

## Temperature-dependent microstructure of evaporated Yb surfaces

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*In situ* evaporated polycrystalline Yb films at different substrate temperatures ( $10 < T \leq 300$  K) were studied by surface-sensitive photoemission ( $h\nu = 40.8$  eV). The presence of substructure in the surface-derived  $4f^{13}$  components allowed an identification of multiple surface shifts as being due to different coordination numbers of surface atoms. The temperature-dependent intensity variation of the surface emission could be correlated with the temperature-dependent change of the surface microstructure.

A detailed knowledge of the surface structure of a solid is one of the fundamental ingredients of an understanding of surface processes. In particular, for a microscopic view of the chemical and physical reactions at solid surfaces a resolution on an atomic scale is needed, i.e., experimental methods such as low-energy electron diffraction, surface extended x-ray absorption fine structure, photon stimulated desorption, or photoelectron diffraction have to be employed. These structural tools run into difficulties, however, if the surface is polycrystalline and/or chemically identical with the substrate. Recently, photoemission spectroscopy has proved to be useful for structural analysis on single-crystal surfaces. In the case of Ir and Au different orientations of the surfaces could be discriminated and surface reconstruction could be discerned.<sup>1,2</sup> This was achieved by carefully studying core-level binding energies which undergo characteristic changes due to the reduced coordination at the surface.<sup>3</sup>

In this Rapid Communication we report for the first time on a temperature-dependent photoemission study ( $10 < T \leq 300$  K) of surface core-level shifts (SCS) on evaporated and filed polycrystalline Yb samples. Yb metal exhibits a simple  $4f^{13}$  final-state spin-orbit split doublet (1.27 eV) with small linewidth and high photoemission cross section for photon energies of 40 eV and shows a clearly discernible and large SCS of 0.6 eV at 300 K.<sup>4-9</sup> At low temperatures this value remains unchanged for filed Yb samples while for evaporated films an increase of the shift with decreasing substrate temperature is observed (0.5 eV at 300 K to 0.9 eV at 10 K). On the other hand, cooling after Yb deposition does not effect the SCS pointing to the fact that the temperature dependence of the SCS reflects the dynamics of the condensation process. Since the SCS is a function of the mean coordination at the surface<sup>1,2</sup> we correlate this behavior with the increase of lower coordination numbers with decreasing substrate temperatures.

Thus we show for the first time that surface-sensitive photoemission allows a detailed investigation of the influence of substrate temperature on the surface microstructure of evaporated films.

The data are taken (a) with a VG ESCA3 spectrometer (0.1-eV resolution) using He II (40.8 eV) radiation for photoexcitation and (b) at the Synchrotron Radiation Center of the University of Wisconsin—Madison using a display-type analyzer with a resolution of 0.2 eV at photon energies of 40 eV.<sup>10</sup> The base pressure in (a) amounts to  $4 \times 10^{-10}$  Torr and in (b) to  $4 \times 10^{-11}$  Torr. High-purity samples (99.99%) of Yb are evaporated from tungsten baskets onto stainless steel, Ta, and Cu substrates under UHV conditions. Only during evaporation the pressure rose to  $2 \times 10^{-8}$  Torr. For the low-temperature measurements in (a) a Heli-Tran cryostat and (b) a closed-cycle He cryostat (Air products) was used with substrate temperatures of 10 and 40 K, respectively. The deposition rates of the Yb films were about several hundred angstrom per second. For reasons of comparison, solid Yb samples were also measured where surface contaminants were removed by scraping with a diamond file. Under these conditions we expect at most an oxygen coverage of 5% of a monolayer. We were unable to detect any oxygen signal with ultraviolet photoelectron spectroscopy (O2p) and x-ray photoemission spectroscopy (O1s) at the sample surfaces. Both experimental setups (a) and (b) led, apart from the slightly lower resolution of (b) as compared to (a), to identical results. Therefore, we present only He II-excited spectra.

Figure 1 shows representative spectra of the Yb valence band of evaporated films at different substrate temperatures. The spectra are dominated by emission from the Yb  $4f^{14}$  orbitals giving rise to a superposition of bulk- and surface-derived  $4f^{13}$  final-state doublets. It is striking that with decreasing substrate temperature an increased shift of the surface derived peaks to higher binding energies is observed.

