A demonstration of Auger electron emission stimulated by secondary radiation: implications for x-ray standing-wave analysis of surfaces

1998 J. Phys.: Condens. Matter 10 L69

(http://iopscience.iop.org/0953-8984/10/3/004)

J. Phys.: Condens. Matter **10** (1998) L69–L72. Printed in the UK PII: S0953-8984(98)88261-1

LETTER TO THE EDITOR

A demonstration of Auger electron emission stimulated by secondary radiation: implications for x-ray standing-wave analysis of surfaces

A G Shard†§ and B C C Cowie‡

† IRC in Surface Science, The University of Liverpool, Liverpool L69 3BX, UK
‡ CLRC–Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK

Received 7 October 1997, in final form 11 November 1997

Abstract. We present direct experimental evidence that adsorbate low-energy Auger transitions can be excited by secondary radiation from a substrate in a photoemission experiment. The system employed is P/Rh(111) and the P LVV intensity is shown to be dependent upon the flux of secondary radiation emitted from the Rh substrate. The implications of this result for surface x-ray standing-wave analysis using low-energy Auger peak intensities is discussed.

X-ray standing-wave (XSW) techniques have proven to be highly useful for the location of adsorption sites on single-crystal surfaces. By manipulating the fringes of an x-ray interference field in a controlled manner and measuring the response of atoms within the interference field it is possible to determine their spatial distribution [1]. One of the critical experimental parameters is the method used to monitor the atomic scattering response to changes in the interference wavefield. It is appropriate when studying adsorbates on a crystal surface to employ surface-sensitive techniques, such as energy-dispersive electron analysis.

Ideally, the scattering response should be followed by observing the intensity variations of photoelectrons in the energy-dispersive curve. This is because photoelectrons are only emitted by interaction with photons and provide a direct measurement of the interference field intensity experienced by the relevant atomic species. It should be noted here that the analysis of XSW profiles taken from photoelectron intensities may be complex, particularly if there is a substantial contribution from multipole terms [2]. Experimentally, the collection of data from photoelectron peaks is sometimes impossible due to a coincidence of other features in the energy-dispersive curve, or the absence of core levels with sufficiently high cross sections for analysis at the photon energies employed. In these cases, other emission channels such as Auger electrons or fluorescent x-rays may be monitored.

Both Auger emission and x-ray fluorescence occur when an atomic species with a core-level vacancy relaxes and the vacancy is filled by an electron from a higher shell. In this type of experiment the core-hole vacancy is predominantly thought to arise from a photo-excitation process, and can therefore be employed to monitor the atomic response to the x-ray interference field. However, since the core-level vacancy may be induced by secondary radiation (electrons and photons) from other atomic species in the interference

§ Present address: School of Applied Sciences, The Robert Gordon University, Schoolhill, Aberdeen AB10 1FR, UK.

0953-8984/98/030069+04$19.50

field, there is a danger that measurements will actually reflect a convolution of different atomic responses to changes in the interference fringes.

Secondary radiation effects will only become appreciable if there is a substantial flux of secondary radiation energetic enough to ionize the core level of interest, this will tend to occur when the core level energy is significantly smaller than the photon energies employed to generate the interference field. Specifically the use of low-energy Auger electrons for this type of analysis has been highlighted as problematic [1]; however, no assessment of the magnitude of secondary- versus primary-radiation-induced Auger emission has, to our knowledge, been published. Woicik *et al* [3] used low-energy Auger electrons to examine the clean InP(110) surface reconstruction and in this case both the inelastically scattered bulk Auger electrons and the secondary-radiation-induced Auger transitions from surface atoms vary in the same manner with changes in the interference field. It was possible to distinguish the XSW profile of reconstructed surface atoms by subtracting an appropriately scaled bulk atom XSW profile from the experimental data. However, in their paper there is no indication of the magnitude of the scaling factor used (i.e. what the contribution of bulk atom and secondary-radiation-induced Auger transitions to the total Auger intensity was), and even if this scaling factor was given it would be impossible to separate the bulk atom contribution from the secondary-radiation contribution.

In this letter we demonstrate that secondary-radiation-induced low-energy Auger emission from adsorbates can be significant and, in an atypical case, greater than the primary-radiation-induced emission. Altering the secondary-radiation flux is achieved by using photon energies close to a substrate adsorption edge. The small changes in photon energy should produce negligible changes in adsorbate primary-excitation processes, but the flux of secondary radiation will be greatly changed and the effect of this radiation on Auger intensities can be monitored.

