Low temperature dissociation of O_2 on Ag(110): Surface disorder and reconstruction

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We studied the dissociation of molecular oxygen adsorbed on Ag(110) by electron-energy-loss spectroscopy. We observe that the dissociation of the adsorbed molecules at 150 K is connected to increased surface disorder. The elastic reflectivity is recovered at 200 K independently of coverage when the added row reconstruction of the substrate sets in.

Several authors have studied in the past the adsorption of oxygen on Ag (Refs. 1–13) and Pt (Refs. 14 and 15) single-crystal surfaces. The interest arises because oxygen chemisorbs on both systems in both atomic and molecular forms and thus allows molecular dissociation to be studied at a fundamental level. The molecular species (peroxy-type O_2^- (Ref. 13)] is in both cases stable at low temperature ($\approx$ 100 K) and dissociation occurs well below room temperature. Moreover both metals are of great importance because of their industrial relevance: Ag is a catalyst for the ethylene epoxidation ($C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$) (Ref. 16) while Pt catalyzes several important heterogeneous reactions as, e.g., the oxidation of poisonous automotive exhaust gases NO and CO.[17]

In this paper we report on a detailed electron energy-loss spectroscopy (EELS) investigation of the dissociation process on Ag(110) with the aim to study the link between the O_2 dissociation and the onset of surface reconstruction. While no definitive conclusion could be drawn on this point we find that the barrier to dissociation is overcome at the temperature of 150 K while the O covered surface reconstructs eventually at 200 K forming adrows already at very low surface coverages.

Near-edge x-ray-absorption fine structure studies of O_2 phase on Ag(110) indicate that at low temperature the O_2 molecule is adsorbed flat on the surface.[11,12] EELS shows a very low frequency for the O-O vibration, 80 meV,[3,4] compared to the gas-phase value, which is indicative that electron transfer has occurred.[4,13] Saturation corresponds to an O_2 coverage $\Theta_{O_2} = 0.25$.[2] When heating the crystal the adsorbed oxygen is partially released into vacuum and partially dissociated as shown by temperature-induced desorption.[2-4] When oxygen is dosed at room temperature or above, $(n \times 1)$ low-energy electron diffraction (LEED) structures form until the saturation coverage of $\Theta_O = 0.50$, which corresponds to a (2×1) overlayer.[1] The $(n \times 1)$ structures were investigated (for $n \leq 4$) by scanning tunneling microscopy (STM),[9] surface-enhanced x-ray absorption fine structure,[10] ion scattering,[8] and inelastic He scattering.[7] They agree that at high coverage O induces the formation of adrows in the $\langle 001 \rangle$ direction. O sits in the adrows, nearly coplanar with the Ag atoms.

The present experiment was performed with a new double pass CDA(127°) EEL spectrometer of our own construction[18] (Ibach design[19]) capable of a monochromatic current of 2×10^{-11} A in the direct beam at the energy resolution of 4 meV at which the EELS was operated. The experimental apparatus was described in Ref. 20. The feature of major relevance for this work is the possibility to dose the oxygen with a supersonic molecular beam, which allows us to obtain sticking coefficients near unity,[21] thus reducing considerably the time needed to reach the saturation coverage. This feature is important to keep surface contamination under control as the surface becomes reactive to carbonate formation in the presence of O_2.[22] The exposure dose to O_2, χ, is given by the flux and the exposure time, normalized to the surface density of Ag(110) (8.4×10^{14} atoms/cm²).[20] The crystal was cleaned by the usual procedures in ultrahigh vacuum (base pressure 1×10^{-10} mbar). The cleanliness of the surface was checked by Auger electron spectroscopy and EELS. EELS is very sensitive to carbonate (CO^{3-}) characterized by a strong dipole active vibration at 30 meV and by a weaker energy-loss peak at 100 meV.[23] Only EELS was used before the experimental runs to avoid surface contamination. The measurements were recorded with the scattering plane of the EELS aligned along the $\langle 100 \rangle$ and $\langle 1\bar{1}0 \rangle$ crystallographic directions.

