Enhanced selectivity towards O$_2$ and H$_2$ dissociation on ultrathin Cu films on Ru(0001)

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The reactivity of Cu monolayer (ML) and bilayer films grown on Ru(0001) towards O$_2$ and H$_2$ has been investigated. O$_2$ initial sticking coefficients were determined using the King and Wells method in the incident energy range 40–450 meV, and compared to the corresponding values measured on clean Ru(0001) and Cu(111) surfaces. A relative large O$_2$ sticking coefficient ($\sim$0.5–0.8) was measured for 1 ML Cu and even 2 ML Cu/Ru(0001). At low incident energies, this is one order of magnitude larger than the value observed on Cu(111). In contrast, the corresponding reactivity to H$_2$ was near zero on both Cu monolayer and bilayer films, for incident energies up to 175 meV. Water adsorption on 2 ML Cu/Ru(0001) was found to behave quite differently than on the Ru(0001) and Cu(111) surfaces. Our study shows that Cu/Ru(0001) is a highly selective system, which presents a quite different chemical reactivity towards different species in the same range of collision energies. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4746942]

I. INTRODUCTION

The possibility of tuning the catalytic activity of a surface has always been very attractive from both the experimental and theoretical points of view. It is generally known that modifying the lateral lattice constant of a surface by introducing strain can strongly influence its reactivity.[1–5] In this framework, metal layers epitaxially grown onto single-crystal metal substrates with different lattice constants have been proposed as very efficient selective catalysts in reactions involving H$_2$ molecules.[6] Certainly, the electronic effects induced by the substrate on the overlayers also must play a central role apart from strain in the renewed catalytic properties. Another fascinating route for artificially tuning surface chemical reactivity is given by metal alloys which in most cases show very complex geometrical and electronic properties and differ deeply from their constituent materials.[7,8] As an example, it has recently been shown by a STM study how isolated Pd atoms alloyed into Cu(111) can efficiently dissociate H$_2$ molecules and allow them to spill over onto the host metal, strongly reducing the dissociation barrier for H$_2$ on Cu(111).[9]

The bimetallic interface of a thin Cu film grown on a Ru(0001) surface has always been considered an attractive system, since the first Cu layer grows pseudomorphic on the Ru(0001) surface.[10–15] The 1 ML Cu film has a next-nearest neighbor distance of 2.73 Å, and is therefore laterally expanded by 5.5% compared to the Cu(111) surface. The 2 ML Cu film relaxes the strain uniaxially, showing three domains of a stripe-phase reconstruction and an average lateral distance of 2.61 Å.[11] Reactivity to oxygen as a function of Cu film thickness was previously investigated by means of STM at room temperature.[14] Evidence for a correlation between surface reactivity and population of the surface electronic state was reported, showing a maximum in the chemical reactivity for 1 ML Cu films, for which the surface state is empty.

Transition metal oxidation processes have attracted a huge interest over the last decades from both an experimental and a theoretical point of view, due to the central role that such materials usually play in industrial catalysis. Calculating potential energy surfaces (PESs) for O$_2$ molecules interacting with transition metals is often a very tough and time consuming task since, in contrast to the case of H$_2$,[16] the adiabatic spin transition from the triplet gas-phase state to the singlet state of the oxygen atom adsorbed on the surface must be included in the simulations. Recently, the experimental sticking coefficient of O$_2$ on the Al(111) surface[17] has been theoretically reproduced by including multiple PESs associated with different spin configurations in the dynamics.[18,19] To get more insight into the non-adiabatic transitions which take place during the molecule-surface interaction, new experimental data about O$_2$ sticking on transition metals are required.

