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Thermal behavior of the Cu(110) surface studied by reflection anisotropy spectroscopy and scanning tunneling microscopy

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The temperature dependence of the reflection anisotropy (RA) of the Cu(110) surface has been investigated over the temperature range 180 to 1060 K. The thermal behavior of the peak observed in RA spectra at 2.1 eV, known to arise predominantly from transitions between surface states at $\overline{Y}$, is monitored and correlated with the temperature dependent behavior of the occupied surface state. We correlate RA spectra with scanning tunneling microscopy data to observe the roughening transition induced at ~ 1000 K which is found to generate a high density of monoatomic steps and results in the irreversible loss of the 2.1 eV RA feature and an enhancement in the response around 4 eV. RA spectroscopy is shown to be a sensitive in-situ probe of thermal induced surface disorder.

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I. INTRODUCTION

The thermal behavior of the Cu(110) surface has received considerable interest both experimentally[1–6] and theoretically.[6–11] The current understanding of the behavior of the surface as a function of temperature is summarized as follows. For increasing temperatures up to 550 K, surface order decreases in a harmonic Debye-Waller fashion. In the region 550 to 900 K, x-ray[1] and He (Refs. 2 and 3) scattering experiments have observed a strongly enhanced mean square displacement of surface atoms with no increase in step or defect density, a result that agrees with theoretical studies.[7,8] These results have lead to the conclusion that anharmonic vibrations of surface atoms are responsible for the increase of disorder in this temperature regime. Structural changes at the surface occur only at temperatures above 900 K (Refs. 3,7,8) attributed to the creation of adatom-vacancy pairs. A roughening transition is believed to occur at $T_R \sim 1000$ K (Refs. 6,10–12) characterized by the proliferation of monoatomic steps across the surface.

In addition to this characterization of the structural behavior, some details of the temperature-dependent electronic behavior at the surface are also known. At the $\overline{Y}$ point of the Cu(110) surface Brillouin zone (SBZ) an occupied and an unoccupied surface state exist in the bulk band gap around the Fermi energy (E_F). At room temperature the occupied surface state is located ~ 0.4 eV below E_F (Ref. 13) and the unoccupied state exists at ~ 2 eV above E_F.[14–16] These crystal-induced surface states have surface-localized wave functions[16,17] and are therefore expected to be sensitive to thermal vibrations occurring in the outermost layer. The thermal behavior of these surface states at $\overline{Y}$ has been investigated by photoemission[13] and inverse photoemission.[14] The energy of the occupied surface state is temperature dependent, following a linear relationship over the range 140 to 630 K.[13] The unoccupied surface state energy was found to be insensitive to temperature variations to within the resolution limits of the experiment, although the intensity of the peak observed in isochromat spectra associated with this state became attenuated with increasing temperature.[14] The temperature dependence of both the electronic and geometric surface structure has interesting implications for optical probes of surfaces and forms the basis of this work.

Reflection anisotropy spectroscopy (RAS) is an optical probe of anisotropy in the surface electronic structure of cubic crystals. RAS probes as a function of energy the optical response of a surface with linearly polarized light by measuring the difference in normal incidence reflection of two perpendicular directions (Δr) normalized to the mean reflection (r). The reflection anisotropy is defined in terms of complex Fresnel reflection amplitudes

$$\frac{\Delta r}{r} = \frac{2(r_{[1\bar{1}0]} - r_{[001]})}{r_{[1\bar{1}0]} + r_{[001]}}. \tag{1}$$

The Cu(110) surface has featured in a number of RAS studies and significant progress has been made in the interpretation of the Cu(110) RA spectrum. It has been established that the dominant contribution to the peak in the RA spectrum at 2.1 eV originates from transitions between surface states at $\overline{Y}$.[18–20] A secondary contribution to this feature may arise from bulk electronic states that are modified by the surface[19] or from local-field effects at the surface.[21] We apply RAS to the study of the temperature dependence of the 2.1 eV RA feature in order to probe the contribution of the surface states at $\overline{Y}$ to this transition and to elucidate the contribution to the RA profile from the surface local-field effect (SLFE).

The electronic structure of a surface is intimately linked to its atomic arrangement, for example, defects such as steps are known to cause perturbations in surface electronic structure.[22–26] By combining RAS and scanning tunneling microscopy (STM) we are able to relate temperature-induced changes in the RA spectra of Cu(110) to differences in surface electronic states arising from changes in surface morphology. RAS has been used to study a range of metal surface phenomena such as reconstruction and molecular adsorption.[18–20] Here we make the first use of RAS as an *in situ* probe of thermal induced surface disorder at a metal surface up to and including the roughening transition.

