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SURFACE CORE LEVEL SHIFT IN POLYCRYSTALLINE HAFNIUM

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Abstract

Photo electron spectra of the 4f core level in polycrystalline hafnium were recorded using synchrotron radiation. The emission from both surface atoms and bulk atoms was identified in the spectra. The surface core levels were found to be shifted 0.42 ± 0.04 eV towards higher binding energies, in agreement with current theoretical calculations.

Surface core level shifts have been extensively studied both experimentally and theoretically during recent years (see e.g. Johansson and Mårtensson 1980,1983 and Citrin and Wertheim 1983). The experiments have to a great extent made use of synchrotron radiation since by proper choice of the excitation energy one can achieve extreme surface sensitivity. The narrow 4f core levels of the 5d elements have been especially attractive. Surface core level shifts in most of these metals have been measured on various single crystal surfaces and in some cases also on polycrystalline surfaces. Compilations of these data and associated theoretical calculations can be found in Johansson and Mårtensson (1983) and Citrin and Wertheim (1983). In this letter we report on the surface core level shift in the 4f spectrum from polycrystalline Hf *).

The experiments were carried out at the Hamburger Synkrotronstralungslabor, HASYLAB, at the storage ring DORIS II with the FLIPPER monochromator (Barth et.al. 1983a). The experimental set-up, incorporating a double-pass cylindrical mirror analyser, has been described by Barth et.al. (1983b). In the spectra reported here the combined resolution of the electron analyser and the monochromator was 0.2 to 0.3 eV. The samples were prepared by electron beam evaporation of the high purity metal

(99.995%) onto a stainless steel substrate. The base preassure in the spectrometer was lower than 30 nPa ($2*10^{-10}$ Torr). During evaporation the preassure rose to 1 μPa ($1*10^{-8}$ Torr).

The cleanliness of the samples was checked by recording photo electron spectra of the valence band region. These spectra were measured at 40 eV photon energy in order to get a high photo ionization cross-section for possible contaminants, e.g. the oxygen 2p band. A weak structure at about 6 eV binding energy could always be detected, but a comparison with samples exposed to oxygen (see below) shows that the small amount of contaminants has no significant influence on the measured surface core level shift.

In Figure 1 we show spectra of the 4f core level recorded at different photon energies. The two prominent structures separated by about 1.7 eV correspond to the $4f_{5/2}$ and $4f_{7/2}$ final states. Each of these spin-orbit components consists of two partly overlapping peaks, labelled S and B. We interpret the peaks B_1 and B_2 as due to emission from bulk atoms and peaks S_1 and S_2 as originating from surface atoms on the basis of the following arguments:

(i) The binding energies of peaks B_1 and B_2 are in perfect agreement with those from XPS measurements (Nyholm et.al. 1980).

(ii) The intensity ratio S/B decreases with increasing photon

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*) A preliminary result from the measurement reported here was quoted in the paper by Johansson and Mårtensson (1983).

energy (see Fig. 1). This is in accordance with the reduced surface sensitivity at higher excitation energies due to the larger electron inelastic mean free path (see e.g. Lindau and Spicer 1974).

(iii) The binding energy difference between peaks S and B is in agreement with the theoretically predicted surface core level shift (Johansson and Mårtensson 1980). This will be further discussed below.

(iv) The peaks S_1 and S_2 are sensitive to adsorption of oxygen (Schmidt-May and Nyholm 1983) while peaks B_1 and B_2 are not. At exposures less than 0.5 Langmuir peaks S_1 and S_2 are significantly broadened while their intensity and center of gravity remain essentially unchanged. At higher exposures (>1 Langmuir) the 4f doublet from hafnium oxide starts to grow up at about 3.8 eV higher binding energy than peaks B_1 and B_2.

Having established the nature of peaks S and B it remains to determine the binding energy difference between these peaks. Since the peaks are partly overlapping a curve fitting procedure was used. In this procedure we used asymmetric line shapes according to Doniach and Sunjic (1970) and a Gaussian broadening function for the instrumental resolution. The background of inelastic scattered electrons was assumed to be proportional to the integrated bulk intensity. In Fig. 1 best fits for the spectra recorded at 70 eV, 100 eV and 150 eV photon energies are shown as full lines. Some comments on the results from the line

fitting procedure are given below:

(i) The life time width of the $4f_{5/2}$ level (0.16±0.03 eV) is found to be slightly larger than that of the $4f_{7/2}$ level (0.12±0.02 eV). This is in agreement with results for Ta and W (van der Veen et.al. 1982). The origin of this difference in line width is an $N_6N_7O_{45}$ Coster-Kronig decay which reduces the life time of the $4f_{5/2}$ core hole state relative to the $4f_{7/2}$ core hole state.

