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Mechanism of hydrogen promotion of field ionization and a new atom-probe field-ion-microscope experiment*

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It is found that at the field strength where hydrogen promotion of field ionization occurs, the field-ion-microscope image spots flicker. This leads us to interpret the promotion effect as a field-ionization enhancement by the field adsorption of hydrogen at the apex of imaged surface atoms. A time-of-flight atom-probe experiment confirms this interpretation.

I. INTRODUCTION

The addition of a few percent of hydrogen to the helium image gas of a field-ion microscope (FIM)[1] surprisingly produces a very sharp image at about $\frac{2}{3}$ of the best image field of pure helium. This strange effect is known as the hydrogen promotion of field ionization,[2] and while it is helpful in extending high-resolution field-ion microscopy to less refractory metals,[3–5] its basic mechanism has not been fully understood. The unusually sharp definition of the promoted helium image was first assumed to be due to improved thermal accommodation when the hopping helium atom collided with chemisorbed hydrogen.[2] Later, a transfer of electronic charge from metal-surface atoms to the adjacently adsorbed hydrogen atoms was thought to produce a locally enhanced field strength at a much lower applied voltage.[6] Most recently, the promoted image was considered to be formed by the apex-field-adsorbed image gas atoms excited to higher energy states by electron showers produced by space ionization of the hydrogen gas.[7,8] Here we report some new observations, suggest a new mechanism, and show additional experimental evidence confirming a prediction of the new interpretation.

II. NEW OBSERVATIONS

Using an ultrahigh-vacuum FIM equipped with a microchannel plate we found the following new phenomena:

(i) In the narrow voltage range[6,9] where the hydrogen promotion occurs, $\Delta V/V \approx 0.025$, the image spots also flicker. The scintillations can be observed practically independent of the hydrogen partial pressure down to 10^{-7} Torr, and are very sensitive to the field strength. Thus when the applied voltage is gradually raised, the regions of flickering shift toward the lower field areas of the surface. The flickering occurs at the regions where the field strength is approximately 3.3 V/Å in the case of tungsten. (Although the average best image field of W is 4.5 V/Å, the local field around {111} regions is ~10% higher.[10]) Thus the flickering may be used as a sensitive means for mapping the relative field strength at various locations of the emitter surface. The fact that the hydrogen promotion can be observed at 10^{-7} Torr hydrogen partial pressure indicates that electron showers do not play an important role. Furthermore, with hydrogen in the system, field adsorption of helium cannot be expected because of its much smaller polarizability compared to either hydrogen atom or molecule. While the chemisorbed hydrogen may enhance the thermal accommodation of helium atoms, this mechanism cannot convincingly explain why the hydrogen promotion occurs only in a very narrow field range.

(ii) An investigation of field-ion energy distribution using the magnetic atom probe[10,11] revealed that there is neither a shift in the peak nor a broadening of the width of the field-ionization-energy distribution of the helium ions coming from a narrow surface site when promoting hydrogen is introduced. Thus there is no change in local field strength, and the helium ions always orginate in the normal ionization zone at the critical distance $x_c = (I - \phi)/F$ as determined by the ionization energy I and the work function ϕ. This observation contradicts the interpretation that a transfer of electronic charge to the adjacently chemisorbed hydrogen is responsible for the promotion effect.

(iii) At very high hydrogen partial pressure, 3×10^{-3} Torr hydrogen plus 4×10^{-4} Torr helium, a severe corrosion of the surface occurred in 5 min at the region where flickering was observed whereas other regions remained intact. The boundary between the corroded area and the undamaged area is quite sharp. This suggests two different adsorption states of the hydrogen in the two regions.

