Ionization Mechanism of H^+ Sputtered from Hydrogenated Silicon

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(Received 3 May 1979)

The emission of H^+ sputtered from hydrogenated amorphous silicon has been studied for 3- to 30-keV noble-gas–ion bombardment. The results suggest that excited silicon atoms can be emitted as $(Si_{2p}H)^+$ molecules. Auger deexcitation in vacuum results in $(SiH)^{2+}$ which disintegrates into Si^+ and H^+ with a corresponding gain in kinetic energy due to Coulomb explosion. Direct emission of H^+ is important only at H^+ energies > 30 eV or at bombardment energies < 3 keV.

The charge state of hydrogen emerging from a solid surface has been investigated in great detail during the last few years. Increasing effort has been devoted to backscattering experiments at low energies.[1] Because of difficulties in the analysis of low-energy neutrals, charge-state fractions of hydrogen could be measured only down to ~200 eV,[1] at which energy the positive fraction of hydrogen backscattered from a clean gold surface, N^+/N_{tot}, is about 10^{-3} or less (angle of emergence 45°). Extrapolation of the results of Ref. 1 suggests that N^+/N_{tot} decreases roughly linearly towards lower energies. Accordingly, hydrogen sputtered from a solid surface should hardly be detectable in the positive charge state because the most probable energy of sputtered atoms is typically $\lesssim$10 eV. Nevertheless, rather intense emission of H^+ (and H^-) sputtered from metals of technical purity[2] or from adsorbed layers[3] has been observed in secondary-ion mass spectrometry (SIMS) experiments. SIMS depth profiling of hydrogen in silicon has been accomplished down to concentrations of 5×10^{17} atom/cm^3 in silicon.[4] Except for measurements of isotope effects,[3] however, fundamental studies of sputtered H^+ and H^- emission has not been reported to date.

In an attempt to evaluate the mechanism of H^+ secondary-ion production we have measured the projectile-energy dependence of H^+ energy spectra observed in noble-gas–ion sputtering of hydrogenated amorphous silicon. The measurements were performed in two ion microprobes of similar design.[5,6] The partial pressures of hydrogen in the differentially pumped target chambers were $\sim1\times10^{-7}$ Pa (at IBM) and $\sim4\times10^{-7}$ Pa (at GSF), respectively. The hydrogenated amorphous silicon sample (a-Si:H) was prepared by plasma decomposition of silane (SiH_4) in an rf glow discharge.[7] The hydrogen concentration was ~20 at.%.

Figure 1 shows energy spectra of H^+ emitted from a-Si:H under bombardment with mass-analyzed noble-gas ions (normal beam incidence, $\delta=0°$, takeoff angle $\varphi\simeq20°$, energy band pass of the spectrometer ~2 eV). The data were recorded under steady-state conditions, i.e., after removal of adsorbed surface layers. Variations in primary ion current density between 0.1 and 10 mA/cm^2 affected the steady-state H^+ intensity from a-Si:H only to a negligible extent (typical beam currents 0.1 to 1 μA). Depending on the primary ion energy and current density as well as on the hydrogen partial pressure, the H^+ intensity emitted from a "clean" silicon reference sample amounted to between 10^{-3} and 5×10^{-2} of the H^+ intensity from the a-Si:H sample (at all H^+ energies). Effects due to adsorption and incorporation of hydrogen from the residual gas

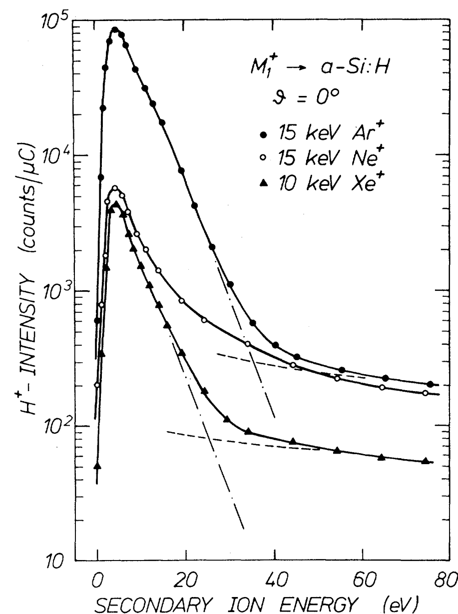

FIG. 1. Energy spectra of H^+ emitted from hydrogenated amorphous silicon under bombardment with different noble-gas ions at normal incidence.