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II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) environment with a base pressure in the 10^{-11} mbar region. The mechanically polished Cu(110) single crystal was aligned using Laue x-ray diffraction to $<0.5°$ before introduction into the vacuum chamber. A clean Cu(110) surface was prepared by cycles of Ar ion bombardment (10 μA/cm^2, 0.5 kV, 300 K) and subsequent annealing to 850 K. Surface order was confirmed by a sharp (1×1) low-energy electron diffraction (LEED) pattern and cleanliness was monitored using x-ray photoelectron spectroscopy (XPS). The specimen was annealed by resistive heating and cooled using liquid nitrogen. To allow sample transfer between the various experimental probes, the temperature was initially measured using an N-type thermocouple positioned at the side of the sample. A separate experiment was performed to calibrate temperature measurements with a thermocouple situated in the sample position.

In situ STM was performed at room temperature in constant current mode using a tunneling current of 1 nA and bias voltage -1.0 V. The STM tip was made from tungsten wire electrochemically etched and prepared *in situ* by annealing. The STM images are conventional greyscale images with contrast from dark to light corresponding to low to high structural elevation.

The RA spectrometer of the Aspnes design[27] utilized an Xe photon source to project and receive light through a low-strain window on the UHV system. Experimental artifacts were removed from the spectra using a correction function obtained by measuring spectra with the sample in two orthogonal positions. Spectra of the real part of the complex RA were taken over a photon energy range of 1.5 to 5.0 eV.

III. RESULTS

Reversible and irreversible changes to the Cu(110) RA spectrum were observed with increasing temperature. We present the results of the temperature dependence of the RA response in the regions 1.5 to 3.0 eV and 3.0 to 5.0 eV separately. Results associated with irreversible effects and the effect of surface cleaning are also presented.

A. RA in the region 1.5 to 3.0 eV

1. Thermal behavior 180 to 730 K

The RA spectra for the clean Cu(110) surface are shown in Fig. 1. The spectral profile at room temperature [Fig. 1(b)] exhibits the main characteristics reported by a number of independent studies,[18,28,29] namely, an intense peak at energy 2.1 eV and a bimodal feature around 4 eV. The peak at 2.1 eV is thought to arise from a combination of two different contributions. The first involves electronic transitions between surface states at the $\bar{Y}$ point of the SBZ.[18,19] At room temperature, transitions occur between an occupied surface state at energy 0.4 eV below E_F and an unoccupied surface state that has been variously located at energies of 1.8,[14] 2.0,[15] and 2.5 eV (Ref. 16) above E_F. The reason for this difference in the measurements of the position of the unoccupied state is not clear. The RAS result is in good agreement with an unoccupied surface state energy of 1.8 eV. The transition at $\bar{Y}$ that generates the 2.1 eV feature is induced solely by light polarized along [001] leading to the observed reflectance anisotropy.[19,29] The assignment of this transition to surface states is supported by the decay of the signal upon molecular absorption[18] and alkali-metal induced surface reconstruction.[20] However, the surface retains anisotropy in this region under ambient conditions[19,21] and upon the formation of the O/Cu(110)-(2×1) reconstruction.[18,19] Since transitions from surface-modified bulk *d* states to E_F occur at ~ 2 eV it has been suggested that such transitions also contribute to the 2.1 eV RA feature.[19] Local field effects at the surface may also contribute to the RA signal in this region.[21]

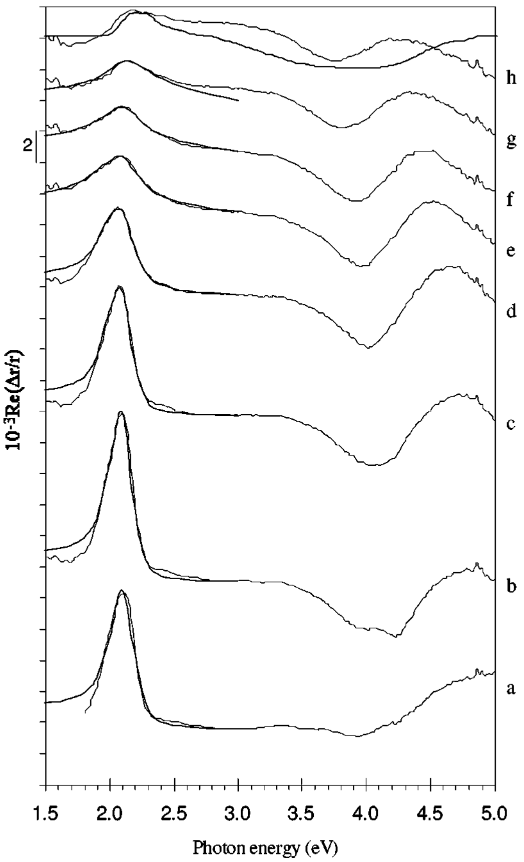

FIG. 1. Experimental and simulated (bold line) RA spectra of Cu(110) as a function of temperature. The peak energy of the simulated transition at each temperature is (a) 180 K:2.11 eV, (b) 295 K:2.09 eV, (c) 430 K:2.06 eV, (d) 555 K:2.04 eV, (e) 730 K:2.01 eV, (f) 850 K:2.05 eV, (g) 965 K:2.18 eV, (h) 1060 K and SLFE model RA spectrum.