(ii) The asymmetry parameter for the bulk peaks, 0.15±0.03, is slightly lower than for the preceding element Lu (0.22, Lang et.al. 1981) but significantly larger than for Ta (0.06, van der Veen et.al. 1981).

(iii) The $4f_{5/2}$ to $4f_{7/2}$ intensity ratio is slightly different from the statistical ratio 0.75 and depends on the excitation energy. The ratio was found to be 0.63, 0.68, 0.72 and 0.75 (with an uncertainty of ±0.03) at photon energies 70 eV, 100 eV, 150 eV and 180 eV, respectively. Such deviations from the statistical ratio have been attributed to different radial wave functions for the two components and a dependence on the kinetic energy of the outgoing electron (Walker and Waber 1974).

(iv) The surface peaks are found to be significantly broader than the bulk peaks. This is probably caused by a distribution of surface shifts due to the polycrystalline nature of the samples (see below), allthough part of this broadening might be due to the small amount of contaminants on the surface. Best fits are obtained using a dominant Gaussian broadening for the surface peaks and with a life time width and an asymmetry parameter which are different from the corresponding bulk values. However, the choice of line parameters for the surface peaks should be regarded only as a means of obtaining a satisfactory line fit assuming single line shapes for the surface peaks, and should not be taken as evidence for a difference in life time width, asymmetry or phonon broadening between surface and bulk peaks. It should be noted, however, that the positions of the surface peaks are rather insensitive to the actual line parameters used.

(v) The surface to bulk core level shift derived from the line fitting procedure is 0.42 ± 0.04 eV.

Johansson and Mårtensson (1980) have shown that surface core level shifts can be calculated using a model based on the assumption of a completely screened final state. Within this model the shift is given by

$$\Delta E_{\mathrm{surf.}} = E_S^{Z+1} - E_S^{Z} - (E_{Z+1}^{\mathrm{imp.}}(Z) - E_{Z+1}^{\mathrm{imp.,surf.}}(Z)) \qquad (1)$$

where E_S^Z is the surface energy of the metal with atomic number Z and $E_{Z+1}^{\mathrm{imp.}}(Z)$ ($E_{Z+1}^{\mathrm{imp.,surf.}}(Z)$) is the heat of solution of a (Z+1) impurity atom in (on) the bulk (surface) of a Z-metal. Since accurate experimental surface energies are very scarce Eq. 1 is usually approximated using an empirical relation between the surface energy and the cohesive energy. Furthermore the impurity terms are usually small and can to a first approximation be neglected. These approximations lead to the following expression for the surface shift (Johansson and Mårtensson 1980):

$$\Delta E_{\mathrm{surf.}} = 0.2 * (E_{\mathrm{coh.}}^{Z+1} - E_{\mathrm{coh.}}^{Z}) \qquad (2)$$

For hafnium Eq. 2 yields a surface core level shift of +0.33 eV, which is in satisfactory agreement with the present experimental result.

In the approximations leading to Eq. 2 no consideration of the actual crystallographic structure of the surface is made. Rosengren and Johansson (1980) have calculated surface core level shifts for different single crystal surfaces of the 5d transition metals. For the most dense surface in Hf, the (0001) plane, a shift of +0.5 eV was obtained. The calculations also show that differences of a few tenths of an eV can be expected between different crystal surfaces. This could explain the broad surface peaks from the polycrystalline Hf films, especially if one consideres the possibilities of having edge atoms, corner atoms etc.. In order to unambiguously explain the broad surface peaks one should perform the measurements on single crystal surfaces.

Acknowledgements

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References

Barth J, Gerken F, Kunz C and Schmidt-May J 1983a Nucl. Instr. and Methods 208 307-12

