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Effect of thermally induced surface defects on the optical anisotropy of Ag(110)

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We show that the temperature dependence of the intensity of the ~1.7 eV peak in the reflection anisotropy spectrum of clean Ag(110) can be explained by considering the effect of thermally induced surface defects and the thermal shift in binding energy of the occupied surface state involved. Two simple models are used to quantify the defect formation energy and the length scale over which the contribution to the intensity of this reflection anisotropy spectroscopy (RAS) feature is quenched due to the presence of thermal defects. We have simulated the decrease in the RAS peak intensity with increased temperature, achieving consistency with related measurements on ion-bombarded and adsorbate-covered surfaces, and previous estimates of the defect activation barrier for the Ag(110) surface. This study demonstrates the potential of RAS as a tool for monitoring surface kinetic behavior.

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I. INTRODUCTION

Reflection anisotropy (RA) spectroscopy (RAS) (Refs. 1 and 2) is a nonintrusive optical probe of surfaces. Initially developed for the investigation of semiconductor growth, RAS has in recent years emerged as a powerful analytical tool for studying metal surfaces.[1] RAS uses linearly polarized light to measure the difference in reflectance Δr between two orthogonal directions in the surface plane normalized to the mean reflectance r. RAS is defined as

$$\frac{\Delta r}{r} = \frac{2(r_x - r_y)}{r_x + r_y}, \tag{1}$$

where, for the Ag(110) surface, r_x and r_y denote the complex Fresnel reflection amplitudes for light polarized along the $[1\bar{1}0]$ and $[001]$ surface directions, respectively. RAS can be used to investigate a variety of electronic and topographical effects such as the destruction of electronic surface states, surface reconstruction, structural phase changes, molecular adsorption, and surface alloying.[1] The sensitivity of the technique to such phenomena coupled with the fact that features in RA spectra may derive from several different electronic transitions means that a quantitative understanding of the RA response from a surface is often nontrivial.

The complexity underlying some RA spectral features can be demonstrated by considering the 2.1 eV peak which dominates the RA response from clean Cu(110). In a recent study, Sun *et al.*[3] simulated the effect of temperature on this feature showing that it can be described as a superposition of three different contributions: electronic transitions involving surface states, surface-modified interband transitions, and a Drude term arising from intraband transitions. The thermal sensitivity of the feature is accounted for in the study by considering photoemission results indicating a shift of the occupied surface state to lower binding energies with increasing temperature. As the state crosses E_f, it depopulates and the difference between its binding energy and that of the unoccupied state decreases. These processes, respectively, induce a reduction in intensity and a shift to lower photon energies of the 2.1 eV peak which are calculated as a function of temperature in the simulation. The effect of temperature on the contributions to the 2.1 eV feature involving interband and intraband transitions are not considered in the model as such details are currently unknown. Various studies have shown the intensity of the 2.1 eV peak, like surface-state-related features in RA spectra from other surfaces, is also sensitive to the presence of surface adsorbates.[1,4] It was put forward by Sun *et al.*[4] that individual adsorbate molecules and surface defects act like circular potential barriers with the ability to isotropically scatter surface electrons such that the anisotropy of the surface state over a considerable area is reduced, subtracting the intensity of surface-state-related RAS features.

In a recent photoemission study by Jensen *et al.*,[5] the temperature-dependent linewidth of a surface state on Al (100) at the $\bar{\Gamma}$ point of the surface Brillouin zone was investigated. An inconsistency between experimental results and the standard model used for describing the effect of temperature on surface states is accounted for in the study by considering the influence of thermally excited surface defects. The effect described is also applied to similar photoemission results from the Au (111) surface in order to reconcile discrepancies between experiment and theory, which as suggested by the authors,[5] demonstrates that the phenomena should be quite general.

Despite the importance of thermal defects in studying surface phenomena such as surface states, relatively little experimental work has been conducted to quantitatively determine details such as their surface concentration, formation energies, and kinetic behavior. The likely reason for this is that the intrusive nature of surface probes, such as the scanning tunneling microscope (STM), makes it difficult to accurately study adatoms and vacancies at elevated temperatures due to their high mobility. RAS, however, is a nonintrusive surface probe with the potential to precisely monitor the effect of surface defects on surface states, making it an ideal tool for such studies.

