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Field Ion Microscope Observations of Cluster Formation in Metal Deposits on Tungsten Surfaces

WHILE studying the mobility of single metal atoms on clean tungsten surfaces by field ion microscopy (ref. 1 and our unpublished results), we have observed the formation of polyatomic clusters in the adsorption layer. The nature and stability of such clusters are of interest in relation to the nucleation of orientated overgrowth layers² and the interaction between adsorbed atoms. Our observations relate to atoms diffusing at temperatures in the range 220°–360° K along the direction of close-packed atom rows on (211) and (321) surfaces, and in all directions over the (110) surface.

For all the adsorbates studied—Ta, W, Re, Ir and Pt—collisions between atoms diffusing in the same channel of a (211) or (321) surface resulted in cluster formation. The individual atoms of dimers were not resolved in the helium ion image at 78° K, and the atoms presumably occupied nearest neighbour sites separated by 0.274 nm. Cluster formation greatly reduced the adsorbate mobility. No dissociation of dimers was observed, so the strength of the bond between adsorbate atoms is unknown.

The behaviour of adsorbates on the (110) plane was very different from that on (211) and (321), and varied with the adsorbate metal. Whereas Ta and W readily formed stable polyatomic clusters, clusters of Ir and Pt were relatively unstable. Re did not form dimers although larger clusters were observed. Ta and W dimers gave unresolved but distinctly oval image spots with the molecular axis at 55°–65° to [110], which does not correspond to the direction expected for atoms occupying nearest-neighbour lattice sites. Furthermore, the mobility of dimers was less by a factor of about ten than that of single atoms on (110) and no dissociation was observed. In contrast, Pt and Ir dimers yielded images in which the individual atoms were resolved (Fig. 1), and were orientated with their molecular axis parallel to the close-packed direction of the substrate. These dimers were only slightly less mobile than single atoms and dissociation occurred at measurable rates. The frequency of dissociation indicated weak bonds between the adatoms of about 7 kJ/mole for Ir dimers and 16 kJ/mole for Pt dimers.

The interatomic distances in dimers cannot be deduced directly from the ion micrographs because of the extra magnification of clusters protruding from the surface. Comparison of the dimensions of the image spots with the jump distance for single atoms measured in diffusion

studies indicates that the bond lengths did not exceed 0.7 nm. For Pt and Ir the low binding energy and the resolution in the image spots are consistent with a spacing of 0.55 nm—twice the spacing in the substrate lattice. The stronger bonding and lack of resolution in the images of Ta and W dimers are consistent with a smaller spacing; the non-alignment of the pair axis with the close-packed direction suggests that these adatoms do not occupy points of the substrate lattice. An examination of possible alternative adsorption sites on a (110) surface shows that the observed axis orientation could be obtained in dimers with a bond length of 0.35 nm. The spacings assigned are, however, subject to reservations about the unknown minimum resolvable spacing in the helium ion image of dimers on (110), and possible distortion of the dimers by the imaging field.

On the (110) plane, clusters larger than dimers could be built up one atom at a time. Individual atoms were not resolved in the cluster image spots, except for linear clusters of Pt or Ir atoms. The spacings in these larger clusters are not known, but the orientation of the cluster edges indicates that the characteristics of dimers are retained.

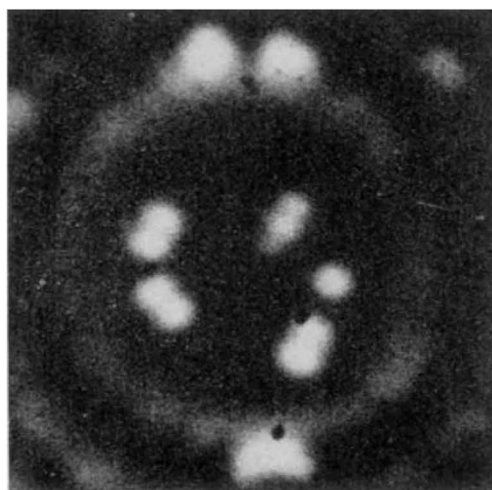


Fig. 1. Three dimers and one trimer (nearest centre of plane) formed by aggregation of single Pt atoms diffusing on (110) tungsten at 240° K.

Our observations indicate that the binding of metal adatoms on the (110) plane of tungsten³ is significantly different from binding on other planes and possibly less essentially metallic. The strength of bonds in small clusters seems to depend critically on the electronic structure of the adsorbate. The absence of strong pair bonds and the assigned spacings in dimers have important implications for the formation of overgrowth layers on (110) W. Either the orientation of the overgrowth should correspond to a lattice spacing in the interface similar to that in the dimers², or a cooperative rearrangement to a more densely packed layer must occur in clusters during nucleation. The binding of atoms in these clusters is being further investigated.

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