

Contributions from surface-modified bulk electronic bands to the reflection anisotropy of Au(110)-(1 × 2)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S4375

(<http://iopscience.iop.org/0953-8984/16/39/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 17:56

Please note that [terms and conditions apply](#).

Contributions from surface-modified bulk electronic bands to the reflection anisotropy of Au(110)-(1 × 2)

D S Martin^{1,3}, R J Cole², N P Blanchard¹, G E Isted¹, D S Roseburgh²
and P Weightman¹

¹ Department of Physics and Surface Science Research Centre, University of Liverpool,
Liverpool L69 3BX, UK

² School of Physics and Centre for Materials Science and Engineering, University of Edinburgh,
Edinburgh EH9 3JZ, UK

E-mail: davidm@liverpool.ac.uk

Received 26 March 2004

Published 17 September 2004

Online at stacks.iop.org/JPhysCM/16/S4375

doi:10.1088/0953-8984/16/39/012

Abstract

We investigate the temperature dependence of the optical reflectance anisotropy (RA) of the Au(110)-(1 × 2) surface and find that transitions involving surface-modified bulk bands contribute to the RA spectrum. The RA peaks observed at room temperature at photon energies of 3.52 and 4.50 eV are assigned to the transitions $E_F \rightarrow L_1^u$ and $L_2' \rightarrow L_1^u$, respectively. The assignments are based upon a comparison between temperature-induced shifts in the energy of these RAS peaks and thermovariation optical spectroscopy results of the temperature dependence of transition energies between bands at the L symmetry point. The application of RAS to Au(110) can be seen as a model system for exploring surfaces in a range of environments including ultra-high vacuum, high pressures and at the solid/liquid interface. The results reported here further the understanding of the RA spectrum of the clean Au(110) surface.

1. Introduction

The low-index single crystal surfaces of Au are well suited to investigations of surface phenomena in a wide range of environments. This is primarily due to the ease of surface preparation and the inert nature of Au to processes such as oxidation relative to other metal surfaces. Reflection anisotropy spectroscopy (RAS) [1] is an optical probe of surfaces able to operate in ultra-high vacuum (UHV), ambient and liquid environments. Thus the application of RAS to Au surfaces can be seen as a model system for exploring surfaces in non-UHV environments. The Au(110) surface is of particular interest due to the variations in its structural

³ Author to whom any correspondence should be addressed.

anisotropy; the clean Au(110) surface exhibits a (1×2) missing row reconstruction at room temperature which converts to a disordered (1×1) phase at higher temperatures [2]. The Au(110)- (1×2) surface has been the focus of a number of RAS studies in UHV [3–8] and at the solid/liquid interface [4, 9–11].

The RA response of Au(110) has been found to be sensitive to surface reconstruction [3–5], surface roughness created by Ar ion bombardment [5], surface alloy formation [7] and molecular adsorption [11]. There are indications of a contribution to the RA response around 1.8 eV from electronic transitions between surface states [3–5, 8]. To date, there have been no *ab initio* calculations of the RA response of Au(110)- (1×2) . The surface local-field model [12] that has contributed to the interpretation of the RA response of Cu(110) [13] has been applied to Au(110)- (1×2) [6], however, the resulting model spectrum does not agree with the experimental profile.

RAS studies of semiconductors have found that electronic bands of the bulk crystal modified by the presence of a surface may contribute structure to the RA profile [14, 15]. It may be expected that similar contributions occur in the RA response of metals. Recent work on the Cu(110) surface by Sun and co-workers [16] has assigned RAS peaks to transitions involving surface modified d-bands near the Fermi level (E_F) at the L symmetry point. The peaks observed at 4.25 and 4.9 eV in the RA spectrum obtained from the crystal at room temperature were assigned to the optical transitions $E_F \rightarrow L_1^u$ and $L_2' \rightarrow L_1^u$, respectively. The temperature dependence of the energy position of these RAS peaks was found to agree with the temperature dependence of the transition energies between the associated d-bands, as determined from thermovariation optical spectroscopy [17]. Prior to the work of Sun *et al* [16], some of the present authors had observed the temperature dependence of the RA response of Cu(110) [18] and we find similar energy shifts as a function of temperature to those measured by Sun *et al* [16].