In this work, we simulate the effect of temperature on the intensity of the peak observed at ~1.7 eV in the RA spectrum of Ag(110) thought to arise solely from electronic transitions between two surface states. By focusing on this particular RAS feature, we eliminate the inherent complexities associated with the Cu(110) and Au(110) surface-state-related features which overlap with other spectral features[1,3] (surface-perturbed bulk interband and intraband transitions) which have unknown temperature dependence. We find that in order to accurately describe the temperature dependence of the Ag(110) RAS peak, the effect of both the thermal shift in the binding energy of the occupied surface state involved and thermally induced surface defects need to be considered. The work presented here reveals the sensitivity of RAS to thermally induced surface defects and thereby demonstrates the potential of the technique as a tool for measuring surface kinetic behavior.

II. RA RESPONSE OF Ag(110) IN THE 1.7 eV ENERGY REGION

The peak in the RA response from Ag(110) at a photon energy of 1.7 eV arises from electronic transitions between two surface states at the $\bar{Y}$ point of the surface Brillouin zone.[6,7] At room temperature, the occupied state is at ~ 60 meV below E_f (Refs. 8 and 9) and the unoccupied state sits at ~ 1.6 eV above E_f.[9–11] The occupied and unoccupied states are p_y type and s type in character, respectively, allowing only light polarized in the [001] surface direction to induce electronic transitions between them. The anisotropy of the ~ 1.7 eV transition therefore derives directly from the symmetry of the occupied surface state.

Photoemission results show that the binding energy of the occupied state reduces linearly with increasing temperature at a rate of $\sim 1.7 \times 10^{-4}$ eV/K between ~ 60 and ~ 450 K.[9] It is predicted using this result that the band completely crosses E_f at a temperature of ~ 620 K. In recent experimental work on the effect of temperature on the RA response of Ag(110), Martin *et al.*[12] noted that the thermal shift of the ~ 1.7 eV RAS peak essentially follows that of the binding energy of the occupied surface state. Results from the same study show that the ~ 1.7 eV peak reduces in intensity with increasing temperature until, at ~ 520 K, it becomes indistinguishable from the background signal. This behavior is very similar to that observed in second-harmonic generation (SHG) data from Ag(110) (Ref. 13) where the $\bar{Y}$ surface-state signal decreases in intensity with increasing temperature until it reaches background level at ~ 500 K. The significant difference in the temperature at which the RAS results indicate that the surface-state transition is quenched and the temperature at which the occupied surface state is predicted to cross E_f suggests the influence of another process on the intensity of the 1.7 eV feature, which we believe is the formation of thermally induced defects.

III. RESULTS

A. Temperature dependence of the occupied surface state

In order to simulate the effect of temperature on the binding energy of the occupied surface state, we adopt an approach similar to that used in other studies to determine the temperature dependence of the ~ 1.7 eV SHG signal from Ag(110) (Ref. 9) and the surface-state contribution to the intensity of the 2.1 eV RAS peak of Cu(110).[3] The parabolic shape of the occupied and unoccupied surface-state binding energies at $\bar{Y}$ can be described using the expression

$$E(k) = E_0 + \frac{\hbar^2}{2m}|\boldsymbol{k} - \boldsymbol{k}|^2, \tag{2}$$

where $\boldsymbol{k}$ is a surface-state electron wave vector, $\boldsymbol{k}_0 = (0, 0.73)$ Å^{-1} (Ref. 9) is the position in reciprocal space of the $\bar{Y}$ point, E_0 is the surface-state energy at $\bar{Y}$, and m is the effective mass of the surface-state electrons. Extrapolating their photoemission measurements, Gerlach *et al.*[9] deduced the occupied band would sit just below E_f at $E_0 = -0.106$ eV at a temperature of 0 K. For the unoccupied surface state we use $E_0 = 1.66$ eV,[9–11] however the thermal sensitivity of this state is unknown. Guided by analogy with Cu(110) (Ref. 3), we assume that the energy of the unoccupied $\bar{Y}$ surface state of Ag(110) is independent of temperature.[14] The effective masses of the occupied and unoccupied states take the values $0.26m_0$ and $0.9m_0$, respectively,[9] where m_0 is the mass of a free electron, and both are assumed isotropic and temperature independent.