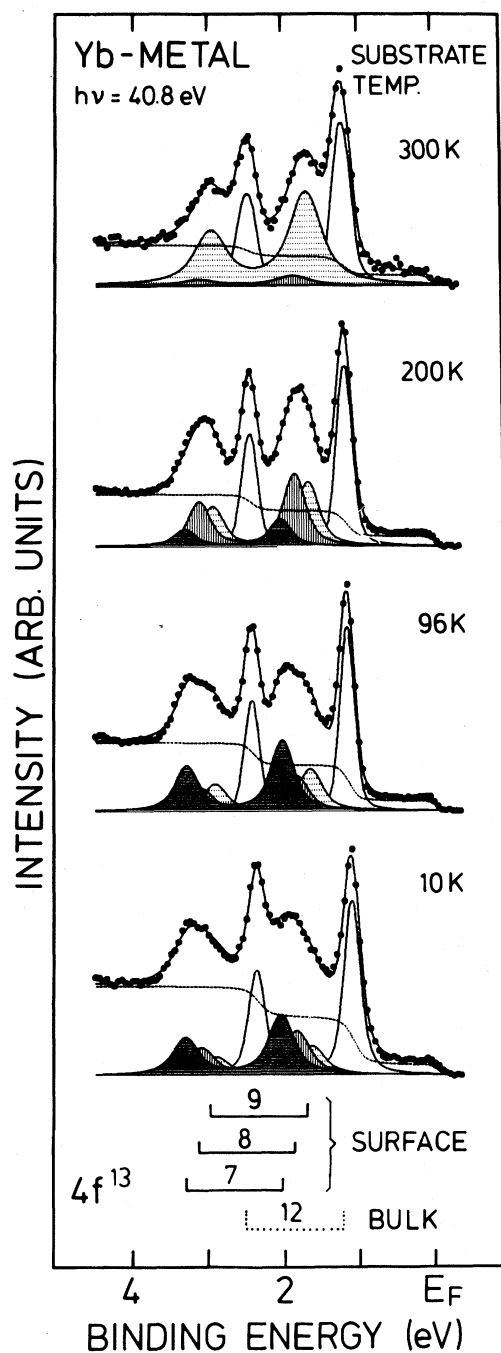


FIG. 1. Valence-band photoemission spectra of evaporated Yb metal at different substrate temperatures. The heavy solid line represents the result of a least-squares-fit analysis of the data points of four  $4f^{13}$  final-state multiplets originating from the bulk [light solid curve (dotted bar diagram)] and the surface [shaded curve areas (solid bar diagram)]. The dotted line represents the integral background. The correlation between the surface peaks and the corresponding surface atom coordination numbers is indicated. Note the strong intensity variation of the surface peaks with substrate temperature.

Furthermore, with *decreasing* temperature the linewidth of the surface peak *increases*. This last observation stresses the fact that the increased linewidth of the surface peak cannot be attributed to phonon broadening. A critical survey of all spectra (not shown here) from evaporated and filed samples shows the presence of peaks and shoulders in the surface emission (seen, for example, in the spectra at 96 K in Fig. 1) corresponding to binding-energy shift of  $0.51 \pm 0.08$ ,  $0.67 \pm 0.05$ , and  $0.86 \pm 0.05$  eV. If these substructures are identified with different coordination numbers of the surface atoms then the smallest binding-energy shift has to be correlated with the highest coordination number.<sup>3</sup> It is known that Yb films mainly condense in the fcc and hcp phases.<sup>11</sup> The coordination in the bulk is therefore 12, while for the surface (depending on the orientation of the microcrystallites) coordinations between 6 and 9 are expected. Consequently, we identify the SCS of 0.5 eV with coordination number 9, corresponding to dense-packed surfaces fcc (111) or hcp (001), respectively. Now, within a simple tight-binding approximation, the magnitude of the SCS is proportional to the square root of the number  $Z$  of nearest neighbors<sup>1</sup>: If the value of the shift  $E_N$  is given for  $N$  nearest neighbors then for a coordination  $Z$  we have

$$\Delta E_Z = [(1 - \sqrt{Z/12}) / (1 - \sqrt{N/12})] \Delta E_N \quad (1)$$

Inserting  $N = 9$  and  $E_N = 0.5$  eV we get for  $Z = 8$  a value of  $\Delta E_Z = 0.68$  eV and for  $Z = 7$  we yield  $\Delta E_Z = 0.88$  eV in good agreement with the position of the observed shoulders. A rough estimate for  $\Delta E_9$  is also obtained from photoemission measurements in the gas phase (coordination 0).<sup>12</sup> In order to compare the  $4f_{7/2}$  position in the gas phase (8.8 eV relative to  $E_{\text{vacuum}}$ ) with the corresponding bulk position in the solid (1.2 eV relative to  $E_F$ ), we add the work function of Yb metal ( $\sim 3$  eV) to the latter and yield for  $\Delta E_0 \cong 4.6$  eV. Then according to Eq. (1) with  $Z = 9$  and  $N = 0$  we get  $\Delta E_9 = (1 - \sqrt{9/12})4.6 = 0.62$  eV. This value is slightly larger than the experimentally observed SCS due to the lack of conduction-electron screening in the free ion.