In the work presented here, we measure the RA response of Au(110) as a function of temperature. We compare temperature-induced shifts in the energy of RAS peaks to thermovariation spectroscopy results [17] of the temperature dependence of transition energies between bulk electronic bands at L. We find evidence that bulk-related transitions similar to those identified in the RAS of Cu(110) contribute structure to the RA spectrum of Au(110).

2. Experimental details

The experiments were performed in an UHV environment with base pressure in the 10^{-10} mbar region. A clean well-ordered Au(110)- (1×2) surface was prepared by repeated cycles of Ar ion bombardment (15 min, $\sim 6 \mu\text{A}$, 0.5 kV, 300 K) and annealing to 900 K. Surface order was confirmed by low-energy electron diffraction (LEED) and scanning tunnelling microscopy (STM). Surface cleanliness was monitored using x-ray photoelectron spectroscopy (XPS). Temperature was measured using an N-type thermocouple with an estimated uncertainty of ± 20 K.

RAS [1] probes as a function of photon energy the optical response of a surface with linearly polarized light by measuring the difference in normal incidence reflection of two perpendicular directions in the surface plane (Δr) normalized to the mean reflection (r). For Au(110) we define the RA as:

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

where the reflections $r_{[1\bar{1}0]}$ and $r_{[001]}$ are complex Fresnel reflection amplitudes for the $[1\bar{1}0]$ and $[001]$ surface directions, respectively. The RA spectrometer based upon the Aspnes design [19]

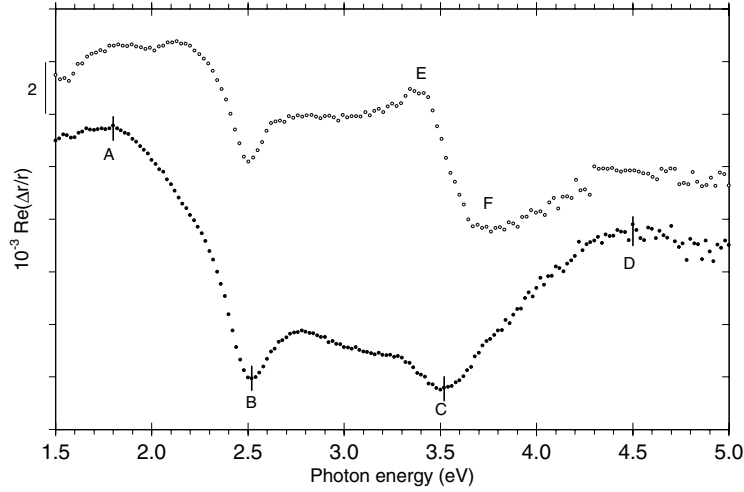


Figure 1. Experimental RA spectra of the clean well-ordered Au(110)-(1 × 2) surface (filled circles) and a heavily (36 min) ion bombarded Au(110) surface (open circles) from [5]. Both spectra were measured at a temperature of 300 K.

projected and received light through a low-strain window on the UHV system. Experimental artifacts were removed from spectra using a correction function obtained by measuring spectra with the specimen in two orthogonal positions. Spectra of the real part of the complex RA were taken over a photon energy range 1.5–5.0 eV. RA spectra were obtained at the constant temperature indicated.

3. Results

The RA spectrum of the clean, well-ordered Au(110)-(1 × 2) surface at 300 K is shown in figure 1. This RA profile is characterized by features at 1.80, 2.52, 3.52 and 4.50 eV (labelled A–D in figure 1) and is in good agreement with previous RAS results of the clean (1 × 2) surface [3–8]. The RA spectrum of the Au(110) surface following Ar ion bombardment is also shown in figure 1. Major changes in the spectral profile following Ar ion bombardment can be seen in the 3–4 eV region. Since the bulk Au single crystal is optically isotropic the RA response observed for both the well-ordered and Ar bombarded surfaces must be associated with the surface layers. The RA response can be simulated using a three-phase model [20] in which the dielectric properties are assumed to vary abruptly at the interfaces between three homogeneous media: vacuum, surface layer and substrate. In the thin film limit where the surface layer thickness d is much less than the wavelength of light λ we have:

$$\frac{\Delta r}{r} = -\frac{4\pi i d}{\lambda} \frac{\Delta \epsilon_s}{\epsilon_b - 1} \quad (2)$$

where ϵ_b is the substrate dielectric function and $\Delta \epsilon_s$ is the dielectric anisotropy in the surface layer. Figure 2(a) shows ϵ_b'' (we use the notation $\epsilon = \epsilon' + i\epsilon''$) determined using spectroscopic ellipsometry data from an Au(110) crystal [21]. In general, peaks in ϵ_b'' arise from interband transitions at critical points. An external perturbation tends to modify the energies E_g and linewidths Γ of these transitions as well as their oscillator strength. It has long been appreciated [22] that the first two effects dominate and so the change in dielectric function is approximately proportional to the energy derivative of ϵ_b . Rossow *et al* have extended this