The model we apply[3] allows vertical electronic transitions to be induced from any point on the occupied state. By integrating over the two-dimensional (2D) Brillouin zone around $\boldsymbol{k}_0$, we obtain the shape of the absorption spectrum and hence the imaginary part of the surface dielectric function ε_s''. The model includes a Gaussian line $\mathcal{L}$ of width $\sigma = 50$ meV $+ (0.1$ meV/K$)T$ to account for hole lifetime broadening[3,9] and the Fermi-Dirac distribution function $\mathcal{F}$ to determine the electronic occupation of the state near E_f for any given temperature. At elevated temperatures, $\mathcal{F}$ allows transitions to be induced from the occupied state at points above E_f. The relationship between ε_s'' and the surface-state transition is

$$\varepsilon_s''(\omega, T) \propto \frac{1}{\omega^2}\int_{-\infty}^{\infty} \mathcal{L}[\omega - E_f(k) + E_i(k), \sigma(T)] \cdot \mathcal{F}[E_i(k), T] k dk, \tag{3}$$

where E_i and E_f are the initial and final energies of an electronic transition as given by Eq. (2). Using Kramers-Kronig relations, the real part of the surface dielectric function ε_s' can be derived from ε_s''. If we assume a complete polarization asymmetry for the surface-state contribution (i.e., $\Delta\varepsilon_s = \varepsilon_{sx} - \varepsilon_{sy} = -\varepsilon_s$), we can calculate the measured RAS signal as a function of absorbed photon frequency ω, using the expression[15]

$$\mathrm{Re}\left[\frac{\Delta r}{r}(\omega)\right] \propto \omega\{A(\omega)\varepsilon_s''(\omega) + B(\omega)\varepsilon_s'(\omega)\}, \tag{4}$$

where the functions $A(\omega)$ and $B(\omega)$ are determined by the substrate dielectric function.[15] For a Drude metal, we have[15]

$$A(\omega) = \frac{\omega^2}{\omega_p^2}, \tag{5}$$

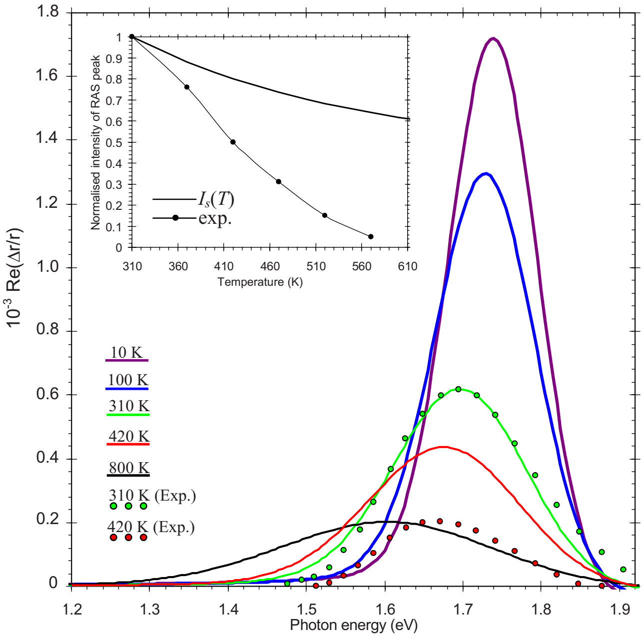

FIG. 1. (Color online) The RA response of Ag(110) simulated using Eqs. (3) and (4) at various temperatures (solid lines) and corresponding experimental data (circles). The inset shows the integrated intensity of the simulated RA response (smooth line) normalized at 310 K to the experimental integrated intensity (dotted line). Experimental data obtained by Martin *et al.* (Ref. 12).

$$B(\omega)=\frac{\omega}{\tau\omega_p^2},\tag{6}$$

where ω_p and τ are the plasma frequency 2.2×10^{15} Hz (Refs. 16 and 17) and the Drude relaxation time 3.1×10^{-14} s (Refs. 16 and 17) for Ag.

