

Vibrational analysis of the 1×1 -O overlayer on Ru(0001)

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A densely packed 1×1 -O overlayer with an oxygen coverage of 1.0 (relative to the number of substrate surface atoms) was prepared on Ru(0001) by sequential dissociation of O_2 and NO_2 and studied by means of high-resolution electron-energy-loss spectroscopy. Two dipole-active modes were observed at 81 and 7.3 meV due to a ν_{\perp} (Ru-O) stretch mode and a new surface mode, respectively. The value of ν_{\perp} (Ru-O) is shifted to higher energy compared to that for the known 2×2 -O and 2×1 -O adlayers at smaller oxygen coverages. These measurements indicate that the O_2 dissociation is kinetically hindered for oxygen coverages larger than 0.5. [S0163-1829(97)03107-X]

I. INTRODUCTION

Chemisorption studies with well-defined single-crystal surfaces are crucial for the exploration of the elementary steps in heterogeneously catalyzed chemical reactions. So far the oxygen chemisorption on Ru(0001) is fairly well understood. Oxygen chemisorbs dissociatively and the oxygen atom is bonded in the hcp threefold-hollow sites. Two ordered overlayers are observed at room temperature, a 2×2 structure at an oxygen coverage of $\theta_O = 0.25$, and three domains of a 2×1 structure, rotated by 120° with respect to one another, at $\theta_O = 0.5$, which is the maximum oxygen coverage that could be achieved so far.¹⁻³ In the unit cell of the 2×1 -O phase, the mutual separation between neighboring O atoms is one and two Ru lattice constants, respectively, so that—at least from purely geometrical arguments—one could speculate that also a 1×1 -O phase with $\theta_O = 1$ might be accessible in which the O atoms form the same lattice as the Ru(0001) substrate. Actually, there has been one speculation on such a high-density phase based on the high-pressure experiments of a catalytic oxidation experiment.^{4,5} The lack of a high-coverage phase for oxygen adsorption on Ru(0001) may be due to kinetic hindrance of dissociation. If this is the case, one may hope to prepare a high-coverage phase by exposure to a high oxygen pressure or by exposure to a more strongly oxidizing molecule such as NO_2 . Indeed, the latter approach has been successfully employed on Pt(111),^{6,7} and more recently also on Ru(0001) for which a 1×1 -O with a negligible amount of subsurface oxygen⁸ and a surface with $\theta_O > 1$ (Refs. 9 and 10) could be prepared.

In the present paper we report on high-resolution electron-energy-loss spectroscopy (HREELS) measurements for the 1×1 -O overlayer on Ru(0001), which was prepared by first exposing the Ru(0001) surface to O_2 at room temperature until saturation was reached, and subsequently exposing it to NO_2 at a sample temperature of 600 K. After preparation, a sharp 1×1 low-energy electron diffraction (LEED) pattern was observed, and the results presented in the following show clearly that this phase is a pure 1×1 -O overlayer. The Ru-O stretch mode ν_{\perp} (Ru-O) is found at 81 meV, i.e., shifted to a higher frequency compared to the $\theta_O = 0.5$ phase. Furthermore, we observe a new loss at 7.3 meV, which is

assigned to a phonon in the RuO double layer taking into account a specific change in the spacing between the first and second Ru layers of the Ru substrate found in a recent structural analysis by LEED.⁸

The paper is organized as follows: after an experimental section II, we present and discuss our results in Sec. III, which is followed by our conclusion.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) apparatus with a base pressure of 1×10^{-11} mbar, which was achieved by a pumping line free of oil consisting of a Ti sublimation pump (TSP), a turbomolecular pump with magnetic suspension (NT 340M, Leybold), a drag pump (TCP015, Balzers), and a diaphragm pump (MD4T, Vacu-brand). The apparatus consisted of two chambers—the upper chamber contained an argon ion gun, a quadrupole mass spectrometer, and LEED optics. The lower chamber housed a high-resolution electron-energy-loss spectrometer for recording vibrational spectra. The two chambers were separated by a valve, so that the lower chamber was kept at a pressure of 3×10^{-11} mbar, during exposure of the sample in the upper chamber to gas doses. The recently developed HREEL spectrometer (DELTA 0.5, Vacuum Science Instruments) delivered 6.1 pA at a full width at half maximum (FWHM) of 0.97 meV of the straight-through beam. The spectrometer consists of a double monochromator and one single analyzer. The analyzer and the sample are rotatable to allow the selection of the angle of incidence and the angle of emission. The HREEL spectra were taken at a 60° angle of incidence with respect to the surface normal and in specular geometry if not noted otherwise. The energy resolution was set to be 1.9 meV across the sample, and typical count rates in the elastic peak of about 3×10^5 counts/s were achieved. All the HREEL spectra were recorded with the sample at room temperature.

