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Study of the inelastic mean free path in ytterbium nanofilms by Auger electron spectroscopy and x-ray photoelectron spectroscopy

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Using Auger electron spectroscopy and X-ray photoelectron spectroscopy, we have measured the inelastic mean free path in ytterbium. This value is shown to be anomalously high in divalent metal films ($\sim 13\text{--}15\text{ \AA}$ at the energy of 92 eV). When ytterbium is transformed to the trivalent state, the inelastic mean free path becomes close to the typical values for most metals. This is due to the promotion of the $4f$ -electron to the $5d$ -level in the valence band and an increase in the excitation cross section for plasmon losses in Yb^{3+} films.

Keywords: inelastic mean free path, electron spectroscopy, ytterbium, electronic structure.

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Inelastic mean free path (λ) of electrons in solids is a fundamental parameter that governs the depth resolution and the intensity and shape of lines in electron spectroscopy [1,2]. Its dependence on energy (the so-called „universal curve“) has a similar shape for different materials, but the scatter of points on this curve may be as large as $\sim 200\%$ of the average value [3]. It is caused, on the one hand, by the diversity of electronic properties and the specificity of electron–electron interactions in solids and, on the other hand, by the imperfection of experimental λ measurement methods.

The thin film deposition method is typical used to measure the inelastic mean free path. These films are deposited onto foreign substrates, and attenuation of the signal from substrates is analyzed. However, the morphology of deposited films and the structure of their interface with substrates are often neglected in this approach [4]. Indeed, errors should arise if the film is significantly non-uniform in thickness and the boundary is chemically diffuse. In the present study, we report the results of correct determination of the inelastic mean free path in ytterbium (a rare earth metal, REM) at energies typical for Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). This object was chosen for study for the following reasons. First, experimental data for ytterbium are virtually lacking in literature. We known of only a single study [5] where λ for this metal was estimated indirectly, by comparing the surface and bulk contributions to photoelectron spectra. Second, ytterbium (and other REMs) is noted for strong localization of the $4f$ -shell near the atomic nucleus, which is likely to suppress the contribution of $4f$ -electrons to inelastic scattering. Third, Yb easily changes valence states from 2 (Yb^{2+}) (electronic configuration $4f^{14}6s^2$) to 3 (Yb^{3+}) [$4f^{13}(5d6s)^3$] and vice versa. It is evident that the valence band transformation

(specifically, the emergence of d -states in it) should affect the inelastic mean free path.

Experiments were carried out in two ultrahigh-vacuum setups with a base pressure $\leq 1 \cdot 10^{-10}$ Torr. One setup included an AES spectrometer with a cylindrical mirror analyzer, and the other featured an XPS spectrometer with a hemispherical conical analyzer. Ytterbium was deposited onto Si(111)(7×7) substrates (n -type, $\rho \approx 1\text{--}7.5\ \Omega \cdot \text{cm}$). The temperature of silicon was maintained at 290–300 K in the process of film deposition and subsequent measurements. The Yb–Si(111) structures formed under these conditions had very low surface roughness and a chemically sharp interface [6]. Evaporators heated by a tantalum or tungsten coil were used for ytterbium deposition. One monolayer (ML) of Yb atoms was assumed to correspond to their surface concentration of $7.84 \cdot 10^{14}\ \text{cm}^{-2}$. The deposition rate was $\sim 1\ \text{ML}/\text{min}$.

Figure 1 shows the intensities of silicon Auger peak L_{VV} (92 eV) for the Yb–Si(111) structures at different metal film thicknesses. It is evident that as the coating thickness increases, the shielding of the substrate by the growing film becomes more pronounced and the flux of Auger electrons passing through ytterbium decreases near-exponentially. Inelastic mean free path λ may be determined in this case using the $I(l) = \exp(-l(\lambda \cos \vartheta)^{-1})$ expression, where $I(l)$ is the intensity of the Si Auger signal at integer values of Yb film thickness l and ϑ is the electron collection angle measured relative to the normal to the surface (42.18°). Calculated $I(l)$ dependences obtained using this expression at different λ are represented in Fig. 1 by solid curves. The best fit between these dependences and experimental data is observed at $\lambda = 4.0\ \text{ML}$.

