Adsorption of oxygen on Cu(110)

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Abstract. This paper describes molecular beam measurements of the initial sticking coefficient for dissociative chemisorption of O_2 on Cu(110). The sticking coefficient has been measured as a function of translational energy (E_i), angle of incidence (θ_i) and surface temperature (T_s). Two sticking channels are identified, an activated, 'direct' dissociation at high E_i and T_s and a precursor-mediated trapping mechanism at low E_i and T_s. The activated channel ($E_i > 50$ meV, $T_s = 300$ K) shows a sharp increase in S_0 from 0.2 at 50 meV and saturates with $S_0 = 0.48$ for energies above 100 meV. The initial sticking coefficient scales with the normal component of the translational energy and this channel is attributed to direct, translational activation via a barrier (≈ 50 meV) located early in the surface O_2 coordinate. Below 50 meV the sticking coefficient is independent of both translational energy and angle, and increases steadily as T_s is reduced. The precursor state is tentatively identified as a weakly bound physisorbed state by analogy with the O_2/Ag and Pt systems.

1. Introduction

The thermal adsorption of O_2 on Cu(110) has been studied using various techniques such as XPS, UPS, LEED and ellipsometry to monitor oxygen coverage as a function of surface temperature T_s and O_2 exposure. Ordered overlayers of atomic O are formed at room temperature, a p(2 × 1) structure with the O occupying the long bridge site and a c(6 × 2) structure at higher exposure, extra O atoms occupying a fourfold site [1]. There is conflicting evidence for molecularly adsorbed O_2 states on copper [2,3,4], at temperatures of 100 K or above oxygen is dissociatively adsorbed on this surface and evidence for a molecular state is weak [1,5,6]. By contrast both Ag(110) [7], Ag(111) [8] and Pt(111) [9,10] show stable molecular chemisorbed and physisorbed states and sticking on these surfaces proceeds via a trapping–dissociation mechanism.

Sticking probabilities for O_2 on copper show a marked face dependence, being facile on the (110) face ($S_0 \approx 0.2$) but rather slower on the (100) and (111) faces ($S_0 \approx 10^{-3}$ [11,12]). The initial sticking probability increased to 0.77 at low temperatures ($T_s = 100$K) [13] and, for coverages $\theta < 0.5$, showed a nearly linear decrease with coverage θ indicating mobile precursor kinetics and island growth [14]. Pudney and Bowker [14] have recently investigated the dependence of S_0 on the gas temperature using a thermal (Maxwell–Boltzmann) beam. S_0 increased with gas temperature, showing an Arrhenius dependence with $E_a = 3$ kJ mol^{-1} (30 meV). Here we report the translational energy and surface temperature dependence of O_2 dissociative chemisorption on Cu(110).

2. Experimental procedure

The experiments were performed in a UHV, molecular-beam scattering system (VSW Scientific Instruments). The chamber was pumped by a 9″ diffusion pump, cold trap and a large aperture liquid nitrogen cooled titanium sublimation pump, giving base pressures of a few times 10^{-11} torr after bake-out at 150 °C. The two-stage beam system comprised a 50 μm quartz nozzle with a 300 μm skimmer and a 1.2 mm final collimating aperture giving a 4 mm spot at the crystal. Both stages were pumped by 6″ diffusion pumps giving typical working pressures of $\approx 10^{-4}$ and $\approx 10^{-7}$ in the first and second stages with the beam on and nozzle backing presures of 0.7 to 1.5 bar. The nozzle temperature could be varied between 300 and 1000 K to control the translational energy of the beam. Gas mixtures of between 1 and 3% O_2 in a monatomic carrier gas (Ne, Ar and Xe) were prepared in a reservoir volume using a capacitance manometer. Translational energies are calculated from the nozzle temperature and carrier gas mixture. The beam could be interrupted by a beam flag in the second beam stage and another flag was positioned in the main chamber, directly in front of the crystal.

