Corrugation enhancement of Cu(001) induced by low-coverage Pb and Bi adsorption

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We report the discovery of a metal-adatom-induced corrugation of Cu(001) studied by surface-sensitive atom beam scattering (ABS). At a Pb or Bi coverage of 0.05 (fraction of Cu layer), and while a (1×1) low-energy electron diffraction pattern is still observed, the ABS diffraction pattern of Cu(001) has changed considerably from that of clean Cu(001). We show that the surface has become up to 10 times more corrugated than the clean Cu(001). The nature of this metal-adatom-induced corrugation is ascribed to the redistribution of the Cu(001) surface charge density.

Surface restructuring, such as reconstruction, relaxation, and faceting, is a fundamental problem in surface physics. Nonmetal-adsorbate-induced surface restructuring has been long observed and studied in the past.[1] Although ultrathin metal films grown on metal substrates have been investigated intensively, studies of induced surface restructuring have been focused on metal substrate reconstruction induced by alkali-metal adsorbates.[2] Recently, Song *et al.*[3] have reported the faceting of W(111) induced by the deposition of ultrathin metal films of Pt. Faceting of stepped Cu surfaces induced by Pb adsorption has also been observed.[4] These are examples of restructuring in which surfaces undergo dramatic rearrangements. However, a possible existence of another kind of surface restructuring, the change of the surface profile corrugation induced by a very small amount of metal adatoms, has not been really discussed in the past. We used the technique of atom beam scattering (ABS) to study the change in the surface profile.

A solid surface can be considered as the profile of the surface charge density. Esbjerg and Nørskov[5] first derived a widely accepted relation between the atom-surface interaction potential and the surface charge density. In its simplest form, it reads

$$V(x,y,z) = a\rho(x,y,z) , \qquad (1)$$

where ρ is the electron charge density of the solid, and a is a constant which depends on the in-coming atom, for He being 53 eVÅ^3. Thus ABS directly probes the surface (electron charge density) corrugation. A 20-meV He atom (a typical energy for most experiments) is turned back, after it reaches the 20-meV equal-potential surface, at about 3 Å from the plane of nuclei. It is a well-known fact that close-packed clean metal surfaces, such as Cu(001), are extremely flat with corrugation amplitudes, as far as He scattering is concerned, of less than 0.01 Å.[6] Specifically, for clean Cu(001), because of its flatness, no ABS diffraction peaks have been obtained.[7]

In this paper, we report the first observation, to our knowledge, of the enhancement of the corrugation of a metal surface induced by metal adatoms. In the paper, we will concentrate mainly on Pb results; the discussion of most of the Bi results will be given elsewhere.[8] Pb and Bi coverages for the effect reported here are very low, much less than those of the observed ordered phases of Pb/Cu(001) and Bi/Cu(001) systems.[9,10] This effect is quite different from most other kinds of adsorbate-induced surface restructuring (such as reconstruction, faceting) for the following reasons: (1) a small amount of adatoms instead of an entire ordered adsorbate layer is involved; (2) no massive surface structure rearrangement takes place, as in alkali-metal-induced reconstruction of fcc (110) metal substrates.[11] Instead, in the case presented here, there is only a redistribution of the surface charge density with no substrate atom displacement: the surface charge density of Cu becomes more atomiclike and localized than for the clean surface. Supporting evidence is presented by analyses of the shapes and intensities of diffraction peaks as well as by their thermal attenuation (Debye-Waller effect).

Our experiment was carried out in a UHV system equipped with He beam scattering, low-energy electron diffraction (LEED), and Auger electron spectroscopy; see Ref. 12 for details. A cold helium beam with energy of 18.4 meV and velocity distribution of about 1% was used in this study. The Cu(001) sample was prepared by repeated cycles of Ar ion sputtering and annealing at 580 °C prior to each run. The well-prepared Cu(001) sample yielded more than 50% of the incident beam in the specular reflection and the specular full width at half maximum (FWHM) was close to the detector resolution, currently set at 0.7°. Pb or Bi of 99.999% purity was deposited by using a liquid nitrogen shielded Knudsen evaporation source with the Cu surface at either 150 or 410 K. Coverages were calibrated with both the ABS real-time deposition curve[10] and the Auger signals.

