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EXAFS Studies of Interfaces in Bilayers and Multilayers

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Abstract. *EXAFS is demonstrated to be a useful probe of interface structure. Glancing angle techniques can be used on bilayer samples for cases in which the overlayer is less dense than the substrate. It is shown that the anomalous dispersion distortions which affect the EXAFS signal can be accurately removed using an analytic model for δ_0 and β_0, allowing quantitative analysis to be carried out. Examples are given for the Cu-Al system. In other cases multilayer samples can be employed to enhance the interface signal, as is illustrated by results on W-C multilayers. A disadvantage of multilayers is that two types of interfaces are simultaneously probed. To deal with this standing wave techniques can be employed to selectivity enhance the EXAFS signal from regions within the multilayer unit cell, and results on Ni-Ti demonstrate the feasibility of this approach.*

Introduction

X-ray absorption techniques can be very useful in studying interface structures. X-rays are a penetrating probe providing the ability to reach buried interfacial regions, and EXAFS is well suited for measurements on the thin and often disordered layers found at interfaces. However, since the x-rays can penetrate deeply, the fundamental difficulty in applying EXAFS techniques to interfaces is separating the interface component from a possibly large bulk signal. This paper reviews recent work which demonstrates two methods for dealing with this problem: the use of glancing angles to confine the x-rays to the interface, and the enhancement of the interface signal using multilayer samples.

Glancing Angle Studies

X-rays at glancing angles can undergo total external reflection at a surface if the incidence angle is smaller than a material dependent critical angle, θ_c. When this occurs the penetration of the x-rays can be very small (as little as 20-30 Å), and can be controlled by varying the incidence angle. Similarly, for a buried interface reflection will occur if the overlayer has a smaller critical angle than the substrate. In this case the x-rays will reflect from the interface if the incidence angle is larger than the surface critical angle and smaller than the substrate critical angle. EXAFS of the substrate atoms near the interface can then be measured by monitoring the energy dependence of either the reflected or fluorescence signal[1]. Fig. 1 shows some examples of the EXAFS $\chi(k)$ obtained for an aluminum on copper sample as the incidence angle is changed. As the angle increases the x-ray penetration increases, and the signal becomes more like

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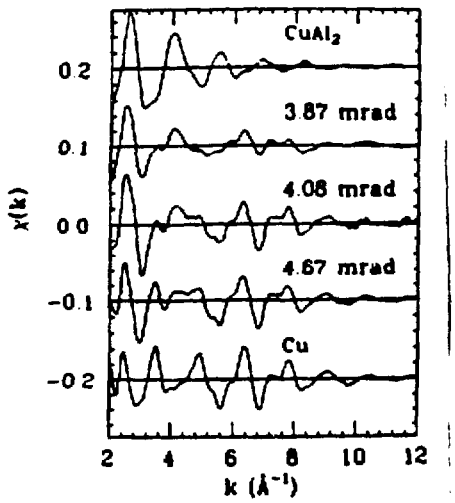

Fig. 1: $\chi(k)$ for Al on Cu compared to Cu and $CuAl_2$.

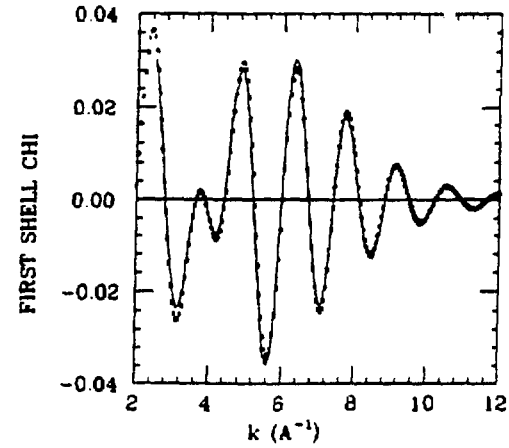

Fig. 2: First shell fit for the 4.08 mrad data in Fig. 1.

that of a Cu standard. It is clear that for the smallest angle the spectrum is distinctly different from Cu, and takes on features similar to the Cu-Al bonding found in $CuAl_2$. This comes from reaction between the Cu and Al layers, which is very sensitive to deposition conditions and temperature. This reaction is discussed in detail elsewhere[1][2], and for illustration purposes only one sample, prepared under UHV conditions, will be considered in the present paper.

The data shown in Fig. 1 were obtained by fluorescence and was background subtracted using standard procedures. This signal is distorted from the true $\chi(k)$, and the standards were arbitrarily reduced by 1/2 for comparison. A similar distortion also occurs in the reflectivity signal, and must be corrected before quantitative analysis can be carried out.