STM studies of the clean surface from which the RAS results of Fig. 1(b) were obtained indicated the presence of a layered surface with steps oriented parallel to each other and aligned in the $[1\bar{1}0]$ direction [Fig. 2(a)]. Step heights varying from monoatomic up to 6 nm height were found on the surface. A very low percentage of steps were of monoatomic height and the majority of steps were of significantly larger height. Terrace widths extended up to 30 nm in the [001] direction. An RA spectrum displaying the same characteris-

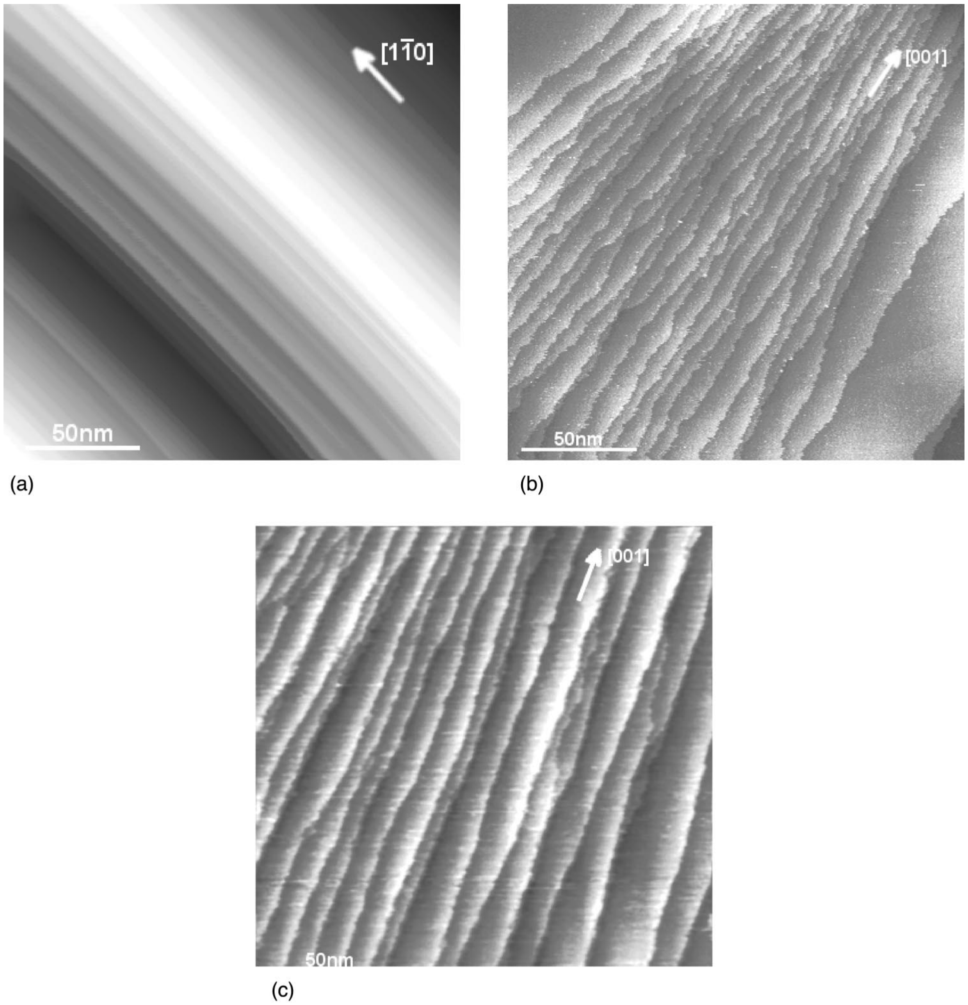

FIG. 2. Room temperature STM data. (a) The Cu(110) surface prepared by cycles of Ar ion bombardment and annealing at 850 K, (b) surface following annealing to 1060 K, (c) effect of further annealing the roughened surface shown in (b) to 1060 K.

tic features as Fig. 1(b) has been observed from a ripple morphology created by a shorter anneal time.[30] These results indicate that the general RA spectral profile is not overly sensitive to a variability in surface morphology arising from the surface cleaning procedure.

The results of the RA as a function of temperature are shown in the sequence of spectra of Figs. 1(a)–1(h). Each spectrum was recorded with the sample held at constant temperature. The RA in the region 1.5 to 3.0 eV was simulated using a Fresnel-based three phase model[31,32] of vacuum, biaxially anisotropic surface layer, and isotropic bulk. Each medium is associated with a complex dielectric function which governs the response of the medium to an applied electric field. For vacuum, surface, and bulk media the dielectric functions are unity, the surface dielectric anisotropy (SDA) defined as $\Delta\bar{\epsilon}_s(\omega)=\bar{\epsilon}_{[1\bar{1}0]}(\omega)-\bar{\epsilon}_{[001]}(\omega)$ and $\epsilon_b(\omega)$, respectively. The reflectance amplitudes are related to the surface and bulk dielectric functions by[33]

$$\frac{\Delta r}{r}=\frac{2i\omega d}{c}\left(\frac{\Delta\bar{\epsilon}_s(\omega)}{\bar{\epsilon}_b(\omega)-1}\right), \tag{2}$$