The RA response in the 1.7 eV energy region simulated using Eqs. (3) and (4) is shown in Fig. 1. With increasing temperature, the peak significantly reduces in intensity, becomes broader, and shifts to lower photon energies. This behavior arises due to three effects: (i) the shift in binding energy of the occupied state with increasing temperature reduces the photon energy required to induce transitions causing the RAS peak to shift to lower energies, (ii) the depopulation of the lower band as it crosses E_f results in a reduction in the number of possible optical transitions, acting to narrow the width of the RAS peak and reduce its integrated intensity, and (iii) the narrowing effect produced by the thermal drift of the lower surface state is overpowered by the combined action of the $\mathcal{L}$ function and the broadening of the Fermi edge at elevated temperatures which allows transitions from occupied states above E_f. In the case of the analogous 2.1 eV surface-state transition at $\bar{Y}$ on Cu(110), the outcome is quite different: only at high temperatures do the lifetime broadening and Fermi-edge smoothing effects dominate the narrowing effect on the RAS peak caused by the thermal shift of the occupied state.[3] The differing importance of these three thermal effects on the width of the surface-state RAS peaks of Ag(110) and Cu(110) arises because of their quite different energy gaps between the bottom of the occupied state and E_f.

The close vicinity of the bottom of the occupied state to E_f, even at room temperature, means that the smoothing of the Fermi-Dirac distribution function at elevated temperatures plays a significant role in the population of the state and hence the RA response. This is demonstrated by the fact that at 800 K, beyond the temperature at which photoemission results predict the lower state to entirely cross E_f (Ref. 9), Eqs. (3) and (4) still generate a RAS peak with significant intensity (Fig. 1). The Fermi-Dirac term in Eq. (3) is considerably less influential when simulating the RA response of Cu(110) where the occupied state sits significantly further below E_f. In the case of Cu, removing $\mathcal{F}$ from the integration in Eq. (3) for a temperature of 700 K has only a minor effect on ε_s'', whereas for Ag it drops dramatically to almost zero.

We find that Eqs. (3) and (4) provide a good description of both the position and width of the Ag(110) surface-state RAS peak, confirming the validity of the approach proposed by Sun *et al.*[3] We now consider its intensity. The change in the experimental intensity of the peak with temperature, using data obtained by Martin *et al.*[12] is shown in the inset of Fig. 1 for 310, 370, 420, 470, 520, and 570 K. (When discussing the "intensity" of this feature throughout the study, we refer to the integrated intensity beneath the peak.) By normalizing this experimental data at 310 K to the calculated intensity of the feature at this temperature using Eqs. (3) and (4), which we label $I_s(T)$, it becomes clear that the thermal shift of the occupied state alone is insufficient to explain the reduction in intensity of the RAS feature at elevated temperatures (inset in Fig. 1). This point is clearly demonstrated by comparing the difference in the simulated and experimental spectra at 310 and 420 K shown in Fig. 1.

B. Effect of defects on RAS peak intensities

In a recent inverse photoemission spectroscopy (IPES) study by Heskett *et al.*,[18] the effect of Ne^+ bombardment on the unoccupied surface state involved in the 2.1 eV peak in the RA spectrum of Cu(110) was investigated. The study found that the intensity of the IPES peak corresponding to this state reduced in an exponential-like manner with increasing ion bombardment. The authors[18] suggest that this behavior indicates that the state is not sustained by contributions from isolated surface atoms but by groups of atoms in undisturbed "patches" on the surface.

In the RAS investigation performed by Sun *et al.*[4] into the effect of CO adsorption on Cu(110), the intensity of the 2.1 eV RAS feature was found to reduce nonlinearly with increased molecular coverage. Such behavior is typical for surface-state-related RAS features and is routinely observed upon the exposure of clean Cu(110) and Ag(110) to surface adsorbates.[1] Sun *et al.*[4] attributed this behavior to the depolarization of the associated surface states in the vicinity of the adsorbed CO molecules which occurs due to the isotropic scattering of surface-state electrons from these adsorbates. This effect causes the anisotropy of the unoccupied *p*-type surface state in the region surrounding the CO molecule to be lost, resulting in the loss of the surface-state contribution

