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Utilization of Photoemission Cross-Section Effects for Monitoring Thin-Film Growth in UHV

N. P. Tucker,[a] R. I. R. Blyth,[a] R. G. White,[a,b] M. H. Lee,[a] A. W. Robinson[a] and S. D. Barrett[a,b]

[a]Surface Science Research Centre, and [b]Department of Physics, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

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Given the tunability of synchrotron radiation, photoemission spectroscopy can be used to monitor the growth modes of thin films in UHV. Cross-section effects such as Cooper minima and resonant photoemission can be exploited to maximize the adsorbate signal and minimize that from the substrate. Under favourable circumstances growth can be monitored in real time at coverages of <1%. As an example the growth of Gd on W(110) is investigated.

Keywords: photoemission; thin-film growth; gadolinium; tungsten.

1. Introduction

It is customary to monitor the growth mode of a thin film in UHV using electron bombardment techniques *e.g.* Auger spectroscopy (Argile & Rhead, 1989), RHEED (Woodruff & Delchar, 1986) and secondary electron current (Barthés & Rhead, 1982). Monitoring the Auger signal of the adsorbate as a function of time (As–t) produces the characteristic signature of various growth modes as shown in Fig. 1. Since most UHV chambers are equipped for Auger spectroscopy this technique is the most commonly used. However, it is not always ideal, as the substrate and adsorbate Auger features may overlap, or the adsorbate Auger cross section may be small.

With the use of synchrotron radiation, photoemission spectroscopy can provide a useful alternative. As with As–t, the photoemission intensity from both the adsorbate and substrate is proportional to the amount of material present, modified by effects due to the low mean free path of electrons through a solid. Thus, the characteristic As–t signatures of Fig. 1 can be used to determine the growth mode from the photoemission signal as a function of time. The tunability of synchrotron radiation allows the exploitation of cross-section effects to maximize the adsorbate signal and minimize that of the substrate, which will favour monitoring the growth using the adsorbate signal. There are two main cross-section effects that can be utilized. The first of these is the photoionization cross section *i.e.* the probability that a photon of given energy will eject a photoelectron from an atom. The cross sections for all elements have been calculated and tabulated by Yeh & Lindau (1985). From the point of view of minimizing the substrate signal the most important feature of photoionization cross sections is the existence of Cooper minima (Cooper, 1962). Atomic subshells for which the wavefunction has a node have a resulting, and often deep, minimum in the photoionization cross section for that subshell. In particular this allows the valence bands of the 4*d* and 5*d* transition metals to be suppressed effectively if the correct photon energy is chosen.

The second cross-section effect, useful from the point of view of maximizing the adsorbate signal, is resonant photoemission. This occurs at core-level ionization thresholds for elements which also have a partially filled level, and causes an enhancement of the photoemission signal. The best example of this is the so-called giant resonance in rare-earth metals (Lenth, Lutz, Barth, Kalkoffen & Kunz, 1978), where the core level (4*d*) and partially filled level (4*f*) are both from the same shell. This is capable of providing very large signal enhancement, as shown in Fig. 2.

It is also possible to suppress the adsorbate signal and enhance the substrate signal by exploiting the same cross-section effects, which then allows the growth to be monitored using the photoemission signal of the substrate. However, this can lead to difficulties as it is known that photoelectron diffraction can cause an enhancement of the substrate signal with increasing coverage (Egelhoff, 1984). At certain angles (corresponding to the axes aligned with the adsorbate atoms) an enhancement of the signal is obtained due to forward focusing and other interference effects. The increase in the substrate signal is particularly noticeable during the deposition of the first monolayer when the number of substrate atoms with neighbouring adsorbate atoms is increasing. However, this is only seen for photoelectrons with a kinetic energy of a few hundred eV or more (Egelhoff, 1990). Therefore, if photoelectrons in this range are to be monitored the adsorbate signal should be used to avoid any diffraction effects.