III. NEW INTERPRETATION OF THE HYDROGEN PROMOTION

Based on the observations described we propose here a new mechanism for the hydrogen promotion of field ionization. Many investigators[12–16] have concluded that at a metal surface hydrogen is chemisorbed in atomic form in possibly two differ-

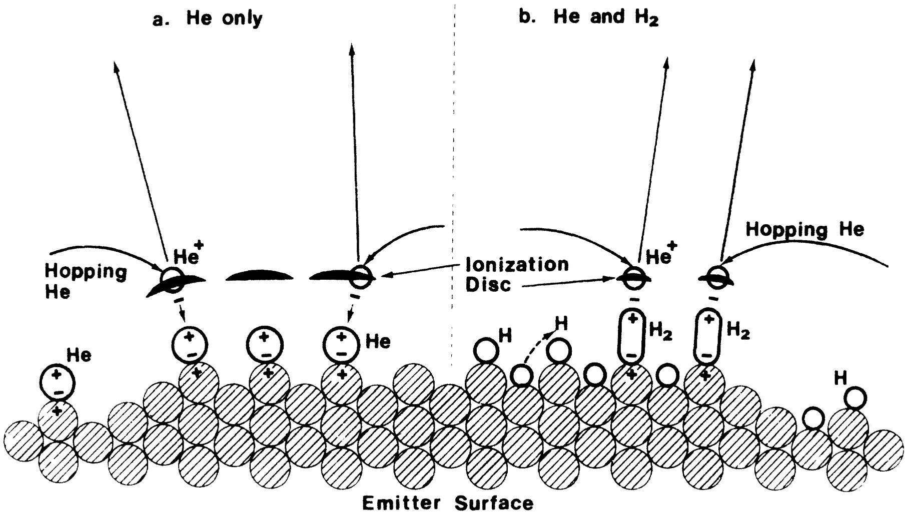

FIG. 1. Schematic of helium-ion image formation on a not closely packed metal surface, at a low field. At the left, the disk representing the ionization zone is diffuse because of the relatively large distance $x_c = (I - \phi)/F$ from the surface (≈ 6.0 Å). At the right, apex-adsorbed H_2 molecules produce a more sharply defined ionization zone and enhance tunneling probability.

ent states. An adatom is sitting on the apex of a protruding surface atom while another adatom is in a recessed position and may perform two-dimensional translations parallel to the surface. According to Mignolet,[17] and others[14] some surface sites are also covered with more weakly bound molecular hydrogen. It has also been discussed that the recessed adatom may be activated to form a hydrogen molecule with an apex adatom.[13,18,19] In the following we point out particularly the consequences of the special conditions in the FIM:

(1) At or below 78 K the metal surface becomes saturated with atomic hydrogen even at a partial pressure of 10^{-8} Torr or less. When the applied electric field at the surface is higher than about 2.9 V/Å, hydrogen can no longer be supplied from the gas phase because of a very high free-space ionization rate.[20] It can, however, be supplied by field-gradient-induced surface migration from the tip shank, as has been directly observed in the FIM.[9]

(2) When the electric field at the surface is increased to 3.3 V/Å, the recessed adatom may flip over to combine with an already present apex adatom (this may be a chemisorbed atom, or a field-adsorbed atom), forming a hydrogen molecule. The molecule will stretch along the field direction and be stabilized by the field-induced dipole-dipole interaction energy.[21–24] A change in the position of an adsorbate, from surface site to apex site, at a threshold field where the total binding energy in the field at the apex site exceeds that at a surface site, has been suggested earlier by Tsong and Müller.[24] In a more general statement, transition from one configuration to a new configuration should occur at a threshold field when the free energy of a system in the applied field becomes lower with the new configuration.

(3) As a consequence of apex field adsorption[23,24] the electron tunneling out of the image gas atom has to pass through the adsorbate, which leads to an enhancement of the field-ionization rate by either resonance[25] or exchange effects.[26] This enhancement has been experimentally verified for neon field adsorption.[27,28] For explaining hydrogen promotion we invoke the enhancement through an intermediate hydrogen molecule (Fig. 1). Its large