The Cu crystal was cut from a 5 N copper rod, polished and oriented to better than 0.25° of the (110) plane. The crystal could be cooled to 100 K and heated to 1100 K using electron-beam heating, the sample temperature being measured using a chromel-alumel thermocouple. The sample was cleaned by repeated cycles of Ar^+ ion bombardment (500 eV, ≈ 1 μA for 10 min) and annealing to 1070 K. Surface analysis facilities consisted of LEED, Auger and atom scattering. The LEED patterns resulting from the clean and the p (2 × 1) and c (6 × 2) ordered oxygen overlayer structures were consistent with those reported by others and showed the usual dependence on oxygen exposure.

Sticking coefficients were measured using the direct reflection technique of King and Wells [15]. The quadrupole mass spectrometer was positioned behind the sample and recorded the mass 32 signal. The beam was admitted to the scattering chamber and then the flag removed allowing it to strike the crystal. Measuring the decrease in O_2 partial pressure gives the absolute sticking probability directly. The O_2 was removed between runs by Ar^+ ion bombardment and annealing. Data points are therefore the result of single measurements which limits the precision of the values for S_0.

3. Results

The initial sticking coefficient for dissociative chemisorption of O_2 on Cu(110) is shown in figure 1 as a function of O_2 translation energy for a 300 K sample and a normal incident beam. The sticking coefficient is nearly constant at ≈ 0.2 for translational energies $16 < E_i < 50$ meV, rising abruptly between 50 and 100 meV to saturate with $S_0 = 0.48$ for higher energies. The value of $S_0 = 0.2$ obtained at low translational energies is in good agreement with the thermal (Maxwell–Boltzmann) measurements ($S_0 = 0.2$ [14], $S_0 = 0.17$ [16]. Pudney and Bowker [14] observed an activation energy of 2.8 kJ mol^{-1} (30 meV) from an Arrhenius plot of S_0 as a function of the nozzle temperature, similar to the translational energy at which we observe S_0 to increase. The lower energy limit of our measurements (16 meV) was as low as could conveniently be achieved using O_2 seeding in Xe carrier gas. No indication was found for any increase in S_0 at low E_i. The abrupt change in the sticking coefficient above
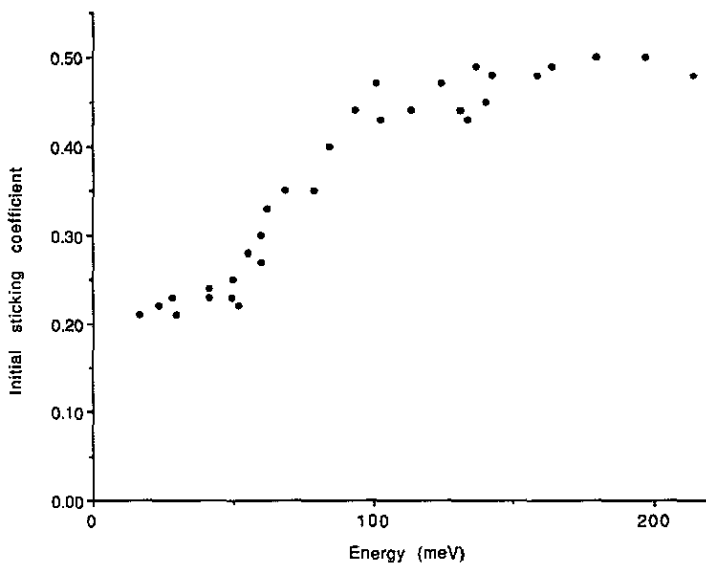
Figure 1. Initial sticking coefficient for dissociative chemisorption of O_2 on Cu(110) as a function of the translational energy of the incident beam. The translational energy is varied by seeding a few percent of O_2 in an inert carrier gas. The data points are individual determinations of S_0 by the direct reflection technique and the scatter in the data reflects short term variations in the beam flux and pumping speed.

50 meV suggests a change of mechanism, dissociation being independent of energy below this with a direct, activated channel opening above $E_i = 100$ meV.