2. An example: Gd growth on W(110)

There has been much recent interest in rare-earth thin films grown on the (110) surfaces of refractory metals *e.g.* W, Nb and Mo. These films are crystalline, and yield low-energy electron diffraction (LEED) patterns with hexagonal symmetry. It has been customary to describe these films as (0001) surfaces, implying a hexagonal close-packed (h.c.p.) structure. The first quantitative LEED study of Gd films grown on a W(110) substrate has now been published (Giergiel *et al.*, 1995). The surface structure of the Gd films determined by Giergiel *et al.* is in good agreement with that published by Quinn, Li, Jona & Fort (1992), who performed a quantitative LEED study of the (0001) surface of a bulk Gd crystal. This result supports the previous designation of a Gd film as having an h.c.p. (0001) surface, and would suggest that this is also the case for other rare-earth films.

Of the rare-earth films, Gd on W(110) is the most extensively studied system, and the growth mode has been previously identified as layer by layer at room temperature and Stranski–Krastanov at elevated substrate temperatures (Kolaczkiewicz & Bauer, 1986). However, As–t is not an ideal technique for monitoring the growth. Fig. 3 shows an Auger spectrum of 3 ML of Gd on W(110). Note that the Gd signal is small and overlaps the W peaks. Compare this with Fig. 2, which is a photoemission spectroscopy spectrum taken of the same film. Fig. 4 shows that the 4*d* giant resonance of Gd occurs very close to the Cooper minimum of the W 5*d* bands, suggesting a photon energy of ~150 eV to be the most suitable for monitoring Gd growth. Fig. 4 also shows that the resonance energies of all the lanthanides occur close to the Cooper minima of W, Nb and Mo, implying that photoemission spectroscopy monitoring may be useful for the full range of rare-earth/refractory-metal combinations.

The measurements were performed on the Liverpool/Manchester photoemission beamline (4.1) (Dhanak,

