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FIELD ION MICROSCOPY OF THE Cu/W SYSTEM: AN INITIAL STUDY*

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Experimental series of neon and hydrogen field ion microscopy and field desorption in the presence of the imaging gases, for copper covered tungsten tips, have been compared with the progress in vacuum field desorption of the copper. Observed changes in the Cu covered surfaces have been discussed in terms of the dependence of the average work function on the average degree of coverage for the Cu/W system. While a few similar stages of the field desorption of copper were observed in the neon and vacuum experiments, the process of copper disappearance in the hydrogen series was considerably affected by corrosion of the surface.

1. *Introduction*

There is still a need to get more information about the chemical physics of metal surfaces. The endless development in such fields as microelectronic technology, catalysis studies and science of materials, so far, stimulates this interest. Some very sensitive methods, e.g. Auger electron spectroscopy, photoelectron spectroscopy or field ion microscopy [1–3], beside other equally modern techniques, have been successfully employed in studies of adsorption, metal thin films, alloys or special crystalline structures.

This paper presents some results of a study of the Cu/W system using field ion microscopy (FIM) techniques. Copper deposited onto tungsten has been studied using field emission microscopy (FEM) by Melmed [4–7] and a few other authors [8–12], and by FEM/FIM methods as well [10–12] — to say nothing of works performed with other experimental techniques. Cetronio and Jones [10] have used helium FIM to investigate the reconstruction of a tungsten surface caused by adsorption of gold, silver and copper.

In the present work, neon and hydrogen were chosen as the FIM imaging gases in order to investigate field desorption, during imaging, which occurs well below the helium imaging field strength of 4.4 V/Å, for copper deposited on tungsten. The field strength for field ion imaging with hydrogen gas is only 2.2 V/Å, and with neon 3.5 V/Å.

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Chemical activity of hydrogen, which is often an obstacle, may be interesting in relation to some other studies, e.g. those made in the field of catalysis, and this was another reason for the choice. However, since Müller [1] has reported that CuH_2^+ ions are a product of the hydrogen promoted field evaporation of copper, good stability of hydrogen FIM images could not be expected for Cu covered tip surfaces.

2. *Experimental*

A slightly modified version of the all-glass field ion microscope described in Ref. [13] was used to perform these experiments. The microscope was bakeable to 420°C. The FIM apparatus was evacuated by two oil (DC 705) diffusion pumps in series and backed by a rotary pump. Traps, cooled by liquid nitrogen, were interposed between the microscope and diffusion pumps. Titanium and molybdenum getters were employed to ensure a low pressure of residual gases. Hydrogen, neon or helium imaging gases were introduced to the FIM working space via heated quartz diffusers, and the gas dosing system was isolated by means of glass indium valves. The FIM operated at liquid nitrogen temperature, and the background pressure was normally $5\times10^{-10}-2\times10^{-9}$ torr.

The FIM apparatus was also used in the FEM mode to receive additional information. Photographic recordings of neon and hydrogen (and also helium) FIM images were made via an E.M.I. external image intensifier, photoelectronic device of type T2001. This was optically coupled to the FIM by simple, good quality optics (Biotar f 1.5/75 lens, C. Zeiss Jena).

The copper vapour source was a droplet fused into a tungsten wire coil and shielded by a glass envelope with a hole in it. The source assembly could be magnetically moved. After fusing and outgassing the copper, the source could be levelled for deposition of copper frontally onto the tungsten emitter surface.

Tungsten emitter tips were prepared with a semiautomatic electropolishing controller [14] and then were spotwelded to loops of tungsten wire 0.2 mm in diameter. The loop had current and potential leads enabling the heating of the emitter and control of tip temperature. To obtain the field evaporation end form W-emitters were imaged in helium, flashed to approximately 900—1200 K a few times, and field evaporated in a helium atmosphere at 78 K. Then the He FIM image of the W-tip surface was photographed. Before the deposition of copper the tip was heated for several minutes to a temperature equal to or higher than that at which the deposition would be made. The tip was additionally field evaporated in vacuum and then copper was deposited onto the W-substrate held at a temperature in the range 300—650 K. Pressure, measured with a Bayard–Alpert gauge, during deposition was mostly below 1×10^{-9} torr.

