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FIELD IONISATION AND FIELD ADSORPTION OF HYDROGEN

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ABSTRACT - The relaxation of the field ionisation rate after depletion of a tungsten surface is studied for hydrogen and helium with a pulsed laser atom probe. The reduction of the field ion rate and its recovery to a steady state value within some milliseconds is due to a correlation between field ion rate and surface coverage. Three possible models are discussed for explaining the enhancement of the rate by an occupied site.

I INTRODUCTION

Very soon after the introduction of the field ion microscope by Müller, it was recognized that while imaging the surface of the field emitter, an invisible coating of the imaging gas, which is adsorbed by a field induced dipole-dipole interactions covers the metal kink sites /1/. The existence of these adspecies is confirmed in many ways. In field pulsed atom probes /2/ as well in atom probes combined with magnetic field mass separation /3/, metal hydride as well as metal helide ions were observed. At some what lower fields, the desorption of the field adsorbed species can be detected by irradiating the emitter with a pulsed laser /4/.

The depletion of the emitter surface due to a heating pulse by a laser or due to a field pulse reduces instantaneously the field ionisation rate, which recovers only after some time. This correlation of surface coverage and FI-rate was first observed by Müller and Krishnaswamy in 1971 /5/. Later in 1981, J.H. Sweeney and T.T. Tsong looked at this phenomenon for He and Ne in more detail, again using a field pulsed depletion /6/. At the same time, Drachsel, Jentsch and Block /7/ made similar observations for C$_2$H$_2$ using pulsed laser field desorption. In this paper now we have studied the relaxation of the field ionisation rate of hydrogen, helium and neon from W(110) in dependence of field strength, emitter temperature, laser power, and gas pressure with the pulsed laser atom probe.

II. EXPERIMENTAL

The pulsed laser atom probe used is based on the instrument described in ref. /8/. It consists of a FIM (fig. 1) with a probe hole (2.5 mm φ) and a 0.4 m path length for time-of-flight analysis. A N$_2$-laser pumped dye laser at 600 nm with a pulse width of 3 ns and 50 Hz max repetition rate was used. The emitter tip was connected to a liquid N$_2$-cool finger, and the tip temperature could be controlled. The residual gas pressure was 5·10$^{-10}$ Torr and gases were admitted for adsorption via leak valves from glass bottles. The TOF ion detector consists of a chevron channel-plate with phosphorus screen. For time of flight analysis a 5-register time-to-digital converter with a time resolution of 2 ns was used. Additionally, the detector signal was fed into a MCA (in multiscaling mode) to look at the dynamic behaviour of the ion rate on a larger time scale. The data were always accumulated over some 1000 laser-pulses. The laser power was adjusted so that nearly all adspecies where desorbed, but no tungsten ions were present in the TOF-spectrum.
Fig. 1. Pulsed laser atom probe.

Fig. 2. Transient of the field ion rate.
Fig. 3. Pressure dependence of K and $\tau_2$.

Fig. 4. Field dependence of $\tau_1$, $\tau_2$ and K.
III. RESULTS

In fig. 2 the typical measured time dependence of the field ion rate is displayed as it is observed by the time of flight electronics (window 30 ps after the He-desorption pulse) and by the MCA on a time scale ~ 100 times longer (starting just behind desorption peak). From the TOF measurement, the He ion rate before the desorption due to the laser pulse is higher than that after. The recovery of the ion rate to its steady state value can only be seen on a larger time scale. The transient curves for all investigated gases showed the same S-like behaviour. After an induction time, here called \( t_1 \), the ion rate increased rather constantly until it again reached saturation after a recovery time, here called \( t_2 \). The enhancement factor \( K \) is defined as the ratio of the rate before the desorption compared to the rate immediately after desorption. The assignment of \( t_1 \) and \( t_2 \) is related to a second order response of a perturbation. With an appropriate theoretical model, the transient curves can be fitted in future by a computer program to evaluate the relevant parameter.

Obviously \( t_2 \), which represents the slope of the rate, is related to the recovery time, as can be seen by the pressure dependence in fig. 3 for He. The value of \( t_2 \) is inversely proportional to the pressure or impingement rate, whereas the enhancement only slightly increases with pressure. These finding were confirmed for all gases investigated.