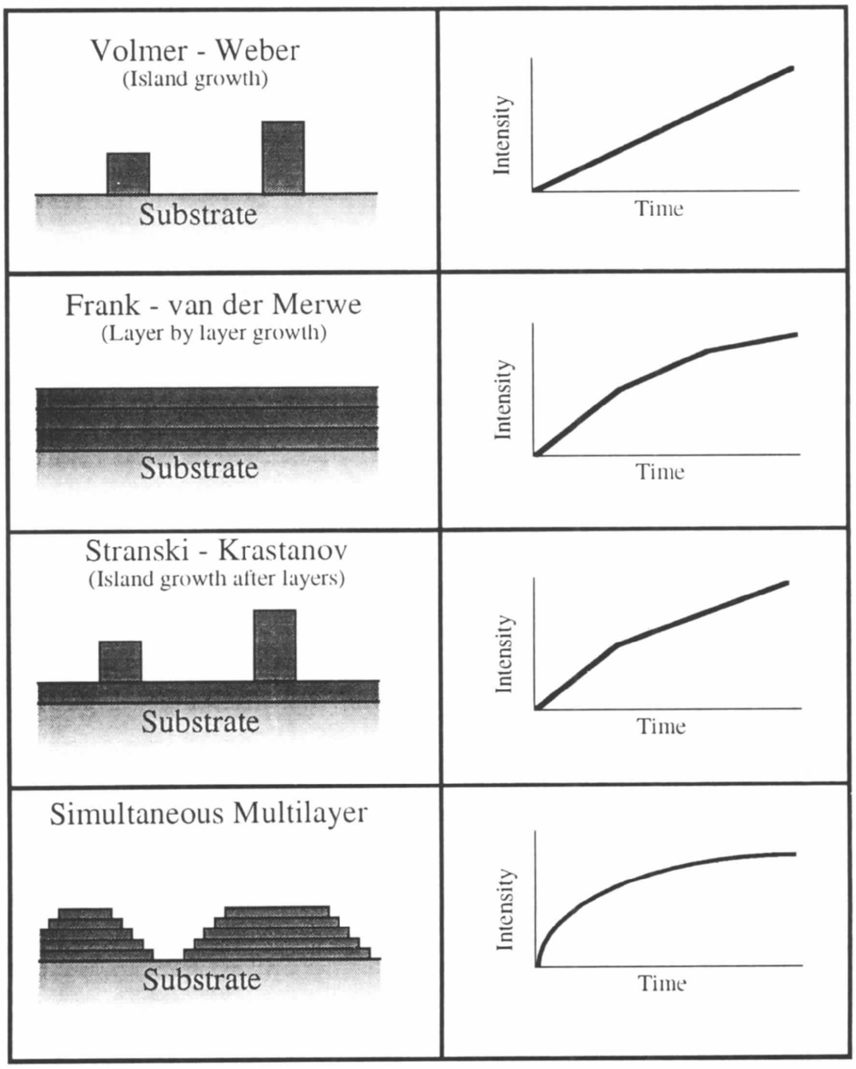

Figure 1
Four types of growth mode and their associated adsorbate As–t signals. For details of growth modes see Volmer & Weber (1926), Frank & van der Merwe (1949), Stranski & Krastanov (1938) and Rhead, Barthés & Argile (1981). Adapted from Nicklin (1993).

Robinson, van der Laan & Thornton, 1992) at the SRS, Daresbury Laboratory. A Vacuum Generators (VG) CLAM2 analyser was used, with a resolution of 0.2 eV. The vacuum chamber, with a base pressure $<10^{-10}$ mbar, was fitted with VG LEED optics, also used as a retarding field analyser for Auger spectroscopy. The W(110) substrate was prepared by roasting at 1500 K in 10^{-6} mbar oxygen to remove carbon, followed by periodic flashing to >2000 K to remove residual O and H, until the surface showed a sharp 1 × 1 LEED pattern. Gd was evaporated from a water-cooled W wire evaporator (Dowben, LaGraffe & Onellion, 1989), with the substrate held at room temperature. The pressure remained below 4 × 10^{-10} mbar during evaporation.

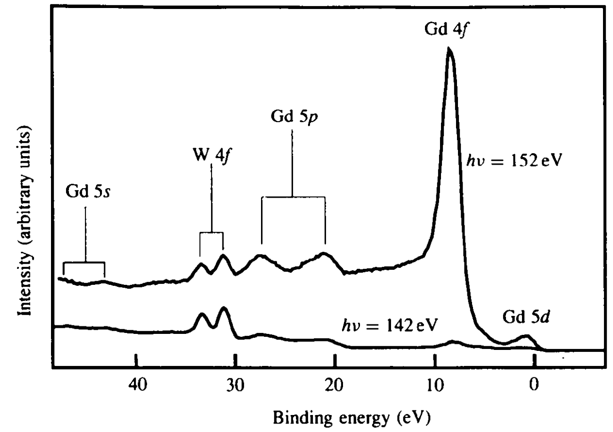

Figure 2
Photoemission spectroscopy spectra of 3 ML of Gd on W(110) showing the effects of the giant 4*d* resonance at *hν* = 152 eV.

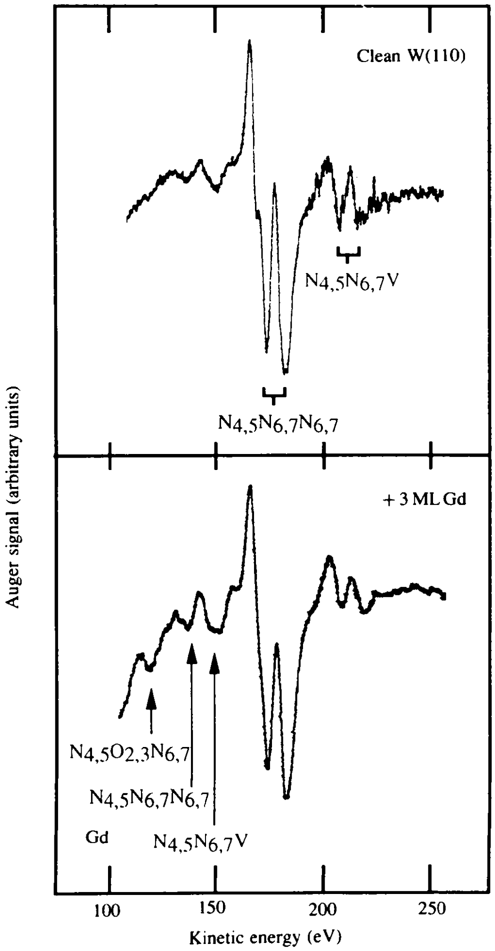

Figure 3
Auger spectra of clean W(110) and with 3 ML Gd.

