Observation of a Possible Surface-Charge-Density Oscillation by the Adsorption of an Impurity

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Neon field-ion image spots of impurities deposited from a Ta wire source on the Ir(100) surface show a halo-ring structure. Using an atom-probe field-ion microscope, these impurities are tentatively identified as tantalum hydrides. This halo-ring image-spot structure is most probably produced by the perturbation of the electronic charge-density distribution of the substrate around the impurity by its adsorption.

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When an impurity atom or molecule is embedded into a metal or adsorbed on a metal surface, the charge density surrounding the impurity will be perturbed and modified in an oscillatory manner. This perturbation is the cause of indirect interactions between atoms in solids and on surfaces.[1-3] The indirect interactions are important in understanding alloy properties, alloy magnetisms, formation of adsorption layer superstructures, etc. These problems have been studied theoretically in great detail by many investigators and the charge-density distributions are sometimes referred to as Friedel oscillations.[4] Evidence of such oscillations comes from interpretation of alloy properties, and is therefore indirect. As far as we are aware, there has been no direct microscope observation of the oscillatory charge distribution resulting from the perturbation of an impurity atom, although in field-ion microscopy Page and Ralph[5] did report an observation of cusp-shaped image spots of Pt and Rh atoms retained on the (100) surface of Ir base alloys when the alloys were field evaporated. The image spots show intensity tails along the ⟨110⟩ directions, or the closely packed atomic row directions, of the substrate. In this Letter, we report an observation of similar triangular cusp-shaped image spots of Ir adatoms deposited on the Ir(111) surface, and a much more exciting and interesting observation of a halo-ring structure of the images of impurities deposited from a Ta wire source on the Ir(100) surface.

In the field-ion microscope (FIM), images are formed by field ionization of image gas atoms above surface atoms in the more protruding positions. The field-ionization rate depends on both the gas supply function and the electronic transition rate.[6] As the gas supply function is determined by a long-range effect of the polarization force of image gas atoms in the inhomogeneous field around the emitter surface, it will not be affected by the small perturbations of the electronic charge-density distribution by the adsorption of impurities at the tip surface. The electronic transition rate, on the other hand, is directly proportional to the unoccupied electronic density of states at the surface near the Fermi level according to[6,7]

$$\kappa \simeq (2\pi/\hbar)\rho(E_F)\,|\langle\psi_k|eV|\psi_a\rangle|^2\Delta E\,, \qquad (1)$$

where $\rho(E_F)$ is the unoccupied electronic density of states at the Fermi level, ψ_k is the metallic state, ψ_a is the atomic state, eV is the perturbation potential of the applied field, and ΔE is the energy width of the ion energy distribution,[8] or the energy range within which field ionization occurs. Thus if the electronic density of states is perturbed by the presence of an impurity either on the surface, or in the lattice just beneath the surface, the perturbation should show up in the shape of the field-ion image spots. For some reasons, except for the report of Page and Ralph, few such features have been observed, possibly because of the smallness of the perturbations by metal adatoms.

In our experiment, the field-ion microscope used is an UHV system with the background pressure in the low 10^{-11}-Torr range. Ir tips used for the study are always carefully degassed and then field evaporated. In the study of the image-spot shape of Ir atoms on the Ir(111) surface, Vyco glass-diffused high-purity helium is used as the image gas. The tip temperature is kept around 30 K. Ir adatoms are deposited from an Ir wire source. Before the Ir wire source is used for the deposition, it is repeatedly degassed at a temperature only slightly below the melting point of Ir. In the study of image-spot shape of Ta impurities on the Ir(100) surface, Vyco glass-diffused high-purity neon is used and the tip is also kept at around 30 to 40 K. Although the Ta wire source is also repeatedly degassed, the deposited particles often are not pure Ta atoms, but compound molecules of tantalum as will be further explained.

