Initial sticking probability of O₂ on Cu(410)

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A B S T R A C T

We present here a supersonic molecular beam investigation of the initial sticking probability (S₀) for the O₂/Cu(410) system. Over the temperature range between 130 and 800 K adsorption occurs dissociatively and S₀ increases up to ~0.7 with beam energy, indicating that the process is activated. S₀ is larger for angles corresponding to molecules impinging on the step rises, implying that defects are more reactive than terrace atoms. The saturation value of S₀ is however lower than for the parent low Miller index surfaces; this indicates that the reactivity at nanosized terraces is reduced compared to extended Cu(100) surfaces. A precursor mediated adsorption path is observed at the lowest translational energy (Eᵢ) below 150 K, as in the case of O₂/Cu(110) and at variance with O₂/Cu(100). At low T and higher energy and for all Eᵢ, at T > 150 K, adsorption occurs directly, yielding a sticking probability independent of surface temperature.

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1. Introduction

Oxygen adsorption on Cu surfaces has been extensively studied [1] in the attempt to clarify the mechanisms underlying Cu₂O formation [2,3]. Cuprous oxide is an industrially important direct-gap semiconductor with a band gap of 2 eV, promising for application to photovoltaic cells. Most investigations concentrated therefore on the high coverage regime required to ignite oxide formation. The initial stages of oxygen adsorption attracted less attention and were limited so far to Cu(110) [4,5] and to Cu(100) [6–8], thus neglecting the role of defects and under-coordinated sites. However a very recent study on sputtered Cu(100) [9] and some investigations on the O/Cu(410) system were performed. Cu(410) is the energetically most stable geometry since it corresponds to the stable faceting observed on Cu upon O₂ exposure [10]; Cu(610), e.g., reorders forming (410) facets and its step rises coalesce to produce smaller (401) facets; the process is complete after exposure to 1000 L of O₂ at room temperature (RT) and subsequent annealing to 520–550 K but, due to the high reactivity of Cu, the first effects are present already after 2 L [11]. Although O/Cu(410) is very well ordered, allowing for a precise structural analysis, the detailed structure of the O/Cu(410) layer remained controversial for a long time [10]. The most recent model, elaborated by Vlieg and coworkers [10] and based on X-ray diffraction experiments and DFT calculations, suggests that for an atomic oxygen coverage Θ = 0.5 ML the adatoms occupy two non-equivalent sites – at the bottom of the step and in the fourfold hollow in the middle of the (100) terrace – of the undistorted Cu(410) surface, thus forming a c(2 x 2) mesh. On the contrary, at low coverage adsorption at twofold sites at the top of the step edges is suggested [12].

O₂ adsorption on Cu(100) and Cu(110) is activated. For hyperthermal energy, the initial sticking probability, S₀, scales with translational energy, Eᵢ, and it is nearly independent of surface temperature, T, for both surfaces. At thermal energy the picture is, however, more complex since S₀ decreases significantly with T for T > 150 K on Cu(110) [5] and on sputtered Cu(100) [8], while it increases on flat Cu(100) [6]. This phenomenon was explained by the presence of a physisorbed precursor in the first two cases and in terms of phonon assisted adsorption for flat Cu(100).

A vast literature deals with the influence of steps and defects on oxygen adsorption at metal surfaces [13], e.g. Pt [14] and Ag [15,16]. Their effect is more or less striking, depending on the nature of the substrate. Generally low coordination sites at steps decrease the activation barrier for dissociation and imply a consequently higher dissociation probability, as it is the case for O₂ on Pt(533) [14].

A similar effect is present also for O₂/Ag(410) [15] and O₂/Ag(210) [16]. While on Ag(100) and Ag(110) adsorption...
occurs molecularly below 150 K, on these vicinal surfaces dissociative adsorption is observed already at 100 K. On Ag(210), where the size of the terraces is limited to one lattice spacing, molecular adsorption is not observed even at 100 K, indicating that the step causes the O₂ molecule to dissociate promptly and that molecular adsorption is destabilized below a critical terrace width.