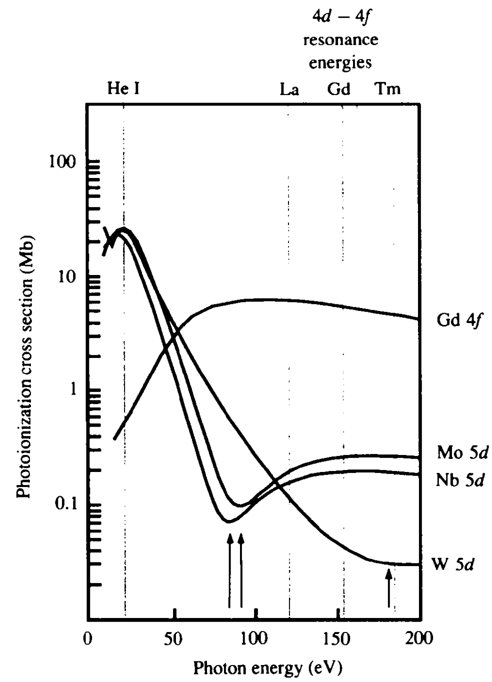

Figure 4
Photoionization cross sections for three lanthanides and the three commonly used substrates showing the resonance energies and Cooper minima. The arrows indicate the Cooper minima. Adapted from the calculations of Yeh & Lindau (1985).

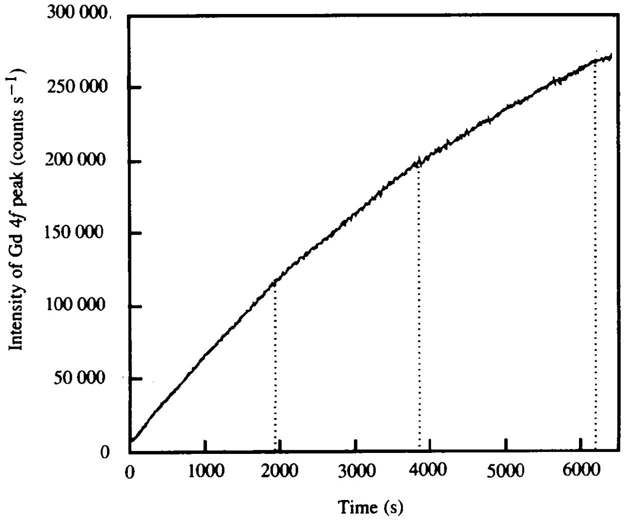

Figure 5
Photoemission spectroscopy scan of growth of Gd on W(110). Distinct breaks are seen in the spectrum, as highlighted by the added lines.

Fig. 5 shows a typical result. By comparison with Fig. 1 it can be clearly seen that the growth mode is layer by layer, in agreement with the conclusions of Kolaczkiewicz & Bauer (1986). The high sensitivity possible with this method is illustrated in Fig. 6, an enlargement of the low-coverage section of Fig. 5. This shows that, with photoemission spectroscopy, coverages of <1% are detectable in real time. A further example of the applicability of photoemission spectroscopy is shown in Fig. 7. These data were taken during the growth of Gd on a faceted W(110) sample, inadvertently prepared by excessive heating. By comparison with Fig. 1 it would appear that the growth mode is simultaneous multilayer, as growth occurs on each crystallite independently.