The sample was mounted using W wires in narrow slits at the edges of the sample and was heated by electron bombardment from the backside. The sample temperature was measured by a Ni-Cr/Ni thermocouple spot welded to the upper edge of the sample. Cleaning of the surface was achieved by cycles of sputtering and annealing. The cleanliness was verified by LEED and HREELS. Coverages mentioned else-

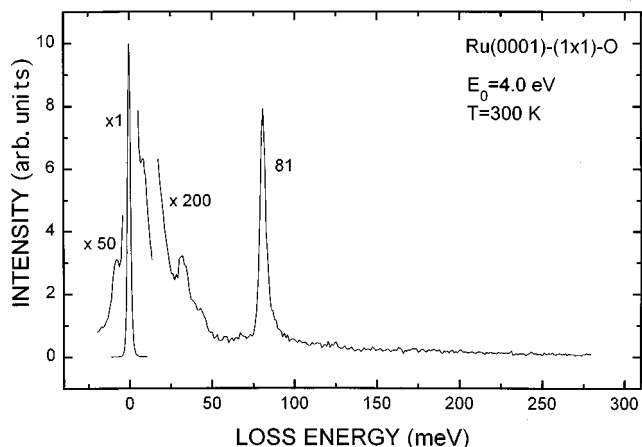


FIG. 1. HREEL spectrum for the Ru(0001) 1×1 -O surface at a sample temperature of 300 K. The primary energy is 4.0 eV. The different scaling factors of the intensity are indicated. The FWHM of the elastic peak, measured on the bare Ru surface, is 1.9 meV.

where in this paper are given relative to the number of substrate surface atoms.

The preparation of the 1×1 -O adlayer with a coverage of $\theta_{\text{O}}=1$ was the same as in Ref. 8, i.e., the 1×1 -O phase was accomplished by first exposing the Ru(0001) surface to O_2 at room temperature until saturation was reached; i.e., the 2×1 -O phase with a coverage of $\theta_{\text{O}}=0.5$ was formed. Subsequently the Ru(0001)- 2×1 -O surface exposed to NO_2 at a pressure of about 5×10^{-7} mbar for 15 min. The sample temperature was set to 600 K so that during decomposition of NO_2 into adsorbed O and NO (the dissociative sticking coefficient of NO_2 is about 1), only O remained on the surface while NO was instantly released into the gas phase. [Note that NO desorption on Ru(0001) is completed at about 500 K.¹¹]

III. RESULTS AND DISCUSSION

A. The pure 1×1 -O phase

The preparation of the 1×1 -O phase has been already mentioned above. After oxygen saturation by dosing O_2 at room temperature a sharp 2×2 (three domains of 2×1) LEED pattern was observed and transformed into a sharp 1×1 one by subsequently dosing NO_2 at sample temperature of 600 K. The HREEL spectrum recorded in a wide energy range is shown in Fig. 1. The dominant feature at 81 meV is assigned to the vibration of O adatoms perpendicular to the surface. This mode is similar to the vibration of O in the 2×2 -O and 2×1 -O phases except for the larger vibrational energy^{2,3,12,13} (see Fig. 2 below). A small feature at 31 meV is attributed to a phonon excitation of the Ru substrate.¹³ Most interestingly, we observe a so far unobserved loss at 7.3 meV including the related gain peak.

In Fig. 1 we present the HREEL spectrum up to 300 meV so that the intramolecular stretch modes of the most likely contaminations, such as CO and NO, may be observable. Apparently there are no other features in the spectrum than those related to O or Ru. This is quite reasonable since for the 1×1 -O phase we do not envisage any adsorption site far enough separated from oxygen to accommodate an adsorbed