A few helium field-ion images of Ir adatoms on the Ir(111) surface are shown in Fig. 1. It is clear that all the image spots appear nearly triangular in shape. The cusps, or corners, are all pointing in the closely packed atomic row directions of the substrate, or along the ⟨110⟩ directions. The spot shape does not change when the field strength is changed. This triangular image-spot shape is similar to what Page and Ralph observed earlier

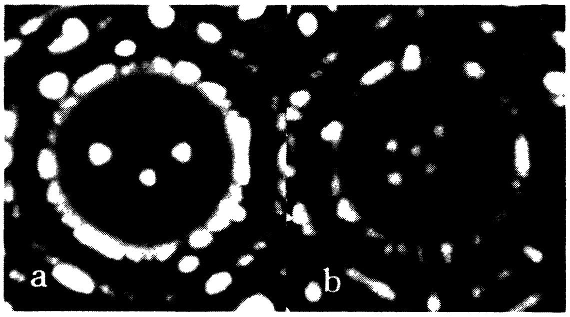

FIG. 1. Helium field-ion images of single Ir atoms adsorbed on the Ir(111) surface.

for Pt and Rh atoms retained on the (100) surface of Ir-Pt and Ir-Rh alloys. They find nearly square-shaped image spots with the cusps pointing also in the ⟨110⟩ directions. We find that Ir adatoms on this surface form regular, circular image spots. These cusp structures may arise from two effects. First, it may be produced by the bond directions of field-adsorbed helium; the size of the image spot is consistent with what can be expected from the resolution of the FIM. Second, it may arise from an electronic charge-density modulation by the adsorption. In any case, the image intensity tails extend for only 2 to 3 Å in distance and there are no oscillatory features.

What is a much more surprising and interesting observation is the spot shape of impurities deposited on the Ir(100) surface from a Ta wire source. We find a Ta wire source is very difficult to clean. Just prior to achieving a complete cleaning of a Ta wire source, two different kinds of image spots of the deposited species can be observed. The ordinary kind produces circular image spots of regular size which are pure Ta adatoms. The other kind, which is very small in number, produces large image spots with their shape dependent on the field strength, as shown in Figs. 2 and 3. At a very low field, these image spots appear as very bright image blobs. In field-ion microscopy, when the field is low, atoms in the more protruding positions always show exceptionally high image intensity. The image resolution is also less good. Thus even if structures exist inside these image blobs, they cannot be resolved. However, as the field is raised, a halo-ring structure starts to appear. When the field is further increased, the size of the outer ring remains nearly constant until the field reaches ~2.9 V/Å; then it increases rapidly. At a field of ~3.2 V/Å, the outer ring may suddenly collapse into a regular image spot or a slightly larger image spot. At this field, regular image spots of Ta also become a little more diffuse and slightly larger. It appears that an impurity atom of some sort has been field desorbed at this field, and as a result the halo-ring structure disappears. In Fig. 4, we show how the approximate range, or the diameter, of the outer ring and that of the central image-spot

