Evidence for Reconstructed {001} Tungsten Obtained by Field-Ion Microscopy

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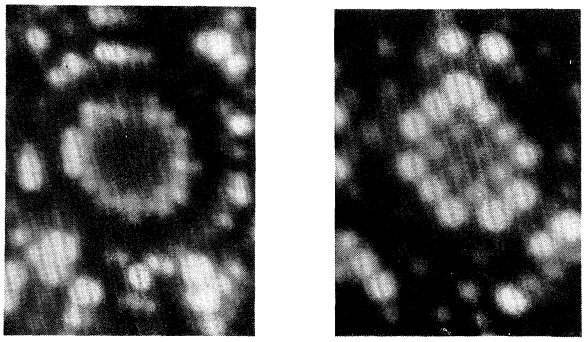
New results have been obtained, by field-ion microscopy, relating to the atomic structure of clean {001}W. The evidence supports a reconstruction model with periodic displacements of atoms having vertical components. The reconstructed atomic configuration prevails over the entire temperature range of this investigation (~15–460 K), suggesting that no phase transition may be needed to account for the structural features of {001}W.

The structure of clean {001}W was shown by Yonehara and Schmidt[1] (YS) to undergo a reversible transition from the ordinary (1×1) to a $c(2\times2)$ symmetry upon cooling to below room temperature, and a lateral ⟨010⟩ displacement model was proposed to account for the reconstruction geometry. Debe and King (DK) subsequently proposed[2] a lateral ⟨110⟩ displacement model, and concluded that their crystal surface, at temperatures below 370 K, consisted of three types of domains, two with $(\sqrt{2}\times\sqrt{2})R45°$ structure and some unreconstructed, (1×1) area as well. Felter, Barker, and Estrup (FBE) suggested[3] the possibility of a periodic vertical displacement of alternate surface atoms along ⟨010⟩ directions, but Barker, Estrup, Jona, and Marcus[4] concluded from a comparison of experiment (low-energy electron diffraction) and theory that the lateral displacement model of DK was more probably correct. A recent paper by Debe and King[5] reviews the subject and provides further support for their model.

According to the analysis given by DK, no reconstruction would be expected to occur for {001}W planes in the range of sizes that can be fully resolved in a field-ion micrograph (FIM), that is, up to dimensions of about 30–35 Å, since all of the atoms would be within 20-Å distance from a plane edge.[5] However, if the zig-zag lateral displacements of the DK model did occur to the extent reported, they would be readily seen by FIM. If the displacements occurred to a much lesser extent, although the geometric details might not be resolvable, we would expect that field evaporation[6] would produce somewhat ragged edges of the {001} planes, but would otherwise be similar to field evaporation of other crystal planes. Similar expectations would hold if the reconstruction were of the lateral kind described by YS. If the reconstruction consists of vertical displacements, as in the FBE model, then it might be possible to directly image the details of the reconstructed configuration, provided that the displacements were of sufficient magnitude. For smaller vertical displacements, although direct imaging might not be informative, we might find anomalous preferential field evaporation of the class of raised atoms in the plane. However, pure vertical displacements have been ruled out by a recent ion-scattering investigation.[7]

We have examined old field-ion micrographs and conducted a new investigation. Among the old micrographs, there are many examples of small numbers of atoms (up to seven) representing the last stages of low-temperature field evaporation of {001}W planes in which the atomic arrangement is a simple $c(2\times2)$. Some planes containing up to 25 atoms, completely resolved, show apparently perfect (1×1) structure, except at the plane edges.

In our recent experiments, we have used single-crystal specimens, with 200–400-Å average radii, oriented with central {001} planes and have field-evaporated surface atoms very carefully, over a temperature range of ~15–460 K. At all temperatures used, we have found that preferential field evaporation of alternate surface atoms occurs and usually results in a $c(2\times2)$, $(\sqrt{2}\times\sqrt{2})$-$R45°$ structure, often not a perfect single domain. When the field evaporation is done at low



(a) (b)

FIG. 1. Low-temperature field-ion micrographs (He, 10% Ne imaging gas) of {001}W. (a) An initial apparent (1×1) structure obtained by low-temperature field evaporation. (b) A final $c(2\times2)$, $(\sqrt{2}\times\sqrt{2})R45°$ structure obtained by field evaporation at 430 K.

temperature (15–20 K, for example), the configuration remains apparently (1×1), except for occasional field evaporation of alternate edge atoms, until the plane is reduced in size to about 4×4 atoms, when preferential field evaporation of alternate interior atoms often leads to a $c(2\times2)$, configuration of a small number of atoms. However, at higher temperatures, the extent of $c(2\times2)$ area which results from field evaporation is greater, and at 430–460 K, for example, planes containing as many as approximately eighty atoms in the (1×1) configuration have been changed by preferential field evaporation to $p(2\times2)$ structures, and finally, to perfect $c(2\times2)$ single domains containing as many as nineteen atoms. Examples of a fully resolved initial apparent (1×1) and a final $c(2\times2)$ configuration are shown in Fig. 1. These higher-temperature experiments, which were done by one of the authors (R.T.T.) will now be described.