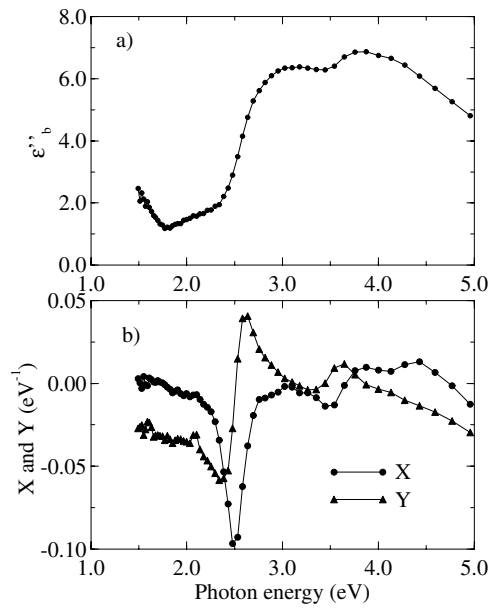


Figure 2. (a) ϵ'_b for Au determined by Blanchard *et al* [21], (b) the functions $X(E)$ and $Y(E)$ defined by equations (3) and (4).

argument to the perturbation of ϵ_b at a surface [23]. For the biaxial Au(110) surface there are different energy and broadening shifts for $[1\bar{1}0]$ and $[001]$ polarized light leading to:

$$\frac{\Delta r}{r} = -\frac{4\pi i d}{\lambda} \frac{(\Delta E_g + i\Delta\Gamma) d\epsilon_b}{\epsilon_b - 1} \frac{d\epsilon_b}{dE} \quad (3)$$

where ΔE_g and $\Delta\Gamma$ are the relative shifts in gap energies and linewidths for the two polarizations, and E is the photon energy.

The real part of $\Delta r/r$ (equation (3)) can be written:

$$\text{Re}\left[\frac{\Delta r}{r}\right] = X(E)\Delta E_g + Y(E)\Delta\Gamma. \quad (4)$$

The $X(E)$ and $Y(E)$ functions for Au, evaluated using ellipsometric measurements of ϵ_b [21], are shown in figure 2(b). The common practice of setting d to 1 nm has been adopted here. It can be seen that $X(E)$ has a number of features in common with the experimental RA spectrum of the well-ordered Au(110)-(1 × 2) surface (figure 1) implying that the spectrum is dominated by the first term in equation (4). We deduce that while particular optical transitions have particular values of ΔE_g and $\Delta\Gamma$, $|\Delta E_g| \gg |\Delta\Gamma|$ throughout the RA spectral range. RAS simulations using equation (4) with the parameters $\Delta\Gamma = 0.0$, $\Delta E_g = 0.05$ eV in the 2–3 eV region, and $\Delta\Gamma = 0.0$, $\Delta E_g = 0.3$ eV in the 3–5 eV region are shown in figure 3. The main features (B, C, D) of the experimental spectrum from the well-ordered surface are reproduced.

RA spectra of Au(110) measured at a range of temperatures between 300 and 1000 K are shown in figure 4. For temperatures up to ~ 820 K, the spectra are in good agreement with previous results presented by Stahrenberg *et al* [3]. The RA spectra show that increasing the temperature above 300 K results in features C and D shifting to lower photon energies. The energy position, 1.80 eV, of the start of the large negative slope (feature A) appears to be independent of temperature (figure 4). The intensity of peak B decreases with increasing