Table 1. Ratios of the intensities at 3010 eV to 2990 eV photon energies.

	(Peak − background)	Background
P LVV	1.9	4.1
P 1s	1.0	3.5
P KLL	1.0	3.7
Sample drain current	—	3.4

The experiment was performed on beam line 4.2 at the Daresbury SRS in an ultrahigh-vacuum chamber equipped with a CLAM-2 concentric hemispherical analyser (VG Instruments). A rhodium (111) crystal was used as a substrate and a layer of phosphorus (approximately 2 ML, estimated by comparison of relative photoelectron peak intensities with a Rh(111)-($\sqrt{7} \times \sqrt{7}$) R 19.1° - P surface, nominal coverage 3/7 ML) deposited on the clean surface. Electron energy-dispersive spectra were acquired of the P LVV (∼120 eV kinetic energy), the P KLL (∼1864 eV kinetic energy) and the P 1s photo-peak (∼2149 eV binding energy) using photon energies just below (2990 eV) and just above (3010 eV) the Rh L_{III} edge. Similar scans were performed on the clean Rh surface for background-subtraction purposes. The Rh(111) crystal was aligned with the surface normal to the electron analyser and at 30° to the photon beam. Figure 1 shows overlays of the background-subtracted spectra collected at both energies and table 1 lists the ratios of peak heights above and below the Rh L_{III} edge; the background levels and sample drain current ratios are also included. The major contribution to secondary-radiation intensity above the Rh L_{III} edge will be Rh LMM Auger electrons at ∼2365 eV kinetic energy and, in simple terms, moving