Conditions for the deposition of copper in neon and hydrogen FIM experiments are given in the captions under Figs. 4 and 1(f–h), respectively. After an FEM pattern of the original Cu covered specimen tip had been photographed, neon or hydrogen imaging gas was introduced to the FIM working space. An FIM image of the specimen surface was observed and recorded at best image voltage (BIV), then higher desorption voltages were applied to the sample step by step, subsequently to FIM imaging and recording the investigated surface at lower best image voltages. To perform the experiment of vacuum field desorption, copper was deposited for 20 min onto the field evaporation end form of the W-tip held at 450 K. The Cu deposit was then equilibrated at 600 K and frozen to 78 K and maintained at this temperature during the desorption course. Fig. 1(a) shows an FEM pattern of this Cu covered W-tip surface. Afterwards, higher and higher desorption voltages were applied to the sample for some seconds, subsequent to the measurements of field emission voltage at a constant electron current, and the FEM images were simultaneously photographed. The vacuum desorption sequence ended in obtaining an FEM pattern of an almost clean tungsten surface (Fig. 1e). FEM patterns in Fig. 1(a–e) illustrate some more characteristic stages of the Cu desorption for this sequence. For FIM imaging and field desorption a Spellman RHSR 60 P power supply with 0.001 % regulation and stability was used. Another unit, type ZWN 4 (0.05 % respectively), was employed in FEM experiments.

3. *Results and discussion*

The experiment of field desorption in vacuum was performed to yield a rough view upon stability of an FIM image of a copper covered tungsten tip. The experimental plot in Fig. 2 shows the dependence on field desorption voltage K_d of FEM voltage, U_e, needed to obtain a constant total field emission current, i_e. The abscissa represents the desorption voltage, K_d, applied to the sample, in precent of an arbitrary voltage at which field evaporation of clean W-substrate in vacuum should occur. Helium FIM best image voltage (He BIV), which had been experimentally found for the same clean W-tip, was used to

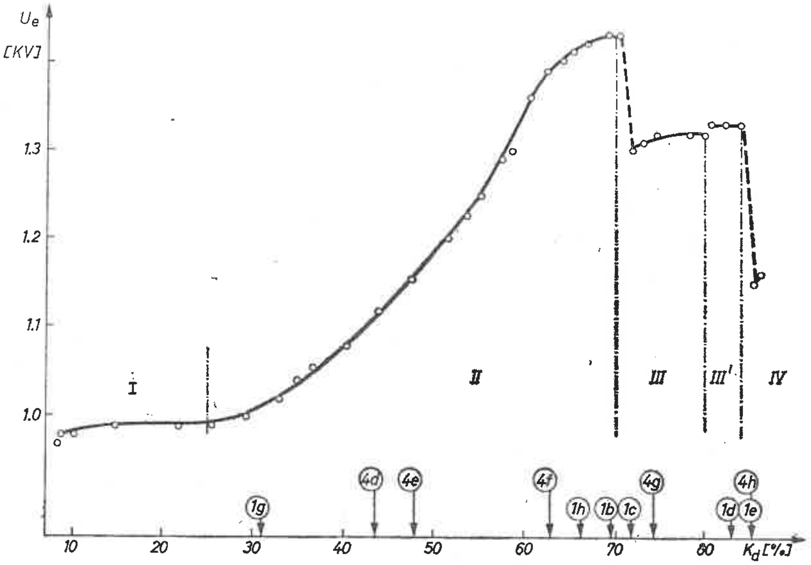


Fig. 2. Field emission voltage U_e at a constant electron current of 6×10^{-7} A vs relative desorption voltage K_d for the Cu covered W-tip. Field desorption at 78 K, in vacuum

calibrate the abscissa scale. Conversion to the evaporation voltage of clean W (i.e. 100% point in the abscissa scale) was made simply by multiplying the He BIV by a factor of 1.295 (the ratio of W evaporation and He best image fields [1]). Because of possible changes in the shape of the sample under adsorption and desorption conditions, the abscissa scale in not linear with the strength of electric field applied.

