Structure analysis of the Cu(110)-(1×2) surface reconstruction induced by alkali-metal adsorption

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The structure of the alkali-metal-induced reconstructed Cu(110)-(1×2) surface has been analyzed by use of low-energy electron diffraction. A missing-row model, a row-pairing model, and a sawtooth model have all been examined. The results confirm the missing-row model for the reconstruction with no long-range order for the alkali-metal atoms. The top interlayer spacing of the reconstructed Cu(110) surface is contracted by 11% and the second layer exhibits a lateral pairing displacement of 0.10 Å.

INTRODUCTION

The (1×2) reconstruction has been observed on nearly all fcc metal (110) surfaces. This interesting phenomenon has stimulated a great number of experimental and theoretical works in recent years.[1–13] It has been known that for the 5*d* metals Ir, Pt, and Au, the (1×2) reconstruction is established on an annealed, clean surface. Low-energy electron diffraction (LEED) analysis and theoretical calculations confirmed a missing-row model with paired rows in the second layer and buckled rows in the third layer for all three 5*d* metals.[1–4] For the 4*d* fcc metals, Pd and Ag, the (1×2) reconstruction was observed after a small amount of alkali-metal adsorption on the (110) surface. A missing-row model without multilayer relaxation or reconstruction was suggested, even though no exact structure was identified.[5,6] For the 3*d* metal Ni, a multilayer reconstructed Ni(110)-(1×2) surface was found after exposure of Ni(110) to H_2 at low temperature. The exact surface structure was reported to be a row-pairing model with second-layer buckling.[7]

Within the fcc metal (110) surface the adsorbate-induced reconstruction of Cu(110)-(1×2) is one of the most attractive subjects for study. Many experimental techniques have been applied to it;[8–10] however, the exact structure of the reconstructed surface has not yet been reported. On the other hand, numerous theoretical efforts have been devoted to explain the fcc metal reconstruction mechanism, especially for the Cu(110)-(1×2) surface. For example, studies have been undertaken in the phonon-softening model within a lattice-dynamical approach,[11] a chemisorption-energy calculation,[12] and a structural-energy calculation within the linear combination of atomic orbitals (LCAO) formulation.[13] Past recent work[8] on alkali-metal adsorption of the Cu(110) surface has shown a 1×2 alkali-metal-induced reconstruction for the Cu(110) surface. Structural analysis by LEED has been, therefore, undertaken in an attempt to more fully understand the mechanism of surface reconstruction and the driving force that initiates it.

EXPERIMENT

The experimental procedure was described in detail elsewhere;[8] only a brief description will be given here. The experiments were carried out in an UHV chamber with a four-grid LEED optics with data acquisition via a video camera interfaced to a personal computer. The Cu(110) surface was cleaned by cycles of Ar-ion bombardment and annealing until there was no indication of impurities in the Auger-electron spectra (AES), and the LEED pattern showed sharp, high-contrast spots. The temperature was measured by Chromel-Alumel thermocouple. Potassium and cesium sources used in this study were Saes-Getters thermal cells.

When the evaporation of K or Cs onto the Cu(110) surface was conducted at 80 K, the alkali-metal overlayer formed a disordered structure or a quasihexagonal structure depending on the coverage.[8] No obvious surface reconstructions were observed. The evaporation of potassium at room temperature produced, however, a sequence of changes in the LEED pattern. At first, streaks in the ⟨001⟩ direction passing through diffraction spots appeared. As the coverage increased, the streaks coalesced into spots which identified a (1×3) superstructure. At a coverage of $\theta > 0.12$, the (1×2) pattern appeared. Here, coverage is defined as the ratio of the number of adatoms to the number of substrate atoms per unit area.

It is very interesting to note that the *I-V* curves of all beams for the K-adsorbed surface are the same as those of the Cs-adsorbed surface despite the large difference in the K and C atomic sizes. This fact supports a reconstruction model for the two structures: the reconstructed Cu(110) substrate produced the (1×2) and (1×3) diffraction patterns, not the alkali-metal overlayer.

Seven LEED intensity spectra for the (1×2) structure,

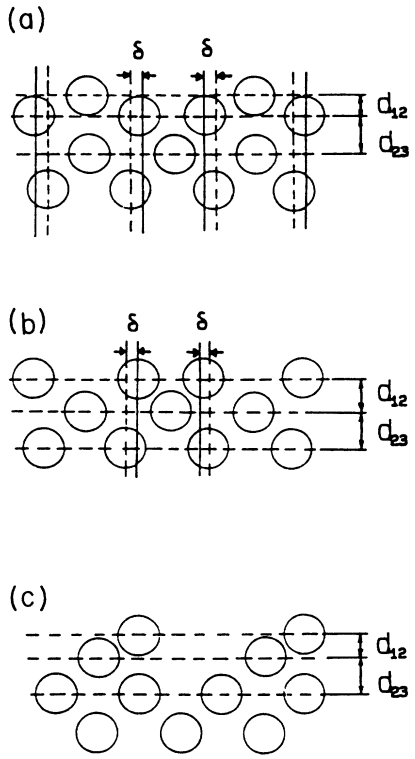

FIG. 1. The three main structure models considered for the reconstructed Cu(110)-(1×2) surface with the definitions of the interlayer spacings d_{12} and d_{23} and the lateral shift parameter δ. (a) missing-row model, (b) row-pairing model, and (c) sawtooth model.