Typical EELS spectra are shown in Fig. 1. The resolution was degraded to 10 meV to improve the signal-to-noise ratio. They were recorded in-specular at different temperatures T of the crystal after an exposure of $\chi = 171$ monolayers (i.e., impinging molecules per substrate atom) to a 3.5% O_2 beam seeded in He at $T = 83$ K. The surface is saturated by O_2 molecules [$\Theta_{O_2} = 0.25$ (Ref. 2)]. The O_2 layer is disordered as demonstrated by LEED analysis which shows a (1×1) structure. The spectra were recorded along $\langle 001 \rangle$ with the electron beam impinging at $\theta_e = 63°$ and an impact energy $E_e = 1.23$ eV to enhance the dipole loss probability.[24] Spectrum (a) was recorded immediately after exposure, spectra (b), (c), and (d) were recorded at different crystal temperatures, which were kept constant within 6 K by switching on and off the circulation of liquid nitrogen in the cooling system. The reported temperatures refer always to the highest reached value. The heating rate was $\approx$ 1 K/min
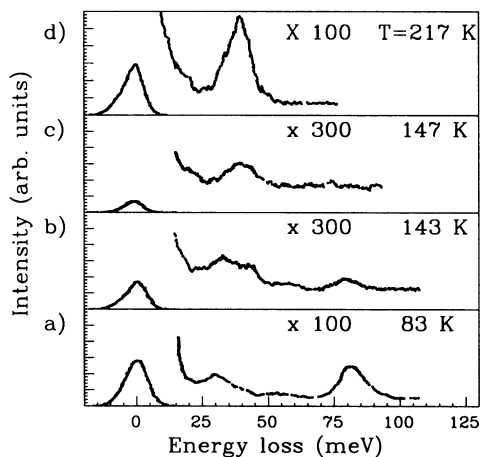
FIG. 1. EEL spectra recorded in specular after adsorption of O_2 at 83 K at $E_e = 1.23$ eV and $\theta_e = 63°$ for the temperatures (a) 83 K, (b) 143 K, (c) 147 K, (d) 217 K.

FIG. 2. Same as Fig. 1 under the experimental conditions for the electron beam $E_e = 4.5$ eV, $\theta_e = 67°$ and at an O_2 coverage $\Theta_{O_2} = 1.5\%$: (a) 83 K, (b) 165 K, (c) 220 K.

around 130 K. In (a) two peaks are present at 30 meV and 80 meV in agreement with literature.[3,4] In (b) the intensity of the 80-meV peak, I_{80}, diminishes and disappears eventually in (c) where a broad peak, of intensity I_{40}, forms at 40 meV, which corresponds to the O-Ag vibration[3,4] indicating that dissociation has occurred. In spectrum (c) the specular reflectivity I_0 has dropped to one-eighth of that in spectrum (b) but recovers to the previous value in spectrum (d), where the surface exhibits a streaky (4×1) LEED pattern. The O-Ag vibration is now well defined and nearly 4 times more intense than in (c). No shift in frequency is observed within experimental resolution. No appreaciable change with time was observed in the spectra over the duration of the experiment in (a), (c), and (d). Desorption of O_2 took place while spectrum (b) was recorded.[3] A time evolution is expected which was not investigated further.

The large change in specular reflectivity is due to surface disorder as is demonstrated by the fact that a similar drop is present under all other investigated conditions, as, e.g., shown in Fig. 2 which was recorded at a resolution of 4 meV with the electron beam impinging along $\langle 1\bar{1}0 \rangle$ at $E_e = 4.5$ eV and $\theta_e = 67°$ for the coverage $\Theta_{O_2} = 1.5 \times 10^{-2}$.