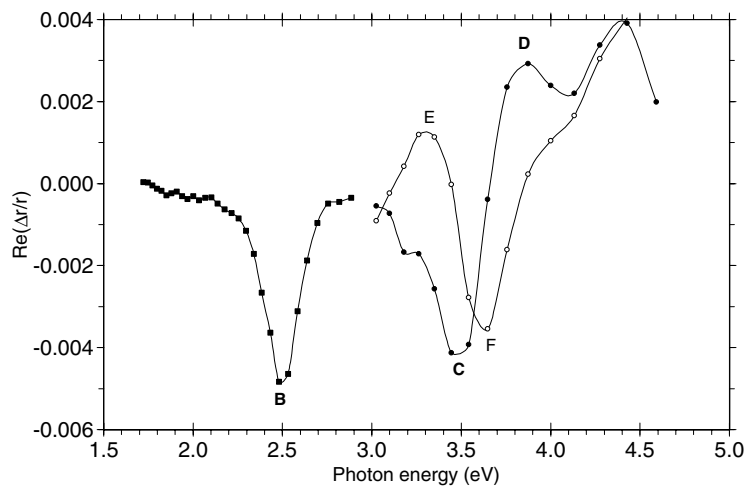


Figure 3. RA simulations calculated using equation (4) using parameters $\Delta\Gamma = 0$ eV, ΔE_g ($1.5 < E < 3.0$) = 0.05 eV (filled squares), ΔE_g ($3.0 < E < 4.5$) = 0.3 eV (filled circles). Open circles calculated using $\Delta\Gamma = -0.3$ eV and $\Delta E_g = 0$ eV.

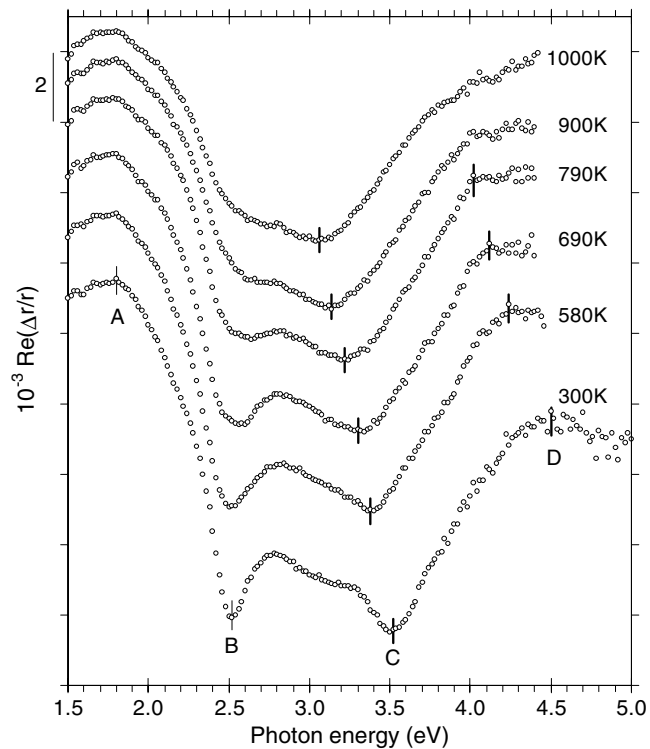


Figure 4. RA spectra of Au(110) as a function of temperature.

temperature and its energy position is found to shift gradually to higher energy upon increasing the temperature above 580 K, residing at ~ 2.6 eV at a temperature of 790 K (figure 4). Above 790 K it becomes difficult to distinguish peak B from the background profile.

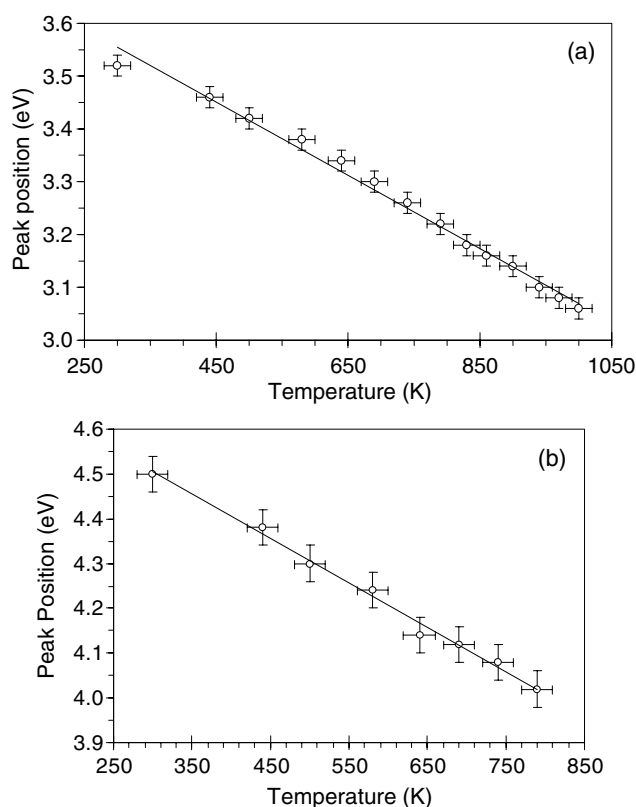


Figure 5. RAS peak position as a function of temperature for (a) peak C and (b) peak D of figure 4. The peak position was measured from the RA spectrum recorded while the crystal was held at that temperature.