The distortion comes from the anomalous dispersion corrections to the complex index of refraction, $n = 1 - \delta - i\beta$, when crossing an absorption edge. The imaginary term β is directly proportional to the absorption coefficient, but the real part, δ, also varies as it can be related to β through a Kramers-Kronig relation. Thus, the reflectivity and correspondingly the fluorescence vary in a complex fashion as the absorption is changed. In general the variation in δ tends to cancel the β variation reducing the overall EXAFS amplitude, but the phase is also affected. To correct for the distortion requires two steps. The distortions in the smooth background can be well modeled using an analytic approximation for the variation of the absorption, μ, with energy[3], allowing the EXAFS to be isolated from the rapidly varying background found in glancing angle data.

The second step makes use of the fact that the EXAFS is small modulation of μ. Thus, a first order expansion of the measured signal with respect to μ is sufficient for generating the correction. For example, the fluorescence signal can be written as $I_f = \mu F(\mu, \delta)$ where F is the integral of the x-ray intensity as a function of depth into the sample multiplied by the concentration of the

fluorescing element. To first order the distortion is given by,

$$\chi' = \chi\left(1 + \frac{\beta_0}{F_0}\frac{\partial F}{\partial \beta} + \frac{\beta_0}{F_0}\frac{\partial F}{\partial \delta}\frac{d\delta}{d\beta}\right)$$

The subscript 0 refers to the smooth part of the functions without the superimposed EXAFS oscillations. These functions and the derivatives can be calculated using the analytic model, using the assumption $\partial F/\partial\mu = \partial F_0/\partial\mu_0$ etc. For more details see Refs. [1] and [4]. This correction procedure has been extensively tested for a pure Au surface, and shown to provide $\simeq$5% accuracy in amplitude, and $\simeq$0.01Å accuracy in the phase correction.

After correction the data can be analyzed using standard procedures as demonstrated in Fig. 2. This shows the results of two shell fitting for the nearest neighbor shell in the 4.08 mrad data. Excellent fits are obtained indicating most of the anomalous dispersion distortions have been removed. The increased Cu-Al reaction for the UHV sample results in the strong beating due to the interference between the Cu-Cu and Cu-Al EXAFS contributions. Further studies have identified O_2 at the interface as a major influence on the amount of reaction at the interface[2]. The fitting results can also be used to estimate the sensitivity of the glancing angle method. For the angles used the penetration of the x-rays past the interface can be easily calculated, and if the Cu density in the interfacial region is known then the relative contribution to the fluorescence signal for the interfacial layers and the substrate layer can also be calculated. Our results indicate an interfacial Cu density similar to that in $CuAl_2$, and adjusting the interface layer thickness to match our observed amplitude ratios gives a thickness of $\simeq$37Å for the UHV sample.

Multilayer Studies

In EXAFS studies of multilayers the interfaces make a strong contribution to the signal because of their relative abundance. As an example we consider the W-C multilayer system. Fig. 3 compares some data obtained W-C multilayers of differing layer thicknesses. For thin W layers the W environment appears amorphous with only C first neighbors present. This indicates that extensive mixing is occuring at the interface. In fact upon annealing the W environment becomes essentially identical to that in W_2C, as shown in Fig. 3(b). However, for thicker W layers distinct W-W correlations are observed for the unannealed sample which can attributed to bcc W in the center of the layers. The W-C bondings are still observed indicating similar interfacial mixing as for the thinner sample. Again with annealing the W-C contribution is seen to convert to W_2C, although the bcc W contribution remains. More details can be found elsewhere[5], but these results clearly demonstrate the utility of EXAFS for studying interfaces in multilayers.

While the interface contribution is easily observed in W-C, it must be kept in mind that the results are the average of two types of interfaces: W on C

