Fabrication of Cu Oxides on Single Crystal Cu Surfaces using Hyperthermal O₂ Molecular Beams

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NANO-related scientific terms:

Cu oxides, cuprous oxide (Cu$_2$O), cupric oxide (CuO), direct-gap $p$-type semiconductor, antiferromagnetic semiconductor, photovoltaic material, nanoparticle, ultra-thin film, nanocrystal, finite size effects, Cu(100), Cu(110), Cu(111), Cu(410), hyperthermal O$_2$ molecular beams (HOMB), collision induced absorption (CIA), nano-structured metal oxide, X-ray photoemission spectroscopy (XPS), low-energy electron diffraction (LEED), X-ray diffraction (XRD), X-ray photoelectron diffraction (XPD), scanning tunneling microscopy (STM), dissociative adsorption, DFT calculations, surface reconstruction, sticking probability, nanofacet, nanostructure, nanoterrace
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<td>auger electron spectroscopy</td>
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<td>AR</td>
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<td>collision induced absorption</td>
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<td>$c_p$</td>
<td>specific heat at constant pressure</td>
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1. Introduction

Understanding the chemistry of the copper-oxygen interaction is one of the outstanding open issues of solid-state physics due to implications for the understanding of high-$T_c$ superconducting oxides, whose basic units are Cu-O chains or layers [1]. Cuprous oxide ($\text{Cu}_2\text{O}$) and cupric oxide ($\text{CuO}$) are regarded as meaningful benchmark materials for theories and experiments. Their bulk structures are shown in Fig. 1 [2,3]. The crystallographic structure of $\text{Cu}_2\text{O}$ (belonging to the space group $Pn\overline{3}$) is highly symmetric with six atoms per unit cell. The O atoms form a bcc lattice while the Cu atoms are on the vertices of a tetrahedron around each O atom. This disposition generates a linear O-Cu-O coordination [2]. In CuO the lattice has a monoclinic symmetry [3]. Each atom has four nearest neighbors of the other kind. Cu atoms are at the center of an O rectangle, while O atoms are at the center of a distorted Cu tetrahedron. The crystallographic parameters and interatomic distances to nearest neighbors are listed in Table 1 for both structures [2-4].

Focusing on the electronic structure, $\text{Cu}_2\text{O}$, an industrially important direct-gap $p$-type semiconductor with a band-gap energy of 2.17 eV [5], is expected to have an essentially full Cu 3d shell. On the other hand, CuO has an open d shell (3d$^9$) and is an antiferromagnetic semiconductor with a gap of about 1.4 eV [6-8].

Both materials are regarded as most promising for applications to photovoltaic cells [9-11], for which a high carrier density and a low leakage current are required to improve the performance in terms of energy conversion. The attractiveness of $\text{Cu}_2\text{O}$ and CuO lies in the fact that they are nontoxic and abundantly available on Earth, and that they have a high absorption coefficient in the visible region of the electromagnetic spectrum and low production costs.

In $\text{Cu}_2\text{O}$ and CuO materials finite size effects are important in physical and chemical properties and were recently demonstrated to affect the magnetic transition temperature in CuO ultra-thin films or nanoparticles [12]. $\text{Cu}_2\text{O}$ is an efficient catalyst for the partial oxidation of propylene to acrolein [13] and CO[14], while CuO is used in gas sensors [15]. The synthesis of $\text{Cu}_2\text{O}$ nanocrystals has been reported recently, further testifying the growing interest for this material [16].

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The structure and electronic properties of Cu$_2$O single crystal surfaces have been studied with surface-science techniques [17]. The termination of the stoichiometric (111) face is nonpolar since the ideal surface is terminated by an outer atomic layer of oxygen anions, a second atomic layer of Cu$^+$ cations, and a third atomic layer of oxygen anions, giving no net dipole moment. Depending on the surface preparations, oxygen vacancies are created on the surface, giving a new periodic structure. The ideal (100) surface is polar with square symmetry. Depending on the surface preparations, either Cu termination or O termination can be produced.

Ordered Cu$_2$O and CuO films and nanostructures are usually grown by controlling O$_2$ pressure (p) and substrate temperature (T) during deposition [18]. From the calculated (p,T) phase diagram [19], this process requires high pressure and high temperature. For the device technology, the growth of the Cu oxides at T as low as room temperature (RT) would be highly desirable.

The use of hyperthermal O$_2$ molecular beams (HOMB) may improve the quality of thin film growth, as demonstrated e.g. for organic films [20], and allows to produce oxide layers at lower crystal temperatures, avoiding contamination problems and reducing film defectivity. Collision induced absorption (CIA) [21, 22] and local heating of the substrate were shown to be indeed effective in inducing oxide nucleation [23], opening up new possibilities for the production of nano-structured metal oxides.

Herein we offer an overview on recent detailed studies of oxygen adsorption and of the initial stages of Cu$_2$O and CuO formation on low Miller index and vicinal Cu surfaces. In chapter 2 we introduce the hyperthermal molecular beam technique and give some details on the experimental apparatuses while in chapters 3 to 5 we discuss the available data for Cu(100), Cu(410) and Cu(110) and Cu(111), respectively.

2. Experiments
All the experiments discussed in the present review were performed under the ultra high vacuum (UHV) conditions. X-ray photoemission spectroscopy (XPS) was recorded with the surface reaction analysis apparatus SUREAC 2000, constructed as an end-station of the soft-X ray beam line BL23SU at the SPring-8 synchrotron radiation source [24],
while high resolution electron energy loss spectroscopy (HREELS) was performed in a dedicated apparatus in Genova [25].

In the BL23SU beam line soft X-rays from about 400 eV to 2000 eV are available with a high spectral resolution (E/ΔE=10000) thanks to a grazing incidence type monochromator system [26]. A photograph and a cross-sectional top view of the apparatus are shown in Figs. 2 and 3, respectively. The surface reaction analysis chamber is equipped with an electron energy analyzer (OMICRON EA125, EA in Fig.3), with a Mg/Al-Kα twin-anode X-ray source (OMICRON DAR400) and with two differentially pumped quadrupole mass spectrometers (SPECTRA Windows Satellite 200D, QMS). The former (QM1), mounted in line of sight with the molecular beam, is used to analyze the HOMB composition; the latter (QM2), at 40° from the surface normal, is used to detect the species desorbed from the surface. Further details about the experimental setup are given in Ref. [27]. The base pressure of the surface reaction analysis chamber is better than 3×10⁻⁸ Pa. The copper sample is mounted on a sample holder equipped with a graphite ribbon heater and coupled with a liquid nitrogen reservoir. The sample temperature can thus be controlled from 100 K to 1300 K.

The HREELS apparatus in Genova [25] consists of a UHV chamber with base pressure better than 1×10⁻⁸ Pa coupled to a supersonic molecular beam similar to the one present at BL23SU. The sample can be heated up to 900 K by electron bombardment and cooled down to 110 K by liquid N₂ flux. The HREELS measurements presented in this review were performed in-specular, at 60° of incidence and with a primary electron energy of 2.7 eV.

The copper samples were cleaned by repeated sputtering with 1-keV-Ar⁺ and annealing to 870 K until no more impurities could be detected by SR-XPS or HREEL and Auger spectroscopy and a sharp low-energy electron diffraction (LEED) pattern of clean the surface is present.

A HOMB generator, consisting of differentially pumped expansion (nozzle) and chopper stages, is coupled to the surface reaction analysis chamber. A two-step differential pumping system separates the HOMB generator and the surface reaction
The supersonic beam in Genova has a similar design but the nozzle is made out of alumina and can be routinely heated up to 1000 K. The spot diameter at the sample is ~6 mm for sticking coefficient measurements and 10 mm for HREELS studies [25].
$E_i=2.3 \text{ eV}$, respectively, indicating a very good adiabatic expansion. This result is confirmed by further checks for HOMB with different seeding ratios and $T_n=1400 \text{ K}$, leading to $0.9<E_i<1.5 \text{ eV}$. Thus, we assumed that the HOMB has a small energy dispersion generated from the adiabatic expansion, although the experimentally estimated value of the translational energy may include a relative large error bar.

The $O_2$ flux at the sample position is estimated experimentally before and/or after the each measurement, following the estimation method described in details in Ref. [29] and briefly recalled in the following. We measure the ratio ($R_b$) between $O_2$ and the inert carrier gas concentration in the direct beam by QM1 (see Fig.3) and the total pressure increase in the surface reaction analysis chamber ($\Delta P$) by an ion gauge. The flux ($Q_a$) is then estimated from the equation:

$$Q_a = \frac{\Delta P}{A(x_a/S_a) + (x_b/S_b)R_b} \text{ [Torr/cm}^2\text{ s]} \quad (2)$$

where $x_j$ and $S_j$ are, respectively, the ionization probability of the mass spectrometer and the pumping speed for the particle $j$ and $A$ is the beam spot area. The typical flux density of $O_2$ molecules at the sample surface is $3\times10^{14} \text{ molecules cm}^{-2}\cdot\text{s}^{-1}$ at $T_n=300 \text{ K}$ for the 0.5 eV HOMB.