where d is the surface layer thickness acting as a scaling factor and $\hbar\omega$ is the photon energy. This result is valid for small anisotropy and within the thin film approximation ($d \ll l$). Bulk dielectric function data for copper were obtained from experimentally determined tabulated data.[34] It is convenient to introduce the bulk dielectric function in terms of the functions $A(\omega)$ and $B(\omega)$ defined by

$$A(\omega)-iB(\omega)=\frac{1}{1-\bar{\epsilon}_b(\omega)}. \tag{3}$$

The real part of Eq. (2) can then be written in terms of $A(\omega)$ and $B(\omega)$:

$$\mathrm{Re}\left(\frac{\Delta r}{r}\right)=\frac{-2\omega d}{c}[A(\omega)\Delta\epsilon_s''(\omega)+B(\omega)\Delta\epsilon_s'(\omega)]. \tag{4}$$

This expression is used to generate simulated RA spectra. The SDA was represented by a single transition localized in the [001] direction and described by a Lorentzian function of transition energy ω_t:

$$\bar{\epsilon}_{[001]}=1+\frac{S/\pi}{\omega_t-\omega+i\Gamma/2};\quad \bar{\epsilon}_{[1\bar{1}0]}=1, \tag{5}$$

where S and Γ are the strength and full-width at half maximum of the Lorentzian line shape, respectively. The simulated RA spectra are shown in Figs. 1(a)–1(g) by the solid line and the parameters used in each fit are given in Table I.

TABLE I. Parameters of the Lorentzian component used to simulate the RA in the region 1.5–3.0 eV. Selected spectra are shown in Fig. 1.

Temperature(K)	ω_t(eV)	Expected ω_e(eV)	S normalized to S (295 K)	Γ(eV)
180	2.11±0.01	2.12±0.03	0.87±0.03	0.30±0.02
295	2.09±0.01	2.09(reference)	1.00±0.03	0.27±0.02
385	2.08±0.01	2.07±0.03	0.91±0.03	0.27±0.02
430	2.06±0.01	2.05±0.03	0.88±0.03	0.30±0.02
555	2.04±0.01	2.02±0.03	0.83±0.03	0.43±0.02
615	2.03±0.01	2.01±0.03	0.83±0.03	0.53±0.02
670	2.02±0.01		0.84±0.03	0.63±0.02
730	2.01±0.01		0.84±0.03	0.73±0.03
780	2.02±0.01		0.84±0.03	0.83±0.03
850	2.05±0.01		0.74±0.03	0.86±0.03
930	2.15±0.01		0.74±0.03	0.98±0.05
965	2.18±0.01		0.74±0.03	1.02±0.06

The data of Table I quantify the changes observed in the 2.1 eV peak as a result of thermal treatment (Fig. 1). As the surface temperature is increased from 180 to 730 K, the RA spectra show a shift in the peak position to lower photon energy [Figs. 1(a)–1(e)].

The spectra of Fig. 1 show that in addition to the shift in the position of the 2.1 eV peak with temperature this feature also shows a significant loss of intensity as the temperature is increased. This loss of intensity was observed directly by operating the RA spectrometer at a single energy of 2.1 eV and the intensity of the peak was monitored as a function of temperature from 295 to 615 K. The results of this experiment are shown in Fig. 3. The surface was subjected to a linear increase in temperature with time while monitoring the RA at 2.1 eV. The inset to Fig. 3(a) shows the decrease in the real part of the RA at 2.1 eV as a function of time. When presented as a function of temperature, a linear decrease in RA at 2.1 eV with increasing temperature is found. As the temperature was increasing continuously during this experiment each data point does not necessarily correspond to thermal equilibrium. However, the decrease in RA with increasing temperature follows a linear relationship suggesting that fast dynamics are associated with the process.

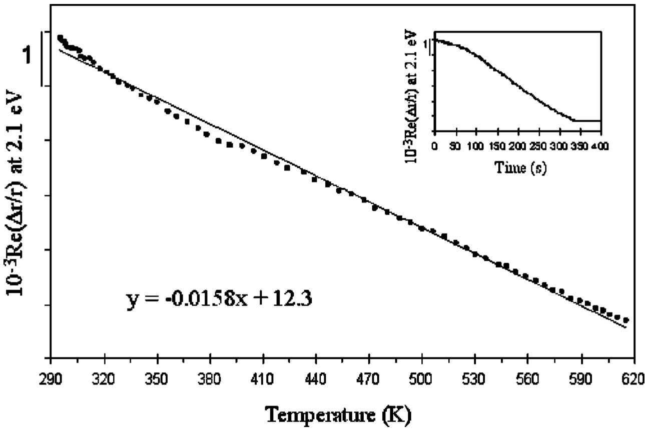

FIG. 3. Fixed energy RA data. The inset shows the decrease in RA at 2.1 eV as a function of time. The main figure shows the decrease in RA at 2.1 eV as a function of temperature.