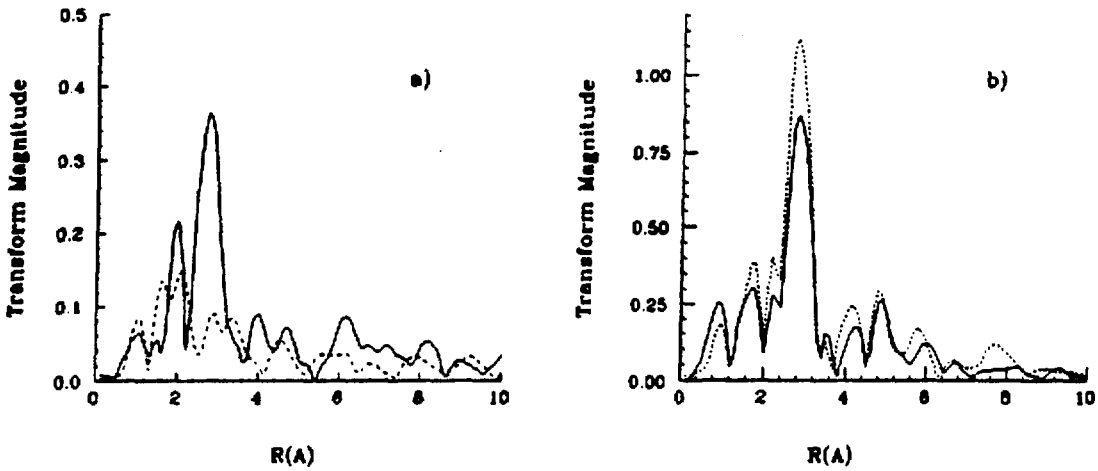

Fig. 3: Fourier transformed EXAFS(k^2 weighted) for some W-C multilayers. a) 43Å W/40Å C(dashed) and 65Å W/18Å C(solid); b) 43Å W/40Å C annealed at 350° C for 3 hrs. (solid) compared to W_2C (dashed).

and C on W. From electron microscopy there are indications that the interfaces are different. To separate the individual contributions requires a more complex technique, the measurement of the EXAFS while standing wave fields are being excited in the multilayer. Standing waves occur when the multilayer is Bragg reflecting, and some examples are shown in Fig. 4 for the Ni-Ti system. It can be seen how selected regions of the multilayer can have their contributions to the absorption enhanced by proper choice of angle. However, since the proper angle depends on the x-ray energy, performing an EXAFS scan under such conditions requires a simultaneous scan of both the energy and angle. Such experiments have been carried for the Ni-Ti system[6], and very little mixing between the components was observed. This meant that very little change in the EXAFS was observed for different standing wave conditions.

The results did, however, confirm that strong standing waves were being excited, as the results in Fig. 5 demonstrate. These show the amplitude of the Ni first shell EXAFS for different incident angles. Since the Ni EXAFS was detected by flourescence and the sample is concentrated, the Ni EXAFS is reduced by the usual self absorption effect for fluorescence measurements on concentrated samples. The result of the standing waves is to change the relative contribution of the Ni layers to the absorption, which is equivalent to changing the concentration. Thus, the amount of amplitude reduction can be used to monitor the strength of the standing wave field. As seen in Fig. 5 the measurements are good agreement with the amplitude reduction calculated for a Ni-Ti multilayer, verifying the existence of the standing waves with the expected strength.

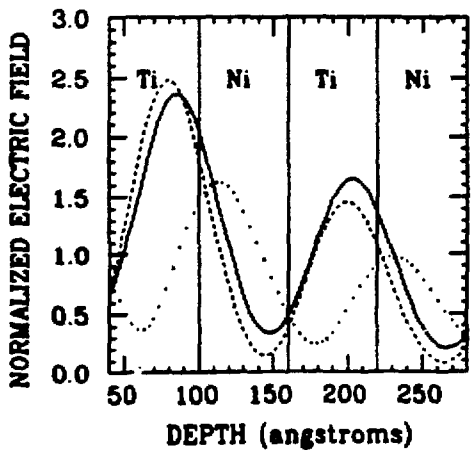

Fig. 4: Calculated electric fields in a Ni-Ti multilayer at 8.23 mrad (solid and dashed) and 9.0 mrad (pts).

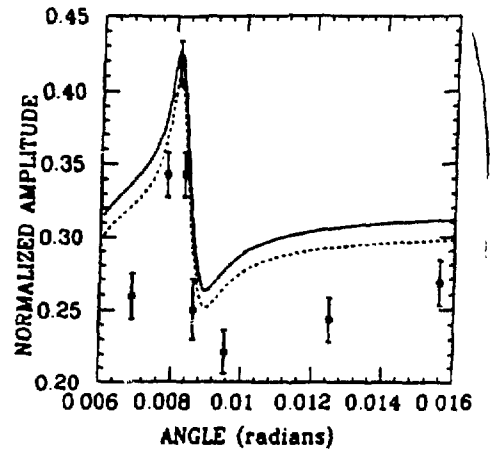

Fig. 5: Ni EXAFS amplitude compared to the calculated reduction.

Conclusions

EXAFS has been demonstrated to be a useful probe of interface structure. Glancing angle techniques on bilayer samples offer extreme sensitivity to interfacial reactions, but are limited to the case of light overlayers on heavy substrates. The use of multilayers to enhance the interface signal avoids this restriction, but gives average information about two types of interfaces. The standing wave technique introduced here offers the possibly of separating the contributions from the individual interfaces, and should prove useful in studying multilayer interfaces. All of these methods have some unique characteristics, and should provide an important complement to more traditional interface probes.

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