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A Glancing Incidence Exafs Study of Evaporated Silver Films on Glass

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Abstract

A glancing incidence EXAFS experiment has been carried out with evaporated silver films on glass substrates. Prior to EXAFS data collection, a reflectivity curve was performed from which the critical angle for total external reflection of x-rays from surface were determined. The analysed EXAFS data revealed that there is a reduction in the coordination number and an increase in Debye-Waller factor compared to bulk values. These changes were explained in terms of grain size effect and the surface effects of the silver film.

1. Introduction

Over the past two decades extended x-ray absorption fine structure (EXAFS) has been developed into a powerful tool for the investigation of the local environment of atoms in condensed matter. Since the absorption edge energy is particular to an element, an EXAFS experiment can focus on one element in the sample and determine neighbour atom types, distances and numbers. Depending on the needed information different EXAFS detection modes can be used. The transmission and fluorescence detection modes are more effective for bulk samples [1] whereas electron detection modes have been used for surface studies [2-4]. Nevertheless, electron detection requires UHV condition since penetration

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depth of electrons in atmosphere is very short and cannot be detected. Another approach to surface studies, which does not require UHV condition provided the x-ray energy is sufficient, is to use x-rays incident at glancing angles, a technique pointed out by Parrat [5]. In this mode, x-rays at glancing angle are totally reflected if the incident angle is smaller than the material dependent critical angle θ_c. Under these conditions only the evanescent wave penetrates into the sample, to around 20-30 Å.

In the x-ray energy region the refraction index of most materials is less than unity and given by

$$n = 1 - \delta - i\beta, \tag{0.1}$$

and the critical angle θ_c is related to the real part of the refractive index of the material by the expression

$$\theta_c = \sqrt{2\delta} = \sqrt{\frac{r_e \lambda^2 N_e}{\phi}}, \tag{0.2}$$

where λ is the x-ray wavelength, r_e is the classical electron radius and N_e is the electron density of the sample. The imaginary part of refractive index β is related to the absorption coefficient μ by

$$\beta = \frac{\lambda \mu}{4\pi}.$$

Using the glancing incident geometry given in Fig.1, one can record the x-ray absorbance either from reflected or from the fluorescence intensity and hence obtain EXAFS data which arises from surface region around 20-30 Å thick.

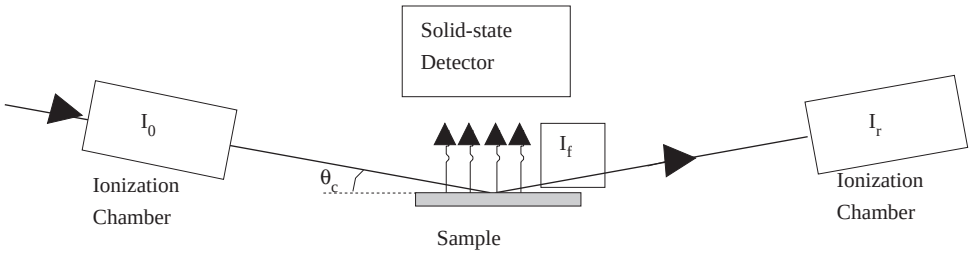

Figure 1. Schematic illustration of glancing incidence EXAFS experiment. I_o, I_r and I_f stand, respectively, for intensity of incidence, reflected and fluorescence of x-rays.

In this study, the glancing incidence fluorescence EXAFS technique was applied to determine the surface structure of silver films evaporated onto glass substrates. Prior to the EXAFS measurements the reflectivity curves were carried out to determine the critical angle. The behaviour of the reflectivity curves are discussed and the EXAFS results of the silver film were compared to the silver bulk structural parameters.

2. Experimental Details

Thin films of Ag, typically about 1000 Å thick, were prepared by vacuum evaporation onto float glass substrates (size 2×8 cm^2) at typical pressures of about 10^{-6} Torr [6]. All the EXAFS and reflectivity data were collected using beamline 9.3 at the sychrotron radiation source in Daresbury, UK using dedicated glancing angle instrumentation[7].