When heating the nozzle, the internal excited states of the $O_2$ molecular beam must be considered. During the free jet expansion binary collisions among the molecules occur about $10^{2}$--$10^{3}$ times [30], leading to internal energy relaxation and to energy transfer from the rotational modes to kinetic energy in the direction of the expansion. The vibrational degrees of freedom generally relax little during supersonic expansion, since for a diatomic molecule more than $10^4$ collisions would be required for energy conversion into translational energy [30]. Assuming that oxygen molecules keep their vibrational temperature during a free jet expansion, the relative population in the $i^{th}$ vibration state is given by the Boltzmann distribution:

$$P_{v=i} = \exp(-E_{v=i}/kT_n)/Z_v \quad (3)$$

where $E_{v=i}$ is the energy of the $i^{th}$ vibrational state, $k$ the Boltzmann’s constant, $T_n$, the nozzle temperature and $Z_v$ the vibrational contribution of the partition function. The ratio between the population of the $v=1$ and $v=0$ vibrational states is $5\times10^4$ for $T_n=300$ K and 0.19 for $T_n=1400$ K, respectively, for $E(v=1)=193 \text{ meV}$ [31].
The rotational temperature cools more easily during a free jet expansion; however, the population of rotationally excited molecules may not be negligible as the nozzle temperature increases. The observed decrease of the O\(_2\) sticking probability on copper surfaces [32] is speculated to be due to rotational hindering in dissociative adsorption. Unfortunately no exact information about the rotational state distribution in the expanded beams is available, because a direct determination is difficult and not feasible in our experimental setups. We refer therefore to some literature pointing out the presence of significant rotational excitation at high nozzle temperatures [33-36]; e.g. M. Binetti et. al. measured the rotational temperature of an NO beam using Resonant Enhanced Multi Photon Ionization (REMPI) and observed an increase of such quantity from 36 K to 154 K depending on \(T_n\) and seeding gas [33]. We note that the excitation of the vibrational and rotational degrees of freedom affects the kinetics of dissociative adsorption of O\(_2\) on copper surfaces, which is the first step for the oxidation [32].

3. Oxide Formation on Cu(100) induced by HOMB

3.1. Thermal dissociation of O\(_2\) and Cu\(_2\)O formation

Many experimental and theoretical approaches have been pursued to understand thermal oxidation of Cu surfaces [37-39]. The Cu(100)-(2\(\sqrt{2}\times\sqrt{2}\)R\(45^\circ\))-O (referred to as 2\(\sqrt{2}\) structure in the following) appearing at the initial stage of the Cu\(_2\)O formation has been investigated using various structural-analysis techniques: low-energy electron diffraction (LEED) [40], X-ray diffraction (XRD) [41], X-ray photoelectron diffraction (XPD) [42, 43] and scanning tunneling microscopy (STM) [38, 44]. The associated 2\(\sqrt{2}\) structure corresponds to a missing-row reconstruction with -Cu-O-Cu- chains, as shown in Fig.4. While the surface structure of oxygen-adsorbed Cu(100) is well understood, the oxide-formation processes have been little elucidated from the kinetic and dynamic point of view. From the measurements of the O\(_2\) initial sticking probability [45-48], it was concluded that O\(_2\) adsorption on clean Cu(100) is direct and dissociative while on the 2\(\sqrt{2}\) structure it involves a molecular precursor prior to dissociation.

A Cu(100) crystal can be oxidized into its bulk when exposed to ambient thermal O\(_2\) molecules at temperatures above 450 K [45,49] and Cu\(_2\)O films can be grown
epitaxially. However, rather high exposures (10^5-10^6 L O_2; 1 L = 1.33 x 10^4 Pa·s) are required for oxide-film growth on Cu(100) under thermal O_2 atmosphere, suggesting a low oxidation efficiency. At high exposures and high temperatures, islands of Cu_2O were observed on Cu(100) by transmission electron microscope [50, 51] and STM [52]. Their morphology depends on surface temperature. For applications in technological devices, Cu_2O growth at lower T (possibly at room temperature) and with very strict contaminations limits is required. Dosing by HOMB may solve this issue.

3.2. Dissociative Adsorption by HOMB

Fig. 5 shows representative O-1s XPS spectra, parametric in oxygen coverage (θ), recorded after exposing the Cu(100) surface at 300 K to a 2.3 eV HOMB [22] at normal incidence. The O-uptake curve, determined from the integration of the O-1s spectra, is reported in Fig. 6. The binding energy of the O-1s peak shifts by 0.6 eV, i.e. from E_b=528.9 to E_b=529.5 eV, with increasing HOMB doses up to θ=0.5 ML (Region A in Fig. 6). In this coverage region the O-1s peak is well fitted by a single symmetric component (see the spectrum at θ=0.47 ML in Fig. 5). Its full width at half maximum (FWHM) decreases with increasing θ; such narrowing corresponds to the transition from a poorly ordered phase (inhomogeneous broadening of a peak) to the perfectly ordered one. Indeed a sharp LEED pattern of the 2√2 structure is developed at θ~0.5 ML. In Region A, O_2 dissociatively adsorbs on the surface and θ increases steeply with increasing HOMB dose (Fig. 6 – note the logarithmic scale for exposure). From comparison of the uptake curve for the 2.3-eV-HOMB exposure (full circles) with that for thermal O_2 (blue dashed line) [22, 53], the increased efficiency of HOMB for dissociative adsorption is evident. This result suggests that HOMB helps in overcoming the activation barrier of dissociative adsorption.

3.3. Cu_2O formation on Cu(100) by HOMB

For θ≥0.5 ML (Region B), the oxidation of Cu proceeds slowly as seen in Fig. 6. The FWHM of the O-1s peak grows with θ and the peak shape becomes asymmetric (see spectrum at θ=0.95 ML in Fig. 5). This behaviour suggests that the broadening of the O-1s peak is due to the presence of two different oxygen moieties. The former (blue solid line), at E_b= 529.5 eV, corresponds to surface O atoms and has the same line shape as the single component (red line) at θ=0.47 ML; the latter (blue dotted line), centered
at 530.1 eV and with nearly the same FWHM as the surface component, is assigned to subsurface and/or bulk O atoms which initiate the Cu$_2$O growth. Indeed, the binding energy of 530.1 eV is very close to the value of 530.2-530.5 eV of bulk Cu$_2$O [4, 54]. Further experiments to verify Cu$_2$O formation have been performed on Cu(410), finding that thicker Cu$_2$O films can be grown efficiently, as it will be discussed in the next section. Thus, for Cu(100) most of the O atoms are located on the surface for $\Theta$≤0.5 ML (Region A), while we estimate from XPS analysis that 60% of them are located in the subsurface and/or bulk region for $\Theta$=0.95 ML (Region B).

In the exposure range corresponding to Region B no gradual increase of oxygen coverage was observed for thermal O$_2$ exposure at ~300 K. The oxidation efficiency is thus significant for HOMB doses and almost negligible for thermal-O$_2$ exposure.

From the O-uptake curve in Fig. 6 we can calculate the O-coverage dependence of the sticking probability for dissociative adsorption of 2.3-eV O$_2$ beams. It decreases from 0.03 to $\sim$10$^{-5}$ in Region A [22]. A step-function-like decrease can be seen at $\Theta$≈0.5, suggesting that the $\sqrt{2} \times \sqrt{2}$ structure appearing at the initial stage of the oxide formation is very stable against further oxidation. In Region B, it is as small as $\sim$10$^{-5}$ (see also Fig. 32 in the following paragraphs). This rather slow process corresponds to the initial stage of copper-oxide formation inferred from XPS (vide ante).

We proposed [22] that a collision-induced absorption (CIA) mechanism [21, 55, 56] is responsible for such slow oxidation process of Cu since: 1) no prominent enhancement of the oxidation efficiency vs T was observed in Region B even for T values as high as 700 K (i.e. just below the oxygen desorption temperature); 2) the efficiency of HOMB for oxidation is rather high compared to backfilling experiments.

The CIA mechanism is active when an incident O$_2$ molecule collides with a preadsorbed O atom impulsively and with a small impact parameter. The energy transfer from the incident particle to the preadsorbed O atom occurs effectively and, as a result, the produced energetic O atom may penetrate subsurface, leaving a vacant site for further dissociative adsorption on the surface. Such impulsive collision has a very low cross section, explaining the low sticking probability ($\sim$10$^{-5}$) in Region B. The activation
barrier for subsurface oxidation by preadsorbed O atoms may be smaller than that for
direct subsurface oxidation by incident O\textsubscript{2} molecules because of interlayer relaxation.
XPS analysis shows that, at $\Theta=0.95$ ML, the amount of surface O atoms has reduced by
30\% compared to that at $\Theta=0.5$ ML ($2\sqrt{2}$ surface), while the one of subsurface O
atoms has increased. This result could be due to the competition between dissociative
adsorption on the produced vacant sites and absorption in a CIA mechanism.

We directly confirmed the occurrence of CIA as follows. Fig. 7 shows O-1s spectra
measured in high resolution after exposing the $2\sqrt{2}$ surface ($\Theta=0.5$ ML) at ~300 K to a
3-eV-Ar-beam at normal incidence. The symmetric O-1s shape of the $2\sqrt{2}$ surface (see
the spectrum at $\Theta=0.47$ ML in Fig. 5) becomes asymmetric after an exposure to
$3.3\times10^{19}$ atoms/cm$^2$ of 3-eV Ar. Such change is attributed to the appearance of the,
above-mentioned, second component at 530.0 eV, corresponding to subsurface/bulk O
atoms. 40\% of the O adatoms forming initially the $2\sqrt{2}$ structure are then
pushed/driven under the topmost surface layer. A further increase of the subsurface O
atoms (60\% of the initial surface O atoms) is induced by increasing the Ar dose to
$6.8\times10^{19}$ atoms/cm$^2$. This is the first example of CIA mechanism in oxide-formation
(see the inset of Fig. 7), although energetic-collision processes were known to induce
dissociation of preadsorbed O\textsubscript{2} molecule at low crystal temperatures [21]. The CIA
mechanism is effective on Cu(100) because subsurface O atoms are stabilized by
surface O atoms [57].

3. 4. Comparison with Cu\textsubscript{3}Au(100)

Fig. 8 shows the O-uptake curves produced by the integration of O-1s spectra recorded
after successive exposures of Cu\textsubscript{3}Au(100) at 300 K to HOMB at kinetic energies of 2.3
eV and 0.6 eV and to thermal O\textsubscript{2}. For the latter dosing condition only 0.15-ML-O atoms
are dissociatively adsorbed on the surface even after massive exposure (~9000 L). On
the other hand, at 2.3-eV, a coverage of about 0.6 ML was obtained after a comparable
exposure. Interestingly, decreasing the HOMB kinetic energy from 2.3 eV to 0.6 eV
induces no prominent differences in the O-uptake curve (compare full and empty circles
in Fig. 8). A further reduction of the kinetic energy to 0.3 eV (not shown here) results,
on the other hand, in an O-uptake curve in-between the thermal and 0.6 eV O\textsubscript{2} doses.
Thus, dissociative adsorption of O\textsubscript{2} on the Cu\textsubscript{3}Au(100) surface is an activated process
and an incident energy above 0.6 eV is enough to surmount the barrier. Oxygen exposure induces structural changes to the Cu₃Au(100) surface since Cu atoms segregate and produce the Cu-O layer. Schemes of the clean and of the O-covered surfaces are shown in Fig. 8.