Off specular elastic intensity I_{off} grows in correspondence to the drop of the specular reflectivity as shown in Fig. 3(a), where the maximum of the elastic peak is reported as a function of crystal temperature for saturation conditions. I_{off} grows by a factor of 2–3 between $T_1 = 150$ K and $T_2 = 200$ K. I_0 is nearly constant up to 120 K when it falls within 30 K to one-eighth of its previous value [Fig. 3(a) continuous line]. I_{off} [Fig. 3(a) circles], shows a correlation with the drop in I_0. I_{80}/I_0 [Fig. 3(b) crosses] decreases even faster and disappears eventually around 145 K. At the same temperature a faint and broad loss at 40 meV [Fig 3(b) squares] appears indicating that O_2 dissociation has occurred. At 200 K a rapid recovery of the specular intensity takes place (a), accompanied by a growth of I_{40}/I_0 (b), by a shrinking of the linewidth W_{40} [full width at half maximum (FWHM)] of the 40 meV loss peak [Fig. 3(c) squares], and by a reduc-
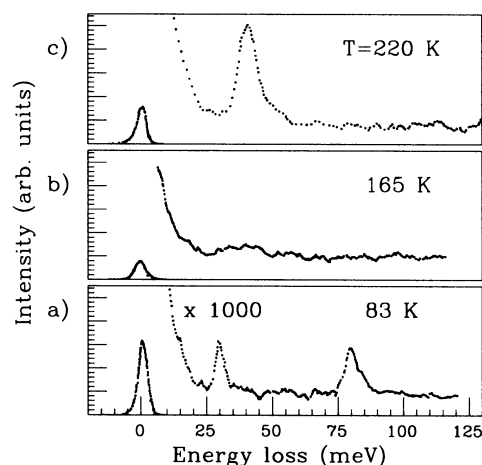
tion of I_{off} [Fig. 3(a) circles]. No LEED superstructure is observed after oxygen exposure at 80 K: neither during the heating up as long as O_2 is present ($T < 150$ K), nor as long as the reflectivity is low ($150 < T < 200$ K). A streaky (4×1) structure appears eventually for $T > 200$ K.

Surface disordering was studied for different coverages following the decrease of the specular intensity quantified by $I_0(\min)/I_0(\max)$ as defined in the inset of Fig. 4. The investigation was performed for O_2 doses χ ranging from 0.19 to 470 monolayers of pure O_2 beam ($E_i = 0.088$ eV) and from 1.5 to 170 monolayers of O_2 seeded in He (3.5%, $E_i = 0.305$ eV). The data in Fig. 4 are reported as a function of I_{80}/I_0, a quantity which is directly proportional to coverage as long as depolarization effects are negligible.[24] A large decrease in specular intensity [$I_0(\min)/I_0(\max) \approx 0.3$] is observed already for $I_{80}/I_0 < 10^{-3}$. The O_2 coverage corresponding to this ratio can be estimated to be lower than 3% by assuming
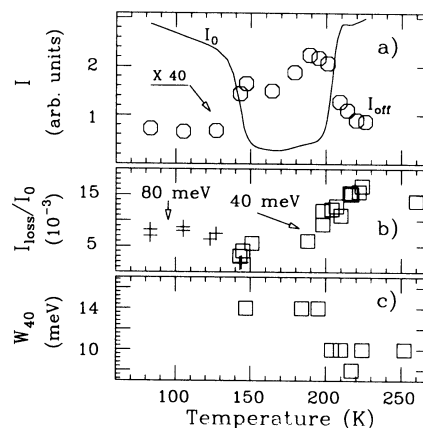

FIG. 3. Intensity of specular peak I_0, loss peak at 80 meV I_{80}, off-specular peak I_{off}, loss peak at 40 meV I_{40}, and width (FWHM) of the loss peak at 40 meV W_{40} vs crystal temperature for saturation adsorption. The correlation of the behavior of the different peaks indicates a disordering of the Ag surface at $T_1 = 150$ K and a reordering at $T_2 = 200$ K.
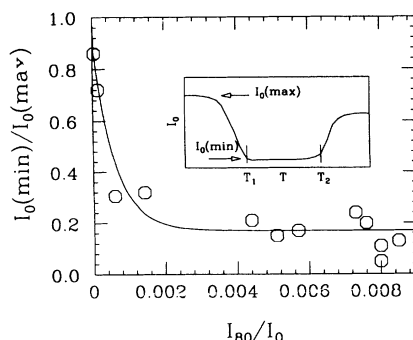
FIG. 4. Collection of the data for the drop in reflectivity $I_0(\mathrm{min})/I_0(\mathrm{max})$ (see inset) vs O_2 coverage monitored by the intensity of the O-O stretching vibration I_{80}/I_0 measured at $E_e = 1.23$ eV and $\theta_e = 63°$. The continous line is a guide for the eye.

