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SURFACE PLASMON PEAK INTENSITY DEPENDENCE ON THE OXYGEN COVERAGE AT METAL SURFACES

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The dependence of the surface plasmon peak intensity on a submonolayer coverage of oxygen in the reflection electron energy loss (REEL) spectra has been investigated for non-monocrystalline aluminium, magnesium, and indium surfaces. It will be shown that the decrease of the surface plasmon peaks can be related to a modification of the surface plasmons dispersion relation. A simple model for this modification introduced by changes of the surface electron density profile is proposed. Parameters of this model will be determined from experimental data.

The surface plasmon (SP) peak shape and intensity in reflection electron energy loss (REEL) spectra depend on the near-surface electronic structure. Hence, REEL spectra contain important information about the near-surface electronic structure of solids. This is a reason, that the adsorption influence on the SP characteristics in the low-energy region of the incident electrons (< 2000 eV) has been studied during the last three decades.¹⁻⁷

The dependence of the SP peak shape and intensity on a submonolayer oxygen coverage (Θ) for Al surface has been determined experimentally in pioneer works on REEL spectroscopy (see Ref.1). It has been shown that for the initial stages of the oxygen adsorption (degree of coverage $\Theta < 0.1$ monolayer (ML)), the intensity of the SP peak decreases rapidly, without visible changes of the peak position in the REEL spectrum. This effect also has been observed for other materials and under different conditions^{3,6,7} although a systematic study of this phenomenon has not been performed yet.

In the present work the SP peak intensity changes in REEL spectra for submonolayer oxygen coverages ($\Theta < 0.1$) at non-monocrystalline surfaces of aluminium, magnesium and indium will be studied. We have found a close relation between SP peak changes and modifications of the SP dispersion relations. These modifications depend on the changes of the surface electronic density profile (SEDP). A simple model is proposed for the SEDP and its changes in the initial stage of oxygen deposition.

The experimental method for the receipt of angle resolved REEL spectra has been described in Ref. 8. For

our purpose we have used an experimental geometry with fixed scattering angle $\theta = 150^\circ$. The angles between the surface and the incident electron beam (γ) and the angles of exit for the registered electrons (β) satisfy equation $\beta = 180^\circ - \theta + \gamma$. The REEL spectra were measured for various magnitudes of the parameter $\varphi = \sin^{-1}\gamma + \sin^{-1}\beta$ ($2.07 < \varphi < 7.30$). The relative energy resolution was about 10^{-3} in the region of the incident electron energy $E = 1000-1500$ eV.

The working pressure in the chamber was about 10^{-10} Torr. Oxygen depositions at the metal surfaces have been performed at partial oxygen pressure of about 10^{-7} Torr. The oxygen input was realized by warming up a CuO source. The purity of the oxygen was checked by mass-spectrometry.

The REEL spectra, obtained at various oxygen coverages at the aluminium surface, are shown in Fig.1. The quantity of adsorbed oxygen at the surfaces was determined by means of both work-function measurements (Anderson's method) and oxygen Auger spectroscopy measurements.⁶ The observed changes in the work-function and REEL spectra correspond to those described in other works.^{1-4,6,7}

The obtained REEL spectra were assumed to consist of several contributions. The contributions are, with respect to their origin, divided into the following categories: elastically reflected electrons, electrons, which loose energy once or twice due to the excitation of surface and/or bulk plasmons, and electrons which had only suffered an energy loss through electron-electron interaction in the solid. The intensities of these peaks in the REEL spectrum were denoted I_{el} , I_s , I_b , I_{sb} , I_{ss} , I_{bb} , I_{e-e} , respectively (see Fig. 1). Here we follow the procedure as described in detail in Ref.8. For all of the investigated

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Table

Metal	P	C	α_0 (a.u.)	D_0 (a.u.)	x_0	d_0 (Å ⁰)	d_a (Å ⁰)	a	Q (a.u.)
Al	4.2	0.4	-0.7 ^a	0.22 ^b	0.83	1.64	0.63	-0.66	0.32
Mg	5.2	2.5	-1.1 ^a	0.11 ^b	0.74	1.47	0.8	-1.05	0.56
In	0.2*	-0.5	-0.8 ^a	0.17 ^b	0.79	1.6	-1.8	-0.36	0.02

*Max. P for In

^aReference 14

^bReference 13

should be much more weaker than $A_s(\Theta)$. For Al and at an incident electron energy of 1300 eV, we find $S/P \approx \alpha_0 \times 0.04$.