With respect to Cu(100) (see uptake curve reported in Fig. 8 for comparison), dissociative adsorption on Cu₃Au(100) has a higher activation barrier. Moreover, it does not occur on Au(111) even when using 2.3 eV HOMB, [58], suggesting that the activation barrier on Cu₃Au(100) falls in between those of the pure Cu and Au surfaces. The reduced reactivity (high activation barrier) may be explained by the shift of the d-band center due to Au alloying [59]: the dissociation barrier is higher for the isolated Cu atoms (possible O₂ dissociation sites) surrounded by Au atoms than for the ones in a pure Cu surface, in analogy with what reported for the Au/Ni system [60]. When comparing the different behaviour of Cu₃Au and Cu at high O₂ doses (≥10¹⁸ molecules·cm⁻² in Fig. 8) it is concluded that the first Cu-O layer and the Au-rich interface work as protection layers against bulk-like Cu₂O formation. The former prevents the dissociative adsorption of gas-phase O₂ and the latter reduces the diffusion of O atoms into the bulk by making the CIA process ineffective.

4. Oxide Formation on Cu(410) by HOMB

The most promising approach to a systematic study of defected surfaces is the use of single crystal surfaces cut along high Miller index planes, i.e. stepped surfaces showing a high density of one majority low coordination site which mimics a defect. This approach allows a shortcut between the need for ordered substrates and controlled conditions and the availability of particular atomic configurations [61]. Here, we use Cu(410) to investigate the role of steps in the oxidation process [62-65]. This vicinal surface consists of 3 atomic row wide (100) terraces separated by monoatomic (110)-like steps (see Fig. 9) and is thus amenable to a direct comparison with Cu(100) and Cu(110) surfaces.

4.1. Cu₂O formation on Cu(410) with thermal O₂

In order to unravel the role of the steps in the oxidation process, in Fig. 10 we compare HREEL spectra recorded for the modified c(2x2) structure at 0.5 ML O-coverage
(monolayer, 1 ML=1.58×10^{15} \text{atoms/cm}^2 \text{ in ML of Cu(410)}) and after oxide nucleation has started. The modified c(2x2) structure, previously investigated by Vlieg et al. [66] by Density Functional Theory (DFT) and X-ray diffraction, is produced by exposing the Cu(410) surface at T=573 K to 108 L of O_2 by backfilling the chamber (preparation (I) in the following). In the accepted structural model the metal-substrate is unreconstructed; half of the oxygen occupies the step-edge sites, organized in Cu-O chains with the O nearly collinear with the Cu atoms, while the other half stays at mid-terrace hollow sites. The HREEL spectrum (solid line) shows a single sharp loss at 38 meV. Two dipole active vibrations would be expected, corresponding to the different adsorption sites; however this contradiction is only apparent, since recent theoretical calculations [67] based on a five Morse potential model showed that the two losses differ in energy only by less than 1 meV and hence cannot be resolved.

After 2250 L O_2 on Cu(410) at 500 K (preparation (II), dotted curve in Fig. 10), the HREEL spectrum shows two additional losses at 19 and 78 meV, respectively. The appearance of these peaks indicates that Cu_2O has formed, since in bulk Cu_2O two infrared-active modes are present at 18.1 and 75.5 meV [68]. A scheme of the corresponding Cu_2O displacement patterns is reported in Fig. 10 as insets. We note that similar vibrations were reported also for Cu_2O films grown on Cu(111) [69] and on Cu(110) [70]; on these surfaces at similar crystal temperature, however, oxide formation was observed only after much larger O_2 doses. No oxide formation was detected for O_2 exposure under UHV conditions at room temperature for Cu(100) [71]. This indicates that open steps promote oxidation. Finally, when O_2 dosing was performed by backfilling and at room temperature, no oxide formation was observed on Cu(410) even after doses greatly exceeding those of the experiment of Fig. 10 [65].

SR-XPS (hv=890.1 eV) confirmed these findings, as shown in Fig. 11 [64]. For preparation (I) the O1s region exhibits a broad symmetric peak at a binding energy \( E_B = 529.8 \text{ eV} \); it consists possibly of two components, corresponding to adsorption at step edge and mid-terrace sites. For preparation (II), the O1s peak has the slightly higher \( E_B \) value of 529.9 eV and is narrower. Its integrated intensity has increased by 17 \% compared to preparation (I). No further growth of the O1s SR-XPS peak was observed after additional O_2 exposure. Since the O1s XPS peak of bulk Cu_2O is located
at 530.2–530.5 eV [4] and HREELS shows Cu$_2$O formation, we conclude that the shift to higher $E_B$ is due to cuprous oxide. Since the large HREELS loss at 78 meV corresponds to only 17% increase in O coverage, the dipole scattering cross section of the Cu$_2$O patches must be quite high; Cu$_2$O formation occurs thus in islands and the oxidation process is kinetically limited [65]. High pressures of O$_2$ and high surface temperatures are then required for the growth of thicker Cu$_2$O films under thermal conditions.

By tracking the energy-loss peak at ~78 meV, we can evaluate the efficiency of Cu$_2$O formation [65]. To this purpose the ratio between the intensity of the 78 meV and of the 38 meV peaks is plotted vs exposure temperature and pressure in Fig. 12. We note that no detectable Cu$_2$O formation is detected at $T=400$ K, independently of pressure. Cu$_2$O formation occurs for $T \geq 500$ K and the energy loss intensity depends then on O$_2$ pressure. Finally, at $T=700$ K Cu$_2$O formation shows reduced efficiency with respect to exposure at $500$ K, at least at intermediate O$_2$ pressure ($5 \times 10^{-4}$ Pa).

We can rationalize our findings as follows. The step edge of the Cu(410) surface can be an efficient source of mobile Cu atoms and acts as an efficient entrance gate for subsurface diffusion of O atoms [72]. Indeed, on clean Cu(410) the step edge has the largest vibrational amplitude and relaxes outwards [73]. Moreover it is expected that atoms at undercoordinated step sites on Cu(410) are less strongly bound with respect to terrace atoms. O adsorption has a double effect: it stabilizes the step edges by forming Cu-O-Cu chains, which look straight in STM images recorded at room temperature [74], and it further weakens the Cu-Cu bonds [66]. Step-edge Cu atoms can be detached in thermally activated step roughening, thus accounting for the initial increase in Cu$_2$O formation with surface temperature (at a fixed O$_2$ pressure). Since migration has the effect of bringing the adatoms back to the step edges, the lifetime of detached Cu atoms is short. This explains why a high O$_2$ flux is necessary for them to act as nucleation centers toward Cu$_2$O.

In fact the higher the oxygen flux, the higher the chance that the mobile Cu atoms are hit by some oxygen and this yields nuclei of Cu$_2$O before returning back to the step edge. We can thus conclude that a kinetic factor, the oxygen flux, limits the amount of
generated oxide. Moreover, since high temperature enhances the mobility of O atoms at the surface and into the bulk, a competition between the increasing amount of mobile Cu adatoms from the step edges and their decreasing lifetime sets in, thus explaining the occurrence of a maximum of Cu₂O production around 500-600 K for the investigated dosing pressure range.

The calculated (p, T) phase diagram for O/Cu [19] shows that, at fixed temperature and below a critical oxygen pressure, Cu₂O is not stable and decomposes. This can be avoided only by lowering the surface temperature and making Cu₂O be stable in UHV conditions. If Cu₂O formation could be formed below a critical O₂ pressure, it should be observed at all possible pressures for large enough O₂ doses, contrary to experimental evidence. When the surface temperature is further increased, the amount of Cu₂O formed for a fixed exposure decreases, as apparent from the series of experiments at P=5×10⁴ Pa. Such a decrease may be due either to the onset of Cu₂O decomposition or to the shortened lifetime of mobile Cu adatoms. In the former hypothesis the limited Cu₂O production at high T would have a thermodynamic origin, in the latter a kinetic origin. In order to address this last issue we performed post-dose annealing to different temperatures (T_{anneal}) of the surface obtained after exposure to 7000 L of O₂ at 500 K. Since an oxide peak of significant intensity is still present upon heating to 750 K, the reduced efficiency of Cu₂O formation at T>600 K [65] cannot be due to decomposition of Cu₂O and is therefore of kinetic origin.

4.2. Cu₂O formation on Cu(410) induced by HOMB

In order to unravel the role of molecular energy in the oxidation process we have also performed O₂ uptakes on Cu(410) at room temperature using a 2.2 eV HOMB impinging along the surface normal [64]. The results are shown in Fig. 13. The O1s SR-XPS peak is now at E_B=529.9 eV for Θ=0.43 ML and its intensity and binding energy increase with O coverage. Fig. 14 shows the results of the peak-shape analysis of representative O1s spectra taken from Fig. 13. The symmetric O1s peak at Θ=0.43 ML is fitted with a Voigt function with parameters G=0.79 eV and Lorentzian width Γ=0.32 eV. It corresponds mainly to chemisorbed O atoms, because peak position and shape are the same as for thermal O₂ exposure at room temperature and HREELS shows no Cu₂O
loss, as discussed in part 4.1 [65]. With increasing coverage, the line shape changes considerably. At $\Theta=1.05$ ML, the O1s peak can be separated into three components: chemisorbed O atoms at 530.0 eV ($G=0.79$ eV, $\Gamma=0.32$ eV), Cu$_2$O ($G=0.71$ eV, $\Gamma=0.21$ eV) at 530.5 eV and a small CuO peak ($G=0.71$ eV, $\Gamma=0.10$ eV) at 529.2 eV [4]. A small amount of the latter phase was also reported for Cu$_2$O formation on Cu(110) [70].

