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The p4g or pgg reconstruction on Cu(100)

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Abstract. The adsorption of atomic hydrogen in the high coverage regime has been investigated. It was found that the surface under these conditions undergoes a reconstruction into the fairly rare pgg or p4g symmetry. The reconstruction was found to coincide with a new HREELS energy loss feature, besides the one present at the low coverage which is interpreted as hydrogen in a hollow site. The new loss feature is interpreted as hydrogen positioned in a bridge bonded site. Two models with the correct symmetry are considered.

1. Introduction

The chemisorption of hydrogen has received much attention lately as it plays an important role in technology and especially in catalysis. Our motivation to investigate the copper–hydrogen system is mainly due to its importance in the synthesis of methanol. Recent experiments have proved that hydrogen can introduce reconstructions on Cu(110) [1, 2] and the nature of the adsorption sites has been discussed from both an experimental [3] and a theoretical [4] point of view. The Cu(100) surface has also been studied [5] and it was suggested, although not proved, that the surface may undergo a reconstruction. The adsorption of hydrogen on copper is a highly activated process and in [5] a molecular beam was used to overcome this barrier. The maximum coverage, when using a beam with a normal energy of 0.4 eV per molecule, was in that case 0.5 monolayer [5]. In this and a previous paper [6] we show that the surface indeed undergoes a reconstruction, however, at a much higher coverage than was achieved in [5]. By using an atomic hydrogen source, a full monolayer of hydrogen can be achieved and it was found by low energy electron diffraction (LEED) that the surface under these conditions undergoes a reconstruction into a ppg or p4g symmetry.

2. Experimental procedure

All the experiments were performed in a UHV chamber with a base pressure P_{base} less than $P_{base} \leqslant 1 \times 10^{-10}$ mbar. The apparatus was equipped with x-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS), LEED and temperature programmed desorption (TPD). As the adsorption of hydrogen is highly activated, the hydrogen molecules were pre-dissociated by a hot tungsten filament prior to adsorption on the Cu(100) crystal. For further experimental details we refer the reader to [6].

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3. Results and Discussion

Figure 1 shows a TPD spectrum of hydrogen from a Cu(100) crystal saturated with atomic hydrogen. The heating rate was 2 K s^{-1} and the high temperature feature compares well with the feature seen in [5], where the saturation coverage was a half monolayer. The saturation coverage in the present experiments, where atomic hydrogen was used, has been estimated to be close to one monolayer, see [6] for details. Figure 1 also shows schematically the results of the investigations of the surface symmetry studied by LEED. A p4g or ppg LEED structure is observed when the surface is saturated with atomic hydrogen. Following the development of this structure, while heating a saturated surface as in the TPD experiment, this LEED pattern is seen to shift irreversibly back to a simple 1×1 at 225 K as indicated by the vertical bar in the TPD spectrum. Thus the rather sharp feature observed toward the lower temperatures is clearly due to atomic hydrogen involved in the reconstruction of the surface. The observed LEED patterns are indicated in the insert of figure 1. As hydrogen is a very weak scatterer the obtained LEED patterns, which were rather sharp [6], must be due to reconstructions of the Cu(100) surface. The LEED pattern of the reconstructed surface is in principle just a 2×2 where the $(n,0)$ and $(0,n)$ beams are missing when n is odd. This LEED pattern has been observed earlier for carbon adsorbed on Ni(100) [7–9] and the symmetry has been discussed extensively. The missing spots are essentially due to the presence of two orthorgonal glide planes.

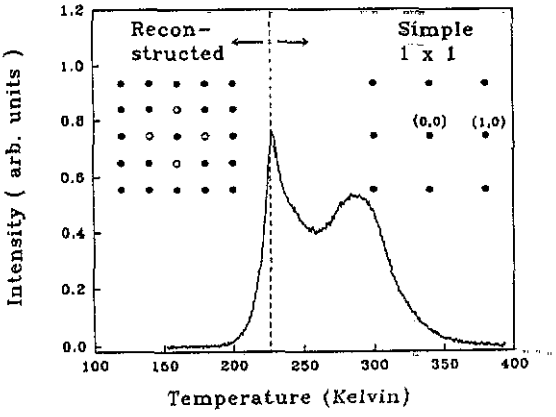


Figure 1. TPD spectrum from Cu(100) saturated with atomic hydrogen. Schematics of the observed LEED-patterns are overlaid.