consisting of three integral-order beams and four fractional-order beams, were collected at normal incidence at a coverage of 0.15 for both K and Cs.

ANALYSIS

A dynamical LEED analysis accompanied by reliability (R) factor evaluation[13] was applied to obtain the atomic structure of the alkali-metal-induced reconstructed Cu(110)-(1×2) surface.

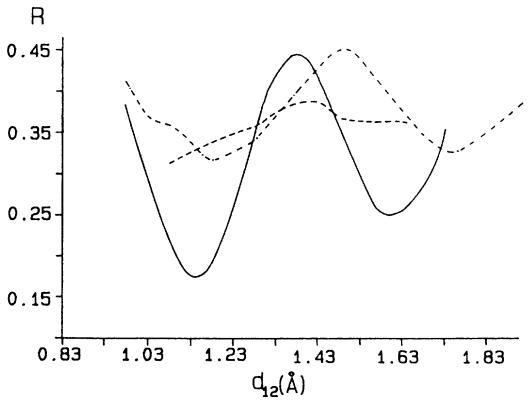

FIG. 2. The R factor as a function of d_{12} for the missing-row model (——), the row-pairing model (—·—·—·), and the sawtooth model (— — —). d_{12} is the interlayer spacing between top and second Cu layers.

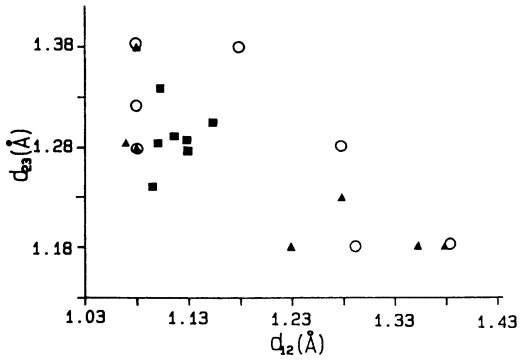

FIG. 3. Best parameters d_{12} and d_{23} defined by R-factor analysis for each individual diffraction beam; missing-row model, row-pairing model, and sawtooth model.

Three main substrate reconstruction models, including the missing-row model, the row-pairing model, and the sawtooth model (Fig. 1), were tested. In the theoretical calculations, seven phase shifts were used. The real part of the inner potential (V_0) was determined to be 15 eV after varying V_0 by a rigid shift of the energy scale to optimize the comparison between theoretical and experimental I-V spectra. A constant imaginary part of optical potential of 5 eV was used. The bulk *Debye* temperature used in the calculation was 343 K, and an enhancement factor of 1.4 was used for the surface layer mean-square vibrational amplitudes. The alkali-metal overlayer was assumed to have no long-range order thus resulting in only a reduction of intensity of all beams and an increase in background, but no other effect on the I-V profiles. Therefore, in theoretical calculations, no special attempt was made to incorporate the disordered alkali-metal overlayer except to extend the inelastic part of the potential above the top Cu layer to account for absorption in the overlayer.

The layer-doubling method and the reverse scattering perturbation (RSP) methods were used in the theoretical calculations.[14] The energy range in the calculations was

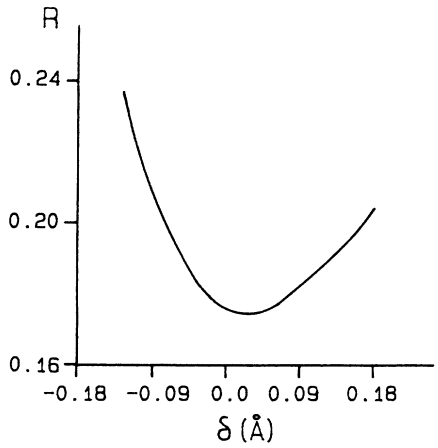

FIG. 4. The R factor as a function of δ (lateral shift parameter) for the missing-row model with row pairing in second layer and $d_{12}=1.13$ Å, $d_{23}=1.28$ Å.

from 50 to 225 eV and 48 beams were used for the missing-row model and row-pairing model, with 70 beams used for the sawtooth model as the calculation used only mirror plane symmetry.