Our main result is the observation of the emergence of a diffraction pattern with the two-dimensional periodicity of Cu(001) from a Cu(001) surface when a small amount of Pb is deposited. In a typical experiment, we proceeded as follows. First, we make sure that no diffraction peaks are present from a clean Cu(001) surface but the specular peak, in agreement with previous investigations.[6,7] Then Pb is deposited on Cu(001) at 410 K. At a coverage of 0.05, in units of Cu atoms, we observe the emergence of diffraction peaks along azimuth $\Phi = 0°$ ($\langle 110 \rangle$ direction of Cu) and $\Phi = 45°$, which are coincident with the $(0, -1)$

and $(-1,-1)$ peaks of Cu(001), respectively [see Fig. 1(a)]. Systematic polar and azimuthal angle scans were done; no other ABS diffraction peak or other features (as due to scattering from isolated adatoms) were seen within our resolution (10^{-4} of specular peak). A small background enhancement due to diffuse scattering was detected. Throughout these low coverage Pb deposition experiments we checked the LEED pattern which always showed a (1×1) pattern with a slight intensity increase of integer spots (see discussion later) and an increased background. The missing of noninteger order diffraction peaks (of both ABS and LEED) clearly indicates that adsorbed Pb atoms do not form a dilute ordered phase; our study is done at coverages much smaller than the one of the most dilute ordered phase of Pb/Cu(001): $c(4 \times 4)$ (coverage of 0.375). Furthermore, the size of a Pb atom (3.6 Å) prevents Pb atoms from forming a (1×1) phase with the above diffraction peaks. From analysis of the attenuation of the specular peak versus coverage and of the shape of the peaks,[8,13] we rule out island formation for both Pb and Bi, although islands form when Pb is deposited with the substrate at 150 K.[8] However, Pb atoms randomly adsorbed on equivalent commensurate sites could give rise to integer order diffraction peaks, as seen for CO on Ni(001).[14] Armand and Salanon[15] have shown that on a flat surface the diffraction intensity $I_G \propto \Theta^2$ (Θ, adsorbate coverage). In our case, we think that the random commensurate adsorption effect gives only a minor contribution to the diffraction peaks for several reasons. First of all, we have not detected any diffraction peaks with the adsorption of Hg (see discussion later on). Second, the diffraction peaks during Pb deposition start to drop at a rather low coverage and disappear at a coverage of about 0.25 [Fig. 2(a)]. This is in contrast to the case of CO/Ni(001), where diffraction peaks increase continuously to 0.3 ML, though we do not expect the square law to hold for relative high coverage. Third, our calculations show that this is a much smaller effect. A chain of 300 Cu atoms with 0.14 ML lattice gas Pb adatoms has been used to calculate the $(0,-1)$ diffraction peak. This is more than 1 order of magnitude smaller than measured intensity [Fig. 1(a)].[8] Thus, we conclude that the ABS (1×1) diffraction pattern observed is generated by a change in the corrugation of the Cu(001) surface.

We use the $(-1,-1)$ peak profile and intensity at different coverages to demonstrate the evolution of the induced Cu(001) corrugation. When more Pb is adsorbed, the $(-1,-1)$ peak intensity first increases with the increase of Pb coverage within the low coverage range, then disappears at a coverage about 0.25 shown in Fig. 2(a). Throughout this process the diffraction peak width remains constant [Fig. 1(b), Fig. 2(a)], which is also in agreement with our model that diffraction peaks come from a corrugated Cu(001) surface with roughly the same correlation as of the clean surface (the random adsorbate does not destroy the preexisting correlations).[16] Upon further adsorption we obtain the series of ordered structures reported in previous papers.[9,10]

The Pb induced Cu(001) surface corrugation can be removed by completely desorbing Pb atoms at 833 K. Then
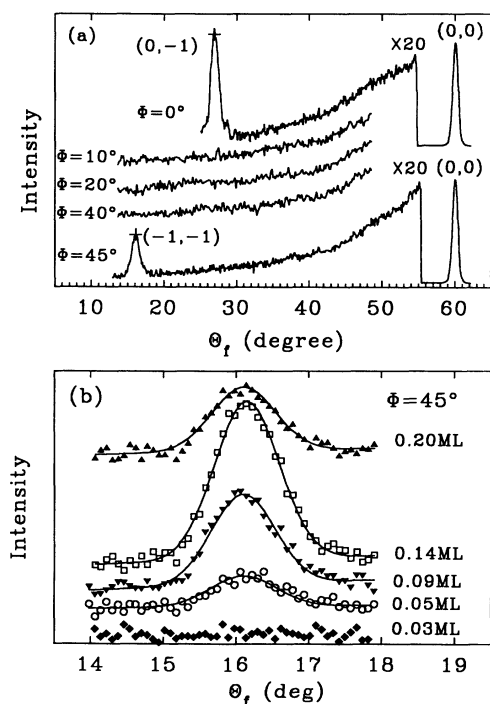