The RA response in the region 1.5–2.5 eV has shown sensitivity to surface reconstruction [3–5, 9, 10]. The reconstructed Au(110) surface is thought to deconstruct via a 2D-Ising transition at a temperature between ~ 650 and 765 K [24] followed by a roughening transition approximately 50 K above the deconstruction temperature [24, 25]. No abrupt changes in the RA spectral features were observed near to these temperatures (figure 4). The smooth decrease in RA intensity observed between 1.5 and 2.5 eV with increasing temperature (figure 4) is consistent with a gradual increase in surface atomic disorder from the well-ordered (1×2) phase to the disordered (1×1) phase.

From figure 4 it is clear that the energies of features C and D shift with increasing temperature. The temperature dependence of the energies of C and D are plotted in figures 5(a) and (b), respectively. The behaviour of both these peaks over the temperature ranges plotted in the figures is well described by linear fits of gradients $-6.9 \times 10^{-4} \text{ eV K}^{-1}$ (figure 5(a)) and $-9.9 \times 10^{-4} \text{ eV K}^{-1}$ (figure 5(b)) for C and D, respectively. In figure 5(b), measurements of D are limited to 790 K since above this temperature it becomes difficult to distinguish the feature from the background profile.

4. Discussion

In the previous section, it was shown that the ‘derivative model’ (i.e. equation (3)) with a non-zero ΔE_g gives a good description of the main features of the RA spectrum of the well-ordered

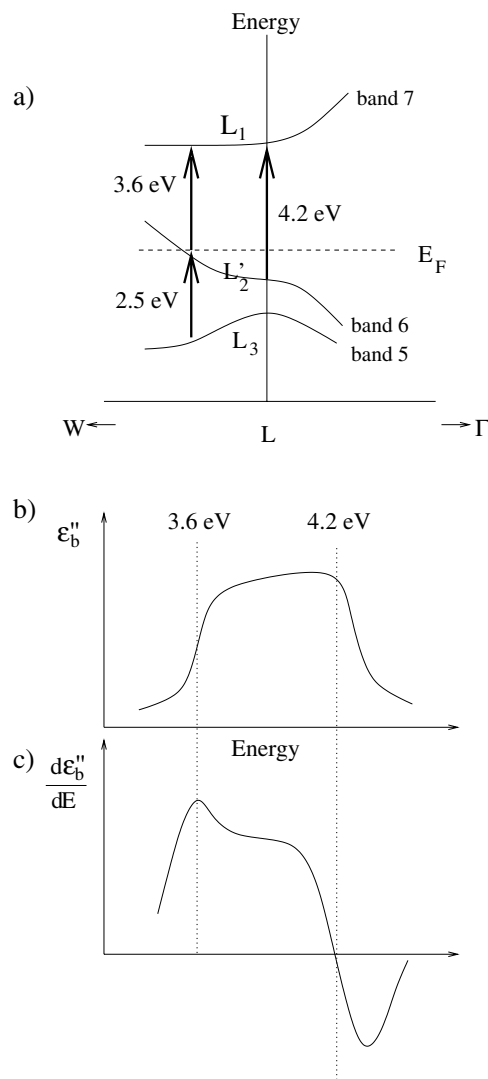


Figure 6. Schematic representation of (a) the energy bands of Au near the L point, (b) ϵ_b'' in the 3–5 eV region, and (c) $d\epsilon_b''/dE$.

Au(110)-(1 × 2) surface. We now explore the relationship between the RA spectrum and the known optical properties of Au, and discuss the possible origin of ΔE_g and $\Delta \Gamma$ parameters.