In this paper, O$_2$ dissociation probabilities for the clean Ru(0001) surface and for 1 ML Cu and 2 ML Cu/Ru(0001) have been evaluated by means of the King and Wells method.[20] Kinetic energy of the incident oxygen molecule has been varied between 40 and 450 meV. A quite high reactivity towards O$_2$ has been observed for both Cu monolayer and bilayer, especially for beam energies higher than 200 meV and the surface at room temperature. This is the most striking finding of the present study, since this value is a factor of 5–10 larger than the one measured on Cu(111) under the same

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incident conditions, which has been measured also in our current work. Moreover, reactivity to H_2 molecules was found to be almost zero for 1 ML Cu and 2 ML Cu on Ru(0001), in agreement with previously reported first-principles six-dimensional dynamics calculations.[21] Besides this systematic study for O_2 and H_2, we checked the adsorption of water employing a D_2O beam of ca. 250 meV incident energy on 2 ML Cu/Ru(0001). Although we could not measure absolute sticking probabilities in this case, our data clearly show that water adsorbs in a very different way on this system than on the clean Ru(0001) and Cu(111) surfaces.

II. EXPERIMENTAL DETAILS

Experiments have been carried out in a helium atom scattering (HAS) apparatus described in Ref. 22. Briefly, it consists of a three-stage differentially pumped beam system and an 18 in. diameter UHV scattering chamber. The free jet expansion is produced through a nozzle of $d = 10$ μm diameter. The nozzle temperature T_n can be varied between 100 and 700 K, allowing a variation of the H_2 beam energy between 25 and 175 meV during diffraction measurements. The estimated energy spread is about 1% for He and 10% for H_2 beams. The angular distribution of the scattered atoms can be analyzed with a quadrupole mass spectrometer mounted on a two-axis goniometer. The base pressure in the chamber is typically $\sim 3 \times 10^{-10}$ mbar. The crystal is mounted on a standard manipulator, modified to allow azimuthal rotation of the sample as well as heating to 1500 K and cooling to 100 K. The sample temperature was measured with a type C thermocouple spot-welded to the sample.

O_2 incident kinetic energies have been varied between 40 and 450 meV. They were controlled by seeding oxygen in a carrier gas (either Ne or He) and varying the oxygen concentration and the nozzle temperature. Since this HAS apparatus is not equipped with a time-of-flight system, the mean translational energy of the incoming O_2 molecules has been estimated as follows:[23]

$$E_T = \left[(1-x)\frac{m}{M} + x\right]^{-1} C_p T_n, \tag{1}$$

where m and M are the molecular weights of the light and heavy gas, C_p is the mean heat capacity averaged according to gas concentrations, and T_n is the nozzle temperature. The estimated uncertainty on the beam energy can reach 10% of its mean value.

Sticking measurements were performed using the method devised by King and Wells.[20] The HAS apparatus has been equipped with two copper flags: the first one is placed in the second stage of the beam system, in order to stop the beam from entering the main chamber. The second one is placed in the UHV scattering chamber, just in front of the sample, to prevent molecules from hitting the surface. It is relevant to underline that in the present experiments the beam quality (regarding angular divergence and energy spread) is the same for both diffraction and sticking probability measurements. The latter have been performed at an angle of incidence $\Theta_i = 15°$. The main reason for using this value, instead
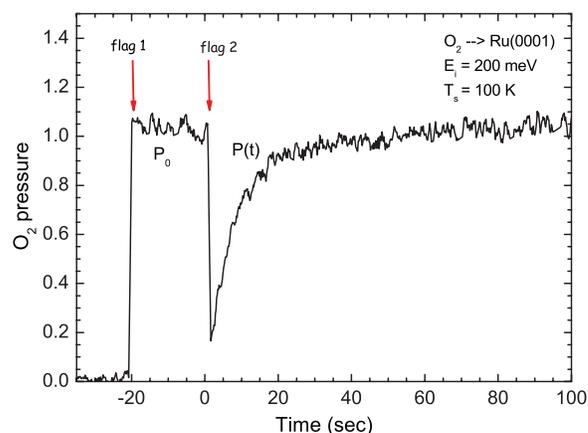

FIG. 1. Typical sticking measurement performed in our helium atom scattering apparatus. Opening of the first flag let the beam enter the main chamber where the oxygen background partial pressure is measured by means of a quadrupole mass spectrometer. When the second flag is open, O_2 molecules strike the crystal surface and stick on it, thus causing a decrease in the background partial pressure (see text). In this measurement, the incident angle is fixed at $\Theta_i = 15°$, beam energy is at 200 meV, and the surface temperature is 100 K.