FIG. 1. (a) Polar scans at representative azimuthals of He beam diffraction from Cu(001) surface with Pb coverage of 0.14, $\theta_i = 60°$, surface temperature is 410 K. The (0,1) and (1,1) peaks are not allowed at these kinematic conditions. The best-fit intensities are indicated by "+." (b) $(-1,-1)$ peak profiles at different Pb coverages. Solid lines are fits to a Gaussian function with a linear background subtraction.
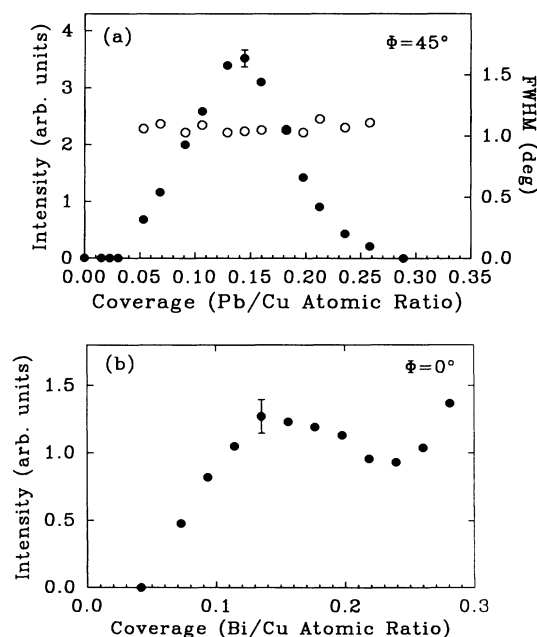

FIG. 2. (a) $(-1,-1)$ peak intensity (solid circles) and FWHM (open circles) vs Pb coverage with Cu(001) at 410 K. (b) $(0,-1)$ peak intensity vs Bi coverage with Cu(001) at 410 K. Increase of peak intensity after 0.2 coverage is due to the incipient $c(2 \times 2)$ phase (Ref. 9).

the ABS specular peak intensity recovers to that of clean Cu(001), and diffraction peaks are no longer observed. This observation is consistent with an earlier work[17] which suggest that Pb atoms do not diffuse into the bulk of Cu. We have also deposited Bi on Cu(001), and found it gives a similar effect on Cu(001) [Fig. 2(b)].

We have also studied the temperature behavior of the diffraction peaks. In Fig. 3 we plot $I(0, -1)$ versus temperature for three differently corrugated Cu(001) surfaces (Pb coverages of 0.10, 0.14, and 0.18). This diffraction peak can be observed at temperature as high as 750 K, which is much higher than the reported melting temperature[17] of all the stable ordered phases for Pb/Cu(001), as well as the melting point of bulk Pb (600.7 K). From the experimental result shown in Fig. 3, and using the formula in Ref. 12, we extracted the *effective* Debye temperatures[18] $\Theta_D = 235$, 221, and 208 K for surface with the above three Pb deposition coverages (see solid lines of fitting in Fig. 3), respectively. In a previous work,[12] we measured the Debye temperature for clean Cu(001) to be $\Theta_D = 320$ K, in agreement with previous determinations[19] (this value is uncorrected for the He size effect). The significance of these results is discussed later.

From our experimental data, there is a clear indication that the Cu(001) surface charge density is rearranged and much more corrugated compared to that of the clean Cu(001). Our model is that Pb or Bi atoms influence the Cu exposed substrate; the increase of diffraction peaks is due to the fact that more area of bare Cu is affected. The intensities then decrease when little exposed Cu(001) remains. We notice that this is in agreement with what is observed for deposition at 150 K. In this case islands are formed and much fewer Cu exposed atoms are effected, thus giving much smaller diffraction peaks, as observed.[8] No effect is observed in case of Hg adsorption at 250 K.[8] Our measurements[20] indicate that Hg adatoms do not form islands and randomly adsorb on Cu(001) at these coverage and temperature ranges. This is in agreement with the fact that Hg adsorbs very weakly[20] and does not

significantly change the substrate charge density distribution.

Now we analyze how the charge density is actually rearranged. For the small corrugations, the hard-wall model in the Eikonal approximation has been used successfully to calculate diffraction intensities and to retrieve information on surface corrugations.[6] Following Eq. (1), the charge density profile is used to obtain equal-density surface contours at the energy of the He beam which are then used in the scattering calculation. It has been shown[21] in many instances that one can obtain the actual surface charge density seen by the He atom by summing the individual atomic contributions of the top layer atoms. There are several successful examples of the use of this approximation, as in the case of a Pb overlayer on Cu, where an atomiclike surface charge density has been used to fit diffraction data.[22] Similarly, we speculate that the clean Cu(001) surface[23] has changed from a very flat into a much more corrugated surface due to a more localized and atomiclike charge redistribution following Pb deposition.