Using thermovariation optical spectroscopy, Winsemius *et al* [17] have shown that the main features of ϵ_b for Au are derived from interband transitions in the vicinity of the L point of the Brillouin zone. Following [17], the relevant bands are sketched in figure 6(a). The sharp rise in ϵ_b'' at 2.5 eV (figure 2(a)) is attributed to $L_3 \rightarrow E_F$ transitions. This absorption is responsible for the sharp peak in $X(E)$ at 2.5 eV (figure 2), as well as the characteristic colour of Au. The main features in the 3–5 eV region were attributed [17] to transitions between bands 6 and 7, as shown in figure 6(a), along with the general form of ϵ_b'' in this region (figure 6(b)). The low energy cut-off indicates band 6 crossing E_F close to L. An M_2 type critical point attributed to transitions between bands 6 and 7 at L was estimated [17] to have

Table 1. Observed temperature dependence of RAS peaks C and D measured in this work over the temperature range in brackets. Also shown are corresponding values measured by Winsemius *et al* [17] using thermovariation spectroscopy. All measurements are in eV K⁻¹. Assignments of the transitions are also shown.

Peak position at 300 K	RAS (this work)	Thermovariation [17]
3.52 eV ($E_F \rightarrow L_1^u$)	-5.9×10^{-4} (300–740 K)	-5.3×10^{-4} (295–770 K)
4.50 eV ($L_2' \rightarrow L_1^u$)	-9.9×10^{-4} (300–790 K)	-10.4×10^{-4} (380–720 K)

energy $\sim 4.2 \pm 0.2$ eV. From these considerations it follows that $d\epsilon_b''/dE$ has a peak at 3.6 eV and an oscillatory structure centred on ~ 4.2 eV, as sketched in figure 6(b).

The form of the Au(110) RA spectrum in the region 3–5 eV can be anticipated from knowledge of $d\epsilon_b/dE$ and the observation that $1/(\epsilon_b - 1)$ for Au is predominantly imaginary and does not vary strongly with photon energy in this region [26]. Under these circumstances we can rewrite equation (2) as

$$\text{Re} \left[\frac{\Delta r}{r} \right] \propto \Delta E_g \frac{d\epsilon_b'}{dE}. \quad (5)$$

It follows that a RA spectrum is predicted with an oscillatory profile centred on 3.6 eV due to $E_F \rightarrow L_1^u$ transitions and a peak at about 4.2 eV derived from $L_2' \rightarrow L_1^u$ transitions, as shown in figure 3. The experimental RA spectrum in figure 1 exhibits a negative feature slightly below 3.6 eV (feature C). The positive component of the expected oscillation is not well resolved in the data of figure 1 but does appear as a small kink around 3.9 eV in the data of Stahrenberg *et al* [3] and Martin *et al* [5, 7]. We associate the 4.5 eV peak (D) with the $L_2' \rightarrow L_1$ critical point. Since peaks C and D are each derived from transitions between the same bands near L_1 , it is appropriate to use a single value of ΔE_g in the 3–5 eV region.

Further confirmation of the assignments of features C and D is provided by analysis of their temperature dependence. In table 1 we compare the gradients of the linear fits of the data in figure 5 with the results of the thermal behaviour of inter-conduction band transitions as determined by thermovariation spectroscopy [17, 27]. The energy shifts obtained from the two techniques compare well (table 1). Thus the general RAS lineshape, the photon energies of the spectral features and their temperature dependence all associate peak C with $E_F \rightarrow L_1^u$ transitions, and feature D with transitions between L_2' and L_1^u .

Association of peak B at 2.5 eV with the $L_3 \rightarrow E_F$ interband threshold is consistent with the assignments proposed by Winsemius *et al* [17]. However these authors have previously noted that the temperature dependence of the $L_3 \rightarrow E_F$ transition is not reliably known. We note that while the intensity and energy of peak B show temperature dependence (figure 4), it appears to be little affected by ion bombardment (figure 1).

We turn now to a discussion of ΔE_g and $\Delta\Gamma$. Sun *et al* [16] have found that the optical anisotropy of the Cu(110) surface around 4 eV is explained by equation (3) with a dominant ΔE_g term. Sun *et al* [16] interpreted this result in terms of the reduced coordination of atoms at the Cu(110) surface. Band narrowing leads to an energy shift to preserve the occupancy of the band, leading to a modification of the E_g gap parameters for optical transitions. The structural anisotropy of the Cu(110) surface causes different band narrowing along [001] and $[1\bar{1}0]$ and hence ΔE_g is non-zero. We adopt the same explanation here for Au(110). Sun *et al* have also noted [16] that the L_1 band in copper is particularly sensitive to changes in nearest neighbour hopping integrals. Similar behaviour in Au is consistent with our observation of a larger ΔE_g for the $E_F \rightarrow L_1$ and $L_2' \rightarrow L_1$ transitions than for $L_3 \rightarrow E_F$. Further evidence for the importance of the coordination of surface atoms is provided by the recent RAS study of vicinal

Cu(111) surfaces by Baumberger *et al* [28] which shows that a RAS peak observed at 4.3 eV derived from the presence of steps has sign determined by the atomic coordination at step edges.