2. Thermal behavior 730 to 1060 K

At a temperature of 730 K and above, the peak at ~2 eV in the RA spectrum is observed to shift to higher photon energy, eventually moving beyond the position observed at room temperature (Table I and Fig. 1). The peak continues to broaden and decreases in magnitude with increasing temperature. At 850 K the main peak is shifted to 2.05 eV [Fig. 1(f)] and is considerably broadened and reduced in magnitude from the room temperature profile. At 965 K the RA feature at ~2 eV has become asymmetric with a deviation from the simulated spectrum on the high energy side [Fig. 1(g)] and at 1060 K, a significant change in the profile of the peak is observed [Fig. 1(h)].

B. RA in the region 3.0 to 5.0 eV

The RA spectrum of the clean surface at room temperature [Fig. 1(b)] exhibits the bimodal structure around 4 eV in agreement with previous studies.[18,28,29] The peak at ~3.9 eV is known to be suppressed upon molecular adsorption whereas the peak at 4.2 eV has been observed to be less sensitive to adsorption and reconstruction.[18]

The 3.9 and 4.2 eV peaks of the room temperature RA spectrum [Fig. 1(b)] are observed to exhibit temperature dependent behavior. A single peak at 3.9 eV is observed from 295 to 850 K [Figs. 1(b)–1(f)] showing that at least one contribution to the RA spectrum in this region is not sensitive to temperature-induced changes. Cooling the sample from room temperature to 180 K suppresses the magnitude of both the contributions observed at room temperature [Fig. 1(a)]. These changes in the RA spectrum are reversible up to 850 K, the temperature regime of harmonic and subsequently anharmonic atomic vibrations.

Above 850 K, the single minimum at ~3.9 eV shifts in energy and decreases in intensity [Figs. 1(f)–1(h)]. At a temperature of 1060 K, the minimum in the spectrum is located at ~3.7 eV [Fig. 1(h)].

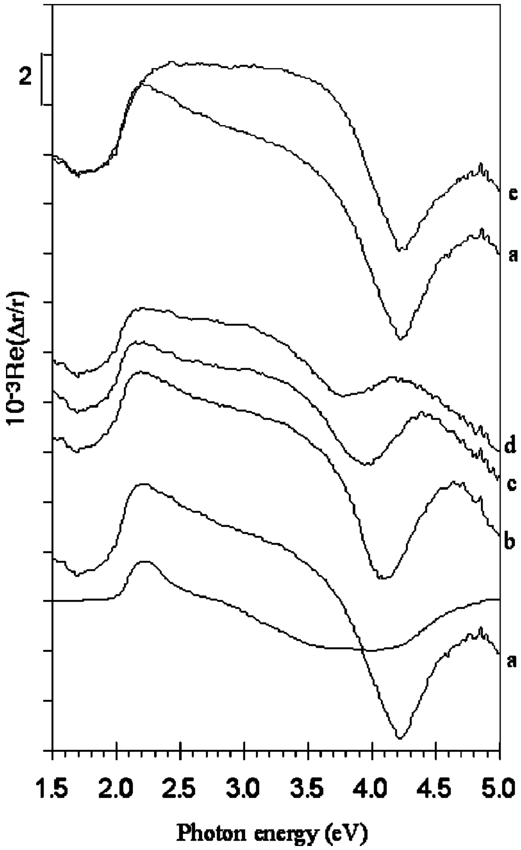

FIG. 4. RA spectrum of the ordered roughened surface prepared by annealing at 1060 K (a) at room temperature with the SLF model RA spectrum superimposed for comparison, (b)–(e) the ordered roughened surface subjected to further thermal treatment: held at (b) 550 K, (c) 880 K, (d) 1060 K, (e) cooled to room temperature.

C. Irreversible changes

We noted earlier that the RA spectrum observed at room temperature was unchanged by thermal treatments up to 850 K. At higher annealing temperatures we observe irreversible changes in the RA spectrum.

The RA spectrum obtained from the surface allowed to cool from a temperature of 1060 K to room temperature is shown in Fig. 4(a). While the absence of the dominant peak at 2.1 eV in the RA spectrum of the surface at room temperature is noted, the structure at 2.2 eV observed at a temperature of 1060 K is retained. A noticeable feature of the spectrum is the strong negative contribution to the RA which has a minimum at 4.2 eV [Fig. 4(a)] and which upon cooling develops from the feature observed at 3.7 eV at 1060 K [Fig. 1(h)]. The RA signal in this energy region is stronger than that observed at room temperature following the initial cleaning procedure [Fig. 1(b)] and no structure at 3.9 eV is observed.