Fluorescence yield x-ray absorption spectra at the Ag-K edge were recorded under conditions of total external reflection at an incidence angle of 80 mdeg. Each scan took approximately 45 minutes and 6-10 such scans were added prior to analysis. A harmonically-rejecting double-crystal Si(220) monochromator was used to monochromate the radiation and fluorescence photons were detected using a 13-element solid-state Ge detector designed by Cramer et al. [8].

3. Results and Discussion

The EXAFS data analysis requires a model compound of which structural parameters are known from x-ray crystallographic studies, in order to obtain phase shifts of the absorbing atom and backscattering atoms. Therefore transmission EXAFS data of a 10 μm silver foil at the Ag K-edge were obtained to determine the central and backscattering phase shifts of silver atoms using the x-ray crystallographic parameters as initial parameters. The calculations were made by using MUFFPOT program within *excurv90* [9]. Central atom phase shifts were calculated assuming a relaxed 1s core hole. Figure 2 shows the calculated least squares fit to the k^3 weighted experimental silver transmission data and Table 1 gives the crystallographic results together with the EXAFS results.

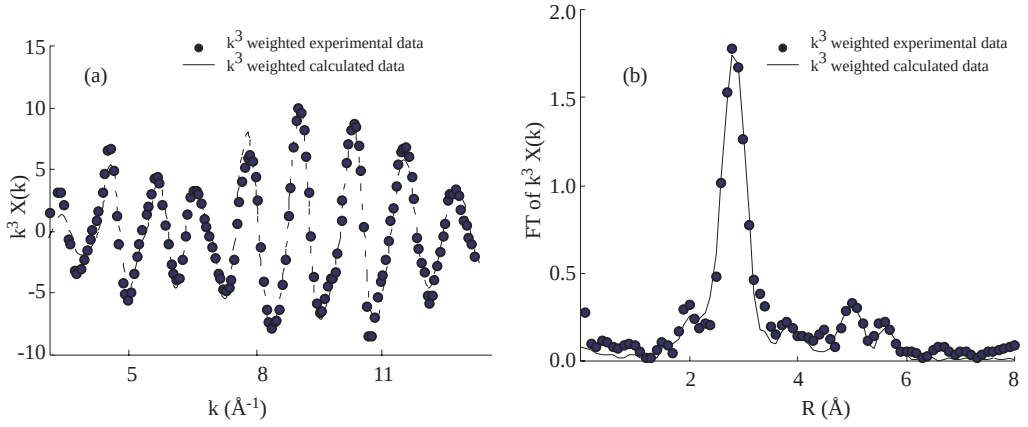

Figure 2. k^3 weighted raw transmission EXAFS of silver foil at the K-edge and best calculated fit by *excurv90* (a) together with Fourier transforms (b). The fitting parameters are given in Table 1.

Table 1. Structural parameters of silver foil determined from least-squares fits of transmission EXAFS spectra at the Ag K-edge and crystallographic parameters.

Crystallographic Parameters			Exafs Results		
Coordination Shell	Coordination Numbers	Distance R / Å	Coordination Number	Distance R / Å	Debye-Waller Factor (σ^2 / Å^2)
1	12	2.889	12.0 ± 1	2.89±0.01	0.009±0.001
2	6	4.087	6 ± 2	4.07 ±0.03	0.016±0.003
3	24	5.005	24 ± 6	5.01±0.02	0.016±0.004
4	12	5.778	12 ± 4	5.69±0.04	0.017±0.005

Reflectivity curves as a function of glancing incidence angle were recorded for energies close to the Ag K-absorption edge to determine the critical angle θ_c below which the EXAFS measurements were performed for the silver film on glass. Figure 3 shows the reflectivity curves of Ag film for two different photon energies. Compared to the reflectivity obtained below the absorption edge, the reflectivity above the edge has a smaller slope at θ_c due to the larger absorption coefficient μ. The effect of this on the slope of reflectivity can be clearly seen from the two curves. Additional structural features are also seen in the region of critical angle (θ_c). These structures in the reflectivity curve are caused by the interference of the reflected and refracted x-rays within the film [10]. From these reflectivity curves the glancing angle used for the EXAFS data collection was chosen as 80 mdeg for the silver film in air.

