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Measurement of metal–metal adhesion and interface segregation energies by core-level photoelectron spectroscopy: Al and Si on Mo(110)

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Abstract. Quantitative information about adhesion and segregation energies in metallic systems can be obtained by means of the binding energy shifts between different layers observed in core-level photoelectron spectroscopy. Layer-dependent Al 2p core-level spectra for Al deposited on Mo(110) are presented. The difference in adhesion energy of Al and Si on Mo is found to be 0.24 eV per atom, with the Si–Mo bonding being the stronger one. It is found that the energetics favour a segregation of Si impurities in the Al layer to the Al/Mo interface. These results are shown to be in good agreement with calculations based on Miedema's scheme.

Photoelectron spectroscopy is a most popular technique for the study of thin-film growth and interface formation. It has been realised for a long time that core-level photoelectron spectroscopy, especially binding-energy shifts, can yield valuable information on thin-film growth modes and intermixing phenomena at interfaces (Nilsson *et al* 1988). Recently it was demonstrated that this technique can also provide quantitative information on the energetics of metallic adhesion and segregation (Mårtensson *et al* 1988). This information, which is essential for a microscopic understanding of phenomena such as wear, friction, metallic lubrication, welding and fracturing, is most difficult to obtain by other methods (Mårtensson *et al* 1988, Valli 1986).

In the present paper we first discuss briefly how information on metallic adhesion and segregation energies can be extracted from layer-dependent core-level binding energy shifts. A more thorough discussion can be found in Mårtensson *et al* (1988). Secondly, this formalism and the layer-dependent 2p core-level spectra of Al deposited on Mo(110) are used to derive the adhesion-energy difference between Al and Si on Mo and the segregation energy of Si impurities in the Al layer. These energies are finally compared with calculations based on Miedema's scheme (Gerkema and Miedema 1983).

The binding energy of a core level is defined as the difference in total energy of the sample before and after core ionisation has taken place. Within the complete screening picture (Johansson and Mårtensson 1980) the core-ionised metal atom (hereafter denoted Z^*) is viewed as an electronically completely relaxed Z^* impurity. (This applies only to the lowest core-level binding energy, whereas e.g. shake-up states must be viewed as excited states of this system. For the rest of this paper only the lowest

binding energy term is discussed). The binding energy of the Z atom core level can be decomposed into two terms; the first term is independent of the specific surroundings of the atom whereas the second term corresponds to the chemical energy required to replace the initial Z atom with a Z* impurity. Thus the shift in core-level binding energy of Z atoms in different environments reflects the difference in the energy required to replace them with Z* impurities at the different sites. The chemical properties of the final state Z* impurity are known (Johansson and Mårtensson 1980) to be well described within the equivalent core or Z + 1 approximation, that is, the influence which the removal of a core electron has on the valence electrons is approximated by increasing the nuclear charge by one.

Turning now to the specific example of the core-level binding energy difference between Al atoms at an Al/Mo(110) interface and at the Al surface, one can, based only on the definition of the binding energy, derive the following symbolic expression for the shift ΔE_{adh} (Mårtensson *et al* 1988):

$$\begin{aligned} \Delta E_{\text{adh}}^{\text{Al,Mo}} &= \left[\text{Al} - \text{Al}^* \right] - \left[\text{Al} - \text{Al}^* \right] \\ &= \left[\text{Al} - \text{Al}^* \right] - \left[\text{Al} - \text{Al}^* \right] \approx \epsilon_{\text{adh}}^{\text{Al}^*,\text{Mo}} - \epsilon_{\text{adh}}^{\text{Al,Mo}} \end{aligned} \quad (1)$$

where the symbols represent the total energy of the individual systems and the small striped square represents a core ionised Al atom. The first bracket is the binding energy for an Al atom at the Al/Mo interface. In the second bracket, which represents the core-level binding energy of a surface Al atom, an Mo slab has been added in both the initial and the final state for the sake of clarity. When taking the differences the Mo slabs cancel, so this does not change the binding energy.