The results of the HREELS investigations are summarized in figure 2. Here the HREELS spectra of atomic deuterium on the Cu(100) are shown for a coverage which is roughly half a monolayer (lower curve) and for a saturated surface (upper curve). For half a monolayer only one frequency is observed at 52 meV. By saturating the surface with atomic deuterium, this loss nearly disappears while two new losses at 42 meV and 86 meV appear. The deuterium case is very similar to the hydrogen case except for the expected $\sqrt{2}$ shift in frequency and the fact that the low-lying energy loss observed for the low coverage does not disappear completely when saturating the surface with hydrogen. This low-lying energy loss is interpreted as hydrogen (deuterium) chemisorbed in a hollow site. When going to high coverage, a new site for adsorption is opened by the reconstruction and the hydrogen chemisorbed in the hollow sites feels a slightly modified potential, thus the small shift downward in

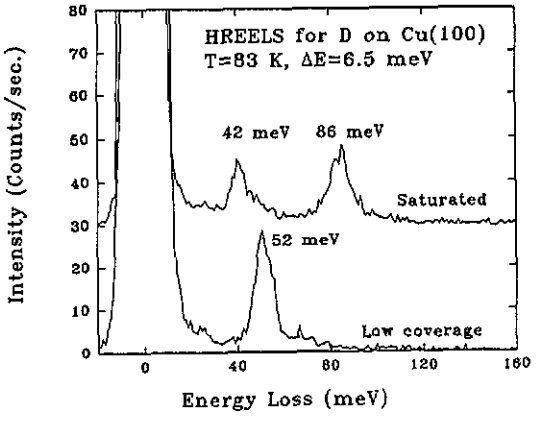
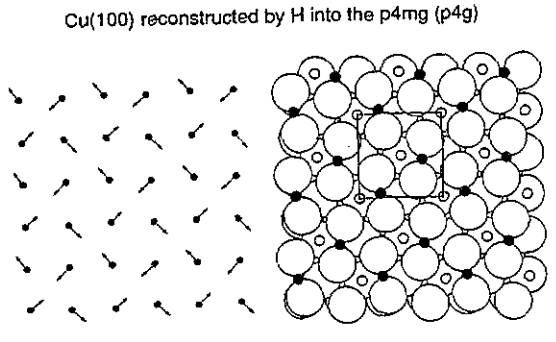


Figure 2. HREELS spectra of atomic deuterium on Cu(100) at low (lower curve) and high (reconstructed) coverages.



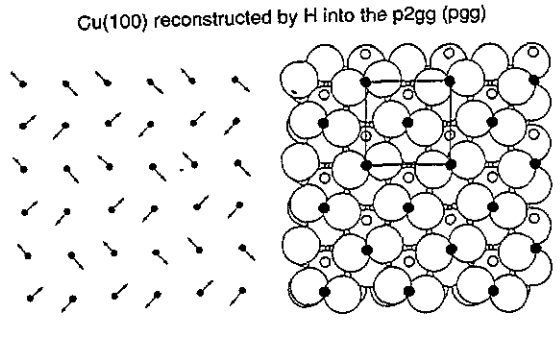


Figure 3. Two models displaying the correct symmetries p4g and pgg. Half a monolayer hydrogen is located in the hollow sites and another half a monolayer is located in the bridge bonded site. The arrows indicate the direction of the distortion of the copper surface atoms.

frequency. The new high frequency energy loss is interpreted as due to hydrogen adsorbed in a bridge bonded site.

Having both the information on the surface symmetry and the information on the bonding geometry, it is possible to set up models for the reconstruction. The observation of the p4g or pgg symmetry where two orthorgonal glide planes are present reduces the number of possibilities considerably. Basically three models can be set up that fulfill the symmetry requirements leading to the observed LEED patterns [6]. As the third model involves transport of half a monolayer of copper atoms and as the reconstruction can be induced by dosing atomic hydrogen at 80 K

where the mobility must be low, this model seems unrealistic and we shall therefore not consider it further here. This leaves us with the two models shown in figure 3. Also shown in figure 3 are the direction of the distortions of the copper atoms leading to the reconstruction. The direction of the distortion does not need to be 45° compared with the unit vectors in order to fulfill the symmetry requirements, but if not, the p4g will be converted into a pgg symmetry. Likewise the hydrogen overlayer does not have to fulfill the symmetry requirements. In order to provide a picture of the surface, the hydrogen atoms have been placed in the most realistic positions, emphasizing that other possibilities exists. It is quite easy to accommodate half a monolayer of atomic hydrogen in the hollow sites of the p4g structure. However, when it comes to the bridge site it will be too expensive energy-wise to place hydrogen over the diagonals where the surface copper atoms are approaching each other. Likewise putting them in the bridge bonded positions between the distorted copper atoms opens a full monolayer of equivalent bridge bonded sites. In the case of the pgg structure, it is easy to accommodate half a monolayer in a bridge bonded site. In this case a full monolayer of equivalent hollow sites is possible. Maybe only one hydrogen atom can be accommodated in each of these extended double hollow sites as indicated in figure 3. The present study does not allow us to determine which of the models is correct.

4. Summary

In conclusion, we have found that the Cu(100) surface undergoes a reconstruction into a p4g or pgg symmetry upon saturation with atomic hydrogen. The bonding at low coverage was found to be in a hollow site, whereas at high coverage the HREELS spectra were interpreted as the presence of both a hollow and a bridge bonded site.

Acknowledgments

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