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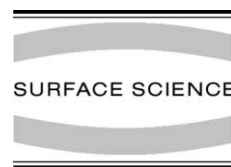
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Growth of 2-mercaptobenzoxazole on Cu(100) surface: chemisorbed and physisorbed phases

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Abstract

We present a high-resolution UV photoelectron spectroscopy study of 2-mercaptobenzoxazole (MBO) adsorbed on clean Cu(100), by sublimation in controlled ultra-high-vacuum conditions, at room temperature and at 100 K. The photoemission data show the formation of an MBO layer chemically interacting with the copper substrate. Saturation coverage is achieved at room temperature with the chemisorbed phase, while a physisorbed multilayer is formed at low temperatures on top of the chemisorbed interfacial layer. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Self-assembly; Chemisorption; Copper; Photoelectron spectroscopy

1. Introduction

Self-organization on a solid surface is a promising tool for growing uniform nanostructures with regular size and spacing. Organic materials are interesting candidates because of their low intrinsic conductivity and their possibility to form monolayers and multilayers of nanometric thickness. Organic thiols constitute an interesting class of self-assembling molecules on metal surfaces. Their technological interest is due to their potential ap-

plication as biosensors and corrosion inhibitors [1]. These interfacial structures are spontaneously formed by the adsorption of molecules with a functional reactive head group which bind chemically to the metal surface, and an organic part (saturated alkyl chain or aromatic ring) which gives rise to the lateral van der Waals interaction between the molecules, driving the molecular packing on the surface. The quality and kind of interaction, the ad-molecule to substrate interaction and eventually the ad-molecule to ad-molecule interaction and the role of the substrate to form ultra-thin ordered layers, are still open questions. A comprehensive range of data has been collected and interpreted for self-assembling of alkanethiols on various substrate [1–3]. In contrast, the literature on the adsorption and self-assembling

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monolayer formation of aromatic and heteroatomic thiols is sparse [4–6], although the introduction of an aromatic system into the two dimensional assembly is interesting in terms of its effects on packing and possible electronic interactions.

In this paper we report a high energy-resolution UV photoemission study of the adsorption of sublimated 2-mercaptobenzoxazole (C_7H_5NOS , in the following MBO) on Cu(100) at room and liquid nitrogen temperature. This molecule may exist in two tautomeric forms: the thione (NH, see inset of Fig. 1) and the thiol (SH) forms, the first with a C=S double bond and the latter having the endocyclic double bond C=N and the hydrogen atom bonded to the sulphur atom instead of the

nitrogen. A previous photoemission study showed that only the thione form is present in the MBO vapour while sublimating it in ultra-high-vacuum (UHV) conditions [7], so this is the species interacting with the Cu surface.

2. Experimental

The experiments, carried out at the surface physics laboratory LOTUS in Modena, were performed in UHV chambers containing a high resolution ultraviolet photoelectron spectroscopy (HRUPS) apparatus and other ancillary facilities for sample preparation. All photoelectron spectra reported here were excited with a high intensity He discharge lamp (HeI_{α} and $HeII_{\alpha}$ photons, $h\nu = 21.218$ and 40.814 eV, respectively). The photoemitted electrons were analyzed in the plane of incidence, with a high resolution Scienta SES-200 hemispherical analyser, with an integration angle of about $\pm 6^\circ$ with respect to the normal emission direction. Calibration of the binding energy scale was carried out in the adsorbed systems using the Cu Fermi edge at 0.00 eV. The gas-phase photoemission spectrum reported in Fig. 1 is calibrated against the C 1s signal of the benzene-like atoms (C_3 and C_4 in the inset of Fig. 1) at 285.0 eV. High purity (99.999%) Cu(100) single crystal was repeatedly cleaned by a series of sputtering–annealing cycles in order to remove the contaminants (carbon, oxygen and sulphur) from the sample surface. Each cycle consisted of sputtering with Ar^+ ions (800 eV, $8 \mu A$) for 30 min, followed by annealing at $420^\circ C$ for a few minutes. After this procedure, the Auger spectra show contaminant signals well below the noise level. Shorter annealing (about 30 s) at $450^\circ C$ allowed better rearrangement of the surface, as evidenced by the well defined low-energy electron-diffraction (LEED) pattern. Aldrich Chemical Company Inc. supplied MBO powder, which purity resulted 98.4% by gas chromatography analysis. The main impurities were crystallization solvents, removed before the insertion in the experimental chamber, by repeated sublimation cycles. The adsorption on the Cu(100) crystal was performed through a leak valve in UHV by sublimating the MBO powder at

