Influence of electron reflectivity on the analysis of surface processes: O$_2$-Ag(110)

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We discuss the influence of elastic reflectivity of the electrons for the analysis of dissociation phenomena on surfaces and adsorbate-induced reconstructions of the substrate. Two situations corresponding to the enhancement of the reflectivity induced by low-energy-electron-diffraction fine structures and by multiple scattering for O$_2$ chemisorbed on Ag(110) are presented.

I. INTRODUCTION

In a recent paper[1] we showed that electron-energy-loss spectroscopy (EELS) can be applied to study the dissociation of gases adsorbed on surfaces and the eventual reconstruction of the substrate. The study was performed for O$_2$ adsorbed on Ag(110) and we showed that the disorder on the surface increases after dissociation. The conclusions were based on the frequency of the adsorbate vibrations, on the intensity of the losses, and on the elastic reflectivity in specular and out of specular. We showed that the dissociation of the O$_2$ molecules is connected to the drop of the specular elastic reflectivity and to the growth of the diffuse elastic intensity. The experimental data were shown for one scattering angle $\theta_i = 63°$ and for one impact energy E_e=1.23 eV for scattering along the $\langle 001 \rangle$ crystallographic direction, where the effect of dissociation on reflectivity is particularly strong.

The reflectivity is, however, also affected by multiple scattering. This is different for different geometries, as is the case before and after a surface reconstruction; it is affected by changes in the work function, which change the wave vector of the electrons in the solid, thus shifting positive and negative interference conditions in energy. These effects were considered in the analysis of the data of Ref. 1, which was performed over a wide range of E_e, but a thorough discussion was omitted in the previous publication and is presented here.

II. EXPERIMENT

The elastic reflectivity was measured by high-resolution EELS (HREELS) for the clean and O$_2$ covered Ag(110) surface. Details on the experiment were given in the previous paper[1] and in the description of the experimental apparatus.[2] Oxygen is dosed with a molecular beam in order to reduce exposure time and the contamination of the vacuum.[3,4] At 83 K O$_2$ adsorbs molecularly without long range order. Dissociation occurs at T_1=145 K, while at T_2=200 K the ($n \times 1$) reconstruction of the substrate sets in. HREELS spectra are recorded as a function of crystal temperature, which is changed from below T_1 to above T_2. To verify that the observed drop in the electron reflectivity depends upon the increased amount of surface disorder and not from a change in scattering cross section for particular impact conditions, the experiment was performed for several E_e.

The comparison of the results obtained for different E_e is, however, not straightforward, as absolute intensities are needed. This is a tough problem with an electron-energy-loss spectrometer as its transmission function and the focus of the lenses depend on impact energy. A fair reproducibility of intensities can, however, be achieved over a not too large impact energy range.

III. RESULTS AND DISCUSSION

The elastic reflectivity is shown as a function of E_e for two experimental conditions for scattering along the $\langle 001 \rangle$ crystallographic direction of Ag(110). They exemplify two typical situations: in Fig. 1 for 1 eV< E_e <2.5 eV and in Fig. 2 for 12 eV< E_e <16 eV. The reflectivity measured for the clean surface is reported by $\diamond$, while + and □ represent the reflectivity after saturation adsorption at T_s=83 K and after dissociation at T_s = 150 K,
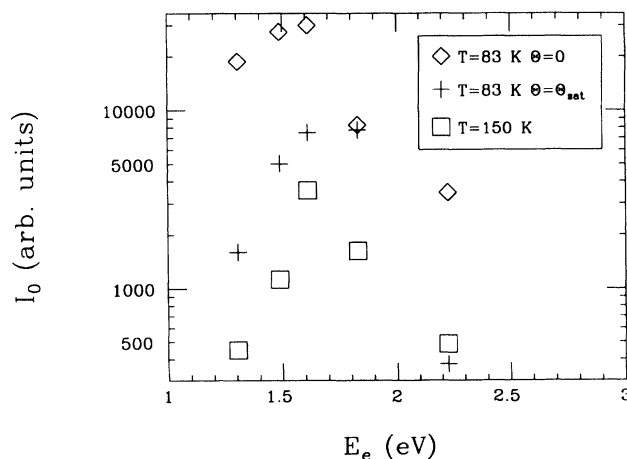