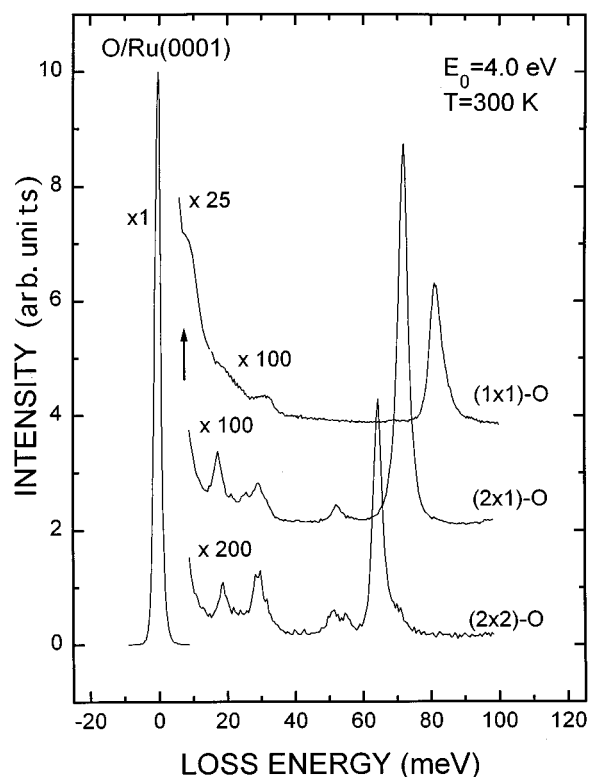


FIG. 2. HREEL spectra of the three ordered oxygen overlayers 2×2 -O ($\theta_{\text{O}}=0.25$), 2×1 -O ($\theta_{\text{O}}=0.5$), and 1×1 -O ($\theta_{\text{O}}=1$).

molecule. The spectrum of Fig. 1 clearly shows that a pure 1×1 -O overlayer was achieved and confirms the result of the LEED intensity analysis⁸ in which a conclusion was drawn on a negligible amount of subsurface oxygen. This differs from the result of Mitchell and Weinberg⁹ who observed the formation of the subsurface oxygen (RuO_x), which was characterized by the appearance of bands at 93 (740 cm^{-1}) and 103 (820 cm^{-1}) meV in HREELS. They also found some residual NO left at the surface.

In Fig. 2 we compare the HREEL spectra of the different oxygen phases. One recognizes that the 1×1 phase fits to the trend of increasing energy of the $\nu_{\perp}(\text{Ru-O})$ stretch mode with oxygen coverage. Furthermore, we have observed that $\nu_{\perp}(\text{Ru-O})$ approaches 54 meV in the limit $\theta_{\text{O}} \rightarrow 0$ (Ref. 14) where we expect isolated oxygen atoms. The latter observation enlarges the energy range of the $\nu_{\perp}(\text{Ru-O})$ mode, which ranges from 54 to 81 meV. The direction of this shift is not well understood. From TDS as well as from calculations based on density functional theory¹⁵ (DFT) the binding energy decreases with coverage. For the hcp site the change is from 5.5 eV (for the 2×2 structure) to 5.28 (2×1) and 4.84 (1×1). If the potential normal to the surface gets shallower one would expect the frequency of the perpendicular motion to decrease accordingly, opposite to the experimental result. Dipole-dipole interaction leads to a shift into the direction indicated by the experiment but the expected amount is only in the percentage range so that this effect cannot explain the large shift observed in the experiment. It seems that, with increasing coverage, the potential well gets stiffer from the lateral repulsive interaction between the adsorbed atoms so that the frequency may be larger although the depth of the potential well is shallower. It is interesting to note that a

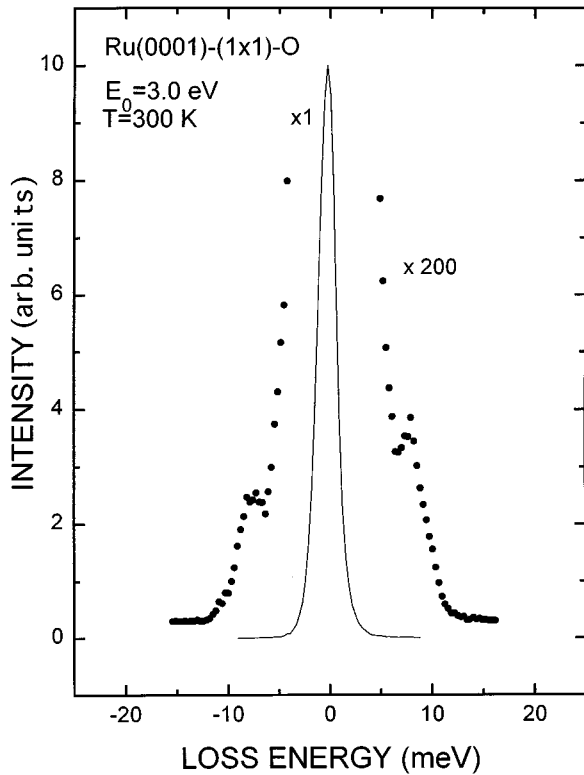


FIG. 3. HREEL spectrum of the Ru(0001) 1×1 -O surface near to the elastic peak including loss (positive loss energy) and gain side (negative loss energy). The elastic peak with a FWHM of 1.9 meV is the same as in Fig. 1.