that the maximum value $I_{80}/I_0 = 0.008$ corresponds to O_2 saturation. The large effect of dissociation on reflectivity may either indicate that disorder increases in the O layer or that the substrate is involved, too. According to Ref. 13 the charge transferred to the O_2 molecule from the substrate $(0.9e^-$ per molecule) is similar to the charge transferred to the single O adatom $(0.8e^-)$. We expect therefore the cross section of the O_2 molecule to be similar to the one of the O adatom. In fact after molecular adsorption (3% coverage of O_2) we observe a drop of 80% of the elastic reflectivity in specular with respect to the bare surface reflectivity under the same experimental conditions ($E_e = 1.23$ eV, $\theta_e = 63°$). The decrease of 70% observed when dissociation occurs is hence not too surprising as the number of scattering centers doubles. This picture is, however, complicated by multiple scattering, which may be altered by adsorption and by dissociation. The EELS data are therefore not sufficient to unambiguously prove whether the disorder is confined in the adlayer or whether it involves also the substrate. Ag-O dimers or Ag-O-Ag trimers could form and be a precursor to the added row structure forming at 200 K. STM and ion scattering investigations of this system are suggested to solve the issue. For $T_1 < T < T_2$, I_0 is very low but not zero. The variation in reflectivity is larger at low E_e where the impinging electrons are more sensitive to the surface barrier. We suggest that the residual reflectivity is due to the contribution of deeper crystallographic planes which are not affected by the disorder localized principally at the surface. This is also the reason why I_0/I_{max} saturates at higher coverages. The temperature T_1, at which the disorder sets in, does not depend

on coverage within the experimental error.

At the temperature $T_2 = 200$ K the reflectivity is recovered independently of O_2 coverage although below $I_{80}/I_0 = 1 \times 10^{-3}$, no LEED superstructure is observed. Above $I_{80}/I_0 = 1 \times 10^{-3}$ streaks or well-defined $(n \times 1)$ superstructures appear with $n \geq 3$; lower values of n are inhibited by the desorption of part of the adsorbed oxygen during the transition.[2-4]

The oxygen effectiveness in restructuring the Ag(110) surface at room temperature and high coverages to missing (or added) row reconstruction was demonstrated by He atom scattering with time of flight detection[7] and by STM.[9] Naively one would assume that the formation of the adrows should strongly affect the vibrational frequency of the O adatoms. However only a difference in the second-nearest neighbors is implied by the reconstruction compared to the twofold adsorption sites originally proposed for the nonreconstructed geometry.[1] Indeed no shift in frequency was observed over the investigated temperature range even at the highest available resolution of 4 meV (see Fig. 2).

The ratio I_{40}/I_0, on the other hand, is observed to be strongly affected at T_2 at all coverages. This effect and the recovery of the reflectivity show that adrows are formed above T_2 also at low Θ_O.

In conclusion the picture that emerges is that at temperatures below 130 K O_2 is stable and the Ag atoms sit in the (1×1) lattice sites. Above 130 K desorption sets in but has no effect on the substrate until at 145 K the dissociation barrier is overcome, and O atoms are formed. The reflectivity and EELS data are unfortunately not sufficient to discriminate between a disorder confined in the adlayer and a disorder involving also the Ag substrate. At 200 K the mobility is large enough to coalesce the Ag-O rows giving rise to $(n \times 1)$ islands as demonstrated by the streaky LEED pattern and by the recovery of the elastic reflectivity at low E_e independently of Θ_O. Following STM results[9] the observed reconstruction is of added row type. The added row mechanism of surface reconstruction is very general in presence of O for fcc (110) surfaces and was observed also for Ni(110) (Ref. 25) and Cu(110).[26,27] On these substrates however no molecularly chemisorbed specie is present as the barrier to dissociation is lower than for Ag.

