

Precursor Adsorption of Oxygen on Ni(111) and the Activation Energy for Chemisorption

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Measurements of electron transmission spectra and work function ϕ of a Ni(111) surface held at $T=5.5$ K during exposure to O_2 provide direct evidence for a precursor adsorption preceding dissociative chemisorption. The form of the electron transmission spectra indicates that the precursor adsorption involves oxygen molecules. Subsequent warming of the oxygen-covered surface leads to the chemisorption state. An analysis of the kinetics of the increase in ϕ that accompanies this transition gives an activation energy of ~ 13 meV for the reaction.

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Despite extensive studies of the adsorption of oxygen on clean metal surfaces, it is still a matter of controversy whether oxygen dissociates and reacts immediately with metal surfaces to form chemical bonds or is first adsorbed in a mobile "precursor" state. Attempts to understand the dependence of the sticking coefficient (s) on coverage (θ) led some years ago to kinetic models based on a mobile precursor adsorption.¹ Such models would account for the experimental observation in many systems that $s(\theta)$ remains essentially constant almost to the saturation value of θ and then rapidly decreases to zero.²

In an attempt to observe the precursor state directly, several studies of the adsorption process have been conducted at low temperatures.³⁻¹³ In the case of metals that react relatively weakly with oxygen, adsorption of molecular oxygen was recently reported [at $T \sim 100$ K for Pt(111)⁷ and $T \sim 140$ K for Ag(110)⁸]. For metals which react strongly with oxygen, however, recent studies of O_2 adsorption on Al(111),⁶ W(110),⁹ Ni(110),¹⁰ and Re(0001)¹² performed at temperatures as low as ~ 20 K have all indicated the existence of physically adsorbed O_2 molecules only after about a monolayer of chemisorbed oxygen atoms has first covered the surface. The reports have therefore concluded that, for these surfaces, either there is no precursor state or that the activation energy (E_A) for chemisorption is very small. On the other hand, studies on evaporated polycrystalline metal films provide persuasive evidence for an adsorption phase that precedes chemisorption. Such a precursor adsorption could be stabilized at 7 K on Cu.¹¹ Temperatures of 15 K or below were found necessary for effective stabilization on Ag, Ni, Pb, Sn, and W.^{4,5} While useful in showing that precursor adsorption of oxygen on metals is a fairly general phenomenon, the film results do not provide information about the behavior of surfaces of known

geometry that is needed for a detailed theoretical understanding. In this report we provide direct evidence, for the first time, for the precursor state to chemisorption of oxygen on Ni(111). We also show that for chemisorption on this surface E_A is indeed very small (~ 13 meV), and that temperatures below 20 K are needed to observe the precursor state.

The low-temperature experiments were carried out in a UHV system with a base pressure of less than 10^{-10} Torr. A variable-temperature ($5.5 \leq T \leq 800$ K) cryostat was used for the oxygen adsorption measurements. The cleanliness and crystallinity of the surface were monitored by Auger electron spectroscopy and LEED. The Ni surface was cleaned by cycles of Ar-ion sputtering, heat treatment in oxygen, and annealing at 800 K. Retarding-potential spectra of sample current $I(E)$ versus the energy E of the normally incident electrons were obtained by use of a field-emission electron source.¹⁴ The derivative of $I(E)$ with respect to E was taken digitally and fitted with the functional form of the energy distribution of the field-emitted electrons to extract the work function ϕ , the threshold energy for electrons to enter the metal.¹⁴ Changes in ϕ could be measured with an accuracy of ± 0.01 eV.

Gas exposure was made by filling the experimental chamber with O_2 for prescribed dosages which are given in langmuirs ($1 \text{ L} = 10^{-6}$ Torr sec). As a result of the low temperature of the radiation shields near the sample surface the temperature of the O_2 gas (which is released from a flask at room temperature) is lower than room temperature, but certainly higher than that of the sample surface. The presence of the radiation shields also reduces the amount of gas that reaches the surface for a given exposure. Calibration of the oxygen exposure was therefore made by use of a quartz-crystal microbalance at 5.5 K in place of the sample and

the assumption $s=1$ (which is realistic for adsorption of oxygen on surfaces at 5.5 K). According to this calibration, believed to be accurate to $\pm 20\%$, an exposure of 1 L (pressure being measured by the ionization gauge) corresponds to 1×10^{14} oxygen molecules/cm² which is equivalent to a coverage of 0.1 monolayer [1 monolayer (ML) coverage defined to be one oxygen atom per Ni surface atom for the Ni(111) surface].