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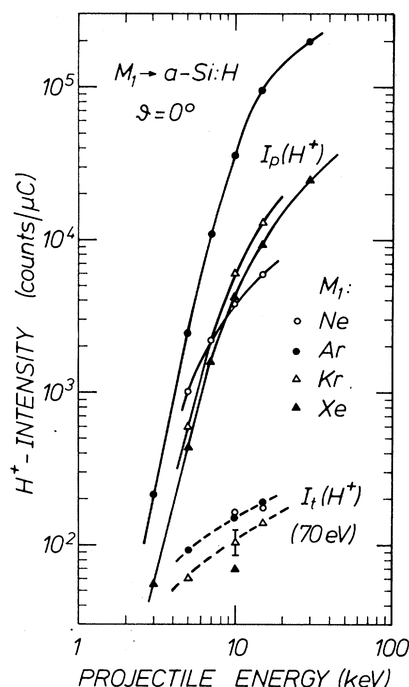

FIG. 2. Projectile-energy dependence of the H^+ intensity at the peak position (full lines) and in the tail of the energy distribution (dashed lines).

can be neglected, therefore.

It is evident from Fig. 1 that a variation in projectile energy, E_0 and/or mass, M_1, causes a pronounced change in the normalized H^+ intensity as well as in the shape of the energy spectra. Two common features are observed under all bombardment conditions. (i) The H^+ spectra exhibit a peak at low energies (~5 eV) followed by a rapid drop in intensity. (ii) Between 30 and 40 eV the steep slope changes into a rather gradually decreasing tail (or "background"). The projectile-energy dependence of the H^+ intensities at the peak, $I_p(H^+)$, and in the tail, $I_t(H^+)$, is depicted in Fig. 2. At low energies, $E_0 < 8$ keV, $I_p(H^+) \propto E_0^5$, whereas $I_t(H^+) \propto E_0^{0.7}$. The results of Fig. 2 suggest that I_t will exceed I_p below 2 keV, i.e., one produces mostly "background" intensity. As a result of limitations in beam current at low energies, reliable data could be obtained in this study only down to projectile energies of 3 keV.

In order to relate the H^+ intensities to other SIMS signals we have also measured the projectile-energy dependence of Si^+ and Si^{2+}. It was found that the respective ion yields from a-Si:H were smaller by about 20% than the yields from pure Si. Within experimental accuracy the shapes

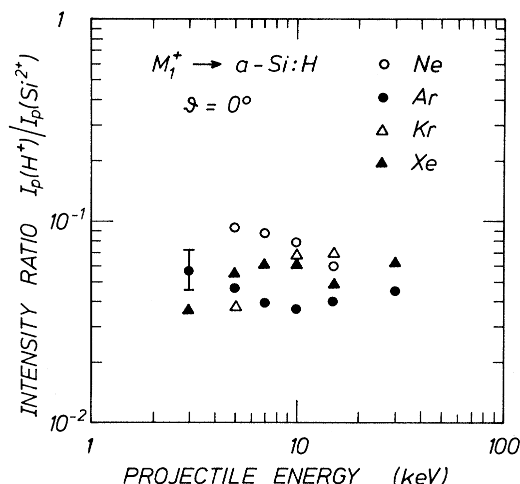

FIG. 3. Intensity ratio $I_p(H^+)/I_p(Si^{2+})$ vs projectile energy. Parameter is the projectile mass M_1.

of the energy distributions of Si^+ and Si^{2+} were not affected by the presence of hydrogen. Comparison of the peak intensities of Si^+ and Si^{2+} (peak position ~5 and ~10 eV, respectively) with $I_p(H^+)$ and $I_t(H^+)$ showed the surprising result that $I_p(H^+)$ is closely related to $I_p(Si^{2+})$ but not to $I_p(Si^+)$, the latter increasing much less rapidly with increasing projectile energy than $I_p(H^+)$. To demonstrate the correlation between $I_p(H^+)$ and $I_p(Si^{2+})$, Fig. 3 shows intensity ratios $I_p(H^+)/I_p(Si^{2+})$ versus projectile energy for bombardment with different noble gases. Clearly, $I_p(H^+)/I_p(Si^{2+})$ is largely independent of the mass and the energy of the projectile. Notice that this statement holds over an energy range within which $I_p(H^+)$ varies by more than three orders of magnitude (Fig. 2).