The STM results of the surface obtained at room temperature following the anneal at 1060 K showed a very high density of steps that were exclusively of monoatomic height on an otherwise flat surface [Fig. 2(b)]. This observation is consistent with the occurrence of the roughening transition while the surface was at the high temperature. A temperature of 1060 K for surface roughening of Cu(110) is consistent with $T_R \sim 1000$ K.[6,10–12] All steps observed were found to have rough edges that were aligned along the [001] direction. The surface resembled a vicinal surface with steps found in a ''staircase'' structure. Terrace sizes were typically 5 nm in the $[1\overline{1}0]$ direction and extended in the [001] direction over distances >500 nm. At high temperature, adatom diffusion is enhanced in the $[1\overline{1}0]$ direction[9] which may be an important factor in the formation of the observed steps. The loss of the 2.1 eV peak and the enhanced RA signal in the region ~ 4 eV is clearly a consequence of the morphology of the roughened surface. The observation of consistent STM images over large areas of the surface indicates that the roughened surface has a greater degree of long range surface order than the surface prepared by annealing at 850 K. LEED showed a sharp (1×1) pattern for this surface indicating the preservation of lattice order through the roughening transition and the primary structural changes induced by the roughening transition are the formation of steps oriented towards the [001] direction.

The surface obtained by cooling from the roughening transition and characterized by the STM results shown in Fig. 2(b) and the RA spectrum of Fig. 4(a) was subjected to further thermal treatments. RA spectra obtained by holding this surface at 555, 880, and 1060 K are shown in Figs. 4(b)–4(d), respectively. The spectrum obtained at 1060 K is similar to that observed previously at this temperature [Fig. 1(h)]. However, spectra observed at lower temperatures [Figs. 4(b),4(c)] are different to those observed earlier [Figs. 1(d),1(f)] in that the strong feature at 2.1 eV arising from the transition between the surface states has not returned. The energy shift of the RA peak at ~ 4 eV with increasing temperature was found to be similar to that observed when first approaching the roughening transition.

When the surface was allowed to cool to room temperature after further annealing at 1060 K the RA spectrum changed to that observed in Fig. 4(e). The STM results of this surface [Fig. 2(c)] show a more ordered array of smoother [001] oriented monoatomic steps separated by an increased average terrace width of ~ 15 nm. The shoulder observed at 2.2 eV in Fig. 4(a) exhibits no change in energy with further thermal treatment [Figs. 4(b)–4(d)].

D. The effect of surface cleaning

We now investigate the effects of the procedure used to prepare a clean Cu(110) surface. Bombardment of the ''ordered roughened'' surfaces shown in Figs. 2(b) and 2(c) by Ar ions (10 μA/cm^2, 0.5 kV, 300 K, 15 min) was found to reestablish the prominent 2.1 eV peak that is the main characteristic of all the RA spectra reported previously for the Cu(110) surface. Furthermore, Ar ion bombardment of the surfaces shown in Figs. 2(a)–2(c) resulted in the appearance of a positive peak with a maximum intensity at ~ 4.1 eV (Fig. 5) that has been observed previously.[35] STM of the bombarded surfaces showed no remaining steps or terrace areas and a disordered surface morphology with no preferred directionality at the length scale of $\geqslant 10$ nm. LEED showed a (1×1) pattern with a low intensity diffuse background. Upon annealing the bombarded surface at 850 K and moni-

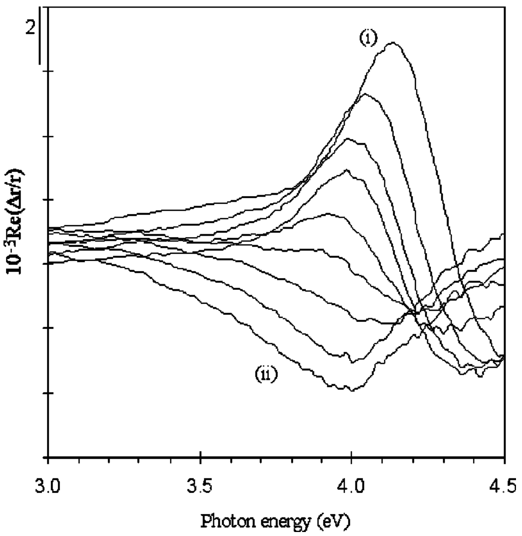

FIG. 5. RA spectra of the Cu(110) surface (i) following Ar ion bombardment and the sequence of spectra from (i) to (ii) shows the effect of annealing the bombarded surface to 850 K.

toring the RAS response as the sample temperature increased from room temperature up to 850 K, a shift in energy and a reversal in sign of the 4 eV RA feature was observed as shown in the sequence of spectra in Fig. 5 from (i) to (ii). A similar behavior has been observed for ion bombardment treatment alone, as a function of bombardment time[35] leading to the conclusion that the RA response around 4 eV was sensitive to the creation of vacancies in the surface layer. The results presented here support the view that the RA response at ~4 eV is sensitive to atomic disorder at the Cu(110) surface.

IV. DISCUSSION

We begin with the assumption that the prominent feature observed at 2.1 eV in the RA spectrum of the Cu(110) surface is made up of two components, a dominant contribution arising from a transition between surface states a weaker contribution arising from the surface local-field effect (SLFE). Calculations by Hansen *et al.*[21] place the peak arising from the SLFE at 2.2 eV, approximately 0.1 eV higher in photon energy than the prominent peak observed experimentally.