Field emission voltage, U_e, depends on two factors: average work function of the emitting surface, and geometry of the sample i.e. the tip shape. Both these factors change during field desorption (FD) or field ion imaging of a Cu covered W-tip. The dependence of average work function, $\bar{\varphi}$, on average degree of coverage, $\bar{\theta}$, for the Cu/W system [15], is shown in Fig. 3.

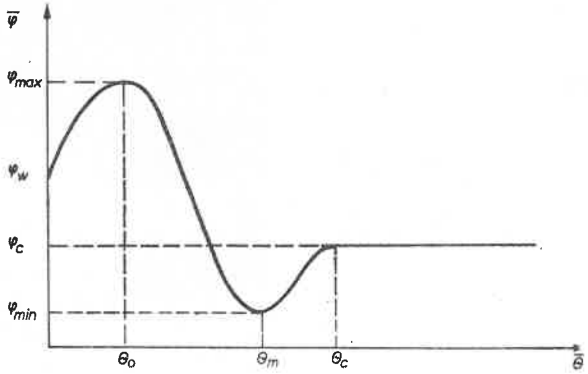
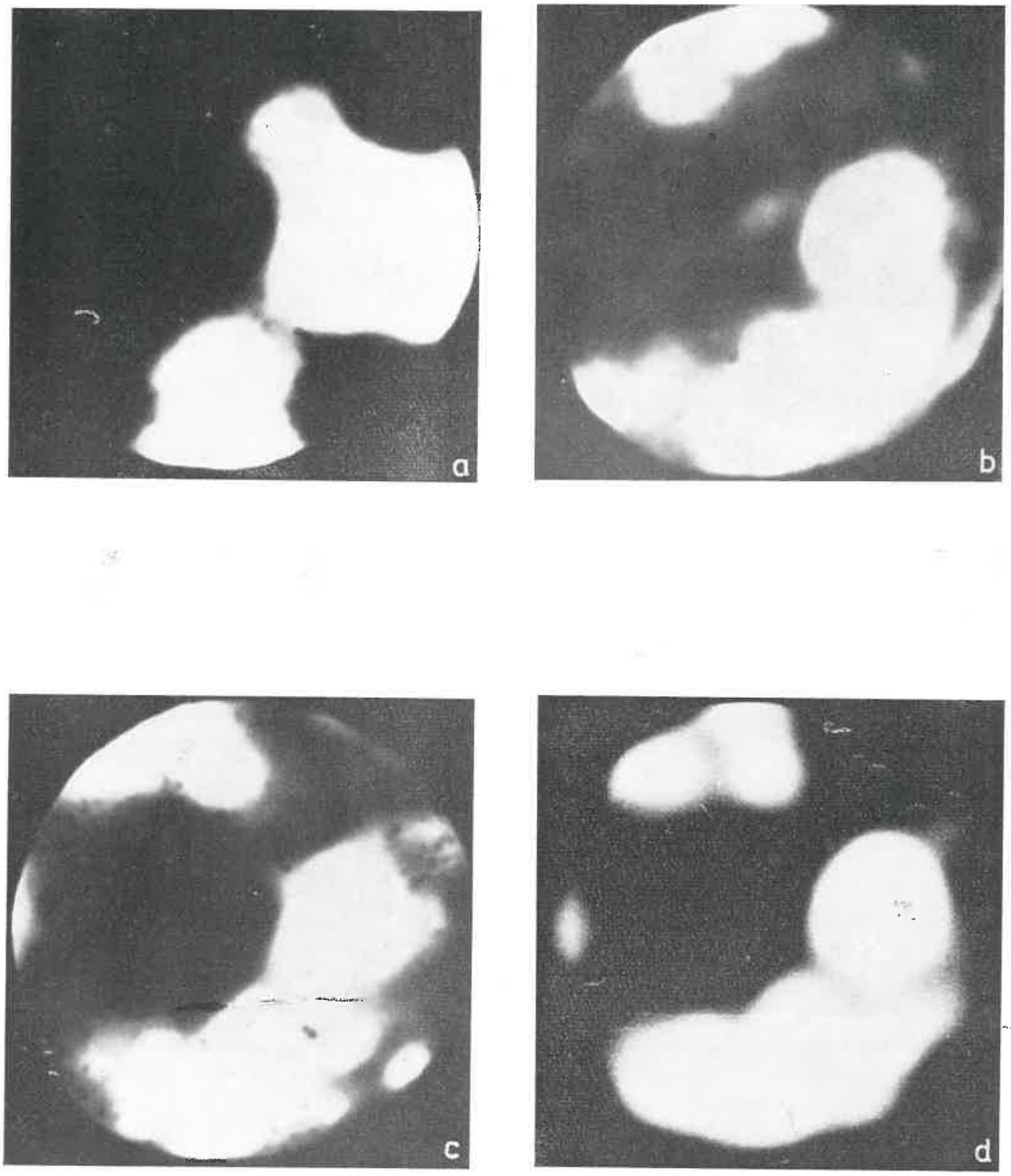