The inelastic mean free path determined above agrees closely with the results reported in [5] ($\sim 3.8\ \text{ML}$). At the same time, it exceeds significantly the values derived from the universal curve ($5.1\ \text{\AA}$ [3]) and determined within the

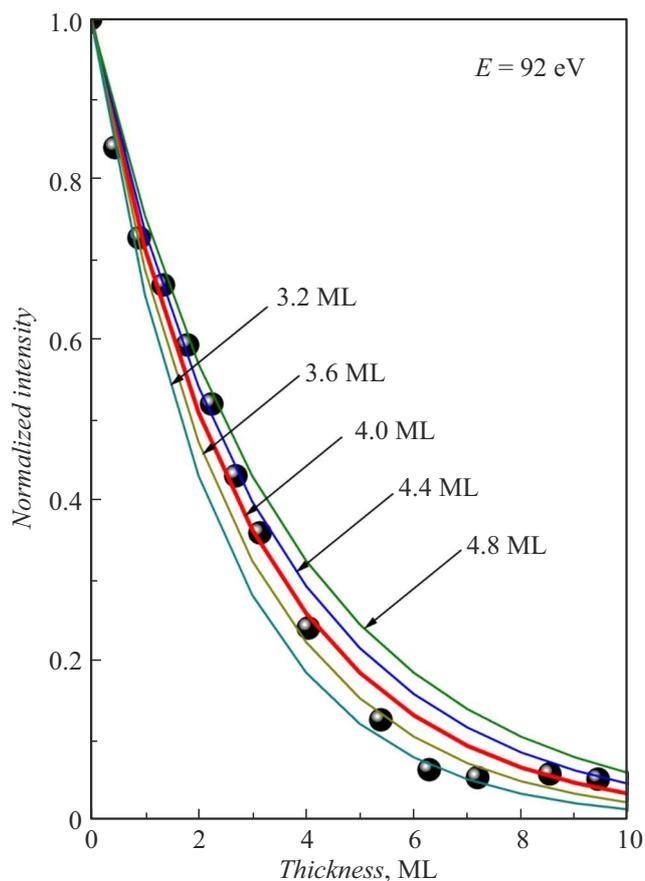


Figure 1. Intensity of Si Auger peak L_{VV} (92 eV) as a function of the ytterbium film thickness. Peak amplitudes were measured in the „peak-to-peak“ mode and normalized to the signal level for a clean surface. Circles and solid curves correspond to experimental data and calculated dependences obtained at different λ values, respectively.

Tanuma–Powell–Penn (TPP) model (5.2 Å [7]). If the thickness of 1 ML Yb (d) is taken to be equal to 3.2 Å [8], the value of λ obtained from Fig. 1 is 12.8 Å. If thickness $d = 3.86$ Å (doubled covalent radius of a Yb atom) is used, $\lambda = 15.2$ Å. This implies that the inelastic mean free path in ytterbium is 2.5–3.0 times longer than the average values.

Two factors should be taken into account in order to obtain an explanation for this. First, as was already noted, the contribution of $4f$ -electrons to inelastic scattering in REMs is likely to be small. This assumption is supported by the data from [5], where λ was found to be unaffected by the degree of filling of the $4f$ -shell in various REMs. Second, the valence of ytterbium in Yb–Si(111) structures is close to 2 [9]. This means that its valence band is formed by s -electrons only, while d -states are located above the Fermi level. Apparently, all these factors combined produce the anomalously large value of λ in metallic divalent ytterbium. Similar values are also observed for simple s -metals. For example, according to the results of calculations performed

in [7], the inelastic mean free path at an energy of 92 eV is 11.1 Å in rubidium and 12.6 Å in cesium.

Given the above, a question arises: how will the inelastic mean free path in ytterbium change when it transitions to the trivalent state? Two ways to induce such a transition are presently known. The first one involves the use of high pressures (~ 40 kbar) [10], while the second method is suited for initiation of this transition in ytterbium films of nanometer thickness upon non-dissociative adsorption of certain molecules on their surface (the depth of its penetration into the bulk of the material is no less than 22 ML [11]). This was the method used in the present study. A layer of O_2 molecules (the dose was 100 L) was adsorbed on the surface of Yb–Si(111) structures with different ytterbium thicknesses. The $Yb^{2+} \rightarrow Yb^{3+}$ valence transition induced by this layer was confirmed by examining the shape of the $4f$ -ytterbium line in XPS experiments [11]. The same method for determining the inelastic mean free path was used to record the dependence of the $4f$ -emission intensity on ytterbium film thickness in the O_2 –Yb–Si(111) structures. This dependence is represented by circles in Fig. 2. Characteristic X-ray radiation with a photon energy of 1253.6 eV (K_{α} -line of the magnesium anode), which specified the kinetic energy of detected electrons (~ 1240 eV), was used to measure the $4f$ -spectra.