A. Reversible changes

We relate the shift in energy of the 2.1 eV RA peak with increasing temperature to the known temperature dependence of the occupied surface state which photoemission[13] has shown to have a linear energy shift with increasing temperature. The position of the unoccupied state is independent of temperature.[14] In Table I we compare the expected change in the energy of the peak in the RA spectrum deduced from the observed change in the position of the occupied surface state with a constant unoccupied surface state energy. The temperature dependent shifts are given relative to the peak position at 295 K. It can be seen that to within experimental uncertainties, the magnitude of the observed energy shifts with increasing temperature from 180 to 615 K (Table I) are in agreement with the shift observed in the occupied surface state energy.[13] We note that within this temperature range surface order is expected to decrease predominantly in a harmonic fashion.

The linear decrease in the RA at 2.1 eV with increasing temperature up to 615 K (Fig. 3) may be caused by a thermal depopulation of the initial surface state. The occupied surface state involved in the transition dominating the RA at 2 eV occurs at $\overline{Y}$ and lies 430 meV below E_F at room temperature and approaches E_F with increasing temperature.[13] At 730 K the occupied state has moved closer to the Fermi energy and the bottom of the surface state band is estimated to be located ~320 meV below E_F extrapolating from the photoemission results.[13] The occupied surface state is of Shockley type and its occupying electrons may be considered as a 2D free-electron-like gas.[22,23] The kinetic energy available from thermal processes to an individual electron within an electron gas is of the order k_BT, which at $T=730$ K is ~60 meV. At room temperature there are 0.04 electrons per atom in the occupied state[36] of average binding energy ~200 meV.[37] Considering a shift in the average binding energy of an electron of a magnitude comparable to that experienced by the bottom of the band, the electrons in the state at 730 K are likely to have an energy approaching k_BT. It is therefore possible that this state experiences charge depopulation due to the gain in thermal energy by electrons and the shift of the state towards E_F as the temperature is increased. This suggestion is supported by the observed reduction in the intensity, the broadening and the shift in energy of the RA peak with increasing temperature.

An exponential decrease in the intensity of the peak observed in inverse photoemission isochromat spectra arising from transitions involving the unoccupied surface state at $\overline{Y}$ has been observed with increasing temperature up to 700 K.[14] This loss of intensity with temperature was attributed to a reduction in the intensity of direct transitions arising from the randomizing effect of momentum transfers caused by electron-phonon scattering. This effect will also contribute to the reduction in intensity of the 2.1 eV RA peak through electron-phonon coupling in both the initial and final states involved in the transition.

As noted earlier, the shift to lower photon energy of the 2 eV RA peak is related to the known shift in the occupied surface state energy (Table I). At 730 K and above, the peak at ~2 eV in the RA spectrum is observed to shift to higher photon energy, eventually moving beyond the position observed at room temperature (Table I and Fig. 1). The peak continues to broaden and decreases in magnitude with increasing temperature. In this temperature range, anharmonic behavior is expected to become the dominant process of atomic disordering at the surface. We attribute the shift of the RA peak to higher photon energy in this temperature range to a combination of the gradual loss of the intensity of the transition associated with surface states at $\overline{Y}$ due to the thermal depopulation of the initial state and the increasing importance of the contribution due to the SLFE which is at a slightly higher energy. This SLFE contribution will be discussed further in the following section.

B. Irreversible changes

With increasing temperature above 900 K, the creation of adatom-vacancy pairs is expected to become the dominant process of surface disordering[3,7,8] and it is likely that the disorder accompanying this process contributes to the loss of intensity from the transition involving surface states at $\bar{Y}$. We assign the structure observed around 2.2 eV at 1060 K [Fig. 1(h)] to the SLFE contribution that is expected to be less sensitive to temperature variations[13] and which we suggest is now directly observable since the transition involving surface states is suppressed. In Fig. 1(h) the thick solid line reproduces the simulated Cu(110) RA spectrum of Hansen *et al.*[21] as generated by the SLFE model developed by Mocán and co-workers.[38–40] This model simulates the surface region by means of a lattice of polarizable cores with *d* electrons that are localized around each core and a screening Drude electron gas describes the delocalized *s-p* electrons. The RA response results from a difference in surface conductivity, due to polarization processes in the presence of an oscillating electric field, between the two principal directions in the surface plane

$$\frac{\Delta r}{r}=\frac{2(\sigma_{[1\bar{1}0]}-\sigma_{[001]})}{c\epsilon_0(\epsilon_b-1)}, \tag{6}$$

where the surface conductivity (σ) is defined as

$$\sigma=-ia\epsilon_0 2^{-3/2}\omega(\epsilon_b-\epsilon_{\mathrm{Drude}})\sum_i \frac{p_i-p_b}{p_b} \tag{7}$$

with p_i the dipole moment of the ith core, p_b the dipole moment of the bulk, and *a* the lattice constant. The simulated spectrum shows good agreement with the experimental RA profile below 2.5 eV [Fig. 1(h)]. In addition, a negative RA response of similar magnitude but a different profile to that observed experimentally is produced at higher photon energy. We suggest that the success of the SLFE model in describing the observed RA response in the region ~2 eV is confirmation both of our view that the contribution from surface states is absent from the RA spectrum at this temperature and of the validity of the application of the SLFE model[38–40] to Cu(110).[21]