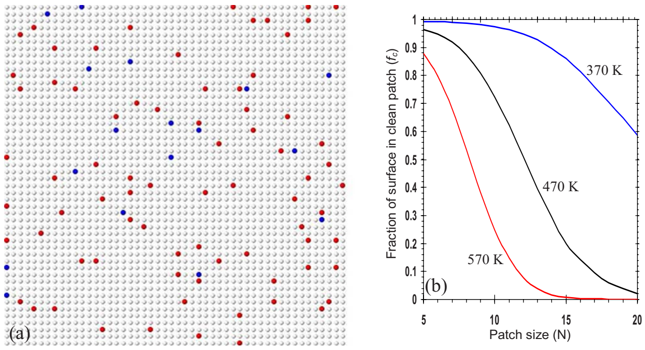

FIG. 2. (Color online) (a) 50×50 atomic site section of the simulated surface showing the location of randomly scattered surface adatoms at 370 K [blue (darker shaded) circles] and 570 K [blue and red (all shaded) circles]. (b) The effect of patch size on the fraction of surface atoms located in clean patches of that size at 370, 470, and 570 K. Data obtained for (a) and (b) using $E_d=0.16$ eV.

to the RAS peak of this surface patch. It is calculated in the study that a single CO molecule quenches the local contribution to the RAS peak over a 1000 Å (Ref. 2) surface area.

In this study, we attribute the anomalous Ag(110) RAS intensities in the measurements of Martin *et al.*[12] (Fig. 1) to the effect of thermally created surface defects. We expect the dominant mechanism for the creation of thermal defects on the Ag(110) surface to be the detachment and subsequent migration of atoms from kink sites on pre-existing step edges.[19] By considering the work of Heskett *et al.*[18] and Sun *et al.*,[4] we suggest that these adatoms reduce the intensity of the ~1.7 eV RAS peak due to one or both of the following processes: (i) the destruction of the unoccupied surface state over areas surrounding defect sites and (ii) the loss of the occupied surface-state anisotropy in the vicinity of defects due to isotropic electron scattering. Although it is unclear which, if either of these effects will dominate, the assumption is made from these studies that an individual adatom will quench the contribution to the intensity of the RAS feature over an area on the Ag(110) surface surrounding the defect site.

C. Thermal defect simulation

To investigate the effect of thermal adatoms on RAS intensities, we adopt a simulation method similar to that used in the surface ion bombardment studies of Heskett *et al.*[18] in which the surface is modeled by a periodic array of "supercells," each comprising a square lattice of 10^6 evenly spaced atomic sites. For a given temperature T, defects are randomly distributed over the supercell with a coverage $C(T)$ calculated using the Arrhenius expression[19]

$$C(T)=\exp(-E_d/k_bT), \tag{7}$$

where E_d is the energy barrier for defect formation and k_b is Boltzmann's constant. The relationship between $C(T)$ and T is illustrated in Fig. 2(a) showing the distribution of randomly positioned thermal adatoms at 370 and 570 K over a 50×50 atomic site section of the simulated surface. In the following section, we reconcile the discrepancy in the experimental and simulated intensities of the ~1.7 eV RAS peak at various temperatures (inset in Fig. 1) by applying two different models: (i) "model *A*" based on the atomic patch size required to sustain a contribution to the intensity of the RAS peak and ii) "model *B*" based on the atomic patch size over which the contribution to the RAS peak intensity is quenched due to the presence of a single thermally created adatom.

D. Patch models

First we will discuss the model based upon the atomic patch size required to sustain a contribution to the ~1.7 eV RAS peak intensity (model *A*). By placing $N\times N$ squares at all lattice positions on the model surface $f_c\ (N,T)$, the fraction of surface sites located within a clean patch can be determined at any temperature. We make the assumption that $f_c\ (N,T)$ is the fraction of surface atoms that contribute to the surface-state RAS peak and therefore can be considered as the normalized intensity of this feature as calculated by considering just the effect of thermal defects. The effect of patch size N on $f_c\ (N,T)$ at 370, 470, and 570 K is shown in Fig. 2(b). Multiplying $f_c\ (N,T)$ and $I_s(T)$ gives a new simulated intensity of the ~1.7 eV RAS peak $I_{sd}(N,T)$, which accounts for both the thermal shift of the associated occupied state and the effect of thermally induced surface adatoms using this model. For comparison with experiment, we normalize $I_{sd}(N,T)$ at 310 K to the experimental intensity observed by Martin *et al.*[12] previously shown in the inset of Fig. 1. Figure 3(a) shows a fit of $I_{sd}(N,T)$ to the experimental data using patch model *A*. In fact, there are two unknown parameters in the model, namely, N and E_d. In principle, it is possible to compensate for an increase in one by increasing the other. Pairs of parameters (N^A,E_d^A) obtained by fitting $I_{sd}\ (N,T)$ to the experimental data are shown in Fig. 4. Heskett *et al.*[18] calculated that a clean patch size of 12×12 atom sites is the minimum required to sustain the unoccupied surface state at $\bar{Y}$ on Cu(110). From Fig. 4, we see that $N^A=12$ in our RAS analysis of Ag(110) implies a defect creation barrier of $E_d^A=0.15$ eV. The $I_{sd}\ (N,T)$ curves shown in Fig. 3(a) use this value of E_d^A. Using the result of Heskett *et al.*,[18] we regard $E_d^A=0.15$ eV as an approximate lower bound.