of normal incidence, is that it guarantees that the incident O_2 beam (with a diameter of 2–3 mm at the sample position) is hitting the sample at its centre for all measured data points. Since the O_2 beam is seeded in He or Ne, we can monitor the reflected He/Ne beam during the beam´s adjustment (the reflected He/Ne signal can only come from the sample). In order to detect the specularly reflected He/Ne beam, we need an angle of incidence different from normal incidence. Owing to limitations in the detector´s rotating system, $\Theta_i = 15°$ is the smallest angle we can use.

As an example, we show in Fig. 1 raw data of sticking measurement of O_2 molecules on the clean Ru(0001) surface, for an incident energy of 200 meV and a surface temperature of 100 K. The quadrupole mass spectrometer initially measures the oxygen partial pressure due to the presence of residual gases in the UHV chamber. By opening the first flag, the O_2 beam enters the chamber and it strikes the second copper flag placed just in front of the sample. In this way, no sticking or adsorption onto the surface is possible, and a reference oxygen background partial pressure due to the beam in the chamber (P_0) is registered. Removal of the second flag (at $t = 0$ in Fig. 1) allows the beam to strike the sample, leading to a transient decrease in the O_2 partial pressure due to molecule sticking onto the surface. As the surface becomes covered, the transient decrease diminishes with time, until the pressure $P(t)$ again reaches P_0 when the surface is saturated. The initial sticking coefficient S_0 is then calculated as[20]

$$S_0 = \frac{P_0 - P_{(t=0)}}{P_0}, \tag{2}$$

and provides an absolute value of adsorption probabilities.

Atomically clean, crystalline Ru(0001) and Cu(111) surfaces were prepared by standard sputtering/annealing cycles, followed by oxygen exposure at 1150 K and a final flash to 1500 K in the case of Ru(0001). Surface cleanliness and order were also checked using low-energy electron diffraction and helium atom scattering.
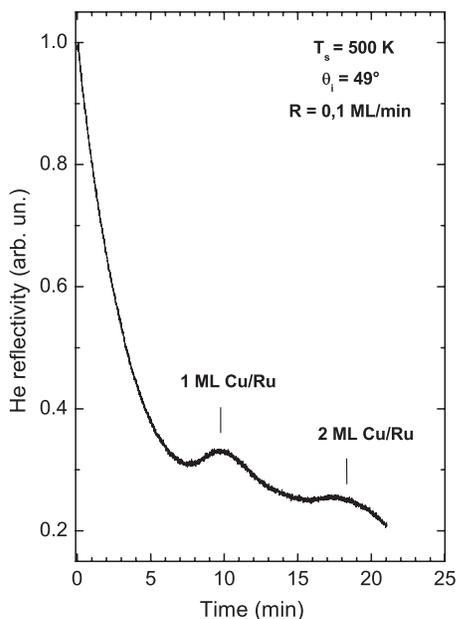
FIG. 2. Intensity of the specularly reflected He beam during Cu evaporation on Ru(0001) versus time. The evaporation rate is about 0.1 ML/min. The two maxima in the spectrum correspond to the completion of the first and second Cu layers, respectively.