The agreement between experiment and theory is quantified by the average of five R factors: R_{OS}, R_1, R_2, R_{RZJ}, and R_{PE}.[15] In the first step of the analysis, one parameter d_{12}, the top interlayer spacing was varied over a wide range for all three models. Figure 2 shows R as a function of d_{12} for the three models. The missing-row models show oscillatory minima which have good regularity and a minimum $R=0.18$ at $d_{12}=1.13$ Å. The minimum value of R for the best row-pairing model is much larger (0.32), and the shape of R as function of d_{12} is less periodic. The R factor for the sawtooth model is the worst being high and nearly flat over the whole d_{12} range.

In the second step of the analysis, two parameters were adjusted simultaneously: the topmost interlayer spacing d_{12} and second interlayer spacing d_{23}. The R factors from the I-V curves of the individual beams were used to obtain a pair of best parameters d_{12}, d_{23} (Fig. 3). For the missing-row model, the chosen "d" parameters are concentrated in a small area around $d_{12}=1.13$ Å, $d_{23}=1.28$ Å. However, for the row-pairing model and the sawtooth model, there was no consistency in the d parameters that were determined for the seven LEED beams. A single structure could not be identified by the analysis of the seven beams for either of these two models. These results exclude the row pairing and the sawtooth model from

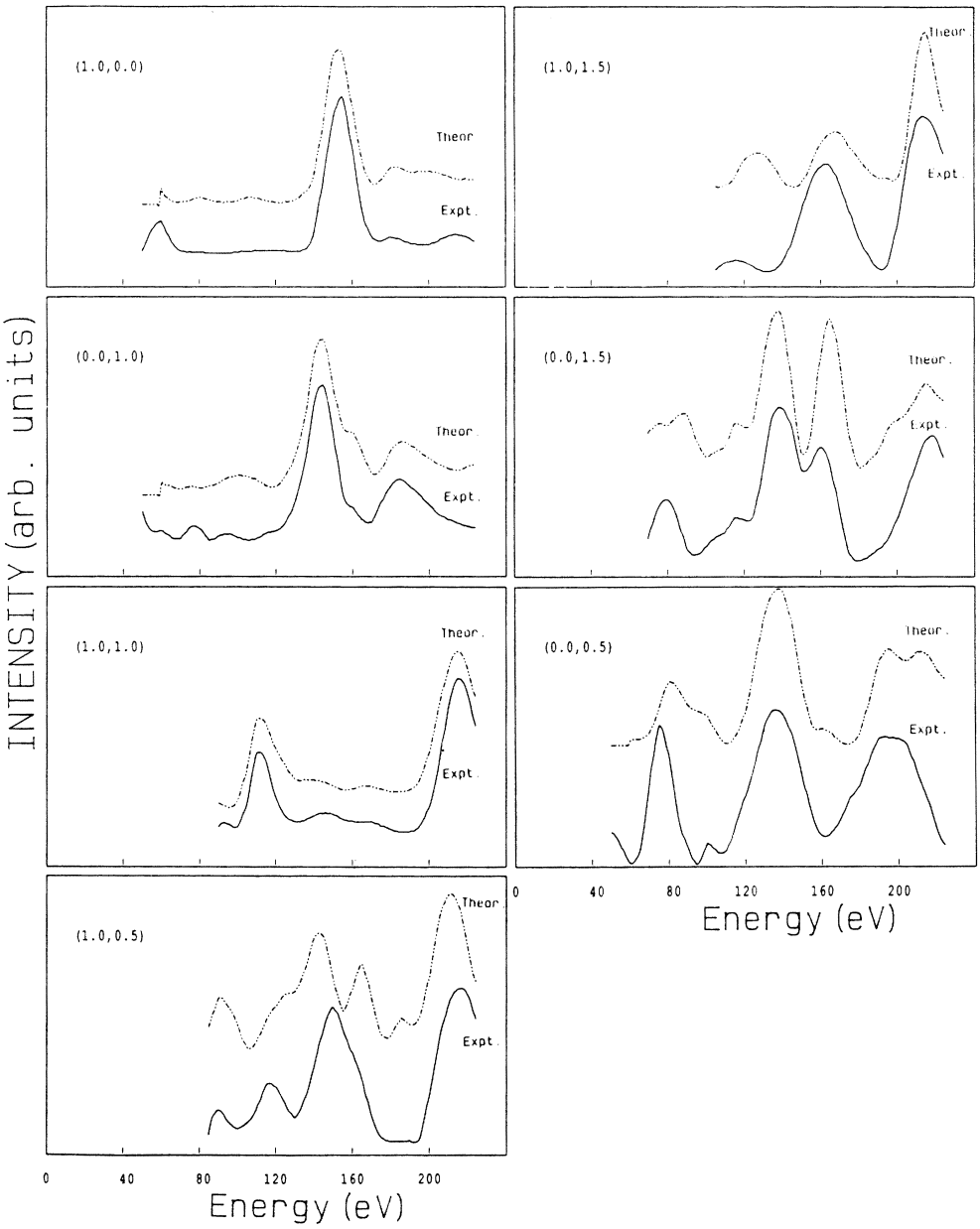

FIG. 5. Experimental and calculated I-V curves for the most probable missing-row model for the Cu(110) alkali-metal-induced (1×2) structure. $d_{12}=1.13$ Å, $d_{23}=1.28$ Å, and $\delta=0.05$ Å.

further consideration.