As demonstrated by figure 1 and [5], the RA response of Au(110) between 3.0 and 4.0 eV is highly sensitive to Ar ion bombardment. An analogous effect has also been observed for Cu(110) [18, 29]. The assignment of the RA response in these regions for both Au(110) and Cu(110) to surface-modified bulk bands implies that these bulk bands must be sensitive to the effects of Ar ion bombardment. We speculate that ion-induced disorder in the near surface region of Au(110) introduces increased broadening of the $E_F \rightarrow L_1$ and $L'_2 \rightarrow L_1$ transitions. It has been found that at sufficiently high temperature (~ 200 K in the case of Cu) anisotropy of the adatom and vacancy diffusion rates due to crystallographic inequivalence of the [001] and [110] directions leads to nanoscale structural anisotropy in the noble metals [30]. We deduce that $|\Delta\Gamma|$ dominates $|\Delta E_g|$ for the ion bombarded surface. LEED results from the ion bombarded Au(110) surface show streaking along the [110] direction [5] implying greater disorder along this direction. This result is confirmed by STM data [5]. An RAS simulation of the ion bombarded surface using equation (4) and $\Delta\Gamma = -0.3$ eV, $\Delta E_g = 0$ eV is shown in figure 3. Comparison with the experimental data in figure 1 suggests that this model reproduces the effect of ion bombardment (features labelled E and F) rather well.

We have previously simulated the RA response of Au(110)-(1 × 2) [4, 5] using a three-phase model [26] incorporating ϵ_b of Au and a parameterized representation of surface electronic transitions. The experimental RA profile was well reproduced [5] using three transitions assigned:

- (1) at the $\bar{\Gamma}$ point between a surface resonance at 1.7 eV below E_F and a surface state at ~ 0.3 eV above E_F ,
- (2) at \bar{X} between a surface state 1.5 eV below E_F and a surface resonance at 2.3 eV above E_F , and
- (3) to inter-band transitions of energy ~ 2.5 eV from d-states to unoccupied states near E_F in the region of L.

The results we present here have implications for this previous interpretation of the RA profile, in particular in the region 3.0–5.0 eV where a contribution from surface state transitions at \bar{X} was proposed. The temperature behaviour of the states at \bar{X} are not known, however, the assignment we propose in this work involving transitions at L accounts well for the observed RAS behaviour. This new interpretation does not exclude a secondary contribution to the RAS from transitions at \bar{X} , however, based upon the results presented here any such contribution is likely to be a small effect.

The earlier suggestion of a contribution from surface state transitions at $\bar{\Gamma}$ at photon energy ~ 1.8 eV remains plausible, since upon exposing the clean surface to ambient air, a significant decrease in the RA response is shown in this energy region [8]. Following exposure to air, STM results [8] show that the Au(110) surface morphology is similar to that before exposure, with (1 × 2) reconstructed terraces and monoatomic steps. STM and LEED data indicate the presence of locally disordered (1 × 1) regions in some areas. No significant difference in the RA response between 3.0 and 5.0 eV is observed following exposure to air. This result is consistent with the assignment of the RA in this energy region to transitions involving surface-modified bulk bands. The surface structure has not altered significantly, following exposure to air, to change the nature of the modification to the bulk electronic bands.

5. Conclusion

We have investigated the temperature dependence of the optical reflectance anisotropy of the Au(110)-(1 × 2) surface and found that transitions involving surface-modified bulk bands

contribute to the RA spectrum. The RA peaks observed at room temperature at photon energies of 3.52 and 4.50 eV are assigned to the transitions $E_F \rightarrow L_1^u$ and $L_2' \rightarrow L_1^u$, respectively. Analogous observations in the RAS spectrum of Cu(110) have been attributed to d-band narrowing at the surface due to the reduced coordination of surface sites. The RA spectrum of Au(110) shows distinctive changes upon ion bombardment of the surface. Model calculations based upon the notion of anisotropic surface disorder reproduce the observed optical anisotropy rather well. We conclude that RAS is a sensitive probe of the nanostructure and electronic properties of the Au(110) surface.