The formation of a CuO phase strongly depends on the surface temperature during the HOMB dose, (see discussion in part 4.4 [63]). Increasing $\Theta$ causes an increment of the Cu$_2$O and CuO peaks and induces the formation of an additional small contribution at 531.4 eV ($G=0.80$ eV, $\Gamma=0.77$ eV), possibly due to chemisorbed O on Cu oxide [4]. The relative weight of the component due to oxygen adatoms (530.0 eV) decreases slowly above 0.5 ML and is no longer present at $\Theta=2.07$ ML, indicating complete surface oxidation.

Cu$_2$O formation was confirmed by the features present in the valence-band spectra and reported in Fig. 15 [64]. After a 2.2 eV HOMB dose at room temperature, the main peak gets narrower and becomes very similar to the one of bulk Cu$_2$O [4]. We note that at 900 eV photon energy the photo-ionization cross-section ratio is $\sigma(O2p)/\sigma(Cu3d)$~0.03 [75], so that the valence band spectrum is dominated by the d spectral weight of Cu$_2$O, concentrated at 1-4 eV. Since the spectra are measured under surface-sensitive condition, the prominent decrease of the density of state (DOS) at the Fermi level indicates the opening of a band gap and the formation of a Cu$_2$O thin-film.

In Fig. 16 we compare the O uptake curve during 2.2 eV HOMB oxidation on Cu(410) with those recorded for Cu(100) [22] (see discussion in section 3) and Cu(110) [76] (see discussion in section 5). It is evident that a dependence of the uptake curves on crystal face symmetry is present for $\Theta\geq0.5$ ML and that the behaviour of Cu(410) is intermediate between those of the constituent low Miller index surfaces (see Fig. 9).

The sticking probability on Cu(100) decreases around $\Theta_o \sim 0.5$ ML and reads thereafter $10^{-5}$-$10^{-6}$, corresponding to the Cu$_2$O formation rate [22]. Such relatively low value of $S$ is consistent with the proposed CIA process [22 and section 3]. On Cu(110) $S$ is by 1-2 orders of magnitude higher during the Cu$_2$O formation process [76]. This leads to the
speculation that such a difference is due to migrating Cu adatoms detached from the added rows acting as additional dissociation centers for impinging O$_2$ [76].

To further elucidate the mechanism underlying Cu$_2$O formation on Cu(410) we performed other experiments by dosing O$_2$ at oblique incidence (see inset of Fig. 17 for details on the angles of incidence) [64]. If oxide formation proceeds dominantly via detachment of copper atoms by impinging O$_2$, we expect the oxidation rate to be largest when the molecules impinge from the upper side of the step edge at large angles (● symbols in Fig. 17). Indeed the experiment shows that this scattering condition is more efficient for oxidation than the one corresponding to molecules colliding nearly normal to the step rises, but the highest efficiency is when O$_2$ molecules impinge along the surface normal. CIA is thus the main mechanism for oxide formation on Cu(410) by HOMB. Detachment of Cu atoms plays only a minor role on Cu(410), contrary to the case of HOMB oxidation of Cu(110) where it was suggested to be relevant [76].

In CIA the important factor is the energy transferred to oxygen adatoms in the direction pointing towards the subsurface region. This argument naturally indicates the efficiency for collisions to be highest along the surface normal, in agreement with experimental observation. According to DFT calculations, subsurface adsorption of O on Cu(100) is energetically favored with respect to on-surface adsorption above 0.5 ML [57]. For Cu(410) (see the model in the inset of Figs. 10 and 11) this condition corresponds to 0.25 ML of adatoms at fourfold hollow terrace sites and the remaining 0.25 ML at the step edges.

A closer inspection of the Cu(410) geometry shows that at an incidence angle $\theta=-30^\circ$ (off normal towards the (100) nanoterrace), O$_2$ molecules hit the O moiety pre-adsorbed at terrace sites at nearly the same angle as for $\theta=0^\circ$ since the surface normal to (100) nanoterraces is at $\theta=-14^\circ$. The adatoms at the step edges are however pushed towards the bottom of the (110) step against the underlying (100) nanoterrace. When moving to $\theta=+30^\circ$ (off normal towards the step rise) the terrace O moiety is hit at 45$^\circ$ while the adatoms at step sites are pushed against the step rise. The larger cross section for oxide formation for $\theta=-30^\circ$ indicates therefore that subsurface incorporation is favoured when O adatoms move towards the fourfold hollow below the step. The same conclusion was
reached investigating direct subsurface incorporation of O on Ag(210), which turned out to be easier when O$_2$ molecules impinge normally to the (100) nanofacet [72].

No traces of oxide formation are detected in O1s and valence-band SR-XPS spectra, when dosing at $E_i=0.5$ eV, indicating that this translational energy is not high enough to induce oxygen incorporation [21]. This experimental evidence strongly supports the CIA mechanism, too.

The oxidation rate is angle-dependent only at intermediate exposure/coverage. For HOMBO exposures exceeding $5 \times 10^{18}$ molecules/cm$^2$, the efficiency of Cu$_2$O formation is independent of the polar direction of incidence. This is quite reasonable since, for such massive exposures, the coverage exceeds 1 ML and the oxide covers a large fraction of the surface area. At this stage, memory of the initial stepped geometry is lost and further oxide formation occurs by growth and coalescence of already existing copper oxide islands rather than by nucleation of new oxide patches. Moreover, the oxide free areas are in the valleys between oxide islands, so that the impinging direction of O$_2$ is no longer relevant. This picture is supported by the absence of clearly ordered LEED patterns upon massive HOMB exposures.

As apparent from Fig. 16, the oxidation rate of Cu(410) falls in between those of Cu(110) and of Cu(100). However, if we take into account the density of step O atoms, the efficiency of Cu$_2$O formation on O-Cu(410) turns out to be comparable to the one of the added-row reconstructed O-Cu(110). O atoms at the step edges of Cu(410) form Cu-O- chains quite similar to those present on added rows of O-Cu(110). This is reasonable since since Cu(410) consists of (100) terraces separated by (110) steps and since the hyperthermal oxidation mechanism, whatever its origin, is more efficient for Cu(110) than for Cu(100) and Cu(111). The reduced efficiency of the closed packed (111) surface, for which subsurface incorporation is more difficult, further supports the suggestion that the CIA mechanism is dominant for Cu(410). Conversely, we notice that the opposite holds true for oxidation under thermal conditions, for which the rate is highest for Cu(111). The mechanism underlying HOMB oxidation is thus entirely different from the one operative one under thermal conditions [50, 65] (see, section 4.1).
4.3. Rate equation model of Cu$_2$O formation

Let us consider a Cu(410) surface with 0.5 ML O-coverage and exposed to a HOMB. When O$_2$ collides with a pre-adsorbed oxygen adatom, there is a finite probability that the latter is pushed subsurface. The incoming molecule, on the other hand, can meet three different fates:

1) it may desorb;

2) it may dissociate leaving one atom at the surface and ejecting the second one into the vacuum [77]. This corresponds to an abstraction reaction which is unlikely but energetically possible for hyperthermal molecules;

3) it may dissociate leaving both O atoms on the surface.

We remember that subsurface sites are unstable by themselves and are stabilized by the presence of an oxygen adatom in super-surface location. Therefore in case 1) the atom hit by the incident molecule can either return back to the surface or move to another subsurface site below an O adatom. We identify this latter condition with the creation of an oxide nucleus (O$_{ad}$+O$_{sub}$); the number of O adatoms without a subsurface companion decreases then by two units.

In case 2) an oxide nucleus (O$_{ad}$+O$_{sub}$) forms and the number of O adatoms without subsurface companion decreases by one unit.

In case 3) the O adatom pushed subsurface by the collision and one of the atoms produced by the dissociation of the incident O$_2$ molecule build up an oxide nucleus (O$_{ad}$+O$_{sub}$). The second O atom arising from the dissociation cannot stay at the surface, since the O coverage would then exceed 0.5 ML; thus it must move subsurface below another O adatom. The net balance is the formation of two oxide nuclei and the loss of two sites with adatoms without subsurface companion.

If n is the number of new oxide nuclei being formed and q is the number of lost O adatoms, it is possible to set up a semi-quantitative model of the HOMB uptake curves using the following rate equations:

\[ \frac{d\Theta_O}{dt} = 2\Phi S_{adatom} - q \Phi P_{oxide} \Theta_O \]
\[
d\Theta_{\text{oxide}}/dt = 2n \Phi P_{\text{oxide}} \Theta_O
\]

where:
\[
S_{\text{adatom}} = S_0 (1 - \Theta_O/\Theta_{\text{Osat}} - \Theta_{\text{oxide}}/\Theta_{\text{max}})^m,
\]
\(P_{\text{oxide}}\) is the probability that an O atom ends up subsurface in a direct molecule-adatom collision, \(\Phi\) is the beam flux, \(S_0\) is the \(\text{O}_2\) initial sticking probability, \(\Theta_O\) and \(\Theta_{\text{oxide}}\) are the coverage of O adatoms without subsurface companion and of O atoms in the oxide, respectively, \(\Theta_{\text{Osat}}\) is the O saturation coverage (0.5 ML for Cu(410)). The factor 2 in the second formula arises from the definition of the oxide nucleus as a \(\text{O}_{\text{ad}}\) + \(\text{O}_{\text{sub}}\) couple, so that the number of O atoms is twice the number, \(n\), of such couples.

