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MODIFICATION OF ATOMIC STEPS BY ADSORBATES OBSERVED BY LOW ENERGY ELECTRON MICROSCOPY AND PHOTOEMISSION MICROSCOPY

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The influence of adsorbates on the structure of atomic steps on a Mo{110} single crystal surface is studied by Low Energy Electron Microscopy and Photoemission Electron Microscopy. Adsorption and proper annealing of a Cu double-layer produces a large number of atoms at atomic step positions along the Mo[001] direction. The number of kink sites increases by the formation of pits. Atoms at atomic step sites multiply as atomic steps migrate past step pinning centers. Cu adsorbs at the bottom of atomic steps modifying Mo step sites there, whereas molybdenum carbide produced by thermal cracking of CO forms at both the top and bottom of atomic steps, modifying Mo sites at both top and bottom.

1. Introduction

Atomic steps are believed to play a fundamental role in many catalytic reactions [1,2]. The effect of catalytic activators, poisons, selective poisons, support materials, and of the reactants themselves on atomic steps is in most cases unknown. The newly developed Low Energy Electron Microscope (LEEM) is capable of observing such effects on model systems. This technique combines low energy electron diffraction with low energy electron imaging of surfaces. Electrons typically in the range between 1 and 30 eV are reflected normal to the surface. Observation of atomic steps is now routine. Lateral resolution is 15 nm, with a theoretical ultimate lateral resolution of 2 nm [3].

Ongoing research includes studies of the fundamental properties of atomic steps on single crystal surfaces. The examples shown are taken from a study of Mo{110} surface. The basic concepts presented should be applicable to many crystalline surfaces.

Details of the instrument, the procedures and earlier results are published elsewhere [4–8]. The microscope has a base pressure of 1×10^{-10} Torr (1.5×10^{-8} Pa) after bakeout. The Mo sample was an ultra high purity single crystal, cut, polished and cleaned by standard surface science methods [9,10]. All experiments were done in situ. Photoemission electron microscopy (PEEM) is used as an auxiliary technique. It is capable of imaging atomic steps under favorable conditions using step decoration techniques [9].

2. Results and discussion

All single crystal surfaces observed by LEEM to date, which are cut and polished by the usual metallurgical procedures, have an atomic step and terrace structure. Figure 1 shows a fairly ideal structure observed after flashing the crystal to 2000 K and then quenching to room temperature. The straight line in the middle is a slip trace produced by thermal stress. It is one atomic step in height [10]. (The irregular dark line seen in all images is a crack in the channel plate.) Typically, the atomic steps are not aligned along any particular crystallographic direction. Rather, their direction and the widths of the terraces between them vary with local orientation. Steps which are not aligned along the most densely packed directions must possess a high density of kink sites. The kink

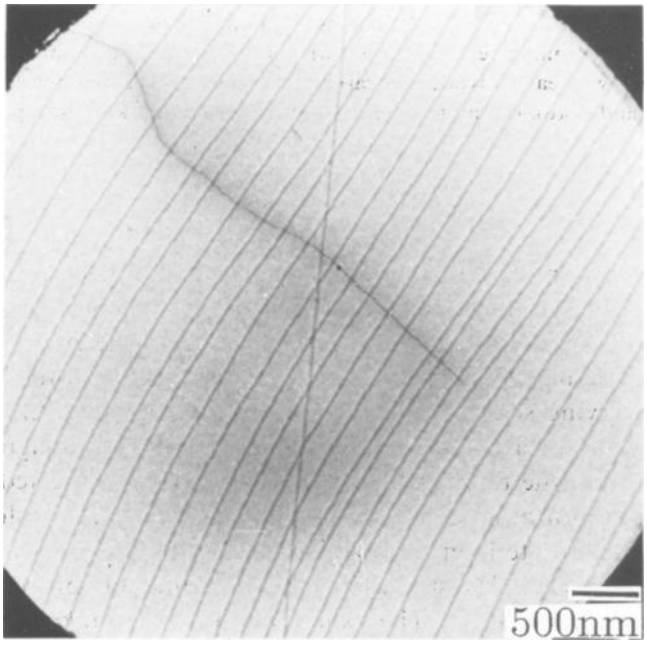

Fig. 1. LEEM image of atomic step and terrace structure on Mo{110}. A slip trace crosses the surface. 4 eV.