Cu was deposited from a commercial evaporator equipped with a W basket filled with Cu pellets. To obtain well ordered Cu films with thickness below 2 MLs, the sample was kept at 500 K during deposition. From STM data it is known that further Cu deposition at 500 K gives rise to an inhomogeneous landscape: extended zones showing the dislocation network corresponding to a local Cu coverage of 2 MLs and large Cu islands attached at the step bunching zones coexist.[14] The quality of evaporated films has been checked by monitoring the changes in the intensity of the specular He beam, taking advantage of its high sensitivity to surface defects.[24,25] The specular peak contains relevant information about the height distribution on the surface, and for compact faces of transition metals is the most intense one. The intensity of higher order diffracted peaks is about 10^{-4} times smaller than the one of the specular peak.[26] The type of growth can be identified by observing the behaviour of the specular intensity as deposition proceeds. When diffusion across steps is easy enough, each atomic level tends to fill up before the next one starts to grow. Surface roughness then varies periodically, reaching a maximum for layer half-filling and a minimum at the completion of each layer. This behaviour gives rise to the well-known periodic oscillations of the specularly reflected intensity in the layer-by-layer growth.[27] Figure 2 shows the evolution of the specularly reflected He beam intensity during the evaporation of Cu on Ru(0001). The evaporated Cu atoms reached the sample at nearly normal incidence, being the evaporator mounted 30° away from the molecular beams incident direction. As it can be seen from Fig. 2, the first and second maxima in the reflected intensity occurred after about 10 and 20 min, which corresponds to an evaporation rate of about 0.1 ML/min. Therefore, using this technique we were

able to grow Cu overlayers with a daily precision in coverage of ca. 1%.

The adsorption of D_2O molecules on the clean Ru(0001) and Cu(111) surfaces and 2 ML Cu/Ru(0001) has also been measured by means of a supersonic molecular D_2O beam. D_2O is used because the m/e = 20 background in the scattering chamber is less than that for m/e = 18. For these measurements, a glass tube was filled with distilled water which was previously purified by repeated cycles of freezing, pumping, and thawing.[28,29] The vapor pressure of water at room temperature is estimated to be 30 mbars. The water was seeded in He, and the mixture was prepared by adding an overpressure of the carrier gas in the glass tube of about 500 mbars. The free jet expansion was produced through a nozzle of $d = 100$ μm diameter. The mixture was rather dilute, with a final concentration in the He beam of D_2O molecules of about 5%. The estimated translational energy for D_2O molecules under these conditions using Eq. (1) is ~250 meV.

III. EXPERIMENTAL RESULTS

Figure 3 shows the initial sticking coefficient as a function of the oxygen molecules normal energy, $E_n = E_i \cos^2\theta_i$, for the clean Ru(0001) surface and for 1 ML Cu and 2 ML Cu surfaces, measured at room temperature. The incident angle is fixed at 15° with respect to the surface normal in all measurements. As it can be seen in Fig. 3, our results for clean Ru(0001) are in very good agreement with the data taken from Ref. 30, which were obtained at a surface temperature of 500 K and normal incidence (normal energy scaling has been also verified in Ref. 30). This gives confidence on the use of Eq. (1) to calculate the incident energy.
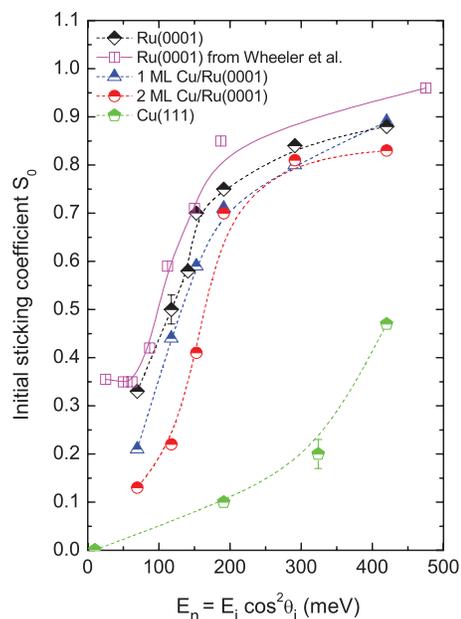