similar effect is observed for other chemisorbed atoms, e.g., N on Ru(0001) (Refs. 13 and 16) and for Cs on Ru(0001).¹⁷

B. The low-energy mode of the 1×1 -O overlayer

In Fig. 3 we show the HREEL spectrum near to the elastic peak in greater detail. Both loss and gain peaks are well resolved. By curve fitting using a standard technique with Gaussian line shapes the average energy between loss and gain is found at 7.30 ± 0.05 meV. The relative intensity of the loss and gain peak is in good agreement with the sample temperature. At 300 K the first excited state of this phonon is occupied to some degree so that the electron beam can pick up its energy by annihilation of a phonon. The loss at 7.3 meV is not observed for the other oxygen phases as can be seen from Fig. 2 and Refs. 2,3,12 and 13. The low energy of this mode indicates that the uppermost Ru layer may participate and that a structural change within the first Ru layer may occur during the increase of θ_O from 0.5 to 1.0. Fortunately, the structures of the different oxygen phases are already determined in LEED intensity analyses.^{8,18,19} The parameters are summarized in Table I, which includes also the values for the 1×1 -O phase from a recent analysis.⁸ Oxygen occupies always the hcp threefold-hollow site. The Ru-O bond length stays nearly constant whereas the Ru-O layer spacing somewhat increases. This curious trend is due to the fact the both the first and the second Ru layers are buckled for the low-coverage phases. The first and second Ru interlayer spacings are taken from the LEED data by averaging the positions of the buckled atoms. The most remarkable

TABLE I. Structural parameters for three oxygen phases on Ru(0001).

	2×2 -O (Ref. 18)	2×1 -O (Ref. 19)	1×1 -O (Ref. 8)
Ru-O bond length (\AA)	2.03 ± 0.06	2.02 ± 0.06	2.00 ± 0.03
Ru-O layer spacing (\AA)	1.18 ± 0.03	1.20 ± 0.02	1.25 ± 0.02
First Ru interlayer spacing (%)	-4.0 ± 1.4	$+0.2 \pm 0.9$	$+3.7 \pm 1.4$
Second Ru interlayer spacing (%)	-1.9 ± 1.4	$+0.0 \pm 0.9$	-0.5 ± 1.8

result in comparing the different structures is the change of the first Ru interlayer spacing, which changes from -4.0 to $+0.2$ and 3.7% . The quarter monolayer of oxygen does not remove the first Ru interlayer contraction of -2.3% found for the bare Ru(0001) surface.²⁰ The interlayer spacing changes with coverage and at $\theta_O = 1$ the trend is even reversed; i.e., there is now an expansion by $+3.7\%$. A similar expansion (of $+3.1\%$) has been found for the O/Zr(0001) system for which 1 ML of oxygen is expected to be accommodated in octahedral sites between the first, second, and third surface layers.²¹ In our case, both LEED intensity analysis⁸ and our HREELS measurements indicate that there is no noticeable amount of subsurface oxygen. According to the work of Mitchell and Weinberg subsurface oxygen gives rise to dipole-active modes at 92 and 102 meV, which are not observed in our measurements. Only after several runs of our experiment we got some indications of subsurface oxygen. The main effect was that the 7.3-meV phonon was smeared out considerably. There is a quite obvious relation between the change in interlayer spacing and the occurrence of the 7.3-meV phonon. Oxygen attracts some charge from the first Ru layer, which leads to a weakening of the bond between the first two Ru layers. These results and the low frequency of the mode lead us to believe that it is a phonon in the RuO double layer. The nature of this mode has to be clarified by future experiments and calculations.