Model *B* is based on atomic patches centered on the adatom site over which the ~1.7 eV RA response is quenched due to isotropic electron scattering and/or the destruction of one of the involved surface states. This model is readily applied to the supercells used in the calculations used in model *A* by redefining $f_c\ (N,T)$ to be the fraction of surface sites not lying within $N\times N$ patches centered on each defect site. For patch model *B*, our numerical calculations of $f_c\ (N,T)$ are essentially indistinguishable from the analytical result used by Sun *et al.*,[4]

$$f_c(N,T)=[1-C(T)]^{N^2}, \tag{8}$$

confirming that the supercell is sufficiently large and the adatoms distributed randomly. Pairs of parameters $(N^B,\ E_d^B)$ obtained by fitting the experimental RAS data with $I_{sd}\ (N,T)$

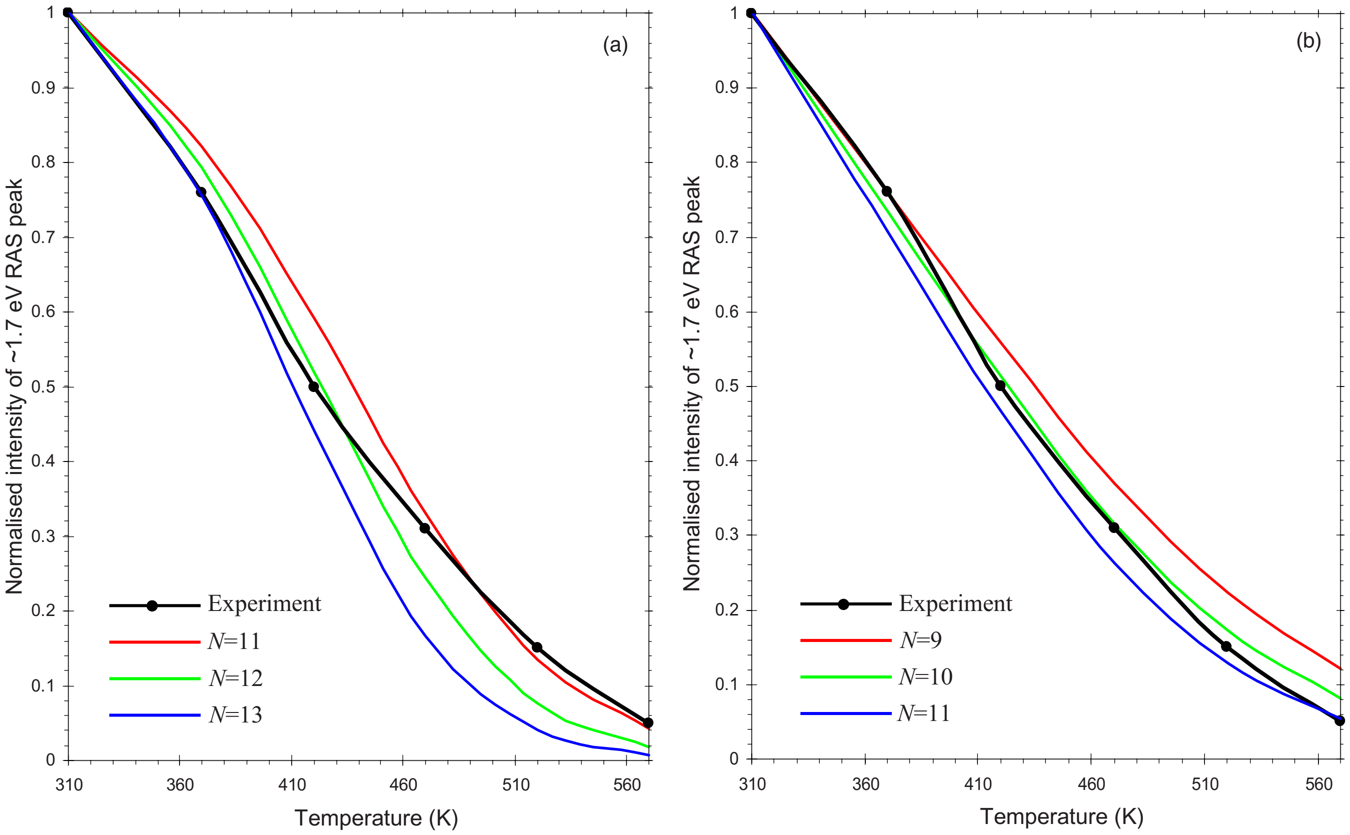

FIG. 3. (Color online) Comparison of the change in the experimental and simulated intensity $[I_{sd}(N,T)]$ of the ∼1.7 eV RAS peak with increasing temperature for (a) patch model *A*, using E_d=0.15 eV, and (b) patch model *B*, using E_d=0.19 eV.

defined using patch model *B* are shown in Fig. 4.

In the low coverage regime, most relevant to the present work, it is calculated by Sun *et al.*[4] that a single CO molecule quenches the local contribution to the surface-state RAS peak of Cu(110) over a surface area of ∼1000 Å,[2] corresponding to N^B=10. With this value we deduce E_d^B =0.19 eV from Fig. 4. The I_{sd} (N,T) curves shown in Fig. 3(b) use this value of E_d^B. In order to accurately model the decrease in the maximum intensity of the ∼2.1 eV Cu(110) RAS peak upon CO deposition, Sun *et al.*[4] utilized an expression equivalent to Eq. (8) but incorporating two values of *N*. The largest cross section required corresponds to N^B =22, implying E_d^B=0.25 eV (see Fig. 4) which we can take as an approximate upper bound.