In order to gain more quantitative information on position and intensities of the observed spectra a least-squares analysis of the data was performed with the following assumptions: (i) The line shape was approximated by a Lorentzian. This procedure is justified since Yb is a semimetal and, therefore, only weak electron-hole excitations are expected. (ii) Energy losses for the photoexcited electrons on their way through the sample were considered only for the bulk  $4f^{13}$  emission and were described by an integral background (see Fig. 1). (iii) Different linewidths were assumed for bulk and surface emission; different surface coordinations, however, were described by identical linewidths. (iv) The spin-orbit splitting and

the intensity ratio of the  $j = \frac{7}{2}$  and  $j = \frac{5}{2}$  components were set identical for bulk and surface emission. (v) Equation (1) was assumed to be valid for the relative positions of the surface peaks; only the positions of the coordinations 12 (bulk) and 9 were free parameters. (vi) In order to simulate the finite resolution of the spectrometer and the temperature-dependent phonon broadening the theoretical spectrum was convoluted with a Gaussian of variable width. From an inspection of Fig. 1 it is evident that this simple model describes the spectra satisfactorily. An analysis of 15 spectra yields for  $E_9 = 0.49 \pm 0.02$  eV in excellent agreement with Ref. 3; for the spin-orbit splitting a value of  $1.27 \pm 0.005$  eV and for the intensity ratio  $I_{5/2}/I_{7/2} = 0.61 \pm 0.02$  is obtained in good agreement with Ref. 5. The ratio of the surface to bulk linewidth is  $1.6 \pm 0.4$ ; however, this value varies strongly with the number of coordinations involved, and, furthermore, since we average over the linewidth of different coordinations this value cannot be taken too seriously. On the other hand, a larger linewidth for the surface emission due to the higher degree of vibrational and rotational freedom of a surface atom or to crystal-field effects may be expected. According to Fig. 1, we note the following observations: (i) While at 300 K predominantly a coordination of 9 is present, there is mainly a contribution from coordination number 7 at 10 K. (ii) With decreasing substrate temperature the inelastic scattering background increases systematically. Figure 2 shows the temperature-dependent variation of the intensities for the surface emission lines corresponding to the coordination numbers 9 and 7. For comparison the results for the scraped samples are also included. In the latter case no pronounced temperature dependence is observed. This behavior may be expected since by filing a statistical distribution of surface lattice planes is obtained independent of the temperature. In the case of the evaporated films the nearly linear increase of the coordination number 7 with decreasing temperature is striking. These results are independent of the substrates used (steel, Ta, Cu) and are reproducible very easily. [The nearly pure coordination number 9 obtained on a highly polished stainless-steel surface (see Fig. 2), however, points to an additional possible surface quality dependent effect for thin films which should be investigated in the future.]

This behavior can be qualitatively understood by the decreasing substrate temperature.<sup>13</sup> At low temperatures, due to the low mobility of the Yb atoms, the nucleation is enhanced, leading to island formation and an increase in surface roughness. With increasing surface roughness the amount of lower coordination numbers should increase which is quantitatively described by the increase of the coordination number 7 with decreasing substrate temperature. Furthermore, with increasing surface roughness an

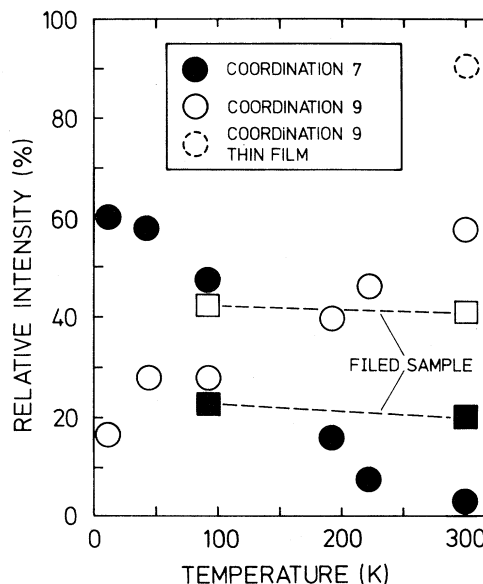


FIG. 2. Relative intensity variation of surface peaks originating from coordinations 7 and 9 with substrate temperature. The intensities are normalized to the sum of the intensities of coordinations 7, 8, and 9. The behavior of the filed samples ( $\square$ ) on cooling is also indicated. Note the value for the thin film ( $< 1000$  Å) which is obtained only on highly polished surfaces.

increase in the inelastic electron scattering background is expected and indeed observed in the experiment (see Fig. 1). These findings are in excellent agreement with structural investigations of evaporated Yb films by electron microscopic and x-ray diffraction techniques which show a decrease in grain size with decreasing substrate temperatures and a nearly amorphous structure of the film below 150 K.<sup>11,14</sup>

To summarize, the dynamic behavior of the nucleation process at the surface of Yb metal could be followed within a broad temperature range by photoemission experiments. Thus, in the future it should be possible to investigate the dependence of the surface structure on other parameters such as type of substrate, film thickness, deposition rate, or annealing temperature in order to gain insight into the fundamental properties of crystal growth and epitaxy.

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