It follows from Fig. 2 that the magnitude of the signal from the ytterbium film increases rapidly with an increase in its thickness at $l \leq 8$ ML. As l grows further, the intensification of the signal becomes less and less pronounced. At $l = 32$ ML, the dependence effectively reaches saturation, which corresponds to $l \gg \lambda$. In general, the dependences in Fig. 2 may be characterized by expression $I(l) = 1 - \exp(-l(\lambda \cos \vartheta)^{-1})$ ($\vartheta = 0^\circ$ is the electron collection angle specified by the geometry of the experiment), which allows one to estimate the inelastic mean free path. A comparison of the calculated dependences (solid curves) for different values of parameter λ with experimental data reveals that the inelastic mean free path in trivalent ytterbium at the electron energy indicated above is 7.3 ML. This corresponds to $\lambda = 23.4$ Å at $d = 3.2$ Å and 25.3 Å at $d = 3.47$ Å (the diameter of a trivalent Yb atom [12]). The obtained values agree completely with the universal curve (~ 24 Å [3]). Moreover, they are very close to similar values predicted in the TPP (25.1 Å) and Gries (26.1 Å) [5] models. Thus, the inelastic mean free path in Yb^{3+} is not anomalously long; it corresponds to the typical λ values for most elements (in particular, d -metals).

Why does the $Yb^{2+} \rightarrow Yb^{3+}$ transition exert such a significant effect on the inelastic mean free path? It is evidently accompanied by a rearrangement of the electronic structure: the emergence of $5d$ -states and their hybridization with $6s$ -electrons in the Yb^{3+} valence band. It may be assumed that the indicated rearrangement raises the excitation cross section of plasma oscillations, which is the process that serves, alongside with single-electron excitations, as the main energy loss channel in inelastic scattering [13]. Note that a similar correlation has already been observed in

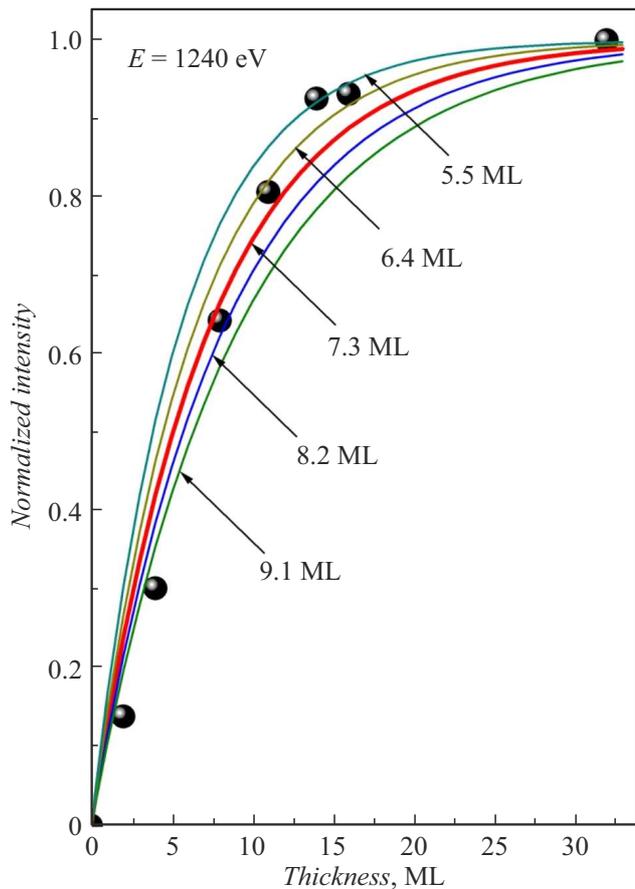


Figure 2. Intensity of 4*f*-emission in XPS spectra for the O₂-Yb-Si(111) structures as a function of ytterbium film thickness. The obtained values were normalized to the signal level at $l = 32$ ML. Circles and solid curves correspond to experimental data and calculated dependences obtained at different λ values, respectively.

earlier experiments; with the Yb²⁺ → Yb³⁺ transition, the intensity of plasmon loss peaks in the Auger spectra of ytterbium increased sharply [14].

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Conflict of interest

The authors declare that they have no conflict of interest.

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