The factor \((1 - \Theta_O/\Theta_{\text{Osat}} - \Theta_{\text{oxide}}/\Theta_{\text{max}})^m\) accounts for two possible effects:

a) when oxide growth is initiated, some surface sites are occupied by oxide nuclei and are thus no longer available for further oxygen adsorption.

b) the sticking probability for surface sites vanishes at \(\Theta_{\text{Osat}}\)

In order to account for the non-layer-by-layer growth of the oxide we introduce the free parameter \(\Theta_{\text{max}}\) (typically 2.1 ML), corresponding to the total coverage for which there are no more free Cu sites available for oxygen adsorption. At \(\Theta_{\text{max}}\), oxide formation via the CIA mechanism stops and another mechanism is required to describe the growth of a thicker oxide layer. \(\Theta_{\text{max}}\) is then a free parameter and does not arise, as a more realistic model would require, from the description of the island growth mechanism in three dimensions. The exponent \(m\) accounts for the rate of the decrease of the sticking probability just below 0.5 ML. In our model it is obtained by fitting the decrease of the sticking probability with coverage below 0.5 ML and reads \(\approx 4\), in agreement with the operation of strong lateral repulsive interactions between O adatoms (\(m = 2\) would be expected for dissociative adsorption with non interacting adatoms). The strong O-O repulsion is also responsible for the occupation of subsurface site being energetically favored for \(\Theta \geq 0.5\) ML.

For mechanism 1) we expect a significant temperature and flux dependence of the oxidation rate, because the atoms pushed subsurface can diffuse back onto the surface if the vacancy is not rapidly refilled by a new O adatom produced in the dissociation of
another incoming O₂. In cases 2) and 3), on the contrary, a purely collisional mechanism is operative, so that neither flux nor temperature dependence is expected. Recombinative desorption is not included in the model since it is negligible for our experimental conditions.

Fig. 18 shows the O coverage vs. exposure obtained for cases 1), 2) and 3). Although it does not determine unambiguously which is the actual reaction path followed, the model captures the essential physics. In fact it shows a semi quantitative agreement with the data, which is the best we can expect with our heuristic approach: very similar curves can be obtained, e.g., by mechanism 3) with Poxide=3×10⁻⁴ or by mechanism 1) with Poxide=6×10⁻⁴. The model predicts a lower growth rate than experiment at Θ≤1 ML and a faster growth rate above 1 ML. At a total oxygen coverage of 1 ML a significant fraction of O adatoms should still be present and their contribution should disappear close to 2 ML. This is in accord with the experimental data of Fig.14, showing that the contribution of O adatoms to the XPS spectra (530.0 eV) has a significant intensity for Θ=1 ML but is no longer present at 2.0 ML. At 2.0 ML, all adatoms have been used to form Cu₂O (component at 530.4 eV) or have been turned into O adatoms on copper oxide (component at 531.4 eV). The existence of an asymptote in the oxide thickness is supported by the decrease in the oxide growth rate for Θ≥1.5 ML. Recent unpublished experiments on Cu(511) [78], for which much longer exposures were performed, indicate that a limiting coverage is indeed approached, thus supporting the existence of a limiting thickness for the oxide film grown via the CIA mechanism.

The data at grazing incidence seem to be better described by a lower value of Θmax (≈1.6 ML instead of 2.1 ML), thus indicating that the morphology of the oxide islands may depend on the angle of incidence of the incoming O₂.

The solution of the rate equations indicates moreover that uptake curves following closely the experimental data can be obtained for Poxide ≈3×10⁻⁴, corresponding to a sticking probability of 3×10⁻⁴ at 0.5 ML. This value is about one order of magnitude larger than for Cu(100) (10⁻⁵, see Ref. 22 ) and only slightly smaller than for Cu(110) [76]. Since it does not scale with the relative area of (110) and (100) nanofacets, the
result indicates unambiguously that the presence of the defect enhances the sticking probability.

4.4 Temperature dependence of Cu oxide formation: Cu$_2$O and CuO

The evolution of the O1s spectra during exposure of Cu(410) at 100 K and at RT to 2.2 eV HOMB was measured with $h\nu$=1092.8 eV and normal emission [63]. The line shape of the O1s peak depends strongly on O coverage and surface temperature during oxidation. In Fig. 19 we show the results of the peak-shape analysis of typical O1s spectra. The symmetric peak of O1s at $\Theta$=0.55 ML at room temperature and ~100 K is fitted by a Voigt function with parameters $G$=0.76 eV and Lorentzian width $\Gamma$=0.36 eV. The O1s binding energy is 530.1 eV at room temperature [64] and 530.0 eV at 100 K. At higher O coverage and for both T, it is necessary to include several additional components, the weight of which depends both on coverage and on oxidation temperature.

At room temperature a fit can be achieved only including contributions of Cu$_2$O at 530.5 eV and of CuO at 529.3 eV [4]. We remind here that a small amount of CuO was observed previously for Cu$_2$O formation on Cu(110) [70]. At the highest investigated O concentration the chemisorbed O component at 530.1 eV is no longer present, thus witnessing that the substrate is now fully covered by Cu$_2$O. The small additional peak at 531.5 eV is assigned to chemisorbed O on Cu oxide [4].

At low T a further component is necessary to fit the data: its binding energy is at 530.1 eV. We associate it to subsurface O [79]. Although this binding energy nearly coincides with the one of chemisorbed O, its introduction is not arbitrary but justified by statistical and physical reasons. In fact with it: a) the $\chi^2$ value per degree of freedom decreases significantly from 1.64 to 1.54 and the Abbe criterion coefficient, estimating the extent of systematic errors, increases from 0.84 to 0.93, indicating smaller systematic deviations [80]; b) at the highest coverage a peak at 530 eV with weight close to 0.5 ML is needed to fit the data. This coverage corresponds to the saturation of chemisorbed O. If the component at 530 eV were due only to supersurface oxygen, we should conclude that only a very small fraction of the surface is covered by Cu oxide.
The latter would then consist of 3-dimensional islands of Cu oxide unphysically elongated normally to the surface.

Cu$_2$O and CuO formation is confirmed by inspection of the Cu L$_3$M$_{4.5}$M$_{4.5}$ Auger electron spectra (AES) and by the Cu 2p spectra reported in Figs. 20 and 21, measured at $h\nu=1092.8$ eV. The reference AES spectra of bulk Cu$_2$O and CuO [4] are also shown in Fig. 20 for comparison. At room temperature exposure to 2.2-eV HOMB produced almost only Cu$_2$O (see also 4.2), as it can be seen in the Cu L$_3$M$_{4.5}$M$_{4.5}$ AES spectra of the oxidized surface. At T~100 K, both AES and XPS (see Fig.19) spectra show, the larger weight of CuO and, conversely, the reduction of the one of Cu$_2$O. Moreover, the satellite and the shoulder of Cu2p, characteristic of the d$^9$ configuration in the ground state of CuO, are clearly observed in the SR-XPS spectra in Fig. 21 in the E$_B$ range 933-945 eV.

The coexistence of Cu$_2$O, subsurface O and CuO for HOMB exposures performed at 100 K suggests that the local heating by high energy HOMB is insufficient for the formation of a homogeneous Cu$_2$O-layer. Mobility of Cu and O atoms, attained at higher T, is thus required for the production of high quality Cu$_2$O film.

While nucleation of Cu$_2$O is expected, the formation of CuO at low T is quite surprising; indeed this moiety is usually produced only at high T and high O$_2$ pressure [81, 82]. It is possible that under the present conditions, CuO reacts with Cu following CuO+Cu$\rightarrow$Cu$_2$O; in this case the CuO phase may act as a metastable precursor for Cu$_2$O formation. It should be also noted that a similar reaction pathway, leading to Cu$_2$O formation, was observed when depositing Cu atoms on CuO thin films [83]. The metastable nature of the CuO phase is supported by the fact that, when heating to 273 K, the O1s component corresponding to CuO disappears in the SR-XPS O1s spectrum [63].

The CIA mechanism [21] plays therefore a dominant role also for the nucleation of the metastable CuO phase, in analogy to the cases of Cu(100) [22] and Si(100) [29]. The transformation to Cu$_2$O occurs eventually at higher T when enough supply of Cu atoms via diffusion becomes possible. The translational energy of the incident O$_2$ is thereby
used mainly to push pre-adsorbed O atoms into subsurface sites, although local substrate heating may also contribute. Fabrication of CuO islands at low T is only attained by HOMB. We do not know whether the Neél temperature of such CuO phase is affected and modified with respect to the value of 229 K of bulk CuO [12].

5. Oxide Formation on Cu(111) and Cu(110) induced by HOMB
The kinetics of oxide formation strongly depends on surface structure. When allowed by the Cu-Cu spacing, Cu-O chains form along the [100] direction. This is however not always the case and different oxide structures form for the different Cu planes [84]. On Cu(100) the Cu-O missing row [38,44] structure forms, while on Cu(110) an added row [85,86] reconstruction is observed. On Cu(111), on the contrary, the impossibility to form Cu-O chains leads to a complicated reconstruction upon oxygen adsorption [87-94]. In this paragraph we compare the two extreme cases of oxidation, namely Cu(111) and Cu(110), focusing on the dependence of the structure on the substrate symmetry.

5.1. Surface oxide formation induced by HOMB on Cu(111)
The formation of stable Cu-O- chains along the [100] direction plays a key role in the surface oxidation of Cu. This process is possibly more intriguing of Cu(111) than on Cu(100) and Cu(110) because of the lack of atoms with the required spacing and arrangement of the [100] direction. Moreover, due to the chemical stability of the close-packed (111) structure, oxide formation on Cu(111) is expected to be much less effective than that on Cu(100) and Cu(110).

Since oxygen adsorption on Cu(111) is accompanied by a rather complex reconstruction, there is no general agreement on the surface structure and on the mechanism underlying surface oxide formation. Briefly, while some researchers reported that no long-range-ordered structure forms at and above room temperature [69, 95-98], others described \((\sqrt[3]{3}R46.1^\circ \times 7R21.8^\circ)\) and \((\sqrt[3]{3}R5.8^\circ \times \sqrt{21}R-10.9^\circ)\) overlayers observed in LEED and STM studies upon oxygen adsorption at high temperatures [87-90]. Such structures have been addressed as ’29’ and ‘44’ structure,
respectively, by comparing their unit cells with the one of the (1×1) substrate. A significantly different overlayer was moreover observed at RT after high oxygen exposures (>10⁵ L) [91]: in the matrix notation it is identified as 32 and consists of a pseudo-(001) structure with the oxygen atoms in local fourfold geometry [91,94]. The existence of so many possible O induced superstructures on Cu(111) obviously complicates the understanding of this system. HREELS inspection of this system evidences only weak losses due to O-adatoms when O₂ exposure is performed by backfilling at or above RT [69] and no loss at all when it is performed below RT [99]: the screening of its vibration implies that the O atoms sit coplanar with the outermost Cu layer.