The final expression of (1) is clearly the difference in adhesion energy on Mo of an Al slab with and without an Al* impurity at the interface. Applying the Z + 1 approximation this equation shows how the adhesion energy changes if an Si impurity is substitutionally added at the Al/Mo interface. Although this in itself is a most interesting result, it is instructive to decompose the expression further. The approximation that adhesion is dominated by nearest neighbour interactions then yields that (Mårtensson *et al* 1988):

$$\begin{aligned} \Delta E_{\text{adh}} &= (N - 1)\epsilon_{\text{adh}}^{\text{Al,Mo}} + \epsilon_{\text{adh}}^{\text{Al}^*,\text{Mo}} - N\epsilon_{\text{adh}}^{\text{Al,Mo}} \\ &= \epsilon_{\text{adh}}^{\text{Al}^*,\text{Mo}} - \epsilon_{\text{adh}}^{\text{Al,Mo}} \approx \epsilon_{\text{adh}}^{\text{Si,Mo}} - \epsilon_{\text{adh}}^{\text{Al,Mo}} \end{aligned} \quad (2)$$

where N is the number of Al atoms at the interface, and ϵ_{adh} is the adhesion energy per atom of Al, Al* and Si, respectively, on Mo. In the last equation the Z + 1 approximation has been introduced.

With these assumptions the core-level binding-energy difference between an Al atom at the Al/Mo interface and at the Al surface is thus simply the difference in adhesion energy (per atom) of Al and Si on Mo. Clearly the above considerations and conclusions do not depend on the specific choice of metals, but apply to all metallic interfaces.

Turning now to the binding-energy shift between Al atoms at the Al/Mo interface and Al atoms in the bulk of the Al layer. By similar reasoning to that given above the

following expression for the interface shift ΔE_{int} is derived:

$$\Delta E_{\text{int}}^{\text{Al,Mo}} = \left[\begin{array}{c} \text{Si} \\ \text{Al} \end{array} \right] - \left[\begin{array}{c} \text{Si} \\ \text{Al} \end{array} \right] = \begin{array}{c} \text{Si} \\ \text{Al} \end{array} - \begin{array}{c} \text{Si} \\ \text{Al} \end{array} \quad (3)$$

Thus the interface shift ΔE_{int} is simply the segregation energy of an Al* (Si) impurity from the bulk of the Al layer to the Al/Mo interface. It may be noted that this result is completely analogous to the interpretation of the binding-energy difference between the bulk and the surface atoms, the surface core-level shift, as the surface segregation energy of a $Z^*(Z + 1)$ impurity in a Z metal (Johansson and Mårtensson 1980).

The layer-dependent Al 2p core-level shifts for Al deposited on Mo(110) have been measured at room temperature. The experiments were performed at the toroidal grating mirror (TGM) beamline of the MAX-lab synchrotron radiation facility. A photon energy of 100 eV was used. Photoelectrons were energy analysed by a double-pass cylindrical mirror analyser (CMA) and the total energy resolution was approximately 200 meV. The Mo(110) crystal was cleaned by heating in oxygen and vacuum.

Al was evaporated from an indirectly heated tantalum tube. During evaporation the pressure increased to about 6×10^{-10} Torr. Contamination of the deposited Al films could easily be detected by photoemission due to the low cross section of the Al (and Mo) valence band at 100 eV. Further checks of the purity were made by Auger electron spectroscopy (AES) and from the Al 2p spectra where a chemically shifted component was easily detectable if oxygen was present. After extensive outgassing it was possible to deposit Al films with less than 2% contamination.