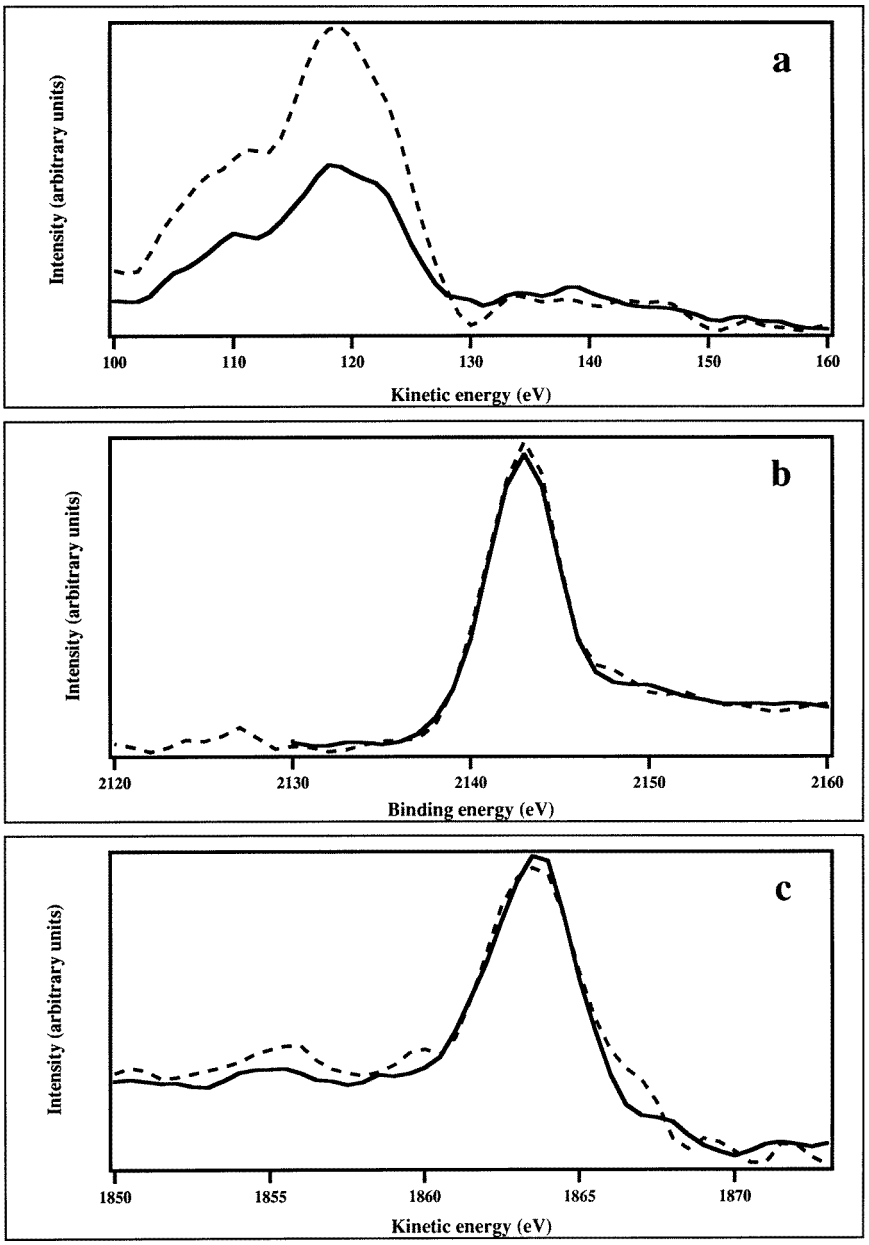

Figure 1. Background-subtracted EDCs of (a) P LVV Auger electrons, (b) P 1s photoelectrons (note the binding energy scale) and (c) P KLL Auger electrons taken with the photon energies $h\nu = 2990$ eV (solid line) and $h\nu = 3010$ eV (dashed line).

the photon energy above the Rh L_{III} edge can be thought of as simultaneously irradiating the sample with photons and a low-power electron gun of 2365 eV electron kinetic energy.

As expected, there is a negligible change in the P 1s photoelectron intensity and also in the P KLL Auger intensity. This latter result is unsurprising since only a small proportion of the secondary radiation is energetic enough to excite the P K shell. However, the P LVV

Auger intensity almost doubles when the photon energy is increased above the Rh L_{III} edge and this increase is solely attributable to the enhanced flux of secondary radiation from the substrate.

Even at 2990 eV (below the Rh L_{III} edge) there is a substantial flux of secondary radiation that is energetic enough to ionize the P L shell. We assume that secondary excitation of P LVV Auger electron emissions is predominantly caused by secondary electrons and not secondary photons. If it is also assumed that the photo-ionization cross sections of the P L orbitals are identical at 2990 eV and at 3010 eV, that the flux of secondary electrons with energies sufficient to cause ionization of the P L shells is proportional to the sample drain current and the normalized energy distribution of the secondary electrons is identical between 2990 eV and 3010 eV (i.e. the inelastic background increases by a constant proportion at all kinetic energies) then it is possible to estimate the proportion of P LVV Auger intensity due to secondary radiation. The latter two assumptions are justified with regard to secondary-electron emission by the observation that the inelastic background at all energies below the Rh LMM Auger intensity increased by a similar proportion to the drain current. The background increase just above the P LVV Auger intensity is slightly larger due to the inelastic tail of Rh MVV Auger features (∼302, 256 and 222 eV). To estimate the fractional intensity of the P LVV Auger feature due to secondary radiation a simple relationship is employed:

$$I_{\text{Auger}} = I_{h\nu} + F_{sr} X_{sr} \tag{1}$$

where I_{Auger} is the observed intensity of the low-energy Auger peak, $I_{h\nu}$ is the intensity due to direct photo-ionization of the P L shell followed by Auger decay, F_{sr} represents the intensity distribution of secondary electrons and X_{sr} represents the probability distribution of secondary electrons promoting a P LVV Auger emission. With the assumptions given above, $I_{h\nu}$ is constant and F_{sr} is proportional to the sample drain current. From the values given in table 1 and equation (1) it can be shown that at 2990 eV, 37% of the P LVV Auger intensity is caused by secondary radiation and at 3010 eV this rises to 67%. This result has important implications for the use of photo-excited low-energy Auger intensities for quantification purposes, and in particular for XSW analyses as outlined above.

References

[1] Zegenhagen J 1993 *Surf. Sci. Rep.* **18** 199
[2] Vartanyants I A and Zegenhagen J 1997 *Nuovo Cimento* **19** 617
[3] Woicik J C, Kendelewicz T, Miyano K E, Cowan P L, Bouldin C E, Karlin B A, Pianetta P and Spicer W E 1992 *Phys. Rev. Lett.* **68** 341