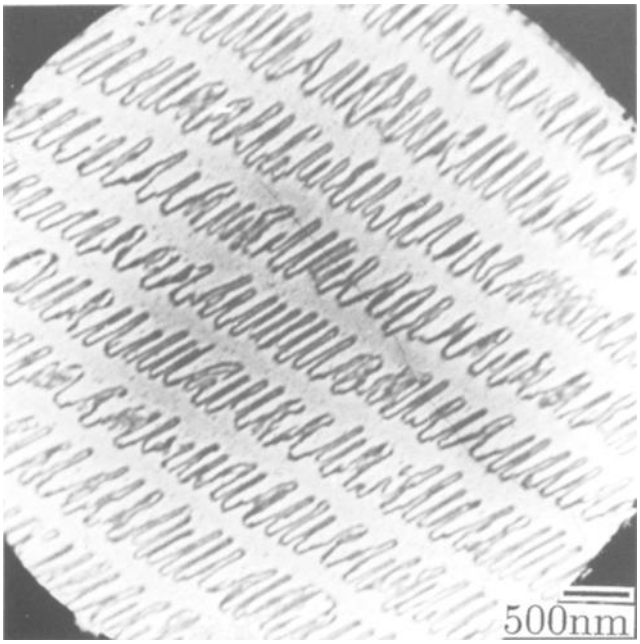

Fig. 2. LEEM image of irregular atomic step and terrace structure after partial desorption from a Cu double layer on a Mo{110} surface. Facets are along the Mo[001] direction. 3 eV.

regions are expected to be highly chemically reactive because of the lower coordination of atoms in these regions. (Indeed for many chemical reactions the kink regions may be too reactive to serve as catalytic centers.) Adsorbates, combined with various heat treatments, can modify the atomic step and terrace structures of the clean surface in a number of ways.

Figure 2 shows a very irregular atomic step and terrace structure produced by the adsorption of two monolayers of Cu at 700 K, followed by desorption of the second layer above 1000 K. The steps have faceted along the Mo[001] direction. The high temperature structure of the copper double layer has a very good epitaxial fit on Mo along this direction [11]. As a consequence, the step free energy is lowest for steps in the [001] direction, and these steps develop preferentially during annealing at high temperatures. The significant point here is that the number of atoms at step edge positions increases. In addition randomly oriented steps are replaced by steps of low Miller index.

One general effect of adsorbates on atomic steps, which has now been observed for many systems, is that they often stabilize step directions of low Miller indices. Just as adsorbates can stabilize non-equilibrium crystal planes of low Miller indices by reducing the surface free energy, so too can adsorbates stabilize non-equilibrium step directions of low Miller indices by reducing edge free energy.

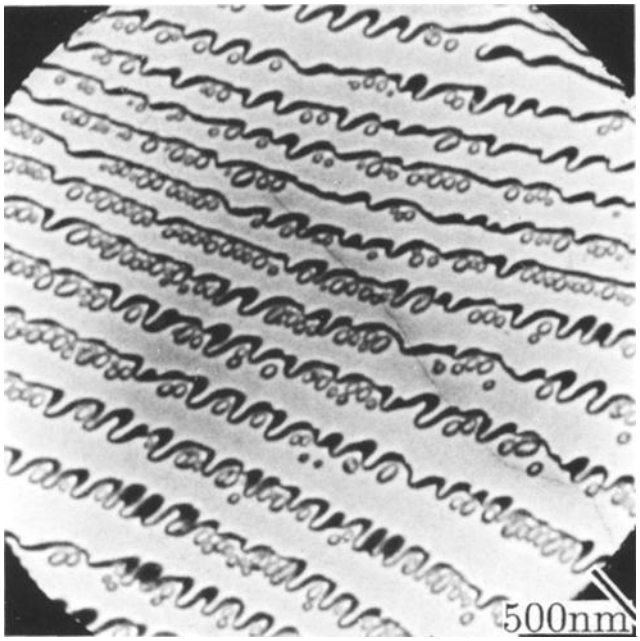

Fig. 3. LEEM image of rounded steps and of pits produced by continued heating and partial desorption of Cu from the surface shown in fig. 2. 3 eV.

Figure 3 shows the evolution of the structure of fig. 2 after continued heating and further desorption of Cu. Bright areas are covered with a monolayer of Cu. Video recordings of the sublimation process show that the dark areas are uncovered Mo at the top of the steps. With continued heating the facets along the Mo[001] direction disappear and the step edges become more rounded. The closed loops are pits one atomic step deep. The formation of the pits greatly increases the number of atoms at step edge sites. Moreover, closed loops must contain a large number of atoms at kink sites, because all edges obviously cannot be aligned along a direction of low Miller index. Figures 2 and 3 demonstrate the subtle effects of heat treatment on adsorbate-covered surfaces on atomic steps. The structures of figs. 2 and 3 were very reproducible.