The mostly glass FIM, described in detail elsewhere,[8] was fully baked and all internal elements were degassed. A controlled field-evaporation sequence then proceeded as follows (we use a specific sequence, parts of which are shown in Fig. 2, as an example). Field evaporation at ~15 K removed the serrated edges of a large {001} plane and resulted in the near perfect apparent (1×1) plane, containing 77 atoms, shown in Fig. 2(a). The tip voltage was then lowered from 9 kV [the image voltage for Fig. 2(a)] to 6.0 kV, and the tip temperature was raised to 430 K. The voltage was then increased to 6.5 kV for 30 sec, and then returned to 6.0 kV. The temperature was lowered to ~15 K and the surface was imaged to 9 kV. After this cycle, vacancies were observed at a number of atom sites as shown in Fig. 2(b). Repeating the cycle produced further vacancies until a $p(2\times2)$ configuration was reached, as shown in Fig. 2(c). Additional cycles produced no further change. Then, raising the high-temperature field-evaporation voltage from 6.5 to 7.0 kV caused further preferential field evaporation, as depicted in Figs. 2(d)–2(f). The topmost {001} plane shown in Fig. 2(f) is a perfect single $c(2\times2)$, $(\sqrt{2}\times\sqrt{2})$-$R45°$ domain containing nineteen atoms. (There is an apparent increase in image magnification as the plane size decreases, related to field effects.[9]) This type of sequence was very reproducible, occurring in all of the thirty field-evaporation sequences thus far conducted at high temperatures. Occasionally, the $p(2\times2)$ and $c(2\times2)$ structures would not be single domains.

It is important to note that during the development of the $p(2\times2)$ structure the production of a vacancy resulting from the high-temperature field treatment was accompanied by an adsorbed atom appearing nearby on the topmost {001} plane. Apparently this adsorbed atom resulted from the field-assisted surface diffusion of an atom from the site of the subsequent vacancy. Such adsorbed atoms were then removed by low-temperature field evaporation just prior to recording the images in Figs. 2(b) and 2(c). Later in the sequence, field-assisted surface diffusion of edge atoms occasionally occurred, slightly enlarging the $c(2\times2)$ domain.

Ordinarily, field evaporation of crystal planes causes the orderly removal of edge atoms so that the planes simply, progressively, and reasonably uniformly are reduced in diameter, ultimately vanishing.[6] Remarkably, however, the {001}W planes, when carefully field evaporated as described above, preferentially lose atoms from alternate interior sites and alternate edge sites.

The occurrence of preferential field evaporation (with or without a precursor surface diffusion step) of alternate surface atoms must be due to a periodic variation in the effective binding energy of {001}W atoms, the most obvious model for which is a vertical reconstruction, as proposed by FBE. In that model[3] {001}W surface atoms are vertically displaced from their "normal" positions with alternate atoms raised and lowered. We designate the raised atoms *A* and the lowered atoms *B*. The *A* atoms should, in general, have a higher probability for field