FIG. 1. Elastic intensity in the specular direction (I_0) as a function of electron energy at $\theta_e = 63°$ for the clean Ag(110) surface at T_s= 83 K ($\diamond$), the O$_2$-saturated ($\Theta_{O_2} = 0.25$) surface (+), and after dissociation (□) at 150 K. In this range of E_e the reflectivity structures are due to LEED fine structures.
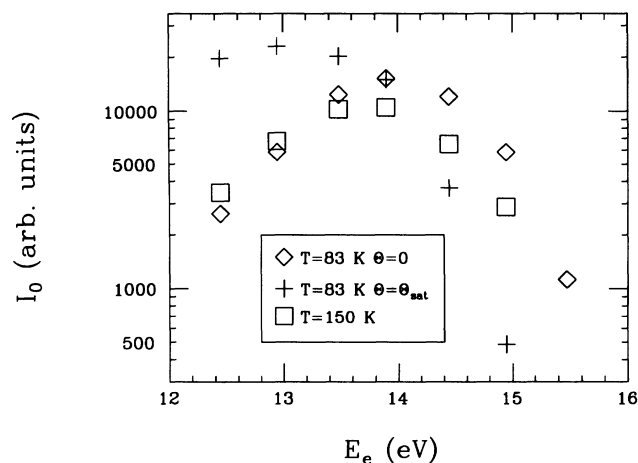
FIG. 2. Elastic intensity in the specular direction (I_0) as a function of electron energy at $\theta_e = 63°$ for the clean Ag(110) surface at T_s=83 K ($\diamond$), the O_2-saturated ($\Theta_{O_2} = 0.25$) surface (+), and after dissociation ($\square$) at 150 K. In this range of E_e the reflectivity is determined by multiple scattering.

respectively. As one can see for the lower energy range the reflectivity is globally reduced by adsorption. In the higher energy range, on the contrary, an increment is observed below 14 eV, while a reduction takes place above that energy. A global reduction is observed, however, in both cases after dissociation takes place, thus justifying the conclusions in Ref. 1. In particular cases, however, as, e.g., at E_e=15 eV, the opposite behavior is observed and the reflectivity increases when O_2 dissociates.

In Fig. 1 the high reflectivity is due to low-energy-electron-diffraction (LEED) fine structures, which appear for scattering conditions corresponding to the threshold for the appearance of an intense diffracted beam.[5] The elastic intensity in the specular direction is then modulated by interference between trajectories involving scattering off the surface barrier and off the planes of surface atoms. This effect was studied in detail theoretically by Le Bossé et al.,[6] who demonstrated that one single reflection at the barrier is sufficient to explain the oscillations in the reflectivity. The energy range at which the phenomenon occurs depends on the lattice con-

stant of the surface. Baribeau and Carette analyzed the effects of the presence of an adsorbate layer on LEED fine structures (LFS) in detail.[7] Ordered adsorption in an interstitial site causes an enhancement of the amplitude of LFS because of the smoothing of the lateral variation of the potential. Disordered adsorption, as in the present case, reduces coherence and consequently the LFS. In accord with the above discussion we observe a reduction of the reflectivity after O_2 adsorption on Ag(110) and a further reduction at dissociation.[8]

For the scattering conditions of Fig. 2 the high reflectivity is due to multiple scattering. The position of the maxima in the reflectivity is determined by the phase of the scattering amplitude and is thus difficult to predict. However, a particular feature in the intensity-energy curve can be associated with specific arrangements of the surface atoms.[9] If the position of the ion cores of the substrate is not modified such a feature will survive adsorption. In a first approximation its position will be shifted by an amount given by the change in the work function. The experiment indicates that indeed the maximum in the reflectivity moves towards lower energies by 0.8 eV after O_2 adsorption and in the opposite direction by 0.4 eV after dissociation, i.e., by the same amount as the variation of the work function.[3]

In the latter case therefore the reflectivity at a particular energy is determined by competing effects and could increase, although the surface disorders and the global reflectivity diminishes: disorder tends to decrease the reflectivity, while the shift in the energetic position of the maximum of the elastic intensity could enhance it. An energy range, wide enough to mediate these effects, should thus be considered before drawing conclusions.

IV. SUMMARY

In summary, we have shown that care must be taken when drawing conclusions based on changes in the elastic reflectivity of low-energy electrons, especially when scattering conditions corresponding to LEED fine structures occur. This analysis completes therefore our previous paper on the dissociation of O_2 molecules on Ag(110),[1] confirming the result that dissociation is connected to an increment in surface disorder.

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