Fig. 3. Dependence of average work function, $\bar{\varphi}$, on average degree of coverage, $\bar{\theta}$, for the Cu/W system. (After Sidorski [15])

Based on the coverage dependence of the work function, $\bar{\varphi}(\bar{\theta})$, the following qualitative interpretation of the vacuum field desorption curve of Fig. 2 seems to be possible. Four regions can be observed in this plot. At stages I and II of the field desorption only the geometry factor contributed to the observed increase in U_e. After original removal of possible contaminations and most protruding Cu atoms or clusters at electric fields up to K_d = ca 10%, a smoothed Cu adsorbate surface was stable at stage I up to K_d = 25%. At stage II, to ca 70%, field desorption of copper caused a gradual decrease in average curvature of the Cu covered W-tip, which resulted in a nearly steady increase in the field emission voltage U_e. After a desorption field higher than ca 70% had been applied, Cu coverage (θ_c in Fig. 3) dropped to a work function minimum level θ_m, and U_e dropped. The work function factor is assumed to assist the geometry factor in further desorption at stage III where the work function increase up to φ_{max} would cause the observed increments of U_e (cf. Figs 2 and 3). The discontinuity of the FD curve between regions III/III′ might indicate that the central (110) W crystal face bared and/or Cu covered {100} W faces were further depleted of their topmost Cu layers, the average work function passed through a maximum, and U_e hopped a little. After the work function maximum coverage, θ_0, had been passed (K_d = ca 84%), U_e again dropped following the average work function at stage IV, and almost clean W substrate was bared, see Fig. 1(e). It should be noted, however,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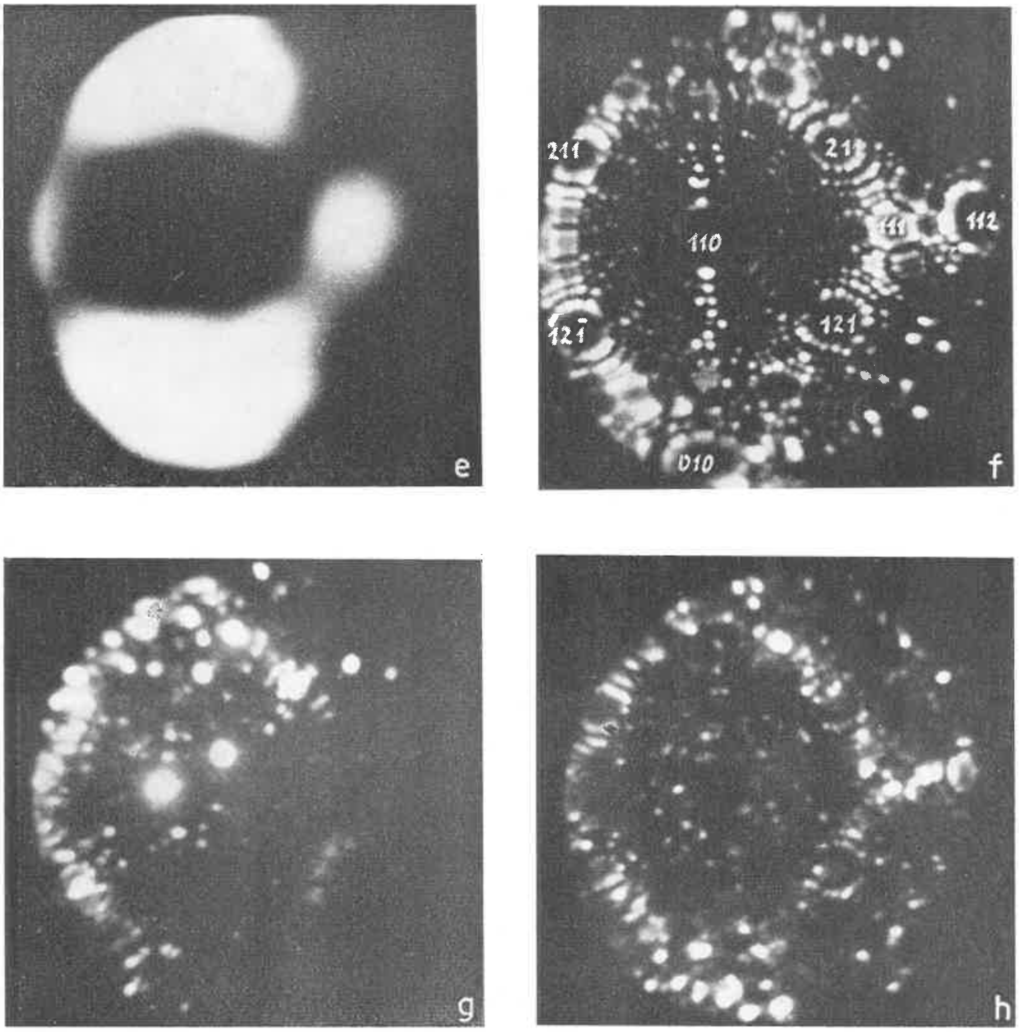
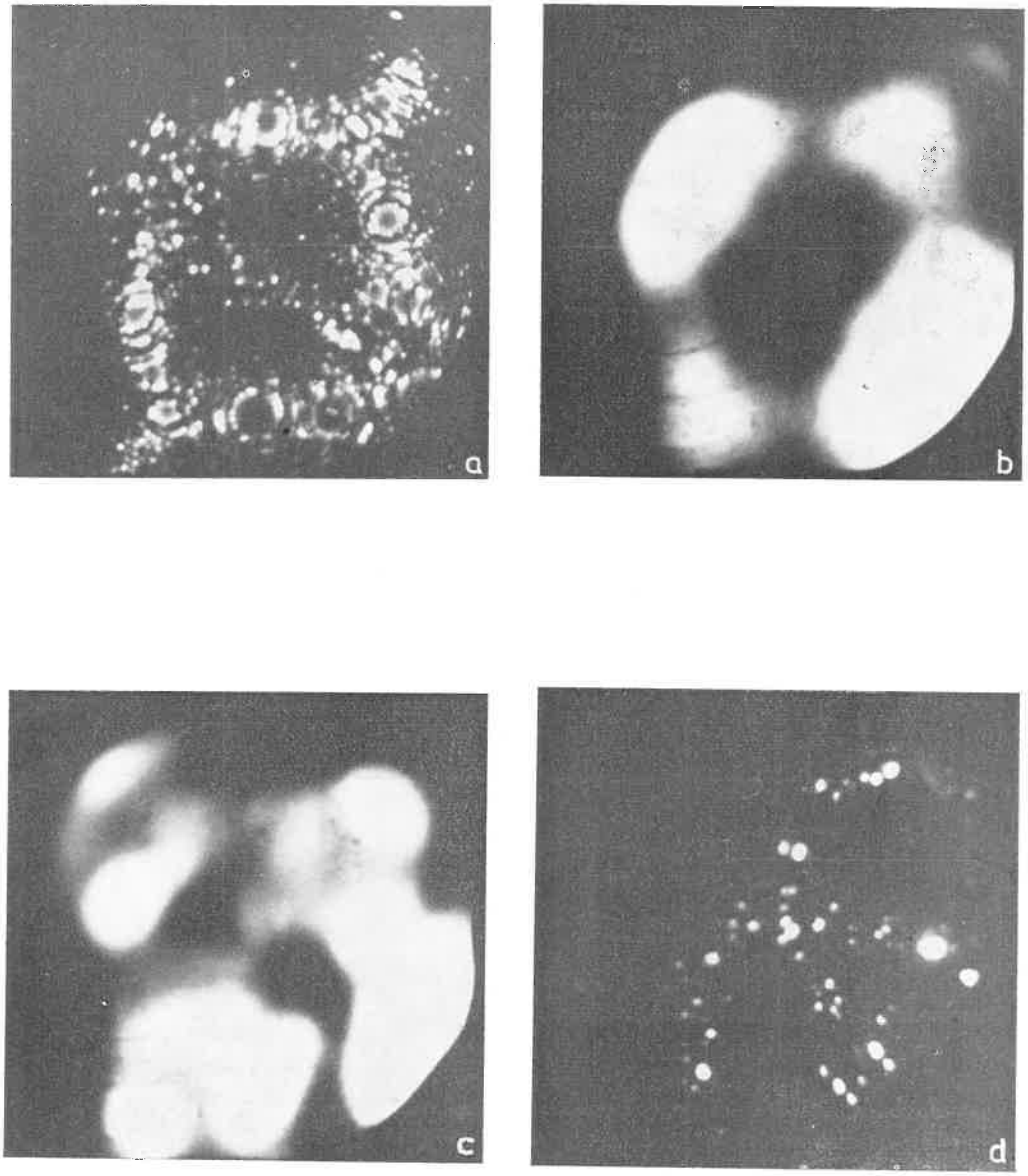