The dependence of S_0 on the incidence angle θ_i was measured for a range of beam energies. Figure 2 shows the angle dependence for translational energies between 16 and 160 meV for scattering along the [110] azimuth. Measurements were also taken scattering along the [001] azimuth, across the rows of Cu atoms, but no difference was apparent in the sticking probability $S_0(\theta_i)$ within the scatter of the data. The normal energy scaling and insensitivity of S_0 to scattering azimuth indicate that the corrugation does not play an obvious role in the dissociation. At low translational energy ($E_i \leqslant 50$ meV) the sticking coefficient is essentially independent of the incidence angle whereas at higher energies S_0 decreases with θ_i . This is shown in figure 3 as a plot of S_0 against the normal translational energy $E_\perp = E_i \cos^2 \theta_i$ The open symbols represent data taken as a function of angle and this shows a good correlation with the normal incidence data (solid points), indicating a normal energy scaling. This is in contrast to the thermal beam data [14] where a total energy scaling was observed. However at low energy S_0 is nearly independent of both E_i and θ_i and no distinction can be made between the two scaling laws.

The initial sticking coefficient was measured as a function of the surface temperature T_s for several translational energies and is shown in figure 4 for beam energies of 52 and 103 meV. For the lower beam energy S_0 shows a steady increase as the surface temperature is reduced, reaching ≈ 0.6 at 100 K, close to the value of 0.77 seen for adsorption at thermal energies on an 83 K sample [13]. The results for the 103 meV beam show the dissociation to be independent of T_s down to 130 K below which the sticking probability increases once again as the trapping channel becomes efficient.
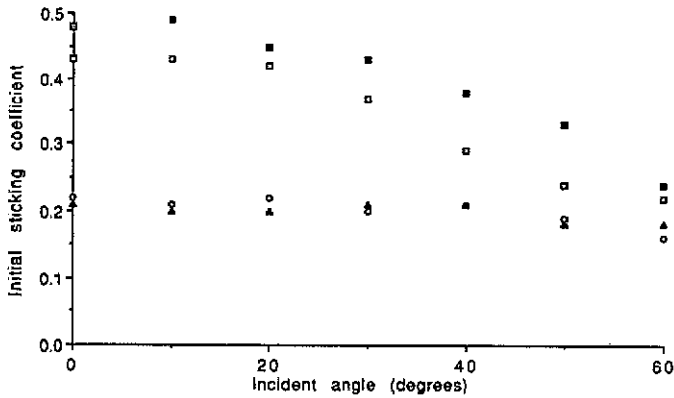
Figure 2. Variation of initial sticking coefficient with angle to the surface normal, (⊡) $E_i = 159$ meV, (□) $E_i = 103$ meV, (○) $E_i = 52$ meV, (△) $E_i = 16$ meV. For the lower beam energies in the range where S_0 is independent of E_i, S_0 shows no dependence on the normal energy, $E_\perp = E_i \cos^2 \theta_i$, whereas at higher energies S_0 decreases with $E_\perp$. No dependence on scattering azimuth was observed.
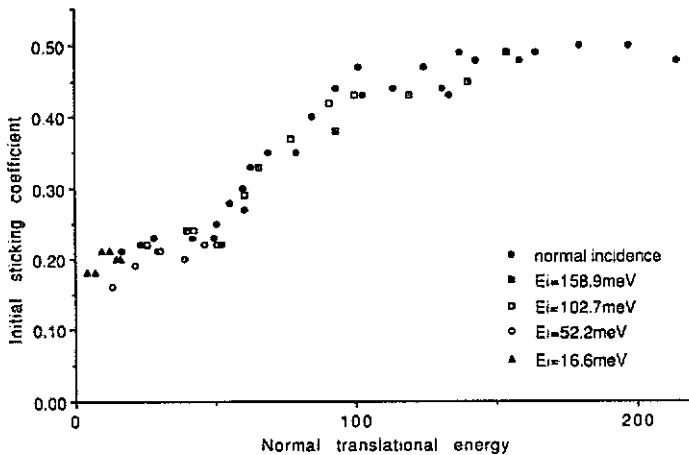

Figure 3. Normal energy dependence of the sticking coefficient. The solid points are the normal incidence data while the open points show the variation of S_0 with angle for a fixed incident beam energy.