Fig. 22 shows the evolution of the O1s XPS spectra during a 2.3 eV HOMB dose at normal incidence on Cu(111) at RT. The changes in the shape of the spectra indicate that the oxidation of Cu(111) proceeds in three different stages: Θ<0.27 ML, 0.27<Θ<0.4 ML, and Θ>0.4 ML.

In the initial stage we detect an O1s peak at E_B=529.4 eV, whose intensity increases with Θ. In this coverage range no ordered superstructures were observed by LEED. Oxygen adsorbs dissociatively at threefold hollow sites without causing surface reconstruction. The assignment to the three fold hollow at low oxygen coverage is supported both by theoretical [19,100] and spectroscopic studies [101,102], so that the XPS peak with E_B=529.4 eV can be reasonably assigned to oxygen adatoms.

The translational energy dependence of the O-uptake curves below 0.4 ML coverage during exposure are shown in Fig. 23 for HOMB and thermal O₂ exposure. The intensity reported in each uptake curve was determined from the integration of the O1s XPS peaks. The nozzle temperature was set at 300 K except for 1.0 eV HOMB data recorded with He and Ar carrier gas mixture and T_n=1400 K. For Θ<0.27 ML, kinetic energy and internal excited states of O₂ are among the important parameters determining the rate of oxygen adsorption [32,94]: on one hand, the high translational energy of O₂ generated by HOMB enhances the adsorption probability by allowing to
the O$_2$ to overcome the activation barrier for dissociation; on the other hand, the vibrational excitation of O$_2$, which is no longer negligible for $T_a=1400$ K, enhances dissociative adsorption [32], most likely because of the reduction of the activation barrier for vibrationally hot molecules.

In the second stage, at $0.27<\Theta<0.4$ ML, a \( \parallel, \parallel \) LEED pattern forms during HOMB exposure. The observed LEED pattern and the schematic representation of the reciprocal lattice are shown in Fig. 24(a) and (b), respectively. One possible structural model is a pseudo-Cu(001)-O where O atoms are placed in fourfold coordinated hollow sites on a Cu(001)-like structure formed on Cu(111) [91]. Although a pseudo-(001) reconstruction has been observed for C, N, and S adsorption on Cu and Ni(111) [84], it is not favoured for O/Cu(111); in fact for the O/Cu system the higher stability on the surface and in the bulk is attained by the formation of -Cu-O-Cu- chains along [100] direction, an arrangement not possible on Cu(111).

Fig. 25 shows the typical evolution of the O-1s XPS spectra on Cu(111) from 0.23 to 0.42 ML during 0.5-eV-HOMB exposure along the surface normal. A new O-1s component appears at $E_b=528.9$ eV in XPS for $\Theta\geq0.27$ ML, i.e. at the onset of the \( \parallel, \parallel \) LEED pattern. The spectra need now to be described by the superposition of two peaks, A and B, at 529.4 and 528.9 eV respectively. Peak B increases with increasing $\Theta$, while peak A (the only one observed below 0.27 ML) decreases. Finally the surface becomes saturated at $\Theta=0.4$ ML. The binding energy of 528.9 eV for peak B agrees very well with that for oxygen adsorbed at the fourfold hollow site on a unreconstructed Cu(001) surface at low coverage [22]. Therefore the LEED pattern in Fig. 24 suggests that oxygen occupies a four-coordinated site in the \( \parallel, \parallel \) structure. A Cu(001)-like reconstruction has been indeed suggested in a photoelectron diffraction (PhD) study of the disordered chemisorption phase on O/Cu(111) [103]. A tentative structural model for the \( \parallel, \parallel \) structure is show in Figure 26.

It is important to note that the saturation coverage is 0.27 ML for HOMB dosing at $E_i\leq0.23$ eV, while it increases up to 0.4 ML for $E_i\geq0.5$ eV. When dosing by backfilling the surface saturates indeed at $\Theta=0.27$ ML, and only after the very large
exposure of $\sim2\times10^{19}$ molecules·cm$^{-2}$ a coverage of $\Theta=0.4$ ML can be attained. No ordered structures were observed in the LEED pattern during thermal O$_2$ exposure even at $\Theta=0.4$ ML. Interestingly the triple domain $\left|\frac{1}{2}, \frac{3}{2}\right|$ structure on the Cu(111) sample at 320 K could be induced even under thermal O$_2$ exposure conditions after the surface had been subjected to several tens of HOMB exposure cycles. This fact indicates that HOMB dosing modifies the copper surface so deeply that usual sputtering doses are not sufficient to restore the initial situation. Elucidating the mechanism of this phenomenon is beyond the scope of this paper, but we mention here that O$_2$ collisions with energy exceeding 0.5 eV may be able to induce step formation on Cu(111). Anyway, a large translational energy (>0.5 eV) is required for oxygen to induce the reconstruction on Cu(111) at $\Theta \geq 0.27$ ML.

Now the question of which mechanism induces such reconstruction naturally arises. The peak B and the $\left|\frac{1}{2}, \frac{3}{2}\right|$ LEED pattern were not observed after bombarding the surface pre-covered by oxygen deposited by backfilling with a 0.5-eV-Ar-beam impinging along the surface normal. This fact implies that the HOMB induced reconstruction cannot be simply explained by a thermal equilibrium process in which the energetic O$_2$ molecules transfer their translational energy to the disordered phase and thermally induce its $\left|\frac{1}{2}, \frac{3}{2}\right|$ reconstruction; a more complicated process, possibly involving also the O$_2$ chemisorption energy, must then occur.

One possible reaction model for the HOMB-induced-reconstruction process is that the growth of $\left|\frac{1}{2}, \frac{3}{2}\right|$ structure is initiated from oxygen adsorbed at steps. Indeed peak B does not increase beyond saturation coverage of 0.27 ML and STM studies have indicated that the step edges play a crucial role for oxide growth [89,90], thus revealing that step edges along $[1\_10]$ initiate nucleation of 2D oxide. We also remind the pivotal importance of open steps for Cu$_2$O formation found for the oxidation of Cu(410) [64]. The simultaneous growth of peak B and decrease of peak A in Fig. 25 suggests that HOMB promotes the growth of the $\left|\frac{1}{2}, \frac{3}{2}\right|$ structure from the step edges onto the (111) terrace. A translational energy of 0.5 eV is still too low to induce the reconstruction because, as mentioned above, an energetic Ar beam is unable to induce it. However, 0.5 eV kinetic energy may be enough to overcome the activation barrier for dissociative O$_2$
adsorption at the step edge and allow the reaction with the low coordinated Cu atoms, although the theoretical value of 0.2 eV [100] at high Θ is probably increased by the O-O repulsion. The energy released in the chemisorption of oxygen is possibly used locally to break further Cu-Cu bonds and produce Cu adatoms and Cu-O complexes. Many experimental [104-106] and theoretical [107,108] studies suggested that oxygen atoms prefer to adsorb at the fourfold hollow site in the {001} faceted step edge whenever a Cu-Cu spacing along the [100] direction is available. Because Cu adatoms and Cu-O complexes are mobile even at RT [109], they may stack up at the step edge at Cu-Cu spacing suitable for copper oxide, although some lattice mismatches to the Cu(111) face must remain.

After annealing at 620 K, the structure changes to the so called ‘29’ structure. The ‘29’ structure is similar to bulk Cu₂O(111) [88] and is thus a more stable oxide structure than the one characterized by the lattice mismatch between the Cu(001)-like overlayer and the Cu(111) substrate. We can thus conclude that HOMB can induce the formation of a metastable surface oxide structure, which cannot be produced otherwise and in particular by dosing at thermal equilibrium by backfilling.

5.2. Cu₂O formation on Cu(111) induced by HOMB

To proceed further beyond Θ > 0.4 ML, oxidation requires an even larger O₂ translational energy. An O coverage above 0.6 ML was obtained on Cu(111) using 2.3-eV-HOMB, to be compared with the 0.4 ML reached for the 0.5-eV HOMB exposure.

Figure 27 shows the O-uptake curves for 0.6 and 2.3-eV HOMB and for thermal O₂ exposure determined by integrating the O-1s XPS spectra. As shown in the figure, oxygen coverage did not increase above ~0.4 ML when dosing with the 0.6-eV-HOMB. In contrast, oxidation gradually proceeds when exposing the Cu surface to the 2.3-eV-HOMB. As shown in Fig. 22, a peak at Eₘ=529.9 eV, corresponding to the formation of the Cu₂O [79], develops in this regime. Figure 28 shows the O-coverage dependence of the sticking probability, estimated from the O-uptake curve, for HOMB incidence on Cu(111). S, decreases from ~10⁻³ to ~10⁻⁶ and remains then constant above
0.4 ML for the 2.3-eV HOMB, while it becomes negligible for the 0.6-eV HOMB. The continuation of oxidation with the small probability of \( \sim 10^{-6} \) above 0.4 ML is interpreted as evidence for a CIA mechanism. Similarly to the Cu(100) case [22], we have indeed confirmed that the energetic Ar beam also induces Cu_2O formation on Cu(111). Although O atoms require a higher substrate temperature of \( \sim 500 \) K [79] to penetrate into the subsurface region, the energetic O atom produced on the surface by a collision with an incident O\(_2\) is therefore able to access subsurface sites and to induce oxide formation.