IV. DISCUSSION

The models used in this study offer two distinct methods for simulating the effect of thermally created surface defects on the intensity of the ∼1.7 eV RAS peak of Ag(110). We have seen that the requirement of consistency with results of Heskett *et al.*[18] and Sun *et al.*[4] provide approximate lower and upper bounds, respectively, on our estimate of the adatom activation barrier, defining the result 0.15 eV$\leq E_d$ $\leq$0.25 eV. Applying Eq. (7) to low-energy electron microscopy studies, Tromp and Mankos[19] deduced the energy barrier for the formation of thermal addimers created via their detachment from step edges on Si(001) is 0.35±0.05 eV. Although a comparative study for Ag(110) could not be found in the literature, it is reasonable to expect a similar but perhaps smaller value for Ag(110). Defect formation energies for Ag(110) have been investigated using various embedded atom models (EAMs).[20–23] Devyatko *et al.*[20] and Zhang *et al.*[21] found adatom-vacancy pairs to be the lowest-energy defects with a formation energy in the range 0.16–0.22 eV. Devyatko *et al.* noted agreement with E_d deduced from medium energy ion scattering results.[20] On the other hand, Silvestri *et al.*[24] interpreted the *T* dependence of

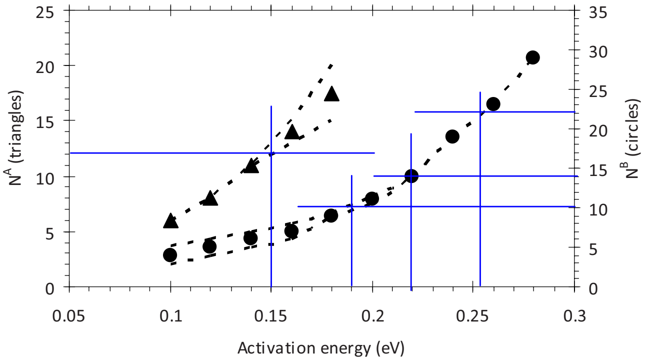

FIG. 4. (Color online) Patch sizes and activation energies deduced from fitting $I_{sd}(N,T)$ to the experimental RAS data of Martin *et al.* (Ref. 12). Results obtained from models *A* and *B* are shown using triangles and circles, respectively. Dashed lines delineate error bars.