Retarding-potential plots of the current $I(E)$ collected by the sample are shown in Fig. 1(a) for clean Ni(111) and for the indicated oxygen cover-

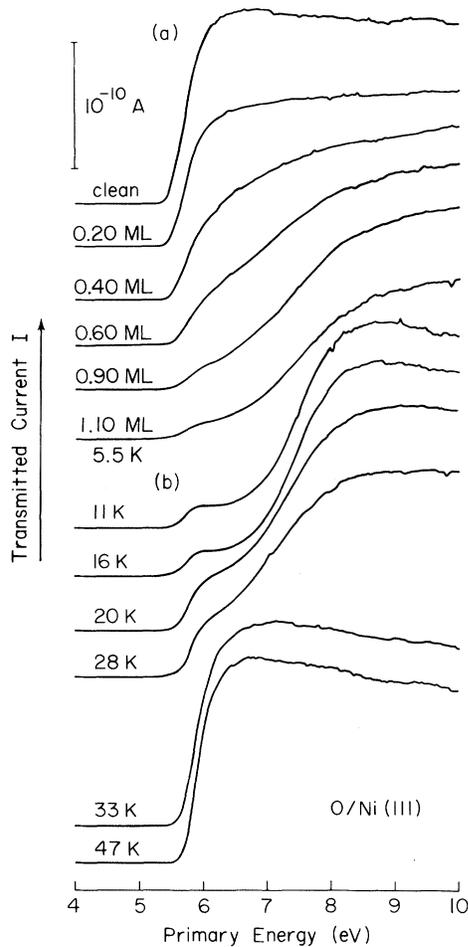


FIG. 1. Retarding-potential plots of the current $I(E)$ collected by the sample as a function of the incident electron energy. (a) $I(E)$ plots are shown for clean Ni(111) and for the indicated oxygen coverages. Sample temperature is 5.5 K. (b) The effect of warming the oxygen-covered surface on the $I(E)$ plots is shown. The change in the shape of the $I(E)$ curves is associated with condensed oxygen molecules which chemisorb/desorb as T is increased (see text). The shifts in the work function of the surface deduced from the onset of these $I(E)$ curves are shown in Fig. 2.

ages. The sample temperature is 5.5 K. The work function of clean Ni(111) determined from the $I(E)$ spectrum is $\phi = 5.4 \pm 0.1$ eV in good agreement with reported values for the (111) face of Ni ($\phi = 5.19$ to 5.46 eV).¹⁵ The effect of warming the oxygen-covered sample is shown in Fig. 1(b).

The presence of chemically adsorbed oxygen was monitored by means of the work-function change ($\Delta\phi$) with respect to ϕ of the clean surface. Figure 2 shows that oxygen adsorption on Ni(111) held at 77 K raises ϕ by an amount, $\Delta\phi$, that increases with coverage and saturates at about 0.32 eV.¹⁶ Exposure with the surface maintained at 5.5 K (Fig. 2) leads to a very different result. The maximum increase in ϕ is now only 0.07 eV, which is much smaller than that observed at 77 K. The majority of the oxygen adsorbed directly on the surface at 5.5 K is evidently in a different physical state than it is at 77 K. Furthermore, the experiments show that the low-temperature phase is converted to the high-temperature phase on heating. Depositing 1.1 ML of oxygen at 5.5 K and then warming the surface to 77 K caused the same large increase in $\Delta\phi$ as a saturation dose of oxygen applied directly at 77 K did. Details of this transition are discussed below.