FIG. 3. Initial sticking probability of O_2 molecules versus incident normal energy for the clean Ru(0001) surface, 1 ML Cu, and 2 ML Cu evaporated on it, and Cu(111). The crystal temperature is 300 K, and the angle of incidence is $\Theta_i = 15°$. The data reported by Wheeler *et al.*[30] for Ru(0001) under similar incident conditions are also shown.
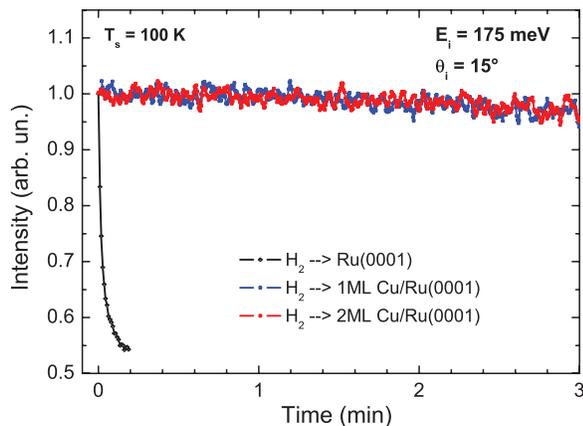
FIG. 4. Intensity of the specularly reflected H_2 molecules versus time for the clean Ru(0001) surface and 1-2 ML Cu/Ru(0001). For the Cu surfaces, H_2 sticking is estimated to be reduced by a factor 10^3 compared to the clean Ru(0001) surface.

For 1 ML Cu and 2 ML Cu, we observe a monotonic increase of the initial sticking probability with incident beam energy, with progressively reduced values as the thickness of the layer increases and for energies lower than 200 meV. In the high kinetic energy regime, the probabilities for the three surfaces are comparable. To put in perspective these results, we need a comparison with the corresponding sticking data of Cu(111). We performed such measurements under the same incident conditions, which are also included in Fig. 3 (lowest curve). From these data, we can estimate a barrier for dissociation of ca. 200 meV on Cu(111), in agreement with previously reported density functional theory (DFT) calculations.[31] This comparison makes clear that the sticking coefficients measured for 1 ML Cu and even 2 ML Cu/Ru(0001) are surprisingly high, since they are a factor of 5–10 larger than the corresponding values measured on clean Cu(111), for the same collision energies.

We have also investigated the adsorption of H_2 on these systems. We could not detect any significant sticking coefficient value using H_2 beams with the method of King and Wells, which means that the sticking should be rather small, below 0.10 (the resolution of this technique using our setup). For this reason, we have employed an alternative way of measuring H_2 sticking values, which consists in exposing the sample to a H_2 molecular beam while monitoring the specularly reflected hydrogen molecules. The values determined using this method are relative values, but can be compared with the values obtained for clean Ru(0001) under the same incident conditions.[24] The results of these measurements are presented in Fig. 4. Here, we can see the evolution of the specularly reflected H_2 beam from the clean Ru(0001) surface and from 1 ML and 2 ML Cu/Ru(0001) as a function of time. The beam energy is fixed at 175 meV and the incidence angle is $\Theta_i = 15°$. The Ru(0001) surface is known to be very reactive towards H_2 molecules, with a dissociative adsorption probability of about 0.5 at this incident energy.[32] This is clearly visible in Fig. 4, where the intensity of the specular beam rapidly decreases to half of its initial value due to the sticking of hydrogen atoms onto the surface. Surprisingly, we see in the same figure that after evaporation of 1 ML Cu on Ru(0001),
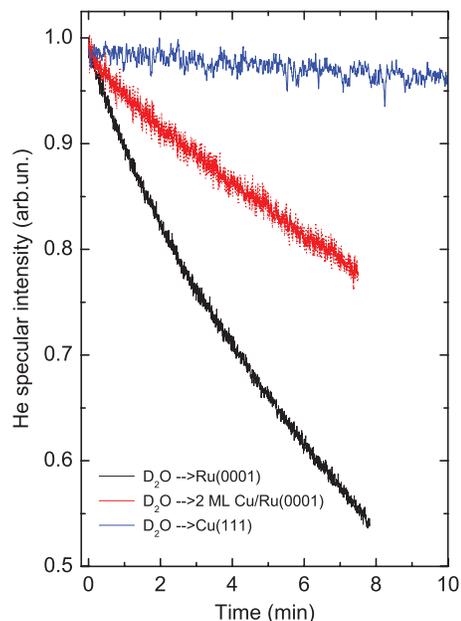

FIG. 5. Intensity of the specularly reflected He beam as a function of time while dosing D_2O with the beam, for the clean Ru(0001) surface, 2 ML Cu/Ru(0001), and Cu(111). The energy of the D_2O molecules is estimated to be 250 meV. Surface temperature is 100 K, and the angle of incidence is $\Theta_i = 15°$.