The above analysis for the alkali-metal-induced Cu(110)-(1×2) surface reconstruction defines the structure as a missing-row model with $d_{12}=1.13$ Å and $d_{23}=1.28$ Å, that is, with top interlayer spacing contracted 11.7% and the second interlayer spacing the same as that of the bulk. This is very different from the clean unreconstructed Cu(110) surface which has oscillatory multilayer relaxation.[16] In order to obtain a more exact structure, a missing-row model with paired rows in the second layer was considered. The lateral shift parameter 2δ (Fig. 1) was varied for the second layer from -0.18 to $+0.36$ Å, while d_{12}, d_{23} were varied independently. Figure 4 shows R for $d_{12}=1.13$ Å, and $d_{23}=1.28$ Å as a function of δ. R reaches a minimum of 0.17 at $2\delta=0.10$ Å. This R is the smallest value obtained for all structures and is supported by minimum in each of the individual R factors.

Finally, buckling was introduced in the third layer as done in previous work.[2,4,7] The vertical displacement of third layer atoms 2β was varied from -0.10 to 0.80 Å, while 2δ was 0.10, to 0.40 Å, and d_{12} and d_{23} were varied independently. Here β is defined such that if the atoms underneath the missing row move up and the atoms underneath the row of the top layer move down, the vertical displacement 2β is positive. The R factor was seen to be very sensitive to the value of β, however, the smallest value of R, 0.17 was found for $0\leq\beta\leq0.02$ Å (with the remainder of the parameters as in the above paragraph) indicating that third-layer buckling is so small that it can be neglected. There has been some recent renewed interest in a buckled-row model for (1×2) reconstruction in fcc (110) surface. For the present case, however, the very poor agreement of the calculated fractional order I-V curves with experiment at values of β (buckling) away from ≈0 and 2δ away from 0.1 Å, and the general poor fit of the integer beams as 2β is increased, negates a buckled-row model for the Cu(110)-(1×2) reconstruction. Figure 5 shows the comparison of the theoretical I-V curves with the experimental spectra for this model. The most probable model for the reconstructed Cu(110)-(1×2) surface is, therefore, described by the following structural parameters: $d_{12}=1.13$ Å, $1.23\text{ Å}\leq d_{23}\leq1.28$ Å, $2\delta=0.1$ Å and $0\leq\beta<0.02$ Å. This structural model is the missing row with second-layer pairing model.

CONCLUSION AND DISCUSSION

The most probable structure of the alkali-metal-induced reconstructed Cu(110)-(1×2) surface as defined by dynamical LEED calculations is a missing-row model with an 11.7% contraction in the top interlayer spacing and a row-pairing lateral shift of 3% in the second layer. There is no clear translational symmetry between the alkali-metal atoms on the surface which induce the reconstruction, however, they are most probably located in the missing-row surface channels. The confirmation of the semidisordered structure of the alkali-metal overlayer and determination of the interlayer spacing between the overlayer and substrate will be described in another paper.[17]

It is very interesting to compare the present results with that of all other fcc(110) surfaces. The Cu(110)-(1×2) reconstruction is the same type (missing row) as that for all 5d metals and perhaps 4d metals as well [the Pd(110) structure has not yet been definitively described]. However, the 5d metal reconstruction is established on *clean* (110) surfaces, while the 4d and 3d metals need additional adsorbates, e.g., alkali-metal adsorbates, to induce the reconstruction. In the (110) surface reconstruction of 5d metals, there are large contractions in the topmost interlayer spacing (20% for Au, 18.4% for Pt, 12.3% for Pd) which smooth the surface corrugations and result in multilayer relaxation and reconstruction. For the Cu(110) surface with an alkali-metal overlayer on the surface, contraction of the topmost interlayer spacing is smaller than for the 5d metals, and only one layer relaxation and two layers reconstruction is detectable. It seems the electrons transferred from the alkali metal mitigate the strain in surface region. On the other hand, the structure of the reconstructed Cu(110) is very different from that of the reconstructed Ni(110) surface which is a row-pairing structure. This difference may come from the full d-shell character of Cu and the unfilled d-shell character of Ni. It is suggested that the structure analysis of the 4d metals Rh(110) and Pd(110), would be very helpful to further clarify fcc (110) surface reconstruction.

ACKNOWLEDGMENTS

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