We refer to the adsorption phase stabilized at 5.5 K as the precursor and identify the adsorption oc-

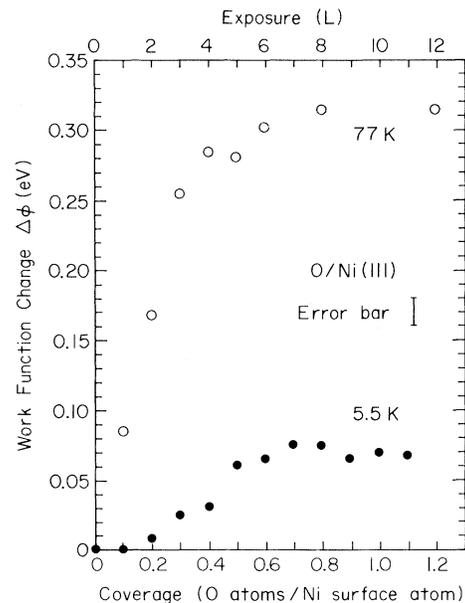


FIG. 2. The change in the work function $\Delta\phi$ as a function of oxygen exposure for Ni(111) at 5.5 K (closed circles) and at 77 K (open circles). The lower scale (coverage) is based on the oxygen exposure calibration at 5.5 K assuming unity sticking coefficient, and is valid for the 77-K data approximately and only for low coverages.

curing at 77 K as chemisorption. This latter assignment is in accord with results of polycrystalline film experiments which show that $T < 12$ K is needed to prevent the formation of strong surface chemical bonds between Ni and oxygen atoms,⁵ and with measurements on the low-index faces of Ni reported in the literature.¹⁶⁻¹⁸ Reported saturation values of $\Delta\phi$ for Ni(110) are the same for deposition of oxygen at 85 K¹⁸ and 20 K,¹⁰ indicating one dominant type of adsorption mechanism for the entire temperature interval. Photoemission measurements¹⁰ of oxygen adsorption on Ni(110) at 20 K confirm that the shift in ϕ is correlated with chemisorption of the first layer of oxygen.

We believe that the adsorption phase stabilized at 5.5 K involves oxygen molecules. Evidence is provided by the electron transmission spectra (Fig. 1) which show a suppression of $I(E)$ in the range $5.5 < E < 7$ eV. This suppression is not observed for any coverage of oxygen at 77 K and it disappears when the condensed layers of O₂ chemisorb/desorb for $T > 30$ K [Fig. 1(b)].¹⁹ A similar suppression of $I(E)$ in the range of 0–1.5 eV above the work function was also observed in spectra taken after O₂ adsorption on Sn(001) and Sn(110) in the temperature range $5.5 < T < 30$ K.¹³ Bader *et al.*²⁰ attribute the suppression, which they observed for multilayers of O₂ adsorbed on polycrystalline Pt at 15 K, to an inner potential of -3.3 eV in the O₂ film. As shown in Fig. 1, the suppression is a sensitive indicator of the presence of molecular O₂.

The small $\Delta\phi$ observed at 5.5 K may be due to a finite amount of chemisorption. This is possibly due to the relatively high temperature of the gas. To illustrate the time (t) and temperature dependence of $\Delta\phi$, the clean surface at 5.5 K was exposed to 6 L of oxygen. Immediately after the exposure, a $\Delta\phi$ of 0.08 eV was observed, consistent with the results shown in Fig. 2. The sample was then held at $T=5.5$ K for about 38 min. During this time, $\Delta\phi$ did not change by more than ± 0.01 eV, indicating no further chemisorption of oxygen at 5.5 K once the gas was adsorbed and brought to thermal equilibrium with the surface. The oxygen-covered sample was then warmed, and $\Delta\phi$ was recorded as a function of both t and T . The data are summarized in Fig. 3, where the circles indicate the measured $\Delta\phi$ as a function of T and the dotted curve shows the relation between T and t . The zero of time in the scale on the right-hand side of Fig. 3 is taken as the time when the oxygen exposure at 5.5 K ended. The varying heating rate indicated by the dotted curve in Fig. 3 was used to illustrate the dependence of $\Delta\phi$ on t as well as T . In particular, note

