26 (1995).

[9] A. Hoffman, S. D. Moss, P. J. K. Paterson, and M. Petravić, J. Appl. Phys. **78**, 6858 (1995).

[10] D. Haneman and D. H. Zhang, Phys. Rev. B **35**, 2536 (1987).

[11] A. Hoffman, D. D. Cohen, and A. Croal (unpublished).

[12] M. Petravić and J. S. Williams, Surf. Sci. **249**, 215 (1991).

[13] M. Matsunami, Y. Hasebe, and N. Itoh, Surf. Sci. **192**, 27 (1987).

[14] D. E. Ramaker, C. T. White, and J. S. Murday, Phys. Lett. A **89**, 211 (1982).

[15] K. Wittmaack, Phys. Rev. Lett. **43**, 872 (1979).

[16] R. A. Baragiola, T. E. Madey, and A.-M. Lanzillotto, Phys. Rev. B **41**, 9541 (1990).

[17] M. Petravić, J. S. Williams, and W. C. Wong, Nucl. Instrum. Methods Phys. Res. Sect. B **78**, 333 (1993).

[18] H. H. Madden, D. R. Jennison, M. M. Traum, G. Margaritondo, and N. G. Stoffel, Phys. Rev. B **26**, 896 (1982).