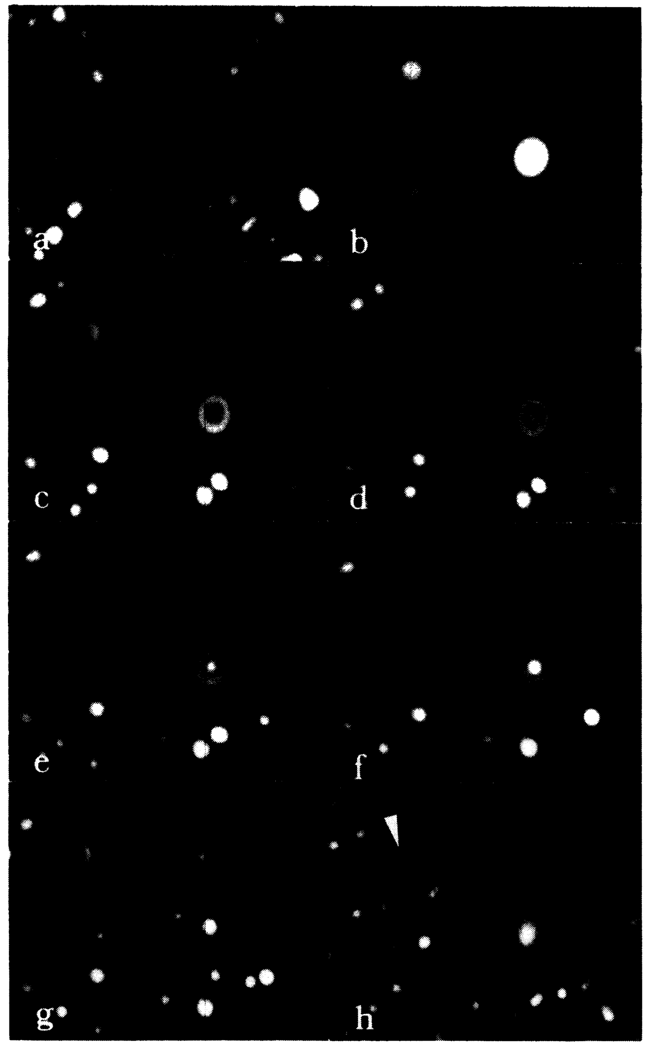

FIG. 2. The first picture is a neon field-ion image of a field-evaporated Ir(100) surface. The rest of the pictures are neon field-ion images at different tip voltages showing two impurities which are deposited on this surface from a Ta wire source. The one near the upper left-hand corner is adsorbed near a lattice step of the substrate. The image voltages for these pictures are 6.75, 4.5, 5.0, 5.05, 5.10, 5.20, 5.40, and 5.7 kV, respectively. The last picture shows that one of the impurities, indicated by an arrow, now has the spot size of a metal atom but the other one is still unusually large.

change with the applied field strength. Length calibration of image spots, however, is not very reliable and can be off by a factor as large as 2.

Exact chemical identification of these impurities is most difficult because of the very small number of such impurities which can be observed for each Ta wire source and also because compound ions can be field dissociated. Using the energy-compensated time-of-flight atom probe we have tentatively identified these impurities to be tantalum hydrides. The detected ion species

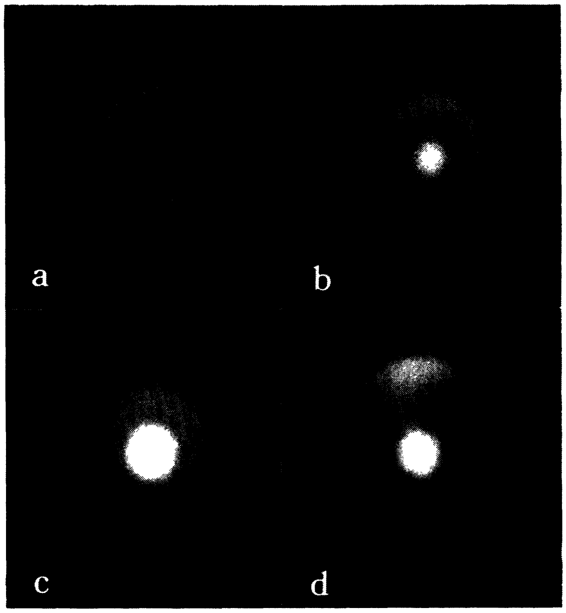

FIG. 3. Enlarged pictures showing a few images of an impurity on the Ir(100) surface at slightly different fields.