5.3. Azimuthal dependence of Cu\(_2\)O formation on Cu(110) induced by HOMB

The Cu\(_2\)O formation process on an open surface as Cu(110) seems to be more complicated than for the Cu(100) and Cu(111) substrates, since it has several directly accessible sites and since it is highly corrugated. Fig. 29 shows the typical evolution of the O 1s SR-XPS spectra during 2.3-eV-HOMB irradiation along the surface normal of the Cu(110) surface at RT. \( \Theta \) was determined from the O 1s intensity calibrated with respect to the saturation coverage of Cu(100)-(2\( \sqrt{2} \times \sqrt{2})\)R45\(^\circ\)-O, with a correction for the face-dependent Cu density. A symmetric single O 1s peak grows upon O\(_2\) exposure at 529.9 eV up to 0.64 ML. At higher \( \Theta \), a further component appears at higher binding energy, corresponding to the contribution of the subsurface (Cu\(_2\)O) O atoms [70]. A (2\( \times \)1) LEED pattern corresponding to the formation of O-added rows (AR) [85] appears above 0.1 ML and changes to a c(6\( \times \)2) pattern [110] above 0.5 ML. Such overlayer is then completed at \( \sim 0.7 \) ML.

Fig. 30 shows the O-uptake curves for 2.3-eV-HOMB and for thermal O\(_2\) exposure on Cu(110). For the thermal O\(_2\) exposure, the surface gets almost saturated at \( \Theta \sim 0.5 \) ML, while with the 2.3-eV HOMB higher coverages are achieved, resulting in a more efficient formation of Cu\(_2\)O. The larger initial sticking probability for thermal O\(_2\) suggests a precursor-mediated adsorption at low incident energy. For thermal O\(_2\), the huge dosage of \( \sim 10^{15} \) L, corresponding to \( \sim 10^{19} \) molecules cm\(^{-2}\), was required to form the c(6\( \times \)2) structure at RT [86,110-112] and it was rather difficult to promote oxidation above 0.7 ML [113] due to the strong repulsive interaction between O adatoms [114].

Commento [le2]: I’m confused. You said before that the Ar beam does not make anything to the O-reconstructed surface with theta<0.4 ML, and now you invoke a CIA mechanism. Energetic O\(_2\) could induce the surface reconstruction and also Cu\(_2\)O formation via CIA mechanism. On the other hand, the energetic Ar could not induce reconstruction, but it could induce only Cu\(_2\)O formation. We have confirmed a little Cu\(_2\)O formation by energetic Ar beam at the dose of 5\( \times \)10\(^{-19}\) atoms/cm\(^2\). Therefore, the energy released in the chemisorption of oxygen is possibly used for the HOMB induced reconstruction. On the other hand, CIA mechanism occurs via the mechanical energy transfer from the incident particle to the preadsorbed O atom. Although the probability of CIA mechanism is very small as shown in FIG.28, it may occur simultaneously with the HOMB induced...
On the other hand, with 2.3-eV HOMB we easily achieved $\Theta > 0.5$ ML and the formation of Cu$_2$O occurred more efficiently thereafter.

The Cu$_2$O formation process by HOMB on Cu(110) is significantly different from that on Cu(100) and Cu(111). We measured the O-1s spectra after 3-eV-Ar-beam incidence along the surface normal on the O-covered Cu(110) surface saturated by thermal O$_2$ gas adsorption at RT; even after the Ar dose of 6.5$\times$10$^{20}$ atoms$\cdot$cm$^{-2}$ no noticeable changes in the line shape of O-1s peak were detected, demonstrating that the effective oxide formation on Cu(110) cannot be explained entirely by the CIA mechanism. Therefore, another oxidation mechanism, peculiar to the Cu(110) surface, must be active.

Fig. 31 shows the azimuthal-incident-angle dependence of the uptake curve for 2.3-eV-HOMB exposure on Cu(110) at RT. The angle of incidence is normal to the surface and 45° from the surface normal along the [001] direction (along AR) or along the [1$\bar{1}$,10] direction (normal to AR). Dissociative adsorption along the AR occurs more efficiently than normally to the AR; i.e., the value of $S$ along AR is larger than it is normally to AR. $S$ is initially independent of the incident azimuth. The onset of the anisotropy occurs at $\Theta \approx 0.2$ ML, almost corresponding to the appearance of the AR. It should be noted that the oxidation efficiency along AR is nearly the same as under normal incidence for $\Theta \leq 0.7$ ML.

In order to account for the experimental data about the formation of Cu$_2$O on Cu(110), we suggest the following reaction mechanism. The oxidation of Cu(110) by HOMB is promoted by dissociation at the troughs of the AR structure for $\Theta \leq 0.7$ ML, possibly via molecular precursors. A theoretical study suggested indeed that a 4-fold hollow site on a Cu(110) surface is favorable for O$_2$ adsorption followed by spontaneous dissociation [115]. A hollow site on the AR structure is accessible by O$_2$ impinging along both AR and surface normal without impediment, while it is shadowed when impinging normal to the AR. This scenario is also applicable to the oxidation at $\Theta \geq 0.7$ ML. On the c(6×2) structure, copper atoms occupy alternatively a short bridge site in the trough along [100] thus shadowing the reactive site for O$_2$ impinging along the AR [116]. This may cause a reduction in oxidation rate for HOMB incidence along AR for $\Theta \geq 0.7$.
ML compared to incidence along the direction normal to the surface (see the blue and the red lines for $\Theta \geq 0.7$ ML in Fig. 31).

The energy barrier to overcome to access to the reactive site on the c(6x2) structure is enhanced due to the repulsive interaction between the existing –Cu-O- chains and the impinging O$_2$ molecule. Therefore a high translational energy is required for oxidation to proceed above $\Theta \geq 0.7$ ML. In addition to dissociation at the hollow site, the energetic O$_2$ may possibly induce new active sites on the surface. Since the translational energy pertinent to the 2.3-eV HOMB exceeds the activation barrier for diffusion of the surface adatoms, which is estimated of several hundred meV [114], the HOMB may promote it. A migrating Cu atom, possibly in the trough, may then act as a reactive site.

Finally, the sticking probabilities on Cu(110), (100) and (111) are compared in Fig. 32 vs. O-atom density for the 2.3-eV-HOMB. S on (100) and (111) surfaces decreases suddenly around coverages of $8 \times 10^{14}$ atoms·cm$^{-2}$ and then maintains a probability of $10^3$–$10^6$ during Cu$_2$O formation. The attainable O density for a give exposure range is thus lower than on Cu(110). The residual S in the region of Cu$_2$O formation on Cu(100) and (111) has been interpreted by CIA. On the other hand, S during the growth of Cu$_2$O on Cu(110) is larger by 1~2 orders of magnitude. This larger value of S is attributed to the newly opened reaction channel for Cu$_2$O formation via reaction in the troughs of the AR structure induced by the 2.3-eV HOMB.

### 6. Conclusions

Oxidation of single-crystal Cu surfaces by HOMB was investigated with high-resolution XPS with SR. The advantage in oxide formation by HOMB dosing is clearly demonstrated and attributed to the high translational energy available with the beam. Cu oxide formation on low-indexed Cu surfaces is dominanted by collision-induced absorption operative with HOMB irradiation. The efficiency of oxide formation is quite sensitive to the crystal face. The stepped surface is more effective in the oxide formation via CIA. On the open (110) surface, another mechanism related to the creation of mobile Cu atoms working as reaction centers is also active.
In the oxidation of Cu with thermal O\textsubscript{2} by backfilling, the growth process is determined by the availability of Cu atoms, which may detach via thermal activation from the open steps or by the availability of channels for subsurface migration at the steps.

We demonstrate that nearly perfect Cu\textsubscript{2}O films can be grown on Cu(410) by HOMB at room temperature, while also CuO forms at \textasciitilde100K. The latter phase disappears when annealing just below RT. This result shows the existence of a reaction route for Cu\textsubscript{2}O formation through a metastable CuO state when dosing by HOMB on a cold substrate.

These HOMB induced oxide formation processes are of general importance for the fabrication of Cu oxide at and below a room temperature, which is quite important for the device technology. Moreover, HOMB has also a great potential for the fabrication of metastable phases for the synthesis of new nanostructured materials.

**Acknowledgements**

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[58] No O-1s intensity in SR-XPS spectra was observed on Au(111) even after doses of $10^{18}$–$10^{20}$ O$_2$ molecules /cm$^2$ with a 2.3 eV HOMB.


[79] Subsurface oxygen on Cu(111) has been identified with an O1s peak at 529.9 by J. Bloch, D.J. Bottomley, S. Janz and H.M. van Driel, J. Chem. Phys. 98, 9167 (1993).
[80] http://www.uni-leipzig.de/~unifit/
Table 1. Crystallographic parameters of Cu$_2$O and CuO [2-4]