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[1] H.A. Engelhardt and D. Menzel, Surf. Sci. **57**, 591 (1976).

[2] M.A. Barteau and R.J. Madix, Surf. Sci. **97**, 101 (1980).

[3] B.A. Sexton and R.J. Madix, Chem. Phys. Lett. **76**, 294 (1980).

[4] C. Backx, C.P.M. de Groot, and P. Biloen, Surf. Sci. **104**, 300 (1981).

[5] M. Rocca, P. Traversaro, and U. Valbusa, J. Electron Spectrosc. Relat. Phenom. **54,55**, 131 (1990).

[6] C.S. Ares Fang, Surf. Sci. Lett. **235**, L291 (1990).

[7] Liqiu Yang, T.S. Rahman, G. Bracco, and R. Tatarek, Phys. Rev. B **40**, 12271 (1989); G. Bracco, R. Tatarek, and G. Vandoni, *ibid.* **42**, 1852 (1990).

[8] M. Canepa, P. Cantini, F. Fossa, L. Mattera, and S. Terreni, Phys. Rev. B **47**, 15823 (1993).

[9] A. Taniguchi, K. Tanaka, T. Hashizume, and T. Sakurai, Surf. Sci. Lett. **262**, L123 (1992).

[10] L. Becker, S. Aminpirooz, A. Schmalz, B. Hillert, M. Pedio, and J. Haase, Phys. Rev. B **44**, 13655 (1991).

[11] R.J. Guest, B. Hernnäs, P. Bennich, O. Björneholm, A. Nilsson, R.E. Palmer, and N. Martensson, Surf. Sci. **278**, 239 (1992).

[12] D.A. Outka, I. Stöhr, W. Jark, P. Stevens, J. Solomon, and R.J. Madix, Phys. Rev. B **35**, 4119 (1987).

[13] P.J. Van den Hoek and E.J. Baerens, Surf. Sci. **221**, L791 (1989).

[14] H. Steininger, S. Lehwald, and H. Ibach, Surf. Sci. **123**, 1 (1982).

[15] H. Gland, B.A. Sexton, and G.B. Fisher, Surf. Sci. **95**, 587 (1980).

[16] C.T. Campbell and M.T. Paffett, Surf. Sci. **139**, 396 (1984).

[17] T. Engel and G. Ertl, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982), Vol. 4, Chap. 2.

[18] L. Vattuone, M. Repetto, and M. Rocca, Int. J. Comput. Math. Elec. Electron. Eng. **11**, 85 (1992).

[19] H. Ibach, in *High Resolution Electron Spectrometers: The Technology of High Performance*, Springer Series in Optical Science Vol. 63 (Springer-Verlag, Berlin, 1991).

[20] M. Rocca, U. Valbusa, A. Gussoni, G. Maloberti, and L. Racca, Rev. Sci. Instrum. **62**, 2172 (1991).

[21] L. Vattuone, C. Boragno, P. Restelli, M. Pupo, M. Rocca, and U. Valbusa, Phys. Rev. Lett. **72**, 510 (1994).

[22] C.T. Campbell and M.T. Paffett, Surf. Sci. **143**, 517 (1984).

[23] C. Backx, C.P.M. de Groot, P. Biloen, and W.M.H. Sachtler, Surf. Sci. **128**, 81 (1983).

[24] H. Ibach and D.L. Mills, in *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

[25] F. Besenbacher, I. Stensgaard, L. Ruan, J.K. Nørskov, and K.W. Jacobsen, Surf. Sci. **272**, 334 (1992).

[26] D.J. Coulman, J. Wintterlin, R.J. Behm, and J. Ertl, Phys. Rev. Lett. **64**, 1761 (1990).

[27] R. Feidenhans'l, F. Grey, M. Nielsen, F. Besenbacher, F. Jensen, E. Lægsgaard, I. Stensgaard, K.W. Jacobsen, J.K. Nørskov, and R.L. Johnson, Phys. Rev. Lett. **65**, 2027 (1990).