The quantity of interest, i.e., the positively charged fraction, $\alpha^+ = I^+/(I^+ + I^0)$, cannot be determined directly from Fig. 2 because the intensity of sputtered hydrogen atoms, I^0, is unknown. I^0 can be assumed to be proportional to the hydrogen sputtering yield, Y_H. From $I(Si^+)$ and $I(Si^{2+})$ measurements we conclude that the (partial) sputtering yields of silicon from either pure Si or a-Si:H are nearly the same so that, in steady state, $Y_H(a\text{-Si:H}) \simeq c_H Y_{Si}(\text{Si})$, where c_H is the hydrogen concentration (in at.%). In the projectile-energy range studied here, the sputtering yield of silicon, Y_{Si}, varies only very little compared to I_p^+ (Y_{Si} variation typically < factor 2).[8] Accordingly, the pronounced variations of $I_p^+(E_0)$ in Fig. 2 must be attributed mostly to α_p^+ variations (assuming that the projectile energy affects

the energy spectrum of *neutral* hydrogen only to a negligible extent). Comparison of Fig. 2 with recent results on ion-excited Auger-electron production[9] reveals striking similarities. More specifically, we have found that $I_p(Si^{2+})$ is directly proportional to the intensity of Si $L_{2,3}MM$ Auger electrons emitted from sputtered silicon atoms. $I_p(Si^{2+})$ may thus be used as a measure of the ion-excited production efficiency of $2p$ holes in silicon. On this basis, the results of Fig. 3 indicate that $\alpha_p{}^+$ is determined by bombardment-induced excitation processes rather than by neutralization effects. It is suggested that low-energy H^+ is formed in vacuum by disintegration of $(SiH)^{2+}$ subsequent to Auger deexcitation of a $(Si_{2p}H)^+$ molecule containing an excited silicon atom with a $2p$ hole. Since SiH^+ is commonly observed with high intensity in SIMS spectra, emission of $(Si_{2p}H)^+$ is also likely to take place. As a result of the large mass difference between H and Si, the maximum energy transfer, T_m, between these two atoms is small ($T_m = 0.13E_{Si}$). Accordingly, Si atoms hitting H atoms in the last encounter before leaving the surface may carry the collision partner with them.

It should be pointed out that a correlation between $I_p(H^+)$ and $I_p(SiH^+)$ was not observed. $I_p(SiH^+)$ was found to increase only very little with increasing (argon) energy (~factor 2 between 3 and 15 keV). This indicates that an excited $Si_{2p}H$ molecule usually leaves the surface in an ionized state rather than as a neutral. Accordingly, Auger deexcitation will produce $(SiH)^{n+}$ with $n=2$ (or 3). Doubly ionized molecules tend to disingrate[10,11] because relatively few bound states exist in that charge state.[12] The kinetic energy gained by Coulomb repulsion of the separated ions is typically 2–10 eV per ion[10,11] and depends upon the respective potential-energy curves. Details for the system $(SiH)^{2+}$ are not known. The measured peak position of H^+ falls into the range observed for other ions.[10,11]

More quantitative statements are not possible here because our mass spectrometer accepted H^+ ions from (nearly) all possible orientations of the $(SiH)^{2+}$ molecule. Accurate measurements of the ion energy associated with Coulomb explosion require coincidence techniques with well-defined geometry[10,11] or other sophisticated methods such as high-energy transmission of stripped molecules through foils.[13,14]

Note that the ratio of the total intensities of H^+ and Si^{2+} (i.e., the intensities integrated over the respective energy distribution) is considerably smaller than the numbers given in Fig. 3. Moreover, $I_p(Si^+)/I_p(Si^{2+}) \gtrsim 5$. Therefore, any gain in Si^+ intensity due to Coulomb explosion of $(SiH)^{2+}$ would be hardly detectable and small compared to the likely differences in sputtering yield between clean and hydrogenated silicon.