Acknowledgments

The authors acknowledge the financial support of the UK EPSRC and the Royal Society.

References

- [1] Martin D S and Weightman P 2001 *Surf. Interface Anal.* **31** 915
- [2] Campuzano J C 1994 The Au(110)-(1 × 2) to (1 × 1) phase transition *The Chemical Physics of Solid Surfaces* vol 7, ed D A King and D P Woodruff (Amsterdam: Elsevier)
- [3] Stahrenberg K, Herrmann Th, Esser N, Richter W, Hoffmann S V and Hofmann Ph 2001 *Phys. Rev. B* **65** 35407
- [4] Sheridan B, Martin D S, Power J R, Barrett S D, Smith C I, Lucas C A, Nichols R J and Weightman P 2000 *Phys. Rev. Lett.* **85** 4618
- [5] Martin D S, Blanchard N P and Weightman P 2003 *Surf. Sci.* **532–535** 1
- [6] Hansen J-K, Bremer J, Seime L and Hunderi O 2001 *Physica A* **298** 46
- [7] Martin D S, Blanchard N P and Weightman P 2004 *Phys. Rev. B* at press
- [8] Isted G E, Martin D S, Marnell L and Weightman P 2004 *Surf. Sci.* at press
- [9] Mazine V, Borensztein Y, Cagnon L and Allongue P 1999 *Phys. Status Solidi a* **175** 311
- [10] Mazine V and Borensztein Y 2002 *Phys. Rev. Lett.* **88** 147403
- [11] Smith C I, Maunder A J, Lucas C A, Nichols R J and Weightman P 2003 *J. Electrochem. Soc.* **150** E233
- [12] Tarriba J and Mochán W L 1992 *Phys. Rev. B* **46** 12902
- [13] Hansen J-K, Bremer J and Hunderi O 1998 *Surf. Sci.* **418** L58
- [14] Del Sole R and Onida G 1999 *Phys. Rev. B* **60** 5523
- [15] Schmidt W G, Esser N, Frisch A M, Vogt P, Bernholc J, Bechstedt F, Zorn M, Hannappel Th, Visbeck S, Willig F and Richter W 2000 *Phys. Rev. B* **61** R16335
- [16] Sun L D, Hohage M, Zeppenfeld P, Balderas-Navarro R E and Hingerl K 2003 *Surf. Sci. Lett.* **527** L184
- [17] Winsemius P, van Kampen F F, Lengkeek H P and van Went C G 1976 *J. Phys. F: Met. Phys.* **6** 1583
- [18] Martin D S, Maunder A and Weightman P 2001 *Phys. Rev. B* **63** 155403
- [19] Aspnes D E, Harbison J P, Studna A A and Florez L T 1988 *J. Vac. Sci. Technol. A* **6** 1327
- [20] McIntyre J D E and Aspnes D E 1971 *Surf. Sci.* **24** 417
- [21] Blanchard N P, Smith C, Martin D S, Hayton D J, Jenkins T E and Weightman P 2003 *Phys. Status Solidi c* **0** 2931
- [22] See, for example, Garfinkel M, Tiemann J J and Engeler W E 1966 *Phys. Rev.* **148** 695
- [23] Rossow U, Mantese L and Aspnes D E 1996 *J. Vac. Sci. Technol. B* **14** 3070
- [24] Sturmat M, Koch R and Rieder K H 1996 *Phys. Rev. Lett.* **77** 5071
- [25] Keane D T, Bancel P A, Jordan-Sweet J L, Held G A, Mak A and Birgeneau R J 1991 *Surf. Sci.* **250** 8
- [26] Cole R J, Frederick B G and Weightman P 1998 *J. Vac. Sci. Technol. A* **16** 3088
- [27] Pells G P and Shiga M 1969 *J. Phys. C: Solid State Phys.* **2** 1835
- [28] Baumberger F, Herrmann Th, Kara A, Stolbov S, Esser N, Rahman T S, Osterwalder J, Richter W and Greber T 2003 *Phys. Rev. Lett.* **90** 177402
- [29] Bremer J, Hansen J-K and Hunderi O 1999 *Surf. Sci.* **436** L735
- [30] Rusponi S, Constantini G, Boragno C and Valbusa U 1998 *Phys. Rev. Lett.* **81** 2735