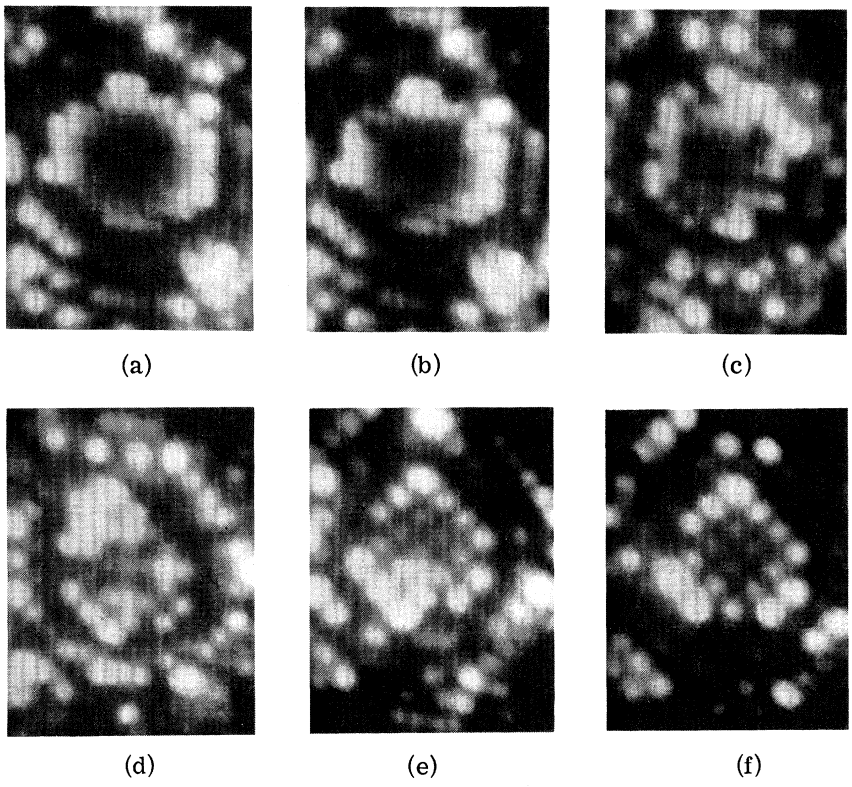


FIG. 2. Low-temperature field-ion micrographs (He, 10% Ne imaging gas) of {001}W field-evaporation sequence. (a) Initial apparent (1×1) structure obtained by low-temperature field evaporation. Plane contains 77 atoms, most of which are resolved in the original micrograph. (b) Same plane with some vacancies produced by field evaporation at 430 K and 6.5 kV. (c) Same plane after sufficient field evaporation at 430 K, 6.5 kV to produce a $p(2\times2)$ configuration. (d) Same plane after field evaporation at 430 K, 7.0 kV. (e) Same plane after further field evaporation at 430 K, 7.0 kV. (f) Final single domain with $c(2\times1)$, $(\sqrt{2}\times\sqrt{2})R45°$ structure resulting from continued field evaporation at 430 K, 7.0 kV.

evaporation than adjacent B atoms because of the combined effects of a (possibly) weaker zero-field binding energy and an enhanced local electric-field strength (arising from the greater protrusion of the A atoms). The actual sequence of field evaporation (with or without a precursor surface diffusion) will then be determined by this alternating variation in field-evaporation probability and the field strength over each atom, which varies with position of the atom in the plane as well as with local atomic geometry.

The observation that when the $p(2\times2)$ structure is reached, further field evaporation requires a higher applied voltage may imply that changes in the binding energy for A atoms occur as a result of the production of vacancies, or that there are actually at least three levels of vertical displacements or binding energies, suggesting that possibly the reconstruction is more complicated than thus far proposed in the literature.

Clearly, the $c(2\times2)$, $(\sqrt{2}\times\sqrt{2})R45°$ structure which results from preferential field evaporation in the FIM is not the structure *per se* deduced from the low-energy electron-diffraction experiments. Rather, the preferential field evaporation is due to periodic variation of vertical displacements of atoms in the {001} W surface and/or periodic variation of binding energy. The vertical displacements apparently are not directly observable in the FIM—hence the "normal" (1×1) appearance of the plane in Figs. 1(a) and 2(a) —but are revealed by the field-evaporation process.

We conclude that the reconstruction of {001} W surfaces at temperatures of 460 K and below, at least down to ~15 K, is such that alternate surface atoms have different binding energies,

suggesting different vertical distances from the immediately underlying atomic plane. This is not consistent with either of the lateral-displacement reconstruction models thus far proposed,[1,2] but is consistent with and supports the vertical-displacement model of FBE,[3] with the possible inclusion of some new features. In addition to the vertical displacement periodicity of atoms along the ⟨010⟩ directions, there may be some other displacement periodicities, so that there are at least three classes of displacements, accounting for our observation of the $p(2\times2)$ structure. Also, we cannot exclude the possibility that the atoms are displaced laterally, to some extent,[10] as well as vertically. In any case, the evidence implies a periodic variation of effective binding energies. We find no inhibiting effects because of the proximity of single-atom-height plane edges.

We wish to emphasize that our evidence for a $c(2\times2)$ structure of {001}W extends from ~15 to 460 K, the lower and upper limits of which range extend beyond the range reported in related work by other techniques. The fact that we find clear evidence for reconstruction at the higher temperatures may mean that the reconstructed configuration prevails over most of the temperature range of existence of stable clean {001}W planes (e.g., at least from ~15 K up to temperatures when surface diffusion becomes prevalent). If this is so, then the configuration does not result from any structural phase transition, but rather represents the true {001}W atomic structure. Alternatively, the persistence of reconstruction at the higher temperatures may be due to the influence of the strong electric field of the FIM.