We report here on a supersonic molecular beam study of the initial stages of O₂ adsorption on Cu(410). The geometry of this surface is reported in Fig. 1. It consists of three atom rows wide (100) nano-terraces separated by monoatomic, (110)-like step rises. The angle of incidence of the impinging molecules, θ, is measured with respect to the surface normal. As the scattering plane is aligned across the steps and the surface forms an angle of 14° with the (100) terraces, θ = −14° and +31° correspond to dosing normally to the terraces and to the step rises, respectively. We find that at low E, the presence of steps increases the surface reactivity with respect to Cu(100). On the contrary, S₀ is globally reduced at hyperthermal energy due to the inhibited reactivity of nanosized terraces, a phenomenon already reported for stepped and nanostructured Ag [15].

2. Experimental

The experimental apparatus consists of a supersonic molecular beam (SMB) coupled to an ultra high vacuum (UHV) chamber [17]. The latter is equipped with a home-made high resolution electron energy loss spectrometer (HREELS), a low energy electron diffraction (LEED) optics, an Auger spectrometer and usual cleaning facilities. The Cu(410) crystal is a 10 mm diameter disk, cut within 0.1° of a single crystal plane. It is mounted onto a Tantalum holder and can be heated by electron bombardment and cooled to 130 K by a liquid nitrogen flux. The sample is cleaned by repeated cycles of sputtering with Ne ions of 1.5 KeV energy followed by annealing to 900 K for 3 min at a base pressure of ∼10⁻¹⁰ mbar; surface cleanliness is checked by HREELS and Auger spectroscopy.

Oxygen is dosed by SMB and its translational energy is varied between 0.09 and 1.4 eV by heating the ceramic nozzle and/or by seeding the gas in He (4% concentration). Systematic measurements of the sticking probability are performed with the retarded reflector method of King and Wells [18] (KW in the following) and are affected by an error of ±0.035. None or negligible recombinative oxygen desorption is detected when heating the sample, in agreement with literature [5]. In accord with this, we find a lower value of S₀ when the O₂ exposure is performed on a surface cleaned only by annealing to 900 K than after a complete cleaning cycle. Since the surface is HREELS clean in both cases, oxygen incorporation into the bulk must occur efficiently. To ensure full reproducibility of the experimental data, a complete cleaning cycle was performed before each experiment.

3. Results and discussion

Previous HREELS investigations [19] showed that oxygen adsorption at Cu(410) occurs dissociatively over the temperature range 130 < T < 700 K and that oxide formation takes place only at high coverage, as confirmed by XPS [20,21]. At low T a single vibrational mode at 46 meV is detected, independently of the angle and energy of the impinging O₂ molecule [19]; such mode has been assigned to disordered adatoms adsorbed both at bridge sites at the step edge and at fourfold hollow sites at terraces. This loss does not correspond to the thermodynamically favoured state since, upon annealing to room temperature, it disappears and a new vibration is observed at 34 meV. We tentatively assigned it to isolated O atoms at the long bridge site. The temperature required to produce such a change indicates that a large barrier is present between the (unstable) 46 meV state and the most stable one. Indeed the 46 meV mode is still observed when dosing at grazing incidence with molecules impinging step down. When temperature and coverage are high enough to generate an ordered overlayer, a loss at 38 meV is found, due to the convolution of two unresolved components at terraces and at steps.

Fig. 2 reports the S₀(T) curve for O₂ beams of E = 0.09 and 0.39 eV impinging normally to the Cu(410) surface. For E = 0.09 eV the initial sticking probability drops abruptly from 0.34 at 145 K to 0.22 at 165 K and remains nearly constant for higher T.

At E = 0.39 eV, on the contrary, S₀ is independent of T. Such behaviour indicates that two adsorption mechanisms are present: a direct one, contributing ~0.2 to S₀ for E = 0.09 eV, independent of T and active at all temperatures and energies, and a precursor mediated one, superimposing to it below 150 K and active only at the

Fig. 2. S₀(T) curve measured for O₂ on Cu(410) at E = 0.09 eV and at E = 0.39 eV. The beam impinges normally to the (410) plane. The presence of a molecular precursor for T < 150 K is evident by the drop of S₀(T) at 150 K for E = 0.09 eV. The line connecting the low energy data is just a guide for the eye. The line passing through the 0.39 eV data results, on the contrary, from a linear best fit and is compatible with S₀ being independent of T.
of note that, on sputtered Cu(100) [9] at 300 K, the large increase only the direct adsorption channel is active and recorded for temperatures in the range from 323 to 383 K, in which

tions, are the most reactive sites. We do not believe this mecha-
ism to be relevant for the present case since at least 0.1 ML of

tancies should be present to account for the observed increase

of vacancies which, according to density functional theory calcula-

tions can overcome it. Since the surface structure is not symmetric

with respect to $\theta = 31^\circ$, the shift in the maximum position may arise from the combination of energetic and geometrical effects.