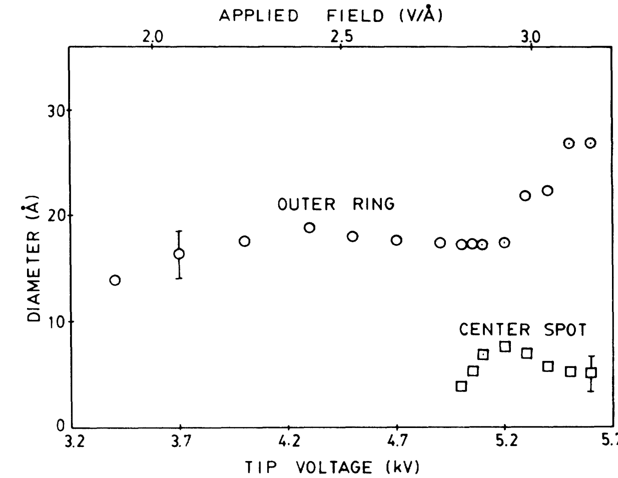

FIG. 4. Approximate ranges, or diameters, of the outer ring and the central spot, as a function of the applied field of the electronic charge distribution resulting from the perturbation of an impurity.

are Ta^{2+}, TaH^{2+}, and H^+. Thus the impurities are most likely TaH, TaH_2, or other small tantalum hydrides. These are definitely not tantalum clusters. The exact identification of the impurities is not important at the present time. The important thing is that these impurities produce a halo-ring structure in the field-ion images. Based on a length calibration of the fully resolved nearest-neighbor atomic distance of the [100] atomic rows of the substrate, the charge perturbation is found to extend to as far as ~ 25 Å from the perturbation centers, as can be seen from Fig. 4. However, the image magnification can be off by a factor as large as 2 for single image spots, and we do not know a way to make an accurate calibration. The charge-density perturbation can, of course, be affected by the applied field; the effect is especially large when the field reaches ~ 2.9 V/Å. An interesting observation is that the halo-ring structure seems to be least affected by the atomic structure of the underlying lattice: It is only when the field is sufficiently high that a faint feature lining up approximately in the [110] direction of the substrate can be seen. The halo-ring structure is seen even for an impurity located near a lattice step. The observed effect is thus more a property of the itinerant conduction electrons of the metal than a property of the lattice, as can be expected from the surface-charge-density modulation by an impurity.

The question is what causes the field-ion image spots to appear as a halo-ring structure. This structure cannot be produced by field adsorption of neon since no such structure has been observed in field-ion images of either single metal adatoms or metal clusters where field adsorption of neon can equally occur. In addition, field adsorption of neon should exhibit a strong structure effect of the substrate, similar to the observation by Page and Ralph of Pt and Rh on Ir(001) and our observation of Ir on Ir(111). In field-ion microscopy, adsorbed hydrogen atoms and molecules cannot be imaged. Thus the halo-ring structure cannot be produced by them alone either. It is also unlikely that the halo-ring structure is produced by an orbital motion of an H atom or molecule around the Ta adatom since H or H_2 is itself not visible in the FIM. All considerations lead us to believe that the halo-ring structure we have observed is most likely the result of a surface-charge-density oscillation induced by the adsorption of the impurity on the surface, which in turn produces a modulation in the field-ion image intensity through the effect of unoccupied density of states at the surface and also through the effect of the local field variation, or both the $\rho(E_F)$ and eV terms in Eq. (1), in field ionization as discussed earlier.

In the future, it will be important to make a systematic study to find out what impurities are most effective in perturbing the charge-density distribution of a metal, and how the applied field will further perturb the distribution. Such experiments would be very difficult since it appears that neither metal nor semiconductor adatoms alone can produce a large enough effect. For the moment, as far as we are aware, this is the first time field-ion image spots with an oscillatory image-intensity modulation have been observed. This image-spot structure is most probably produced by the oscillatory charge-density distribution at the metal surface resulting from the perturbation of the adsorbed impurity.