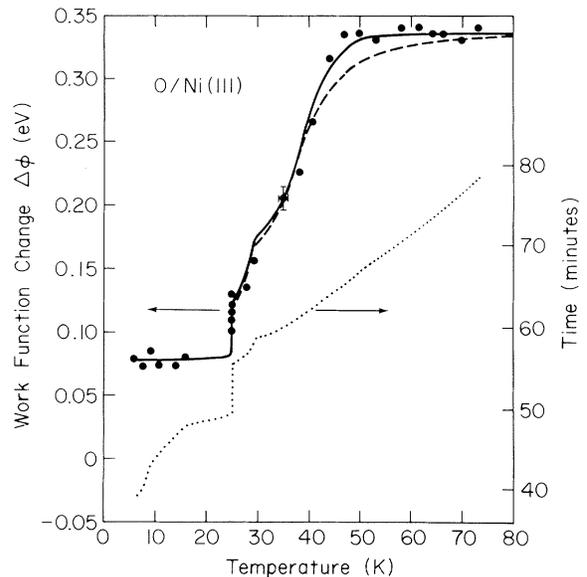


FIG. 3. The change in the work function as the Ni(111) surface covered with 0.60 ML of oxygen at 5.5 K is warmed (circles). The dotted curve shows the dependence of temperature on time. The solid and dashed curves are results of calculations based on Eq. (1).

that while the sample was kept at $T=25 \pm 0.5$ K for about 8 min, $\Delta\phi$ increased by about 0.03 eV. In Fig. 3, the heating was continued up to $T \sim 100$ K. Additional oxygen exposure at this T resulted in no further increase in ϕ .

To explain quantitatively the variation of $\Delta\phi$ with T in Fig. 3, we use a simple model for the time and temperature dependence of the reaction (transition from the precursor state to chemisorbed oxygen). Assuming that $\Delta\phi$ is proportional to the amount of chemisorbed oxygen on the surface, we define $\delta(T, t) = \Delta\phi^{\text{sat}} - \Delta\phi(T, t)$ as a measure of the fraction of the surface which is covered with oxygen and has not yet reacted with it [$\Delta\phi^{\text{sat}} = 0.33$ eV is the saturation value of $\Delta\phi$ for $T > 50$ K (Fig. 3)]. We consider an n th order temperature-activated reaction equation for the chemisorption rate,

$$d\delta/dt = -\alpha\delta^n \exp(-E_A/kT), \quad (1)$$

where α is a constant. If temperature is increased linearly with time, i.e., $dT = C dt$, in Eq. (1) t can be replaced with T to obtain

$$\delta(T) = \delta_0 \exp \left[-\frac{\alpha}{C} \int_{T_0}^T \exp \left(-\frac{E_A}{kT'} \right) dT' \right] \quad (2)$$

for $n=1$, and a similar expression for $n=2$. In Eq. (2), T_0 is equal to 5.5 K and δ_0 is equal to $\Delta\phi^{\text{sat}}$ minus the value of $\Delta\phi$ at 5.5 K prior to heating. With use of the experimental heating rate, and the

assumption that over small temperature intervals (0.2 K) the heating rate is constant, $\delta(T)$ can be evaluated by numerical integration to fit the data in Fig. 3 (α and E_A are adjustable parameters). The solid and dashed curves in Fig. 3 represent the best fits for $n=1$ and $n=2$, respectively. The parameters used are $\alpha=20 \text{ min}^{-1}$ and $E_A=14 \text{ meV}$ for $n=1$, and $\alpha=220 \text{ min}^{-1}$ and $E_A=19 \text{ meV}$ for $n=2$. The solid curve is in better agreement with the data. Considering the experimental uncertainty, however, we cannot rule out the second-order equation. For both $n=1$ and $n=2$, ranges of α and E_A exist for which reasonable agreement between the experimental data and the calculated curves is found. For instance, for $n=1$, $11 < E_A < 17 \text{ meV}$ with $7 < \alpha < 60 \text{ min}^{-1}$ result in fair agreement with the experimental data.

Similar analyses of data obtained by repeating the above experiment for different initial oxygen dosages and heating rates result in values for E_A and α which are comparable to those given in the above paragraph. On the basis of our results so far we estimate E_A to be $13 \pm 6 \text{ meV}$. This value of E_A is compatible with the activation energies measured by Chottiner and Glover for the chemisorption of oxygen adsorbed on thin evaporated polycrystalline metal films at 4 K and heated to higher temperatures.^{4,5} The activation energies found for the initial stages of chemisorption were 12 meV for Ni and 35 meV for Sn.

The low-temperature results presented in this paper are direct evidence for the existence of a precursor adsorption state of oxygen on Ni(111) prior to chemisorption. Because of the small size of E_A , temperatures below about 20 K are required for a direct observation of this state. It is also demonstrated in this report that accurate work-function measurements provide quantitative information which can be used to characterize the adsorption process and obtain activation energies.

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