We have determined that the changes of the SP peak amplitude are related to a modification of the SEDP through a modification of the SP dispersion relation. It is attractive to reconstruct characteristics of the SEDP using experimental data and the simplest available theoretical model. For this purpose we use the "jellium model" with a δ -like oxygen coverage. The localization of a part of the electronic charge is a suitable way to describe the adsorption of more electronegative atoms on a metallic surface.¹³ In this model the electronic density $n_-(z)$ and the smeared positive charge of the ionic cores of the solid $n_+(z)$ (located at $z > 0$) are

$$n_-(z) = n_s \Theta(z + d_0 - z_d) +$$

$$+(n_0 - n_s)\Theta(z - z_d) + N_a \delta(z + d_a),$$

$$n_+(z) = n_0 \Theta(z)$$

where n_s and n_0 are uniform densities in a near-surface region and in the bulk, respectively; d_0 is an effective thickness of the near-surface region with electronic density n_s ; z_d is an effective thickness of the near-surface electron depletion region in the solid; N_a and d_a are an effective surface density of the adsorbate charge and centroid of this charge, respectively, and $\Theta(z)$ is the Heaviside step-function. Finally, we assume that $N_a \approx Q \cdot \Theta / (n_0 \cdot s_0)$ and $n_s/n_0 = x(\Theta) = x_0(1 + a \cdot \Theta)$, where Q is an effective charge of the adsorbed ions; s_0 is an average one-atom metal area at the surface. Eigenfrequencies of the adsorbed ions are much smaller than ω_p , and Q may be introduced as a non-oscillating charge. For the represented model we can determine α_0 and P as functions of the parameters of the model

$$\alpha_0 = d_0 x_0 (x_0 - 1) / (2x_0 - 1)$$

$$P = a(1 - 2x_0 + 2x_0^2) / (x_0 - 1)(2x_0 - 1).$$

Since the experimental information on the work-function should be described by the model too, we now calculate the dipole part of the work-function as a function of the Θ .¹³ If we take into account the system neutrality

condition, we obtain

$$D(\Theta) = 4\pi \int dz z [n_+(z) - n_-(z)] = D_0(1 - C\Theta),$$

where $D_0 = 2\pi n_0 d_0^2 x_0(1 - x_0)$ and $C = a(1 - 2x_0 + 2d_a/d_0)/(x_0 - 1)$.

In order to determine the parameters x_0 , d_0 , a_0 and d_a we can use both experimental values for P and C , and the known literature data for α_0 and D_0 . The results of this calculation are shown in the Table. It is quite remarkable that the magnitudes of the obtained parameters are in a very reasonable region.

The near-surface effective electronic charge decreases for all materials when the total adsorbate electronic charge is increased. However, there is a difference between Al and Mg, on one hand, and In on the other hand, with respect to the determined position of the oxygen atom at the surface. The oxygen atom is located outside the positive core for Al and Mg surfaces, whereas for the In surface d_a corresponds to a configuration, where the O-atom is located inside the near-surface region of the In positive ionic core charge ($z > 0$). This explains the sign of the C_{In} and is in good agreement with other experimental data published by other authors.⁷

The proposed model is too simple for far-reaching conclusions, but it shows a possibility to obtain additional information from the REEL data. It will therefore be very interesting to measure the $\alpha(\Theta)$ dependence at the initial stages of oxygen adsorption and to compare it with Eq.(7).

Summarizing, we can to conclude that changes of the SP peak intensity in the REEL spectra for the initial stages of oxygen adsorption are related to a modification of the SP dispersion relation. This modification corresponds to a change of the SEDP parameters and there is a possibility to determine the SEDP parameters using the experimental REEL spectroscopy data. The expression for the SP dispersion relation and the simple jellium model, described above, yields reasonable magnitudes for the SEDP and oxygen-adsorbate parameters in the case of the non-monocrystalline surfaces Al, Mg and In.

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