<table>
<thead>
<tr>
<th></th>
<th>Cu$_2$O</th>
<th>CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameter</td>
<td>Cubic, $a=4.27$ Å</td>
<td>Monoclinic, $a=4.6837$ Å</td>
</tr>
<tr>
<td></td>
<td>$b=3.4226$ Å</td>
<td>$b=3.4226$ Å</td>
</tr>
<tr>
<td></td>
<td>$c=5.1288$ Å</td>
<td>$c=5.1288$ Å</td>
</tr>
<tr>
<td></td>
<td>$\beta=99.54^\circ$</td>
<td>$\beta=99.54^\circ$</td>
</tr>
<tr>
<td>Shortest distance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_{\text{Cu-O}}$</td>
<td>1.84 Å</td>
<td>1.95 Å</td>
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<tr>
<td>$d_{\text{Cu-Cu}}$</td>
<td>3.02 Å</td>
<td>2.90 Å</td>
</tr>
</tbody>
</table>
FIG. 1. Schematic representation of bulk Cu$_2$O and CuO structures. Gray and black circles are copper and oxygen atom, respectively.
FIG. 2. Photograph of the experimental station for surface chemistry studies installed at the soft X-ray beamline BL23SU in the SPring-8. The dotted line indicates the surface reaction analysis apparatus (SUREAC2000).
FIG. 4. Left: ball model of Cu(100)-(2√2 × √2R45°)-O. Right: LEED pattern of Cu(100)-(2√2 × √2R45°)-O prepared at room temperature with 2.3 eV HOMB.
FIG. 5. O-coverage dependence of the O-1s XPS spectra recorded after exposure of Cu(100) at ~300 K to a 2.3-eV-HOMB impinging along the surface normal. Data are taken from Ref. [22]. From the bottom, spectra correspond to $\Theta=0$, 0.19, 0.32, 0.42, 0.47, 0.73 and 0.95 ML. The spectra at $\Theta=0.47$ and 0.95 ML consist of one and of two components, respectively. The LEED pattern at $\Theta=0.95$ ML is shown in the inset.
FIG. 6. O-uptake curves on Cu(100) for 2.3-eV HOMB incidence (full circles) and ambient O$_2$ exposure (dashed line). Data are taken from Ref. [22, 53]. Regions A and B are indicated by arrows.
FIG. 7. O-1s XPS spectra measured after the 3-eV Ar-beam incidence along the surface normal on the $\sqrt{2}$ surface ($\Theta=0.5$ ML) at ~300 K. Data are taken from [22]. Lower and upper spectra correspond to the 3-eV-Ar exposures of 3.3 and $6.8 \times 10^{19}$ atoms/cm$^2$, respectively. Each spectrum can be separated into two components, corresponding to surface and subsurface and/or bulk O atoms.
FIG. 8. Uptake curves of O on Cu$_2$Au(100) for the 2.3 (●) and 0.6 (○) eV HOMB incidence and for thermal O$_2$ exposure (⊗). Data are taken from Ref. [23]. The uptake curve on Cu(100) for 2.3-eV-HOMB incidence (open squares) is shown for comparison. The incidence direction is along the surface normal and the surface temperature is 300 K. The insets report a scheme of the clean (bottom) and O-covered surface. In the structural models, small open, middle, and large circles correspond to O, Cu and Au atoms, respectively. Black balls indicate Cu atoms in the layer without Au atoms.
FIG. 9. Schematic view of Cu(410). The angles corresponding to the normal to the (110) and (100) nanofacets (+31° and -14°, respectively) are reported in the side view.
FIG. 10. HREEL spectra recorded in-specular after preparation (I) (bottom, solid line) and (II) (top, dotted line). Data are taken from [64] Schematic models of optical phonon modes of Cu$_2$O and a picture of the c(2x2) O-Cu(410) surface are shown as insets.
FIG. 11. XPS spectra of O 1s after preparation (I) (bottom, solid line) and (II) (top, dotted line). Data are taken from [64]. A picture of the c(2x2) O-Cu(410) surface is shown in the inset.
Fig. 12. Temperature and background pressure dependence of the ratio between the 78 meV and 38 meV EELS intensities measured after exposure of Cu(410) to 4000 L of O₂. Data are taken from Ref. [65]. The EELS peaks were fitted with a Gaussian functions on an exponential background. The peak intensity was estimated from the height of the fitted Gaussian peak. The normalization of the 78 meV peak intensity to the one of the 38 meV peak reduces the scatter of the absolute loss intensities in the data.
FIG. 13. Evolution of O-1s XPS spectra for exposure of Cu(410) at room temperature to a 2.2 eV HOMB along the surface normal. Data are taken from Ref. [64].
FIG. 14. Line-shape analysis of representative O-1s SR-XPS spectra of Fig. 13. Data are taken from Ref. [64]. The four components, corresponding to chemisorbed O on Cu, Cu$_2$O, CuO and chemisorbed O on Cu$_2$O, are indicated by thick grey, thick dashed, thick solid, and thick dotted lines, respectively. The background is indicated by the thin dashed line.
FIG. 15. Valence-band SR-XPS spectra of Cu(410) clean (continuous blue) and covered by 2.07-ML-O (dashed red) dosed by 2.2 eV HOMB at room temperature. Data are taken from Ref. [64]. The thin dashed line corresponds to the XPS spectrum of bulk Cu$_2$O [4]. The spectra are measured at 70° from the surface normal. The calculated valence band peak positions of Cu$_2$O are marked by vertical bars at 7.95, 6.70, 2.78, and 1.29 eV [4].
FIG. 16. O uptake curves for HOMB at normal incidence on Cu(110) [76], Cu(410) [64] and Cu(100) [22] at room temperature. $E_i$ is 2.3 eV for Cu(110) and Cu(100) and 2.2 eV for Cu(410).
FIG. 17. O uptake curves for 2.2 eV HOMB on Cu(410) at room temperature, parametric in angle of incidence. Data are taken from Ref. [64]. θ is either normal (triangles) or at ±30° from the surface normal, i.e. nearly normal to (100) terraces (circles, θ=-30°) or to step rises (open squares, θ=+30°) (see inset).
FIG. 18. Comparison between the experimental total coverage of O atoms vs O₂ dose and the total coverage obtained by numerically solving the rate equations model described in the text.
FIG. 19. Line-shape analysis of the representative O-1s SR-XPS spectra at (a) T=100 K and (b) room temperature for 2.2-eV HOMB incidence along the surface normal. Data are taken from Ref. [63]. Four components are present. They correspond to chemisorbed O on Cu (530.1 at RT and 530.0 at 100 K), subsurface O (530.1 eV, only at 100 K), Cu$_2$O (530.5 eV), CuO (529.3 eV) and chemisorbed O on Cu oxide (531.5 eV).
FIG. 20. Cu L_{3}M_{2,3}M_{4,5} Auger electron spectra measured at 70° from the surface normal after 2.2-eV HOMB incidence along the surface normal. Data are taken from Ref. [63]. From the bottom: bare surface, 1.74 ML prepared at a room temperature, and 2.12 ML O coverage prepared at 100 K. Spectra corresponding to bulk CuO (dashed line) and Cu₂O (thin continuous line) are also shown [4].
FIG. 21. Cu-2p XPS spectra of Cu(410) measured for emission along the surface normal after the surface was exposed to 2.2-eV HOMB at normal incidence. Data are taken from Ref. [63]. From the top: magnified spectra for clean and O covered surfaces (1.74 ML at RT and 2.12 ML at 100 K). Bottom spectrum: non-magnified spectrum of the clean surface.
FIG. 22. Evolution of the O-1s XPS spectra during the 2.3-eV-HOMB exposure along the surface normal on Cu(111) at RT. Data are taken from Ref. [93]. The dotted and broken lines show the peak positions at 529.4 and 529.9 eV. The essential steps of Cu(111) oxidation are indicated on the right side (see text).
FIG. 23. O-uptake curves for 1.0, 0.5 and 0.23 eV-HOMB incidence along the surface normal and for thermal O$_2$ exposure on Cu(111) at RT. Data are taken from Ref. [94]. Oxygen coverage is determined by integrating the O-1s XPS spectra. ML unit represents the number of atoms per surface Cu atom. Thick and thin dashed lines are a guide to the eye for thermal O$_2$ and 0.23 eV HOMB data, respectively.
FIG. 24. (a) LEED pattern (Ep= 86.5 eV) of the oxygen covered Cu(111) surface at $\Theta$ =0.42 ML after 0.5 eV-HOMB incidence at RT. (b) Schematic representation of the reciprocal lattice of the $\frac{1}{2}, \frac{1}{2}$ structure.
FIG. 25. O-1s XPS spectra recorded during 0.5 eV HOMB incidence along the surface normal on a Cu(111) surface at RT. Data are taken from Ref. [94]. A and B peaks are reproduced by one single Voigt component.
FIG. 26. A tentative structural model for the \( \frac{1}{1} \frac{3}{2} \) oxide phase on the Cu(111) surface. Large grey and small black circles represent copper and oxygen atoms, respectively. Intensity of shading in the copper atoms indicates the difference of relative heights of these atoms. The white dotted line represents a \( \frac{1}{1} \frac{3}{2} \) unit cell.
FIG. 27. O-uptake curves for 0.6 (open circle) and 2.3 eV (solid circle) HOMB incidence and for thermal O₂ exposure (dashed line) on Cu(111). Data are taken from [92].
FIG. 28. O-coverage dependence of sticking probability for 0.6 (open circles) and 2.3 eV (solid circles) HOMB incidence on Cu(111). Sticking probability was calculated from the uptake curves in Fig. 27.
FIG. 29. Evolution of the O-1s XPS spectra during the 2.3 eV HOMB incidence along the surface normal on Cu(110) at RT. Data are taken from Ref. [76].
FIG. 30. O-uptake curves for 2.3 eV (solid circles with solid lines) HOMB exposure and thermal O$_2$ dose (open circles with broken lines) on Cu(110). Data are taken from Ref. [76]. Schemes on the right show the different overstructures forming in the different coverage ranges.
FIG. 31. The azimuthal incident angle dependence of the oxygen uptake curves on Cu(110) at RT. Data are taken from Ref. [76]. A schematic drawing of the AR structure and the incident direction is reported in the inset. The red solid triangles and line, the blue open circles and dotted line and the green solid circles and broken line are correspond to 2.3 eV HOMB exposure along the surface normal, along the [001] direction (along AR) and along the [1\bar{1},10] direction (normal to AR), respectively. The angle of oblique incidence is 45° from the surface normal. The observed LEED patterns are indicated on the left.
FIG. 32. Face dependence of the sticking probability vs O coverage for the 2.3 eV HOMB incidence at RT on Cu(110) (triangles), Cu(100) squares) and Cu(111) (circles). Data are taken from [76].
I'm confused. You said before that the Ar beam does not make anything to the O-reconstructed surface with theta<0.4 ML, and now you invoke a CIA mechanism.

Energetic O2 could induce the surface reconstruction and also Cu2O formation via CIA mechanism. On the other hand, the energetic Ar could not induce reconstruction, but it could induce only Cu2O formation. We have confirmed a little Cu2O formation by energetic Ar beam at the dose of 5x10^19 atoms/cm2. Therefore, the energy released in the chemisorption of oxygen is possibly used for the HOMB induced reconstruction. On the other hand, CIA mechanism occurs via the mechanical energy transfer from the incident particle to the preadsorbed O atom. Although the probability of CIA mechanism is very small as shown in FIG.28, it may occur simultaneously with the HOMB induced reconstruction. I have corrected the sentence on p.28 l.11.