(c) $S_0$ is nearly angle independent at the highest $E_i$. This behaviour corresponds to saturation of $S_0$ above the adsorption barrier.

(d) At $E_i = 0.09$ eV $S_0$ is larger at positive than at negative $\theta$, in accord with a higher reactivity of the step rises. In Fig. 4 the initial sticking probability is plotted vs. $E_i$ for three different $\theta$. The experimental curve for $\theta = 0^\circ$ is compared with the corresponding ones for Cu(100) [6,8] (solid curve) and Cu(110) [5] (dashed line). We notice that

(e) $S_0$ increases monotonously saturating for higher energies.

(f) The data for $E_i > 0.2$ eV fall below those of the corresponding low Miller index surfaces indicating that at hyperthermal energy the high reactivity at the steps is overcompensated by a reduced reactivity of (100) nano-terraces. A similar result was found also for sputtered Ag(100) [26,27].

![Fig. 3. $S_0(\theta)$ curves measured for O$_2$ on Cu(410) parametric in translational energy (the corresponding $E_i$ values, expressed in eV, are indicated for each set of data). The directions corresponding to normal incidence on the (110) and (100) nanofacets are shown by arrows. The error bar is the same for all curves.](image)

The data shown in Figs. 3 and 4 of this paper were recorded for temperatures in the range from 323 to 383 K, in which only the direct adsorption channel is active and $S_0$ is constant within experimental error. They are therefore directly comparable with each other.

The identification of the two different paths is based on the different temperature dependence of $S_0$ and it is supported by the angle or energy dependence of the latter quantity [22]. We further note that, on sputtered Cu(100) [9] at 300 K, the large increase of $S_0$ at low translational energy was explained with the formation of vacancies which, according to density functional theory calculations, are the most reactive sites. We do not believe this mechanism to be relevant for the present case since at least 0.1 ML of vacancies should be present to account for the observed increase of $S_0$ while the surface was sputtered and annealed before each experiment and it presented a sharp LEED pattern.

In Fig. 3 we show the initial O$_2$ sticking probability as a function of the angle of incidence and parametric in $E_i$. Coherently with the lowest $E_i$. The data shown in Figs. 3 and 4 of this paper were recorded for temperatures in the range from 323 to 383 K, in which only the direct adsorption channel is active and $S_0$ is constant within experimental error. They are therefore directly comparable with each other.

![Fig. 4. Left panel: Initial sticking probability vs. translational energy $E_i$ for O$_2$ on Cu(410) at different angles: $\theta = -45^\circ$, $0^\circ$ and $+45^\circ$. The right panel compares the data at normal incidence with those of Cu(100) (continuous line [8]) and Cu(110) (dashed line [5]).](image)
For $E_i < 0.2$ eV the data are lower than $S_{\text{Cu}(110)}^0$ and close to $S_{\text{Cu}(110)}^0$. From Fig. 3 we see that $S_0$ is larger for positive than for negative $\theta$. Since the fraction of the impinging molecules colliding with the step rise is higher at positive than at negative angles (vanishing at $\theta = -59^\circ$), the larger value of $S_0$ is indicative of the higher reactivity of under-coordinated sites.

4. Conclusions

In summary we find that dissociative $\text{O}_2$ adsorption at Cu(410) is activated, similarly to the case of the parent low Miller index surfaces, and that different adsorption mechanisms are present. At low energy both a direct path and a precursor mediated channel exist. The former is independent of $T$ and contributes $\sim 0.2$ to $S_0$, while the latter is operative only below 150 K. Such an additional, precursor mediated, adsorption path, present on the Cu(410) surface at low $T$, exists also on Cu(110) [5] and on sputtered Cu(100) [8], but not on pristine Cu(100). At high energy $S_0$ is independent of $T$ and saturates at $\sim 0.7$. This result indicates that the enhanced reactivity at the under-coordinated step sites, is overcompensated by a reduced activity at nanosized terraces, as observed also for stepped Ag surfaces.

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