Based upon the model outlined above, one may interpret the energy spectra of H^+ in Fig. 1 as being composed of two contributions: (i) an intense distribution at low energies, peaked at ~5 eV, which is due to the disintegration of $(SiH)^{2+}$; and (ii) a "background," represented by $I_t(H^+)$, which is probably due to direct emission of H^+ from the solid. Separation into the two contributions is indicated in Fig. 1 by the dashed-dotted and dashed lines, respectively. $I_t(H^+)$ decreases very slowly with increasing H^+ energy, $I_t(H^+) \propto E^{-0.5}$. Assuming an E^{-2} energy distribution of sputtered *neutral* hydrogen,[15] we find that $\alpha^+(H)$ increases rapidly with increasing energy, $\alpha^+ \propto E^{1.5}$. Since $I_t(H^+)$ tends to decrease with increasing projectile mass (Fig. 2), projectile-hydrogen collisions seem to be mostly responsible for direct hydrogen emission (notice that recoiling hydrogen atoms can be backscattered from silicon atoms). Variations in projectile mass might also result in different degrees of preferential hydrogen sputtering.

In conclusion, intense H^+ production in noble-gas–ion sputtering of *a*-Si:H can be observed at bombardment energies at which $2p$ holes in Si are produced with high efficiency. Direct sputter emission of H^+ becomes important only at high secondary ion energies and/or low bombardment energies. Finally, we mention that a projectile-energy dependence identical to that of $I_p(H^+)$ has recently been observed for $I_p(D^+)$ in argon depth profiling studies of deuterium implanted in silicon.

I would like to thank M. H. Brodsky for providing the *a*-Si:H sample.

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Simultaneous Fermion and Boson Spin Dynamics in a One-Dimensional Antiferromagnet

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(Received 24 July 1979)

The proton NMR spin-lattice relaxation time T_1 has been measured in the spin-$\frac{1}{2}$ one-dimensional antiferromagnet (1DAF) α-*bis*(N-methylsalicylaldiminato)-copper (II) (CuNSal) at low temperatures and high fields. T_1 is dominated by electron spin fluctuations of the 1DAF, and we show that these fluctuations are described by Fermi-Dirac statistics for the one-magnon contribution to T_1 but that the two-magnon part is given by Bose-Einstein statistics.

The spin-wave excitations of ordered magnetic systems have traditionally been treated by the Holstein-Primakoff (HP) transformations[1,2]

$$S_i^z = S - a_i^\dagger a_i \tag{1}$$

in which z is the equilibrium direction of the spin $\vec{S}_i$ at the ith lattice site and $a_i^\dagger$ (a_i) is a spin-deviation creation (annihilation) operator. HP further treats the spin deviations as bosons and, to lowest order in the spin deviations, has the transverse operators $S_i^\dagger$ (S_i^-) proportional to a_i ($a_i^\dagger$). Low-temperature thermodynamics and spin dynamics have therefore been described by boson elementary excitations, and the HP treatment has remained a valid and useful description in spite of more recent developments in the theory of ferromagnets and antiferromagnets at low temperature.[2-4]

The one-dimensional antiferromagnet (1DAF) for spin $\frac{1}{2}$ is an exceptional and particularly interesting case of a strongly interacting magnetic system. First, in contrast to the basic premise of the above HP description, it has no long-range order in zero field at finite temperature. In spite of this it is still possible to treat the 1DAF by bosons provided higher-order terms are included.[4,5] However, an alternate description, which is uniquely simple for spin $\frac{1}{2}$ and 1D, is possible in terms of fermions. That is, $a_i^\dagger$ (a_i) in Eq. (1) is treated as a fermion creation (annihilation) operator and a nonlinear transformation[6] relates S_i^+ (S_i^-) to a_i ($a_i^\dagger$). As a result the *XY* model becomes exactly soluble in terms of noninteracting fermions,[6] and the isotropic Heisenberg model is quartic in the fermion operators.[7] It is clear that exact treatments in either the fermion or boson representations must ultimately produce the same result. It is not so obvious, however, which of the two pictures is more amenable to simple approximations which utilize the statistics of noninteracting fermions or bosons.

This Letter reports proton NMR relaxation measurements in a spin-$\frac{1}{2}$ Heisenberg 1DAF which are novel in that contributions from the transverse ($S_i^\pm$) and longitudinal (S_i^z) dynamical spin fluctuations have been measured separately. We further show that the transverse (one-magnon) dynamics are in agreement with the fermion picture but that the longitudinal (two-magnon) ones are better given by a boson model.

The system studied is the Cu^{2+} salt α-*bis*(N-methylsalicylaldiminato)-copper (II), referred to as CuNSal, which is a well-documented 1DAF. In an extensive work[8] elsewhere we have shown that one of the inequivalent protons is tightly coupled to a single Cu^{2+} ion. The angular and field dependence of the NMR frequency of this proton in single-crystal CuNSal was used to show that the