Fig. 1(a–e). Some stages of field desorption in vacuum illustrated by FEM patterns. Relative desorption voltages are indicated in Fig. 2 by arrows. (a) Cu covered W surface before desorption, (b–e) progress in field desorption, (f) helium FIM pattern of the same W substrate surface, original in the hydrogen series, after some field evaporation, (g) hydrogen FIM pattern of Cu covered W-tip. Copper was deposited for 10 min with W-tip held at 300 K, (h) H_2 FIM pattern at a higher voltage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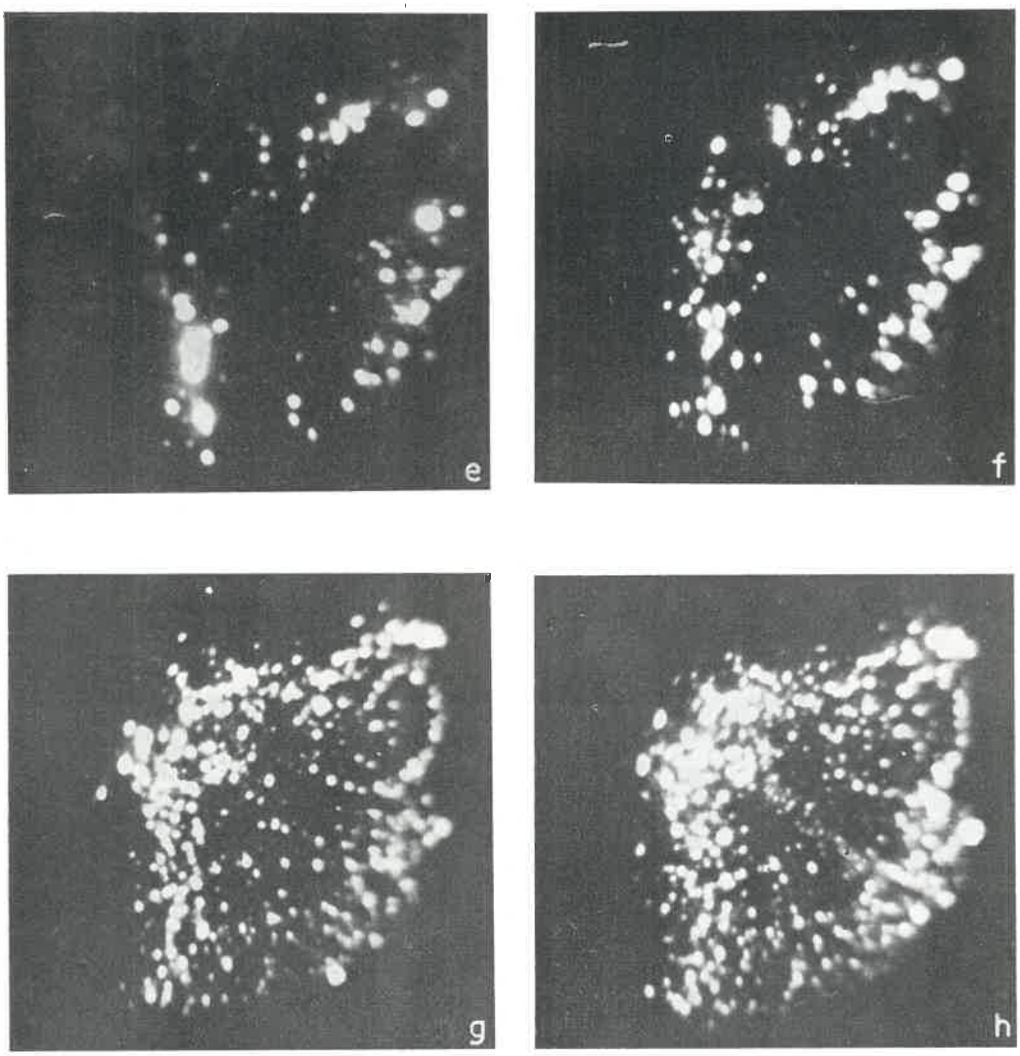