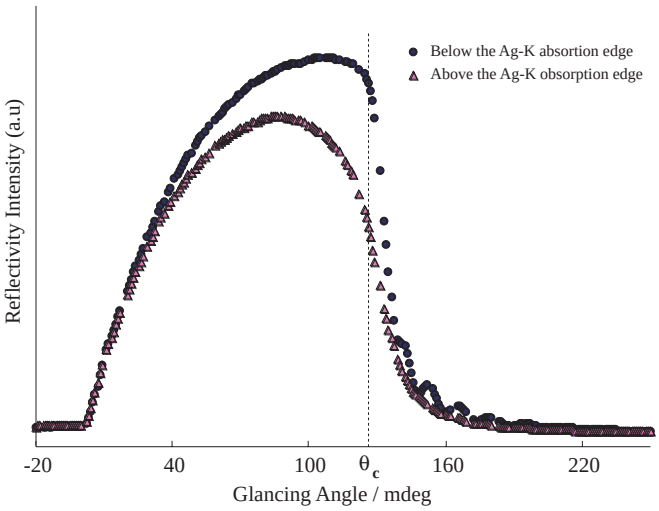

Figure 3. Reflectivity measurements of silver film on glass at energies below and above the Ag-K absorption edge.

Figure 4 shows the theoretical fitting to k^3 weighted experimental fluorescence EXAFS data and corresponding Fourier transforms. The derived structural parameters from the data analysis are presented in Table 2. Comparing the results in Table 1, it can be seen that shell distances of the silver film perfectly match with the silver foil but there is a reduction in the coordination numbers and a slight increase in the Debye-Waller factors from these of bulk values.

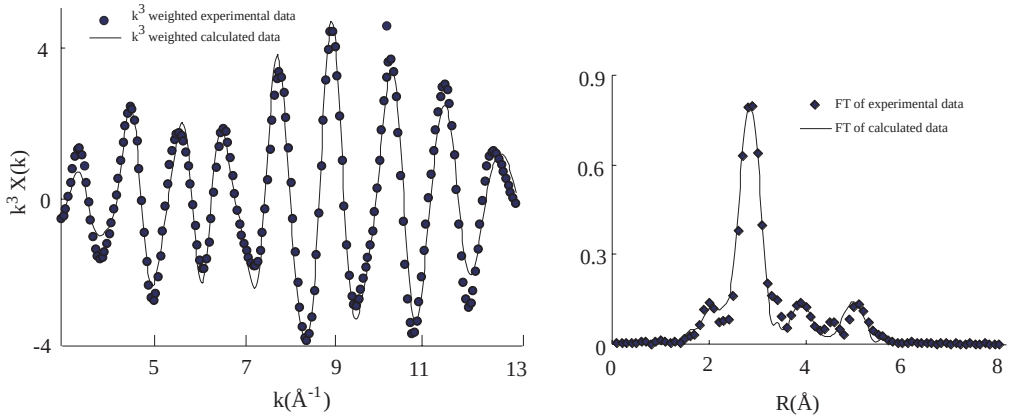

Figure 4. Fourier filtered fluorescence EXAFS data for silver film on glass and least squares best fit (a), with corresponding Fourier transforms (b).

Table 2. Refined structural parameters of fluorescence EXAFS data of silver film on glass.

Coordination Shell	Coordination Numbers	Distance R / Å	Debye-Waller Factor (σ^2 / Å^2)
1	10 ± 1	2.89± 0.01	0.010±0.001
2	5 ± 2	4.03± 0.02	0.017±0.003
3	18 ± 5	4.99 ± 0.04	0.020±0.004
4	11 ± 4	5.66 ± 0.08	0.021±0.005

Similar reduction in the coordination numbers for the fluorescence EXAFS data of films was also observed by others [11,12] and has been attributed to the small grain size in the film. Surface effects can also cause reduction of the coordination numbers since much of the signal in total external reflection geometry comes from a few top layers of the film where average coordination numbers are different from bulk values. Thus the reason for the reduction of coordination numbers can be given in terms of a mixture of these effects.

An increase in the Debye-waller factors can also be expected due to surface effects since the atoms in the surface will have larger amplitude motion than these in bulk increasing the mean square displacement of the atoms. This will affect the vibrational component and lead to an increase in the Debye-Waller factor.

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