Barth J, Gerken F and Kunz C 1983b Nucl. Instr. and Methods 208 797-804

Citrin P H and Wertheim G K 1983 Phys. Rev. B27 3176-3200

Doniach S and Sunjic M 1970 J. Phys. C3 285-91

Johansson B and Mårtensson N 1980 Phys. Rev. B21 4427-57

Johansson B and Mårtensson N 1983 Helvetica Physica Acta 56 405-26

Lang J K, Baer Y and Cox P A 1981 J. Phys. F11 121-

Lindau I and Spicer W E 1974 J. Electron Spectrosc. Relat. Phenom. 3 409-13

Nyholm R, Berndtsson A and Mårtensson N 1980 J. Phys. C13 L1091-6

Rosengren A and Johansson B 1980 Phys. Rev. B22 3706-9

Schmidt-May J and Nyholm R 1983 Annals of the Israel Physical

Society 6 348-50

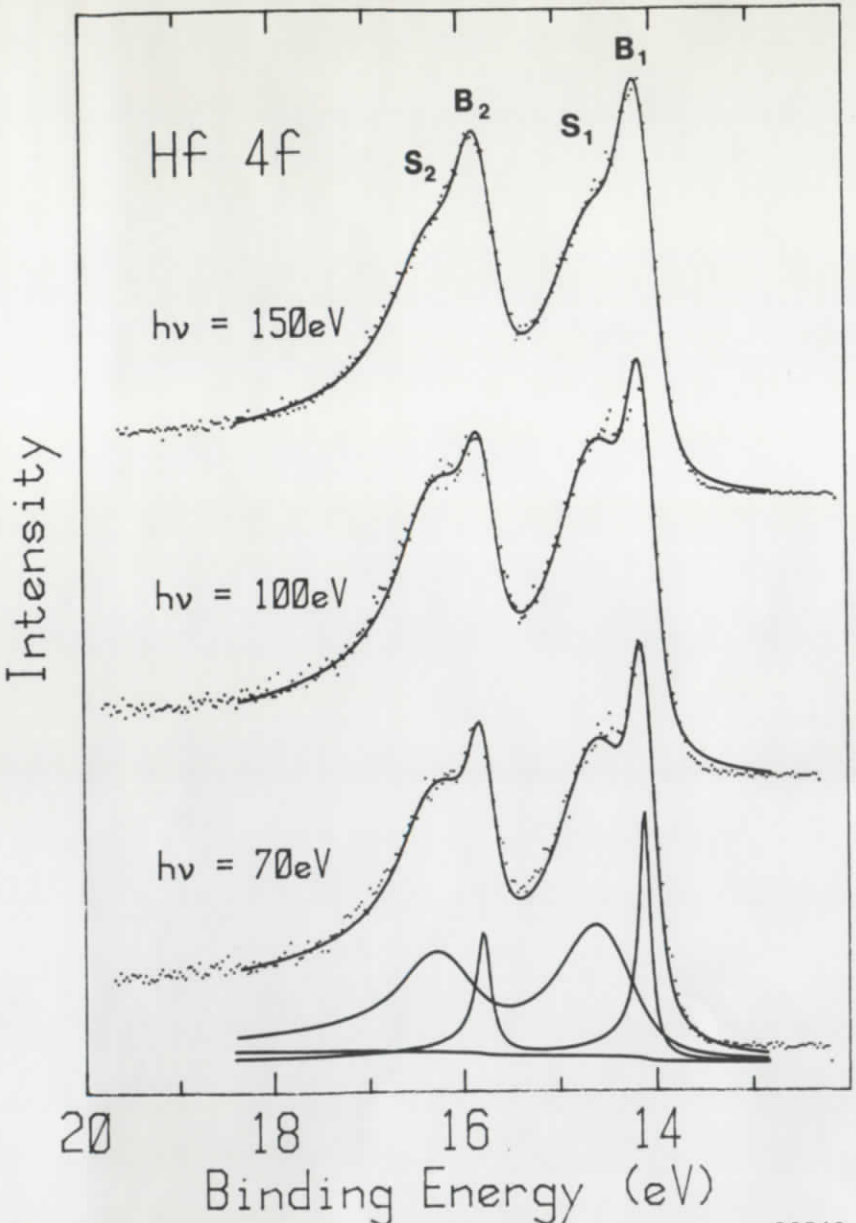
van der Veen J F, Meimann P, Himpsel F J and Eastman D E 1981 Solid State Commun. 37 555-9

van der Veen J F, Himpsel F J and Eastman D E 1982 Phys. Rev. B25 7388-97

Walker T F H and Waber J T 1974 J. Phys. B7 674-92

Figure Caption

Photo electron spectra from polycrystalline hafnium showing a binding energy shift between the 4f core levels from bulk and surface atoms (peaks B and S, respectively). The full lines are results from a curve fitting procedure.


B1
B2
S1
S2
Hf 4f
hν = 150eV
hν = 100eV
hν = 70eV
Intensity
20
18
16
14
Binding Energy (eV)

36542