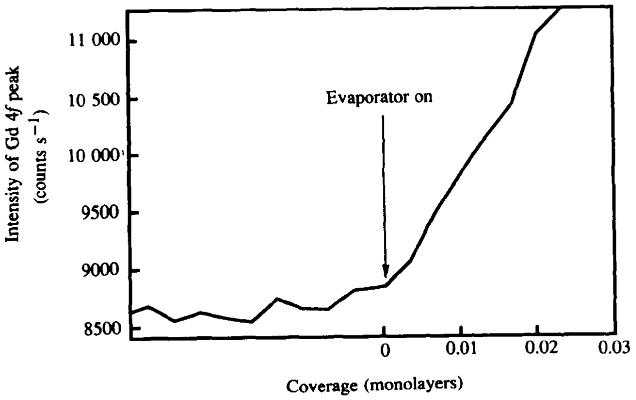

Figure 6
Photoemission spectroscopy scan of the initial stages of growth of Gd on W(110). The coverage is inferred from the first break (one monolayer) assuming a constant deposition rate.

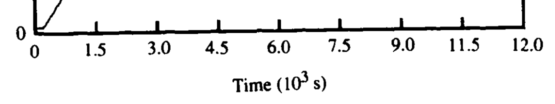

Figure 7
Photoemission spectroscopy scan of Gd growth on a faceted W(110) substrate. The absence of any breaks in gradient of the line suggests simultaneous multilayer growth.

3. Conclusions

We have shown that photoemission spectroscopy monitoring is a complementary technique to As–t. It is likely to be of particular use in monitoring the growth of samples for photoemission spectroscopy. By default once growth has been completed the sample is in position for spectroscopy, with the added advantage that the area thus sampled is the same as that for which the growth had been monitored. The fortunate coincidence that the rare-earth 4*d* resonances occur at similar energies to the refractory-metal *d*-band Cooper minima suggests one area of applicability for this technique.

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References

Argile, C. & Rhead, G. E. (1989). *Surf. Sci. Rep.* **10**, 277–356.
Barthés, M.-G. & Rhead, G. E. (1982). *Surf. Sci.* **116**, 217–224.
Cooper, J. W. (1962). *Phys. Rev.* **128**, 681–693.
Dhanak, V. R., Robinson, A. W., van der Laan, G. & Thornton, G. (1992). *Rev. Sci. Instrum.* **63**, 1342–1345.
Dowben, P. A., LaGraffe, D. & Onellion, M. (1989). *J. Phys. Condens. Matter*, **1**, 6571–6587.
Egelhoff, W. F. Jr (1984). *Phys. Rev. B*, **30**, 1052–1055.
Egelhoff, W. F. Jr (1990). *Crit. Rev. Solid State Mater. Sci.* **16**, 213–235.
Frank, F. C. & van der Merwe, J. H. (1949). *Proc. R. Soc. London Ser. A*, **198**, 205–216.
Giergiel, J., Pang, A. W., Hopster, H., Guo, X., Tong, S. Y. & Weller, D. (1995). *Phys. Rev. B*, **51**, 10201–10204.
Kolaczkiewicz, J. & Bauer, E. (1986). *Surf. Sci.* **175**, 487–507.
Lenth, W., Lutz, F., Barth, J., Kalkoffen, G. & Kunz, C. (1978). *Phys. Rev. Lett.* **41**, 1185–1188.
Nicklin, C. L. (1993). PhD thesis, Univ. of Leicester, UK.
Quinn, J., Li, Y. S., Jona, F. & Fort, D. (1992). *Phys. Rev. B*, **46**, 9694–9699.
Rhead, G. E., Barthés, M.-G. & Argile, C. (1981). *Thin Solid Films*, **82**, 201–211.
Stranski, J. N. & Krastanov L. (1938). *Ber. Akad. Wiss. Wien.* **146**, 797–801.
Volmer, M. & Weber, A. (1926). *Z. Phys. Chem.* **119**, 277–282.
Woodruff, D. P. & Delchar, T. A. (1986). *Modern Techniques of Surface Science*. Cambridge Univ. Press.
Yeh, J. J. & Lindau, I. (1985). *At. Data Nucl. Data Tables*, **32**, 1–155.