C. Quenching of the lower symmetry derived modes

In general, HREELS is a very appropriate tool in exploring surface phonons including their dispersion. This is achieved by recording HREEL spectra in off-specular geometry. In the case of adsorption, if the overlayer is ordered and has a smaller surface Brillouin zone (SBZ) compared with the substrate SBZ, some substrate phonon modes can be folded back to Γ from the high symmetry points of the substrate SBZ and may become observable in specular geometry if they are dipole active.²²⁻²⁴ This quite general phenomenon is also observed for the O-Ru(0001) system as discussed in the following.

The O adatoms occupy hcp threefold-hollow sites in all three oxygen phases.^{8,18,19} The bare Ru(0001) surface and its 2×2 -O adlayer exhibit C_{3v} symmetry.^{2,3} The symmetry is lowered to C_s in the 2×1 -O phase^{2,3} while it is raised again to C_{3v} in the 1×1 -O phase. By folding the M point of the substrate SBZ back to Γ in the 2×2 -O phase two dipole-active substrate phonons were observed, besides the perpendicular $\nu_{\perp}(\text{Ru-O})$ mode. They are found at 18 meV

(145 cm^{-1}) and 29 meV (230 cm^{-1}), respectively, and are assigned to the shear vertical (SV) and the parallel (P , similar to a breathing mode together with the oxygen atom) mode, respectively.³ In the 2×1 -O phase, two substrate phonons, which are dipole active and derived from the M point of the substrate SBZ folded back to Γ , are observed and assigned to the SV (17 meV) and P (28 meV) modes, respectively. In addition, there is one parallel mode $\nu_{\parallel}(\text{Ru-O})$ at 55 meV (440 cm^{-1}) observed at Γ , which is due to the lower symmetry of C_s ,³ i.e., because of this lower symmetry, the two Ru-O normal modes [$\nu_{\perp}(\text{Ru-O})$ and $\nu_{\parallel}(\text{Ru-O})$], which lie within the reflection plane perpendicular to the surface, belong to the A' symmetry and are therefore dipole active. The other parallel mode is not dipole active and is not observable in specular HREELS.^{2,3}

In contrast, the 1×1 -O adsorbate SBZ is the same as that of the substrate and there is no folding back of substrate modes in this phase. Since the symmetry is raised to C_{3v} , out of the three normal modes of oxygen, only the A_1 mode, $\nu_{\perp}(\text{Ru-O})$, which is polarized perpendicular to the surface, is dipole active and, therefore, observable in specular HREELS. The other two degenerate modes of E symmetry are polarized strictly parallel to the surface, and are dipole inactive.²⁵

Figure 2 exhibits HREEL spectra for the three different oxygen phases. The results for the 2×2 -O and the 2×1 -O phases are in good agreement with the data in the literature.^{2,3,12,13} In the 2×2 -O phase the adsorption-derived substrate SV and P modes are at 19 and 29 meV , respectively, while in the 2×1 -O phase, the SV and P modes are at 17 and 29 meV , respectively, and the lower C_s symmetry derived parallel mode $\nu_{\parallel}(\text{Ru-O})$ is at 53 meV .

Now we come back to the 1×1 -O phase. In Fig. 2, we can clearly see, as we expected, that the SH and P modes are not observed for the 1×1 -O phase due to the change in

symmetry. A small peak at 31 meV is observed now, which is due to a Ru phonon since it is also observed on the bare surface.¹³ In the 2×2 and 2×1 phases this loss is probably hidden by the surface phonon modes at 29 meV .

IV. CONCLUSION

Using HREELS evidence is given that a well-defined densely packed 1×1 -O overlayer can be prepared on Ru(0001) by sequential dissociation of O_2 and NO_2 . This result confirms that O_2 dissociation on Ru(0001) is kinetically hindered for oxygen coverages above 0.5. The oxygen Ru stretch mode $\nu_{\perp}(\text{Ru-O})$ is observed at 81 meV in the dipole scattering mode, i.e., at the Γ point of the surface Brillouin zone. Its energy is shifted to a higher value compared to the other oxygen overlayers at lower oxygen coverages. The amount and direction of this shift are not understood yet. From the decrease in binding energy with oxygen coverage one would expect a shift into the opposite direction. The potential well perpendicular to the surface becomes steeper with coverage although its depth decreases. A second dipole-active mode is found at 7.3 meV . Its low energy indicates that it may be due to a phonon in RuO double layer, which is somewhat decoupled from the second Ru layer as indicated by a recent structure determination.⁸ The nature of this mode has to be clarified by future experiments and calculations.

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