the surface is practically passivated towards H_2 molecules, as the intensity of the specular beam remains almost unchanged. By considering the initial slopes of the two curves,[24] we can estimate that the H_2 sticking probability on 1 ML and 2 ML Cu/Ru(0001) is reduced by a factor 10^3 compared to the clean Ru(0001) surface. An important consequence of the results shown in Fig. 4 is that they allow us to exclude the existence of uncovered Ru islands as the possible source of the high reactivity observed towards oxygen, since in this case also a high reactivity to hydrogen must have been observed.

The adsorption of D_2O molecules for the same system has also been measured. Figure 5 shows the normalized helium-scattering intensity as a function of time while D_2O dosing through the supersonic beam at an angle of incidence of 15°. The estimated kinetic energy of the D_2O molecules is 250 meV. The surface temperature is 100 K. The slope measured on the 2 ML Cu/Ru(0001) system is about three times smaller than on the Ru(0001) surface. The slope of a reflectivity curve is proportional to the product of the initial sticking probability times the water cluster size formed on the surface.[24] Since the cluster size might be different on the different substrates studied, it is not straightforward to conclude from these data that larger slopes correspond to larger sticking probabilities. Although further work is needed to get a more detailed description of these systems, our data clearly show that the adsorption properties of water on 2 ML Cu/Ru(0001) are quite different from those observed on the clean Ru(0001) and Cu(111) surfaces.

IV. DISCUSSION AND CONCLUSIONS

The 1 ML Cu film is laterally expanded by 5.5%, compared to clean Cu(111), whereas the corresponding value for

the 2 ML Cu film is just 2.2%. The data plotted in Fig. 3 show a strong similarity between the dependence of the oxygen sticking probability with incident energy for the three surfaces investigated (1 ML Cu, 2 ML Cu/Ru(0001), and clean Ru(0001)). If we compare the results for 1 ML and 2 ML Cu films, we see that essentially the same curves are obtained, in spite of the large difference in the corresponding lateral lattice parameters. Thus, it seems that the high reactivity of the 2 ML Cu film cannot be explained only in terms of strain in the Cu layer (which is expanded just 2.2%), but points instead to the strong influence of the Ru(0001) substrate. The presence of exposed clean Ru islands during the oxygen sticking measurements on 1 ML Cu and 2 Cu ML can be excluded, since these surfaces were found to be inert to hydrogen, even at incident energies of 175 meV. Moreover, both He and H_2 scattering has been measured from 1 ML and 2 ML Cu surfaces,[33] and narrow diffraction peaks observed. This points to a very low defects density in the Cu overlayers.

The observed strongly reduced reactivity of the Cu overlayers to H_2 molecules is consistent with the calculations reported in Ref. 21, where the dissociative adsorption of H_2 on a pseudomorphic Cu monolayer grown on Ru(0001) has been investigated by means of first-principles six-dimensional dynamics calculations. The authors show that the system H_2/Cu/Ru(0001) is activated with a threshold of ~160 meV. The reactivity of the resulting surface is, therefore, strongly reduced compared to the Ru(0001) substrate, but still high compared to Cu(111). The calculated energy threshold for dissociation reduces to about half of the value estimated for the clean Cu(111) surface (which is about 360 meV). Concerning the dissociation threshold for H_2/Cu/Ru(0001), our results show that it must be above 175 meV, in contrast with the ~160 meV reported in a theoretical study.[21] This discrepancy might be partially due to the use of the PW91 functional in the calculations, which sometimes slightly underestimates activation energy barriers,[34] and also to the fact that our data were not taken at normal incidence, but at an angle of incidence of 15°.[35]