diffuse He atom scattering from metal surfaces in terms of adatom evaporation from steps. Following this approach, Pedemonte and Bracco[25] obtained an adatom barrier of 0.38 eV for Ag(110), in very good agreement with the EAM barrier calculations of Ferrando and co-workers[22,26] which gave E_d=0.38 eV for the adatom-vacancy barrier. Parametrizing such results using a so-called "bond breaking model" leads to a barrier of 0.40 eV for adatom-vacancy formation and barriers of 0.38 and 0.22 eV for evaporation from ⟨110⟩ and ⟨001⟩ oriented steps.[25,26] In the same way, a barrier for kink sites of 0.20 eV is obtained. Pedemonte and Bracco concluded that both terraces and ⟨110⟩ steps supply adatoms and explained the apparent absence of adatoms from ⟨001⟩ oriented steps by the relative rarity of such steps; an observation also noted by Martin *et al.*[12] Thus, both experimental and theoretical estimates of the defect activation barrier for Ag(110) lie in the range 0.16–0.38 eV. In this context, the estimate of 0.20 ± 0.05 eV in the current work is reasonable, but we note that a dominant role for adatom-vacancy pairs (i.e., two scattering sites per defect) would increase our estimate slightly (by ~0.03 eV).

Our estimate of E_d yields consistency with both the IPES results of Heskett *et al.*[18] and the RAS study of CO adsorption by Sun *et al.*,[4] provided the appropriate model is used for each comparison. Which model is to be preferred? The answer is that which correctly describes $f_c(N,T)$: the RAS renormalizing factor due to defects. Model *A* is expected to be most relevant at high defect density where only a few undisturbed atomic patches remain and less well matched to describing the low-density regime. In accord with this expectation, we find that model *A* leads to a poorer description of $I_{sd}(N,T)$ with increasing E_d, as demonstrated by the growing error bars in Fig. 4. We can deduce the form of $f_c(N,T)$ empirically by dividing the experimental RAS intensity by $I_s(T)$ derived from Eqs. (3) and (4). This process yields an approximately linear function between 300 and 600 K. Model *A* reproduces such behavior only for E_d less than 0.16 eV. Model *B*, on the other hand, is expected to be most appropriate at low defect densities. Again this expectation is confirmed in our data analysis—we find that this patch model gives a less satisfactory description of the empirical $f_c(N,T)$ for low defect barriers and hence high defect densities. For $E_d \geq 0.22$ eV, not more than one of the $I_{sd}(N,T)$ intensity curves produced using model *B* crosses the experimental intensity curve. From this result, we estimate that a 14×14 atomic patch (see Fig. 4) is the minimum surface area over which the RAS contribution to the intensity of the ~1.7 eV RAS peak is lost due to a single thermally created defect. The neglect of defect interactions, such as adatom clustering, that are likely to occur on the Ag(110) surface at elevated temperatures along with our relatively crude geometric treatment doubtless contribute to the imperfect agreement between our simulations and the experimental RAS measurements. However, considering the simplicity of the models, we deem this degree of uncertainty to be acceptable but acknowledge that improvements, incorporating effects such as temperature-dependent adatom-adatom interactions, could further improve its quantitative accuracy.

V. CONCLUSION

We have shown that the effect of temperature on the intensity of the ~1.7 eV peak in the RA spectrum of Ag(110) can be explained by considering both the effect of thermally induced surface defects and the thermal shift in the binding energy of the associated occupied surface state. Using two simple models, we have simulated the decrease in the RAS peak intensity with increased temperature, achieving broad consistency with related measurements on ion-bombarded and adsorbate-covered Cu(110) surfaces, and previous estimates of the defect activation barrier for the Ag(110) surface. Our results reveal that RAS is highly sensitive to the presence of thermal defects on the Ag(110) surface and demonstrate the potential of the technique as a tool for monitoring surface kinetic behavior.

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