The simulated RA profile of the SLFE model shows some similarity with the magnitude of the RA response in the region around 4 eV observed at 1060 K [Fig. 1(h)]. The creation of adatom-vacancy pairs is expected to become significant at temperatures ⩾900 K (Refs. 3,7,8 and our results indicate that the RA response in this energy region is sensitive to this disorder mechanism. This result is in agreement with previous work that has suggested that the RA signal around ~4 eV is sensitive to the presence of vacancies at the surface created via Ar ion bombardment.[35] Deviations from the SLFE profile at high temperature [Fig. 1(h)] may arise from the effects of adatom-vacancy pairs which are not considered in the SLFE model.

It is clear that the 2.1 and 3.9 eV peaks in the RA spectra are lost irreversibly upon inducing the roughening transition. Given the sensitivity of the intensity of the 2.1 eV RA peak to the population of the occupied surface state at $\bar{Y}$ and the closeness of the binding energy of this state to E_F it is possible that the narrow terrace structure generated by the proliferation of monoatomic steps across the surface prevents the surface state from returning to the energy, ~0.4 eV below E_F, that it has on the original surface. Upon cooling from 1060 K to room temperature the occupied state may be held at a higher energy by a confinement of the state by the steps. This behavior has been observed for the Shockley-type surface state on a vicinal Cu(111) surface which shifts in binding energy as a result of lateral confinement of the surface state wavefunction to terraces.[25] On the Cu(111) surface the width of terraces was found to affect the binding energy of the surface state with narrow terraces shifting the state towards E_F. This shift was found to be consistent with a 1D Kronig-Penney model of δ function potential barriers[26] that yields a value for the surface state energy for the case of a periodic array of monoatomic steps. The bottom of the surface state band is reduced in binding energy by an amount[25,26]

$$\Delta E=(\hbar^2/2m^*L^2)[\cos^{-1}(|T|)-\phi]^2, \tag{8}$$

where L is the mean step-step distance, m^* is the effective surface state electron mass, and $T=|T|e^{i\phi}$ is the energy-dependent transmission coefficient through the step barrier. For the case of total confinement by the steps separated 5 nm apart [Fig. 2(b)] and using $m^*/m=0.26$,[13] $\Delta E=60$ meV which is comparable with the shift in energy necessary to cause significant depopulation of the state.

The strong RA response observed at 4.2 eV from the roughened surface [Fig. 2(b)] is significantly different from that simulated by the SLFE model [Fig. 4(a)] and from that observed on the original surface [Fig. 1(b)]. It is likely that this RA signal is associated with the monoatomic step array. The narrowing of the RA feature at ~4.2 eV observed following further annealing of the roughened surface [Fig. 4(e)] and the creation of more uniform steps [Fig. 2(c)] supports its association with [001] monoatomic steps. The shoulder observed at 2.2 eV in Fig. 4(a) exhibits no change in energy with further thermal treatment [Figs. 4(b)–4(d)]. This observation together with the STM results of increased terrace widths [Figs. 2(b)–2(c)] indicate that the structure observed at 2.2 eV on this surface is unlikely to derive from transitions involving the surface states at $\bar{Y}$ and closely resembles the contribution expected from the SLFE.

We suggest that the absence of the 2.1 eV peak in the RA spectrum observed from the surface showing an ordered array of monoatomic steps [Figs. 2(b)–2(c)] and its presence on the RA observed from the surface following the Ar ion bombardment can be explained in terms of the local nature of the RA probe and the sensitivity of the energy of the occupied surface state to the terrace structure. The energy of the initial surface state is close to E_F and on the ordered surface the narrow terraces and arrays of [001] monoatomic steps confine the surface state and lower its binding energy resulting in charge depopulation. On the disordered surface there will always be regions of the surface in which the initial surface state is occupied. The intensity of the 2.1 eV peak will then be a measure of the fraction of the surface over which the initial surface state is occupied.

V. CONCLUSIONS

The RA response of the Cu(110) surface has been found to be sensitive to temperature-induced surface disorder. The RA peak at 2.1 eV shifts in energy between 180 to 615 K by an amount that is in agreement with the observed shift in energy of the occupied surface state at $\overline{Y}$. We suggest that the reversible decrease in RA intensity at ~2 eV up to 850 K is related to the temperature-dependent electronic occupancy of the surface state. Irreversible changes to the RA spectrum are observed upon inducing the roughening transition that we suggest are caused by changes in the surface state occupancy due to confinement by the terrace structure and the response from monoatomic steps. The relative contributions from surface state transitions and surface local-field effects to the RA response around 2 eV are determined. We suggest that the feature observed at 4.2 eV dominating the RA spectrum of the roughened surface is associated with monoatomic steps.

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