The deposition rate was determined by AES by using peak-to-peak amplitudes of the Al 86 eV and Mo 186 eV lines in dN/dE spectra. The AES growth curve exhibited a sharp kink at 20 min deposition time corresponding to the completion of the first Al monolayer (ML) on top of Mo(110). All coverages given in ML are obtained by simply dividing the deposition time by the time for depositing the first monolayer. Figure 1 shows Al 2p photoemission spectra for 1 ML and for several coverages above 1 ML. From these spectra it is seen that the growth of a second Al layer leads to the appearance of a new spin-orbit doublet at about 0.2 eV higher binding energy, whereas the doublet characteristic of the 1 ML situation shows only a minor shift in energy (but of course a gradual damping) as deposition increases. Clearly the development in the spectra allows for an assignment of the low binding-energy component to the interface Al and of the high binding-energy component to Al at the surface or the bulk of the Al film.

Figure 2 shows an example of how the 2.4 ML spectrum can be separated into two 2p doublets. The 4 ML spectrum, which is identical to a spectrum from a thick Al film, was used as model spectrum for the individual 2p doublets. In the fitting procedure the intensities and energy positions of both doublets were allowed to vary freely. This leads to one component with the same binding energy as the 4 ML spectrum and another component with 0.24 eV lower binding energy. Similar results are obtained when applying the same procedure to the 2 ML spectrum. Thus the adhesion shift ΔE_{adh} of Al on Mo(110) is equal to -0.24 eV, i.e. Si on Mo has 0.24 eV higher adhesion energy than Al on Mo. Instead of the above model spectra one could use the 4 ML spectrum for the high binding-energy component and the 1 ML spectrum for the low binding-energy component. The change in adhesion shift resulting from using these model spectra instead is of the order of 10 meV, which is certainly insignificant in the present context. The fit, however, becomes worse because the interface component becomes too broad. This indicates that the growth of the second ML somewhat diminishes the broadening

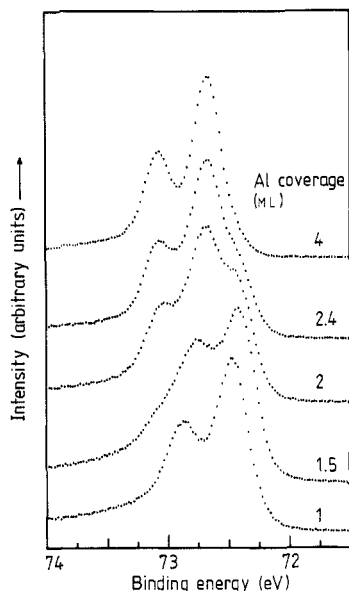


Figure 1. Al 2p photoemission spectra for Al deposited on Mo(110) at room temperature ($h\nu = 100$ eV).

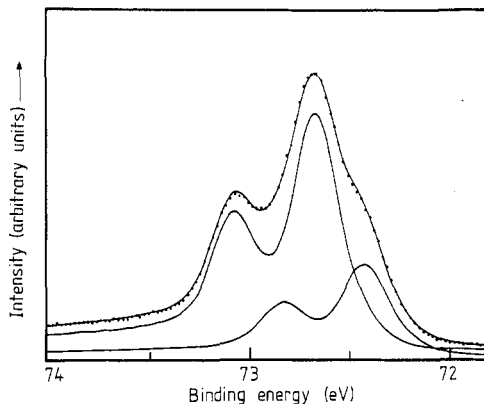


Figure 2. The decomposition of the Al 2p spectrum for Al deposited on Mo(100) for the 2.4 ML situation (dotted line) into two shifted 2p spectra (full line) ($h\nu = 100$ eV).

found for the 1 ML situation. From this analysis it is further seen that the interface peak has 0.06 eV higher binding energy than the peak in the 1 ML spectrum, probably due to a reconstruction of the first ML. The surface core-level shift of Al is very small (Johansson and Mårtensson 1980, Chiang and Eastman 1981, Kammerer *et al* 1982), which makes it very difficult to extract an exact value since the mentioned changes in the interface layer as the second monolayer is deposited may very well dominate the shift. The smallness of the surface shift is also reflected by the fact that, as shown above, the 2.4 ML spectrum can be fitted excellently by two shifted spectra from a thick Al film. This would not be possible if the thick-film spectrum contained a significantly shifted surface component. Since no surface core-level shift of Al can be resolved, it is assumed to be zero. The value for the interface shift ΔE_{int} then becomes equal to the adhesion shift. Thus it is found that Si impurities in the Al layer will segregate to the Al/Mo interface with a segregation energy of 0.24 eV.