The reduction of the field ionisation rate after depletion of the emitter surface is very pronounced at fields below the best image field strength, as shown in fig. 4 for hydrogen. The enhancement factor decreases from 8 to 1 within 0.5 V/Å and above 3 V/Å the ion rate shows no relaxation. For helium and neon above the best image voltage again no enhancement is visible. The time \( t_1 \) according to fig. 4 decreases from ~ 3 ms to practically zero at 2.5 V/Å, indicating that with increasing field this process gets much faster. We interpret this as a proceeding diffusion step, where the diffusion is enhanced by the field. The recovery time \( t_2 \) of 3.8 msec does not change much below 3 V/Å but above is reduced to ~ 1 msec. It should be noted that this latter value is rather uncertain, as the enhancement is only very weak in this field region. The surface coverage of hydrogen and the field ion rate in the same field range are compared in fig. 5 for the same area on the (110) face of the tungsten tip. At about 2.5 V/Å where the \( \text{H}_2^+ + \text{H}^+ \) desorption rate, which is a measure of the surface coverage, is maximum, the enhancement factor is reduced to 1 and the increase in the ion rate with field is less steep. The reduction of \( K \) to one at high fields we interpret as a consequence of the cut-off of the gas supply due to the complete field ionisation of the incoming flux.

The correlation of enhancement and surface coverage also can be seen from the temperature dependence in fig. 6. Within the measured temperature range from 90 K to 250 K, \( K \) decreases from 2 to 1. This means, at the high temperatures where no hydrogen is field adsorbed, no change in the ion rate after the applied laser pulse is observed. The field ionisation rate is reduced also by a factor of 2 from 90 K to 250 K. Obviously the ion rate at the high temperature is of the same magnitude as the one at 90 K for a bare surface. The time \( t_1 \) drops from 3 ms to zero at 150 K because diffusion is enhanced by temperature such that it is not measureable with this technique. The recovery time over this temperature range (not shown) is nearly constant.

IV. CONCLUSIONS

As was deduced in the cited papers /5, 6/, there is a strong correlation between the occupancy of the emitting sites by field adsorbed image gas and the observed field ionisation rate. The enhancement of the ion rate by an occupied site can be explained in one of the following ways:
Fig. 5. Field dependence of field ion rate and pulsed laser desorbed hydrogen at 90 K.

Fig. 6. Temperature dependence of $\tau_1$, $K$, ion rate and pulsed laser desorbed hydrogen.
(a) The field ionisation rate is coupled strongly to the field desorption rate with \( K = \frac{(i_{FI} + i_{FD})}{i_{FI}} \).

(b) The ionisation probability increases strongly if a kink site is occupied \( K = \frac{P(\text{occupied})}{P(\text{empty})} \).

(c) The rate is mainly due to a collision induced field desorption, where a gas atom kicks out a field adsorbed atom (of equal mass), \( K = \frac{(i_{FI} + i_{CIFD})}{i_{FI}} \), where \( i_{CIFD} \) is proportional to coverage \( x \) supply rate.

In discussing these models, possibility (a) can be ruled out as the desorption rate dependence on probe temperature or similarly on laser power makes a negligible contribution to the total ion rate. Only by a field pulse technique, leading to fields of more than 3.8 V/Å, field desorption of hydrogen at 78 K is observed /9/. However, at these high fields no enhancement is detected.

Concerning model (b), Sweeney and Tsong /6/ saw strong evidence from their results that an ion rate enhancement due to an increased electron emission rate from a hopping He-atom above a He occupied site could be assumed. This is supported by observed promotion of helium field ionisation by traces of neon (flickering of image spots). This enhancement of the order of 6 to 10 in the ion rate decreases at higher substrate temperatures, which is explained by Ernst /10/ as due to an increasing vibration amplitude of the field adsorbed neon. In /6/ just the opposite temperature behaviour would be expected as in this case was found, but the transfer of the results of He-Ne interaction to the case of self field adsorption has to be questioned. With our experimental technique we have seen no difference in ion rate enhancement if we compared the TOF-spectra, where field desorbed hydrogen or helium was detected with those were no desorption event was present. Since our detector has only 50 % detection efficiency and we looked at more than one site, this statement is not so reliable though.

According to model (c) where an impact induced field desorption is assumed, the enhancement at low fields can be understood as arising from a more efficient accommodation of the impinging gas in the apex area because a collision partner of equal mass exists on the surface. This would lead to a higher ionisation rate compared with a depleted apex area, where a much higher portion of the gas supply would leave this area as neutrals. This is supported by the increase of \( K \) with pressure in fig. 2, with a still increasing hydrogen coverage in this pressure range. We favour mechanism (c), as the explanation for the above described effects but stress that a site dependent measurement of field ionisation rate and simultaneous coverage by field desorption is necessary to form a definitive conclusion. For all models, the time \( t_1 \) can be interpreted as a refilling time of the kink sites by field enhanced diffusion from adjacent terraces. The terraces inturn are replenished from the gas phase as governed by a recovery time \( t_2 \), which is reciprocal to the actual pressure.

REFERENCES

/10/ N. Ernst, to be published.