Figure 4 is a photoemission image showing the influence of a step pinning center on the step distribution. The atomic steps here are decorated with Cu, which was deposited onto the Mo substrate held at 700 K. Cu adsorbs at the bottom of the steps. Step pinning centers are observed on a variety of substrates and occur whenever localized impurity aggregates prevent the free desorption of the underlying substrate material. During sublimation atomic steps migrate approximately parallel to one another. In fig. 4 the Mo steps, free of Cu, were migrating from left to right. The steps bunch together behind the pinning center. However, the regions of the steps away from the pinning center can continue to migrate and eventually encircle it. When steps at the same level meet beyond the

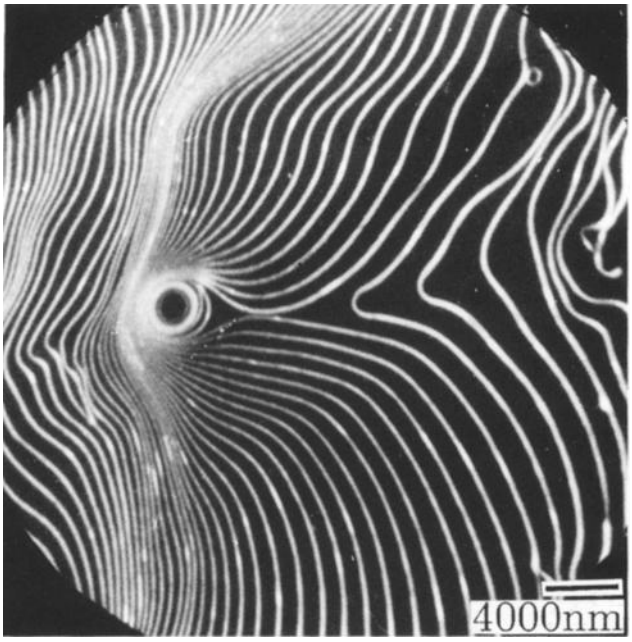

Fig. 4. PEEM image of step pinning center, showing local multiplication of atomic steps on Mo{110}. Cu decoration.

pinning center they caolesce. The step is no longer pinned and is once again free to migrate. However, as each step migrates past the pinning center, the pinning center is encircled by a ring one atomic step in height. The rings are of ever increasing diameter and the pinning center grows into a cone. In this manner the number of atoms at atomic step sites multiplies on the surface. A relatively negligible amount of impurity is all that is necessary to start the process. The pinning centers can grow to large size. Because the loops are circular, they must contain many kink sites. Similar multiplication of atoms at atomic step edge sites should occur during chemical etching if an impurity resists the etch. Impurities must be concentrated in islands for this effect. If the adsorbates are distributed along an extended front only step bunching occurs. This is the most probable explaination for the step bunch [13] seen in the upper left of fig. 4.

Figure 5 shows two-dimensional carbide islands on Mo{110}. They were produced by thermal cracking of adsorbed CO below 500 K. Transition metal carbides are now of great catalytic interest [12]. The carbide islands form in two domains, with the major axes of the islands oriented along the two ⟨111⟩ directions of Mo{110}. An unusual feature shown in fig. 5 is that the carbide has formed at both the top and bottom of the atomic steps. Typically adsorbates will nucleate either at the top *or* bottom of the steps. The distinction is important because atomic sites at the tops of atomic steps may possess different catalytic activity than sites at the bottom. Possibly some selective poisons act by blocking

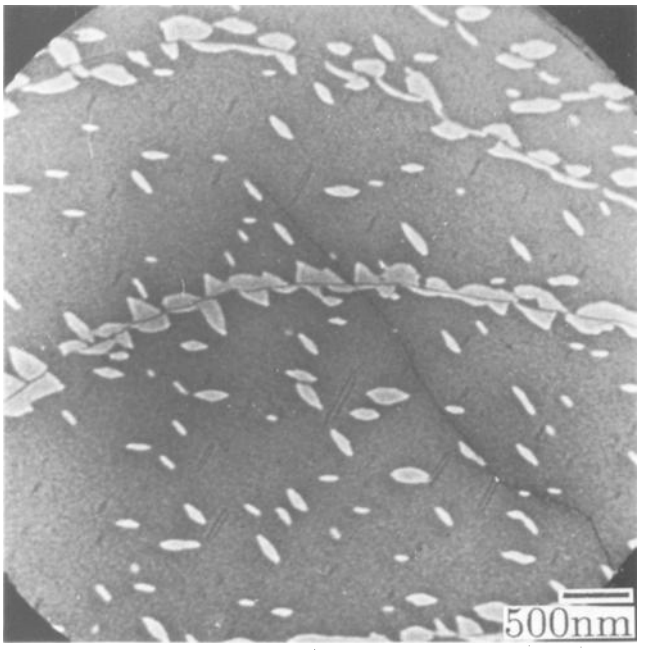

Fig. 5. LEEM image of carbide islands on Mo{110} formed by CO cracking below 500 K. 17 eV.

sites at the top or bottom of steps. LEEM is capable of distinguishing between these two situations. The carbide islands did not always form at steps. More often islands grew exclusively on the terraces [13].

3. Conclusions

Atomic steps may be modified by adsorbates in a variety of ways. The changes are often quite subtle and are not easily detected by most techniques of surface science. LEEM is capable of observing the effects of adsorbates at atomic steps on many model systems of catalytic interest.

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