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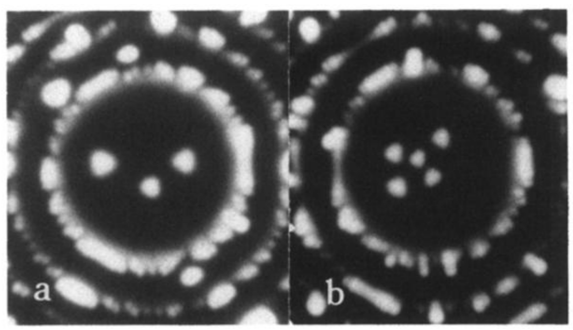

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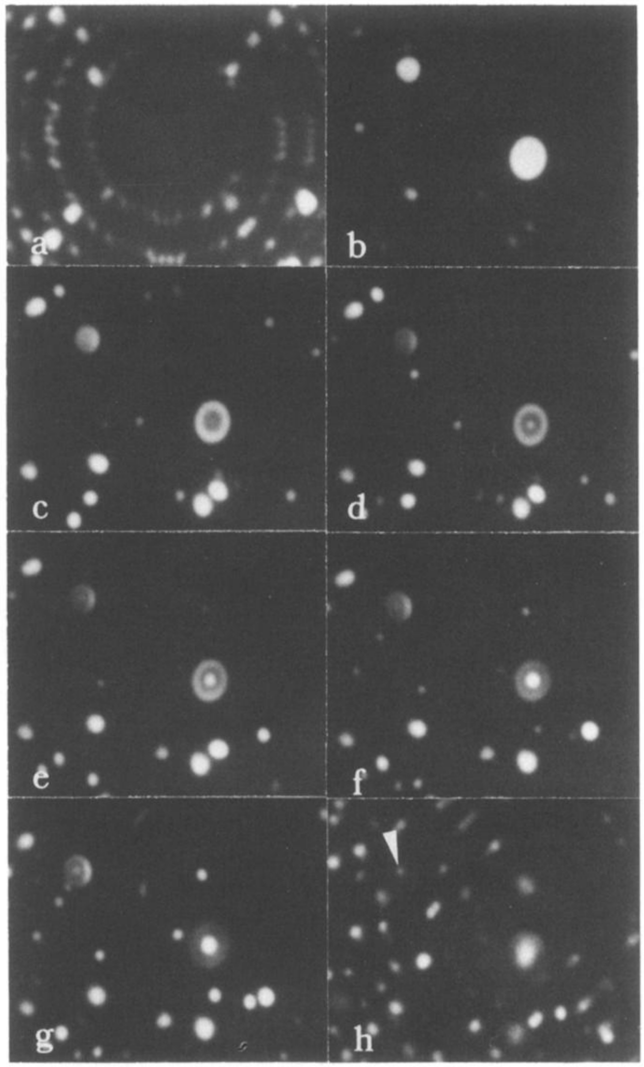

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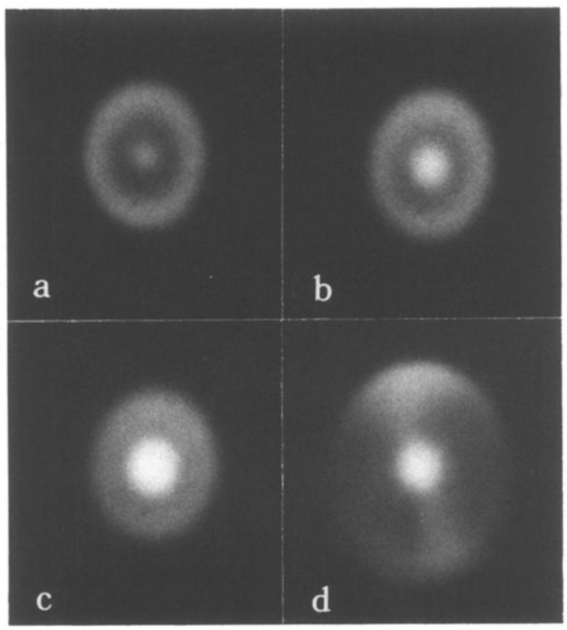

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