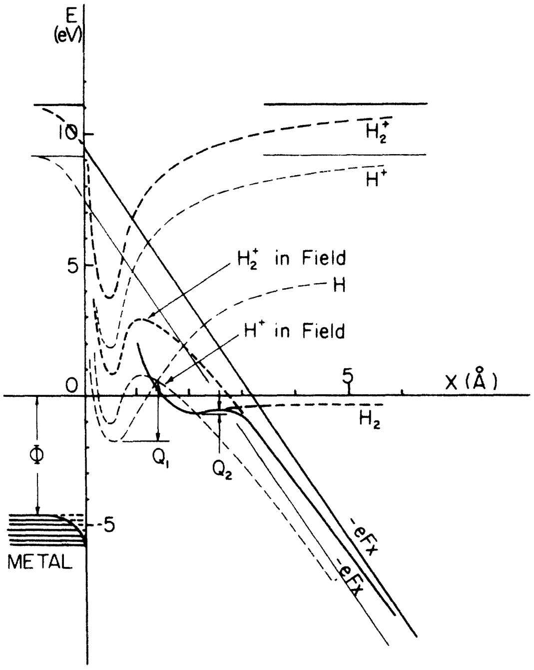

FIG. 2. Potential-energy diagram for field desorption of H and H_2 at 3.3 V/Å. The activation energy for H (Q_1) is very much larger than that for H_2 (Q_2).

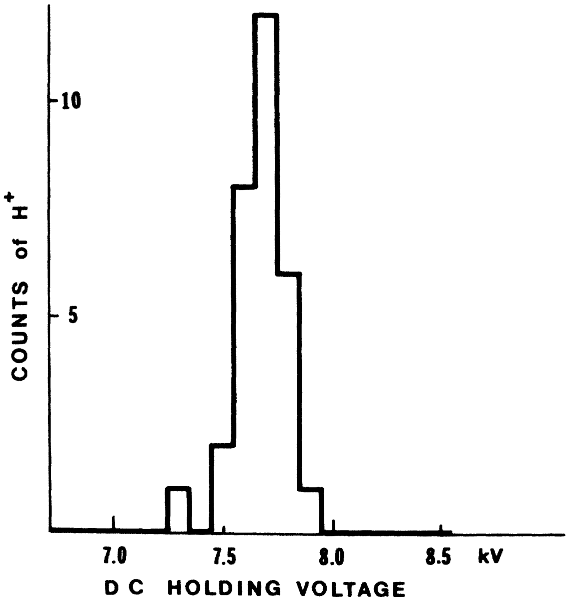

FIG. 3. Atom-probe histogram showing the appearance of H^+ ions in a narrow range of dc holding voltage exactly coinciding with the appearance of the promoted image.

dipole moment results in a strong mutual repulsion of neighboring hydrogen molecules. Thus the promoted image spot is more sharply defined due to a well localized field-ionization zone. By comparison the ionization disk above a helium adsorbate with its smaller dipole moment is more diffuse.

(4) Using the charge-exchange model of field desorption[29] and available potential-energy data,[30] it can be shown (Fig. 2) that at a field of 3.3 V/Å the activation energy of desorption is very low and the field desorption rate is very high for molecular hydrogen. Thus once a hydrogen molecule is formed at the apex of a metal atom, it may be desorbed in a short time. The flickering of the promoted image reflects the dynamic process of replenishment by field-enhanced surface diffusion and field desorption of field-adsorbed hydrogen. At fields higher than 3.4 V/Å the lifetime of the newly formed hydrogen, and also the probability that an incoming helium atom finding a field-adsorbed hydrogen are much too small to produce an appreciable enhancement of field ionization, therefore the promoted image disappears. We thus expect the hydrogen promotion to occur in a very narrow field region as is indicated by a sensitively voltage-dependent position of maximum promotion within a given net plane.[9] We are aware that the complex interplay of several processes governed by rates of unknown field and temperature dependences makes a quantitative understanding quite impossible. It is appropriate here to state our reasons for invoking the promotion as due to field adsorption of molecular hydrogen rather than atomic hydrogen. Even though our present understanding of field desorption does not allow us to calculate desorption field accurately, available methods[31] give a slightly higher desorption field for atomic hydrogen than molecular hydrogen. Thus at a field of ~3.3 V/Å, a molecular hydrogen can be formed from two flipped-over atomic hydrogens. Recently, Paulson and Schrieffer[32] conclude from a theoretical investigation that an apex chemisorbed atomic hydrogen is partially immersed in the metal atom. The desorption field of atomic hydrogen is therefore even more unlikely to be as low as 3.3 V/Å.