A more detailed exposition will be given in the near future.

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Excited-State Absorption Spectrum of F_2^+ Centers and the H_2^+ Molecular-Ion Model

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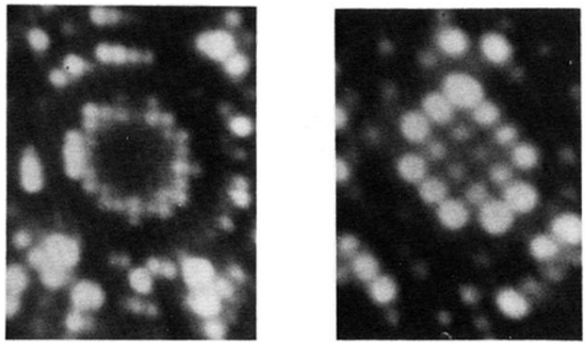
Five principal transitions, three of which from the first excited state, have been measured in absorption for the F_2^+ center in KF. With one significant exception, these data are in essential agreement with predictions of the simple H_2^+ molecular-ion model. The measurements were made by way of a novel optical pumping technique, which allows for direct, accurate determination of band strengths and shapes, even in the presence of strong overlapping absorptions by other species.

As a single electron trapped by a pair of adjacent anion vacancies, the F_2^+ center has been compared to an H_2^+ molecular ion embedded in a dielectric continuum.[1] That model was given considerable support by measurements in KCl, principally on the $1s\sigma_g \rightarrow 2p\sigma_u$ (Refs. 2 and 3) and $1s\sigma_g \rightarrow 2p\pi_u$ (Ref. 3) transitions (see Fig. 1). Furthermore, the model has been quite useful in predicting and interpreting phenomena relating to F_2^+ center lasers.[4-6] Nevertheless, the predictive abilities of such a model are limited, and a rather complete empirical determination of the electronic structure is ultimately required. This Letter describes such a determination, involving measurement in KF of all *five* of the principal transitions indicated in Fig. 1. Based on modu-



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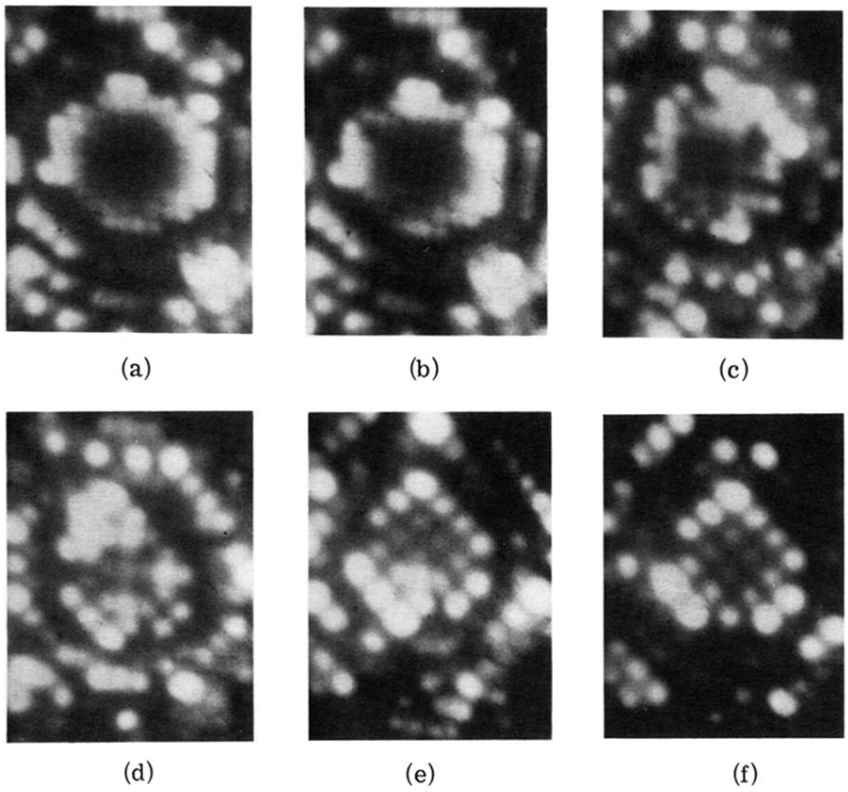

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