As noted earlier, at low Pb coverage range, the $I(0, -1)/I(0,0)$ ratio increases to 4–5 % as more Pb is deposited. For a quick estimate of the average corrugation enhancement, we can use a simple corrugation function to represent the surface profile[6,20] which is valid for a small surface corrugation and a simple square lattice. We use

$$\xi(x,y) = \xi_{0,1}\left[\cos\left(\frac{2\pi}{a}x\right) + \cos\left(\frac{2\pi}{a}y\right)\right]$$
$$+ \xi_{1,1}\cos\left(\frac{2\pi}{a}x\right)\cos\left(\frac{2\pi}{a}y\right) \qquad (2)$$

with $a = 2.55$ Å. For experimental data in Fig. 1, the best-fit values are $\xi_{0,1} = 0.06$ Å, $\xi_{1,1} = 0.08$ Å, and this yields an overall corrugation (top to hollow sites) of 0.14 Å. We note that if the clean Cu(001) had one-tenth of the above corrugation, we would already be able to see diffraction peaks with the resolution of our apparatus.

Our measured temperature behavior of the ABS diffraction peaks from the corrugated Cu(001) surface supplies further evidence that the surface charge density becomes localized and atomiclike after Pb deposition. The substantial drop of the effective Debye temperature for Cu(001) with an enhanced corrugation can be attributed to a decrease of the Cu-Cu force constant. The weakening of the Cu-Cu bond is consistent with a change in the charge distribution, which becomes more localized. With more Pb deposited, an increased corrugation of the surface leads to a further weakening of the Cu-Cu bond and thus to smaller Debye temperatures as shown in Fig. 3.

We find that there is no reconstruction in the direction parallel to the Cu(001) surface although a displacement localized at the adsorption site could exist. Within our system accuracy of 1.5%, the lattice constant of the corrugated Cu(001) surface, 2.55 Å, is unchanged from the clean Cu(001) surface. However, there could be a change in the interlayer spacing perpendicular to the surface, as frequently occurs in adsorbate-induced restructuring.[24]
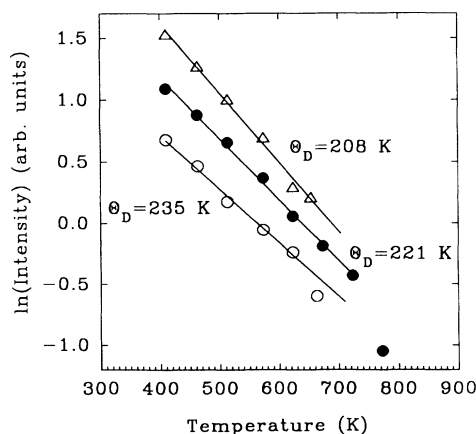

FIG. 3. $(0, -1)$ diffraction peak intensities vs temperature from Cu(001) surface with Pb coverages of 0.10 (O), 0.14 (●), and 0.18 (△), respectively. Error bars are of the size of the symbols. The solid lines are fits to experimental data.

Because of the insensitivity of ABS to nonexposed layers, we are unable to obtain this kind of information. However the slight intensity increase of Cu(001) integer LEED spots mentioned earlier could be (partially) due to the Cu interlayer spacing relaxation, although this increase is also consistent with a corrugation enhancement. This possible relaxation supports our discussion above. The tendency of smoothing out the overall (including adatoms and Cu surface) charge density contour in order to lower surface kinetic energy (Smoluchowski effect)[25] can result in a surface relaxation as Finnis and Heine suggested.[26] The relaxation of the top layer Cu atoms makes the Cu charge density distribution more localized and atomiclike.

In summary, we have shown that a clean Cu(001) surface becomes more corrugated upon low coverage adsorption of Pb and Bi, but no change is observed for Hg. A surface charge density reconfiguration has been addressed and analyzed as the direct cause of the metal adatom-induced corrugation. No large reconstruction of the corrugated Cu(001) surface has been detected. For further investigation of related issues, other techniques, like photoemission, electron-energy-loss spectroscopy, scanning tunneling microscopy, and LEED dynamical calculations, should be of help in checking possible electronic structure change, local displacement, and interlayer spacing relaxation.

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