Fig. 4. The "neon FIN/FD series". Copper was deposited for 25 min, with W-tip held at 650 K. (a) helium FIM pattern of initial W surface, BIV = 14.5 kV; (b) FEM pattern of the same W surface, (c) FEM pattern of Cu covered W tip, (d–f) neon FIM patterns of Cu covered W tip, relative image voltages are indicated in Fig. 2; (g, h) neon FIM patterns of the same Cu/W tip field desorbed in the presence of neon, BIV = 12 kV

that the changes in average degree of coverage during the field desorption process need not necessarily run following (reversely) those which go during the copper deposition process.

The results of neon and hydrogen FIM imaging and field desorption in the gases, of the Cu/W system with different Cu deposits, are illustrated in Figs. 4 and 1(f–h), respectively. Progress in the removal of the copper, which was viewed with observed and recorded FIM images, is compared to the vacuum field desorption plot (the FIM image and desorption voltages are indicated by arrows in Fig. 2). The relative voltages have been calculated in the same way as for the vacuum FD series.

Two first photomicrographs in Fig. 4 show the initial field evaporated W-tip surface (Fig. 4a — He FIM pattern, Fig. 4b — FEM pattern), of another W emitter. The Cu covered W-tip surface with multilayer coverage is shown in Fig. 4c (an FEM pattern). Figs. 4(d–h) illustrate some stages of field ion imaging the Cu deposit in neon gas; the patterns were recorded at imaging-desorbing voltages indicated in region II of Fig. 2 by the arrows. Fig. 4(g, h) illustrate the desorption stages which correspond to regions III and IV of the vacuum FD curve, where the imaging voltage was lower than the desorption voltages applied in this case and only slightly higher than the Ne BIV of 11.85 kV for the pattern of Fig. 4(f).

It can be deduced from this neon FIM series that the desorption of copper, during the action of electric fields, went originally through similar phases in neon gas as during the vacuum field desorption experiment. Figs. 4(d–f) show only a gradual removal of the Cu deposit. From Figs. 4(f, g) a dramatic change in Cu average coverage is seen, which would mean the transition from stage II to III. Comparing the patterns 4(f–h) one could believe that the Cu coverage at stage III, illustrated by the photomicrograph 4(g), would amount to one Cu monolayer or so for the region of the central (110)W face. The rest of the Cu "cap", which had existed in the surroundings of the central crystal face, must have left the surface during the transition, and the tip got in result a new state of the relative equilibrium at stage III of the desorption — Fig. 4(g). Another transition can be seen from Figs. 4(g, h). The central region of the investigated surface, which had been randomly covered by Cu atoms (Fig. 4g, stage III), bared at the next stage, showing an almost clean tungsten (110) face — see Fig. 4(h). These FIM patterns can indicate that at least for the central (110) crystal face, Cu coverage in the region of $\theta_0 - \theta_c$ is somewhat lower than certain reported values [5, 8]. However, because of the relatively rough character of these experiments, there no sensible comparison of the results can be made with the quantitative ones by Cetronio et al. [12] and Polański and Sidorski [9], with regard to the (100)W plane coverage.