The experimental results here presented can be generally explained in the frame of the *d*-band model, according to which the closer the center of the *d* bands to the Fermi level is, the larger is the chemisorption energy.[2, 36] The *d* bands are narrow, and small changes in the environment can modify the *d* states and their interaction with adsorbate states significantly. The presence of tensile strain on a surface correlates to the upward shift of the centroid of the *d* bands. Indeed, when the lattice is expanded parallel to the surface, the overlap between the *d* electrons on neighboring metal atoms becomes smaller, the bandwidth decreases and, to keep the *d* occupancy fixed, the *d* states have to move up in energy.[2] This effect results in a stronger interaction with adsorbates. Thus, a laterally expanded metallic surface is predicted to become more reactive compared to the unstrained one. Calculations for H_2 dissociation on transition and noble metals have shown a similar correlation between interaction strength and centroid of *d* bands.[37] Our results for the adsorption of D_2O molecules also show the same trend: assuming that similar cluster sizes are formed (as discussed above), water molecules stick with a higher probability on the strained 2 ML Cu/Ru(0001) sur-

face than on clean Cu(111), at an incident energy of ca. 250 meV.

Nevertheless, there are many effects that can influence the chemical reactivity of a metallic surface apart from the shift of the centroid of the *d* bands, such as the presence of defects in the film, steps or threading dislocations, and the proximity of the Ru(0001) substrate. Calculations performed in Ref. 15 indicate that the centroid of the *d* bands is shifted with respect to Cu(111) for the 1 ML Cu film, while it is constant above 2 ML Cu. Moreover, the strongest decrease in the oxygen sticking probability was found to occur when going from 2 to 3 ML, by a factor of about 30. For this reason, the authors attributed the observed decreasing reactivity with film thickness to the progressively population of the surface state, since only the position of the surface state could track the layer-by-layer evolution of the strain.[14]

Evidence against the validity of the simple picture given by the *d*-band model for 1 ML Cu/Ru(0001) has been provided by the DFT-based, six-dimensional dynamics calculations reported in Ref. 21. In effect, these authors showed that the barrier for hydrogen dissociation in a laterally expanded Cu(111) surface (up to the value of the Ru(0001) lattice constant) is about 130 meV higher than for the Cu/Ru(0001) system. The authors attributed such a difference to the influence of the Ru(0001) substrate on the electronic properties of the Cu overlayer. In addition, local density of states (LDOS) calculations performed by the same authors suggest that Cu/Ru(0001) should be less reactive than Cu(111), since there is a net downshift of the *d*-band center, but the opposite is obtained from the 6D-PES calculations. Although this difference in reactivity for H_2 is not observed in our experiments (we measured a sticking probability very close to zero for H_2, up to 175 meV incident energy), the situation for O_2 is quite different. In effect, at the same energy we get a sticking probability of 0.6 for 1 ML Cu at 300 K. Since the corresponding value for Cu(111) is 0.1, this can be taken as strong evidence for a failure of the *d*-band model for this system. If this is due to the presence of the underlying Ru(0001) substrate, or perhaps to the occurrence of non-adiabatic effects, remains to be explored.

In conclusion, initial sticking probabilities have been measured for O_2 molecules impinging on the clean Ru(0001) surface and on 1 ML Cu and 2 ML Cu/Ru(0001) in a broad energy range, for a room temperature crystal. Surprisingly, even upon the growth of 2 Cu ML, the resulting surface still exhibits a high reactivity to O_2 molecules. Interaction with hydrogen has been studied by following the intensity of the specularly reflected H_2 beam at 175 meV versus time. The adsorption probability of H_2 was found to be virtually zero for 1 ML Cu and 2 ML Cu/Ru(0001), even with the surface at $T_s = 100$ K. In addition, the adsorption properties of water on 2 ML Cu/Ru(0001) were found to be intermediate between the values observed on Ru(0001) and Cu(111). These results show up the exciting possibility of selectively tuning the reactivity of a surface towards different gas molecules by simply growing a single layer of a different material on it. The Cu/Ru(0001) system shows an energetic barrier of more than 175 meV for hydrogen adsorption and dissociation, while the interaction with oxygen molecules is non-activated and

practically the same as for the Ru(0001) substrate. These results are expected to stimulate new theoretical studies of oxygen adsorption on Cu/Ru(0001).

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