4. Discussion

The sticking data is interpreted in terms of two distinct mechanisms for dissociative chemisorption on Cu(110). At high translational energy ($E_i > 50$ meV) and high surface temperatures the dissociation occurs via a direct, activated process which becomes increasingly dominant as the energy is increased. The sticking coefficient scales with the translational energy normal to the surface and is independent of surface temperature. This can be interpreted as the phase space above the barrier opening up as E_i is increased in the 50 to 100 meV range. In a simple one-dimensional picture the barrier is assumed to lie in the surface O_2 coordinate and to be sensitive to the surface site and geometry, giving rise to the observed energy dependence. It is not clear whether this barrier lies before or after the predicted O_2^- molecular state. The
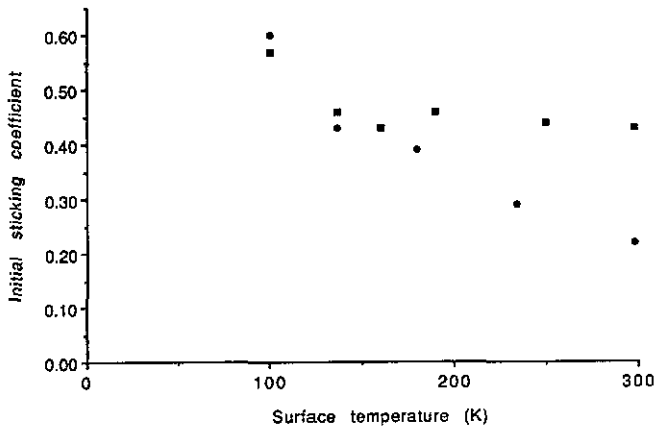
Figure 4. Surface temperature dependence of S_0 for different beam energies, (■) $E_i = 103$ meV and (●) $E_i = 52$ meV.

normal energy scaling indicates that conversion of parallel and perpendicular energy prior to the barrier is inefficient. Such mixing might be expected to occur if trajectories sampled the molecular state for a significant time period prior to arriving at a barrier sited between the molecular and dissociatively adsorbed states [17,18]. The apparent absence of a stable molecularly chemisorbed state indicates that there is only a low (or no) barrier to dissociation on copper and suggests that the barrier to activated dissociation lies in the entrance channel, prior to any chemisorbed molecular state.

At low translational energy and low surface temperature dissociation occurs via trapping into a precursor state followed by thermally activated dissociation. Unlike the Pt(111) and Ag(110) surfaces, where stable molecularly chemisorbed and physisorbed species have been identified, there is little evidence for a stable molecular state on copper. Oxygen dissociation on Pt(111) has been studied in detail and shows a similar $S_0(E_i, T_s)$ dependence and magnitude to that observed here, but with an energy scaling that is intermediate between normal and total energy scaling [9]. In both the Ag (110) [7] and Pt(111) [10] cases trapping occurs directly into both the physisorbed and chemisorbed molecular wells. The identity of the trapping state on Cu is unclear. Unlike the $O_2/Pt(111)$ system, $O_2/Cu(110)$ shows a T_s dependence only below 300 K. S_0 does not show an increase at low E_i as would be expected from classical models of the trapping probability when E_i becomes comparable to the well depth. This suggests that the well depth of the trapping state is rather low, although it was shown for $O_2/Pt(111)$ that the trapping coefficient was rather less than predicted from the well depth of the molecularly chemisorbed state [9]. If the trapping probability is assumed to be independent of T_s at low E_i, a kinetic model for the competition between desorption and dissociation gives a difference of 12 meV between the barrier heights for the two steps, reflecting the rather low temperature at which S_0 starts to increase. The small difference in barrier heights may be fortuitous but suggests a weakly bound physisorbed state is responsible, as has been invoked for the Pt and Ag trapping channels [8,10]. The small well depth of this weakly bound precursor would also help to explain why no enhancement was seen for the trapping probability at low translational energy.

5. Conclusion

Dissociative chemisorption of O_2 on $Cu(110)$ occurs via two channels, an activated, direct dissociation via an early barrier at high translational energies and high surface temperatures and a trapping-dissociation channel, probably via a weakly bound physisorbed precursor, at lower energies and temperatures.

Acknowledgments

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