Because of a difference in average radius of curvature of the used emitters there could exist some shift between the calibration points for the voltage series of the neon FIM/FD experiment and for that of the vacuum experiment, the points of which had to be established in the abscissa scale of Fig. 2 for the purpose of comparing the results. This shift may well be ignored but the effect of a possible reduction of field desorption voltages, caused by the presence of neon, should be considered. Nishikawa and Müller [18] have reported that field evaporation of clean W, Mo and Pt occurs in neon at slightly lower fields than in vacuum. The reduction of the evaporation voltage in Ne for W at liquid nitrogen temperature amounts to 6% [18]. Such an effect could be expected also for this case of field desorption. Thus, the discussed field desorption stages of the Cu/W system for the neon series might occur at desorption voltages which would be a few percent lower than for the vacuum FD series. This possible shift between the above mentioned calibration points can also be ignored in this discussion.

It should be noted that the observed field desorption of the copper deposit in neon gas preferred the low-field central (110) tip surface region, which caused this area to flatten (see Fig. 4d–h). This result is in very good agreement with the model of field evaporation in neon, proposed by Nishikawa and Müller in Ref. [18].

Two more desorption steps — the final one up to 96% — were made in the Ne sequence, but they did not result in a perfectly clean W surface. An experiment of helium FIM and FD, if made, would allow us to continue the study of the final transition layer and of possible displacements of tungsten substrate atoms.

Micrographs in Fig. 1(g, h) illustrate the behaviour of a Cu deposit under conditions of high electric fields and the presence of hydrogen. Deposition of copper was made here with the W-tip held at room temperature. The initial Cu coverage was lower than those in both former cases and the deposit was not equilibrated at a higher temperature. A helium FIM pattern in Fig. 1(f) shows the original substrate surface of the experimental series. Hydrogen FIM imaging the initial Cu deposit (see Fig. 1g) at a constant low field of K_d = ca 31%, lasting several minutes, revealed a striking development in the depletion of the surface, which would indicate that the effect occurred of hydrogen stimulated field desorption or field induced corrosion of the surface. Even at so relatively low field applied as K_d = ca 42% (Fig. 1h) some characteristics of the latter stages of the neon series could be found. However, the differences in the initial coverages and the tip temperatures during copper deposition should be taken into account. It should be noted here that the former difference seems to have only a marginal effect in the applied procedure of investigation since before FIM image fields are reached, the top-most layers of the copper deposit will be field desorbed. The copper covered tips of the vacuum FD and Ne FIM FD series were heated to 600 (i.e. equilibrated) and 650 K (deposited at), respectively. Melmed [5] has found that the surface diffusion of copper on tungsten for thicker than one monolayer Cu coverages should occur at 300 K easily, though not at 78 K. On the other hand, surface diffusion of W on W initiates at a temperature in the region 500—550 K [16, 17], but it could result in a more essential surface rearrangement of the W substrate only at a temperature higher than 700 K [17] which was not reached here. Nevertheless, the prevalent corrosion of copper in hydrogen contributes more to such an inadequacy of the comparison of the three experimental series than the difference in Cu deposition temperature does alone.

4. *Summary*

Another attempt to receive physical information by means of field ion microscopy has been made, using the Cu/W system as an example and based on FIM image interpretation and existing experimental and theoretical results.

Neon FIM observations enable one to supplement the hitherto existing results up to the very copper deposit structure. Neon field ion microscopy has revealed in this study a couple of states of the Cu deposit which were in good agreement with the coverage dependence of work function for the Cu/W system. The procedure which has been used here is suggested for "visual" comparing quantitative results on work functions and coverages for the purpose of better understanding surface phenomena for similar metal systems.

Though the field strength for hydrogen FIM image is lower than that for neon FIM best image, field induced corrrosion of the copper covered surface was considerable as could be expected.

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