(5) The field-induced occurrence of single artifact vacancies[9] limited to the regions where hydrogen promotion of field ionization takes place, and an excessive vacancy formation or severe surface corrosion at high hydrogen partial pressure indicate another effect of field-adsorbed hydrogen. Obviously, the binding energy of metal atoms in the substrate is reduced, and excitation of the surface complex by the electron shower leads to field evaporation.

IV. TIME-OF-FLIGHT ATOM-PROBE EXPERIMENT

If the above mechanism is indeed correct, the following atom-probe experiment may be suggested: By maintaining a dc field at exactly the promotion field, and applying nanosecond high-voltage pulses, one must be able to detect the apex adsorbate in regions where hydrogen promotion is observed. Of course, the desorbed molecule would be seen as field-dissociated atomic ions, as it has been shown that H_2^+ ions in a field of ~3 V/Å dissociate within 10^{-14} sec.[33,34] If the dc holding field is slightly below or above the promotion field, one must not detect field-desorbed hydrogen ions since there should be no apex field adsorbed hydrogen.

We have performed the experiment with our new energy-focused high-resolution time-of-flight (ToF) atom probe,[35] although any atom probe of more modest performance would have sufficed provided mass one is accessible. At liquid-hydrogen temperature with He-H_2 mixed gas, an iridium tip was field evaporated at 11.8 kV to obtain an atomically perfect surface. The voltage was then lowered to 7.7 kV where hydrogen promotion occurred. Vivid flickering was observed at the $\{113\}$ and $\{012\}$ regions in the voltage range of 7.6–7.9 kV. Then 2-kV pulses of width 17 nsec were applied to field desorb the molecules. We varied the dc holding voltage from 6.7 to 8.5 kV with increments of 100 V. In the entire range, the total applied voltage is low enough to avoid field evaporation of the metal atoms. Figure 3 shows a histogram of the atom-probe spectra. H^+ ions appear only in the narrow voltage range around 7.7-kV dc holding voltage in which image flickering and promotion are observed. This correlation confirms our interpretation that the hydrogen promotion is due to field adsorption of hydrogen. It is also consistent with our assumption that the field-adsorbed species is molecular hydrogen.

V. SUMMARY

It is found that in the field range where hydrogen promotion of field ionization occurs, the FIM image spots scintillate. This leads us to propose a new mechanism of the promotion as a field-ionization enhancement by the field adsorption of hydrogen molecules. At a threshold field, a hydrogen atom in a surface site flips over to the apex position of a surface atom to combine with an already present adatom, forming a hydrogen molecule. A time-of-flight atom-probe experiment confirms the apex field adsorption, and is also consistent with the assumption that the field-adsorbed species is a hydrogen molecule. This experiment also confirms the occurrence of a flipping process at a threshold field, which has been suggested earlier from an energetic consideration.[24]

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[30] The data are semiquantitative in nature. They are from J. H. de Boer, Adv. Catal. Relat. Subj. 8, 51 (1956).

[31] The activation energy of field desorption of atomic hydrogen as seen from the semiquantitative potential-energy diagram of Fig. 2, is about 2 eV or higher at 3.3 V/Å. One may also use $F_d \approx (I + \Lambda - \phi - e^2/4x_0)/(x_0 + \delta)$ to estimate the desorption field (see Ref. 1 for notations). Reliable data for binding energy Λ, interatomic separation x_0, and field penetration depth δ are unavailable. For the purpose of estimation, we use $\Lambda_{H_2} = 0.4$ eV, $\Lambda_H = 1.6$ eV, $\phi = 4.5$ eV, $x_0 = 1.37 + 1.1$ Å for H_2, $x_0 = 1.37 + 0.53$ Å for H, and $\delta = 0.5$ Å. The desorption field for H_2 is found to be 3.4 V/Å and for H is 3.7 V/Å. Thus both methods consistantly give higher desorption field for atomic hydrogen.

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