These results can be compared to values calculated on the basis of Miedema's semiempirical scheme (Gerkema and Miedema 1983). The adhesion energy gained when bringing two metals A and B into contact may be decomposed into contributions from the surface energies γ_A and γ_B and from the interfacial energy γ_{AB} . The latter consists of a chemical term, which is related to the energy of alloying, and another term, which is the average grain boundary mismatch energy

$$E_{\text{adh}} = \gamma_A + \gamma_B - \gamma^{\text{chem}} - \gamma_{\text{mm}}. \quad (4)$$

The grain boundary mismatch energy γ_{mm} is, in the case of poor matching given by $0.15(\gamma_A + \gamma_B)$ (Gerkema and Miedema 1983). The chemical term can be estimated from the heat of solution (Miedema and den Broeder 1979) which can be calculated from Miedema's formulae (Miedema and Dorleijn 1980). These expressions give the rela-

tively large values of 3.42 J m^{-2} and 3.75 J m^{-2} for Al/Mo and Si/Mo, respectively. These absolute values are dominated by the surface energy terms, which account for about 90% of the value. The difference is, however, determined by the chemical terms, which contribute around 75% of the difference. This is so because in taking the difference, the surface energy of Mo cancels and, as the surface energies of Al and Si are almost equal, these surface energies and the mismatch terms also almost cancel. Thus the dominating terms in the adhesion energy difference are the solution energies of Al and Si in Mo.

Assuming a close-packed interface Al layer, Miedema's scheme leads to a difference in adhesion energy per atom of 0.15 eV and an interface segregation energy of 0.07 eV, favouring Si enrichment at the interface. This should be compared with the experimentally obtained 0.24 eV for both energies. Some of the discrepancy between these values comes from the fact that Miedema's scheme includes a surface core-level shift of 0.08 eV for Al, while the value used in the experimental analysis is zero. This value is correct within 0.05 eV, while the theoretical value has an uncertainty of at least 0.1 eV. Within this uncertainty, the semi-empirical values are seen to be in good agreement with the experimental ones, showing that the Miedema scheme accounts well for the change in adhesion energy on Mo from Al to Si. Also the segregation of Si impurities to the Al/Mo interface is reproduced by the calculation. It should be noted that for the combination Yb/Mo (Mårtensson *et al* 1988) the Miedema calculations also yielded values for the adhesion and segregation energies in very good agreement with experimental results.

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References

- Chiang T C and Eastman D E 1981 *Phys. Rev. B* **26** 6836
- Gerkema J and Miedema A R 1983 *Surf. Sci.* **124** 351
- Johansson B and Mårtensson N 1980 *Phys. Rev. B* **21** 4427
- Kammerer R, Barth J, Gerken F, Kunz C, Flodström S A and Johansson L I 1982 *Phys. Rev. B* **26** 3491
- Mårtensson N, Stenborg A, Björneholm O, Nilsson A and Andersen J N 1988 *Phys. Rev. Lett.* **60** 1731
- Miedema A R and den Broeder F J A 1979 *Z. Metallk.* **70** 14
- Miedema A R and Dorleijn J W F 1980 *Surf. Sci.* **95** 447
- Nilsson A, Eriksson B, Mårtensson N, Andersen J N and Onsgaard J 1988 *Phys. Rev. B* **38** 10357
- Valli J 1986 *J. Vac. Sci. Technol. A* **4** 3007