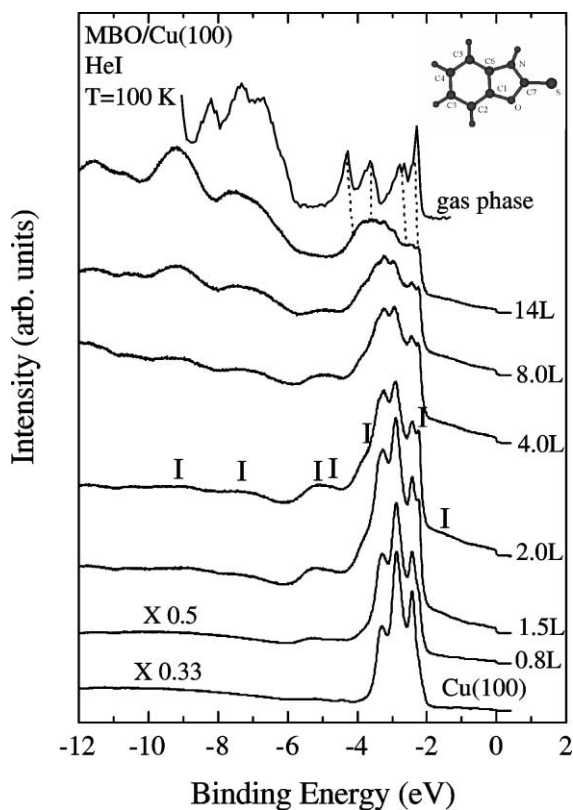


Fig. 1. High resolution UV (HeI photon energy, 20.218 eV) photoemission spectra of MBO on Cu(100) as a function of MBO exposure at 100 K. Data from gas phase MBO are shown as the top spectrum, for comparison (from Ref. [7]). The structure of the MBO molecule in the thione form is schematically sketched in the upper-right part of the figure.

115 °C, after repeated heating-pumping cycles for further cleaning. All the depositions were carried out at a comparable value of the MBO pressure (in the range of 10^{-6} Pa), only varying the exposition time. The exposures were measured in Langmuir units ($1 \text{ L} = 1.33 \cdot 10^{-4} \text{ Pa s}$).

3. Results and discussion

A selected set of photoemission spectra recorded with unpolarized HeI radiation at increasing MBO exposures on the Cu(100) surface kept at 100 K (low temperature, LT), are collected in Fig. 1. Significant changes in the spectral features are observed as a function of the MBO deposition. For exposures up to $\sim 2 \text{ L}$, the main change observed in the photoemission spectra is the appearance and progressive growth in intensity of new features at -1.5 , -2.2 , -3.7 , -4.75 , -5.2 , -7.5 and -9.2 eV (labelled in Fig. 1 with vertical bars), concurrently with the progressive attenuation of the copper d-like bands. Moreover, an uptake of spectral density is measured close to the Fermi energy. Upon increasing the exposure to MBO, further changes in the photoemission spectrum are observed: the components at -7.5 and -9.2 eV binding energy continue to increase, the peaks at -4.75 , -5.2 and -1.5 eV progressively decrease in intensity, while a multiple band is progressively superimposed on the d states energy-region, affecting its spectral shape. The gas-phase MBO photoemission spectrum [7] is reported in Fig. 1 for comparison purpose. The first peak in the gas-phase spectrum due to the HOMO orbital of the molecule, that is a π delocalized orbital, corresponds to the signal at -2.2 eV in the adsorbed phase. The second peak in the gas-phase spectrum, which is splitted for vibrational effects and is correlated to a molecular orbital localized mainly on the sulphur atom [7], seems to contribute to the change of the d region shape at high exposure while is not observed at lower exposure. The third and fourth peaks in gas phase coming from delocalized π orbitals seem to correspond to the large component at -3.7 eV in the adsorbed system, taking into account a possible shift of the fourth peak due to intermolecular interactions. The peaks

at lower energy are the convolution of signals coming from different orbitals and cannot be clearly attributed. The signals at -4.75 , -5.2 and -1.5 eV in the adsorbed system, which are clearly observed at low coverage and quenched at high exposures, do not correspond to any signal in the gas-phase spectrum, thus can be ascribed to new electronic states which arises from MBO–copper interaction.

We performed analogous experiment at room temperature (RT), by depositing successive doses of MBO on Cu(100), and the photoemission valence band spectra are reported in Fig. 2. The spectral signal evolution in the whole coverage

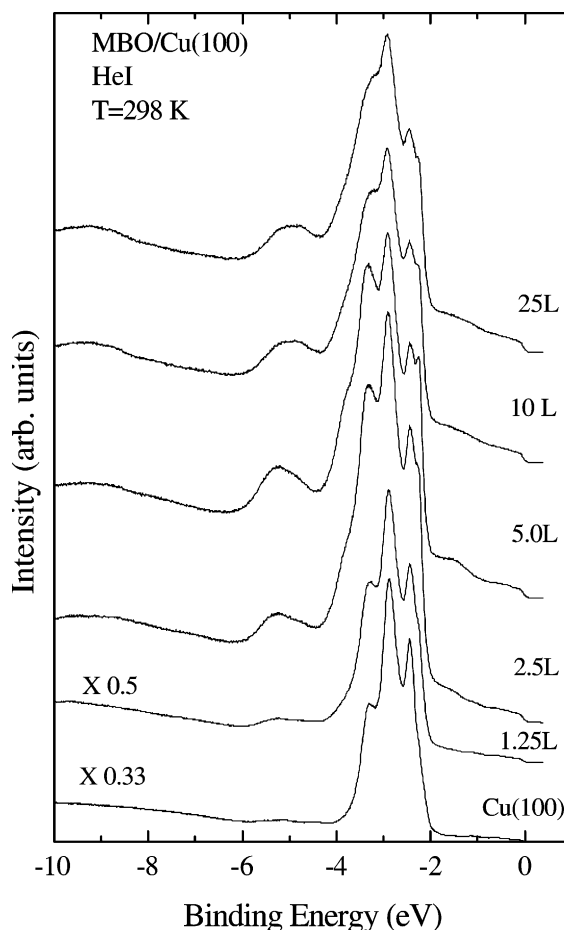


Fig. 2. High resolution UV (HeI photon energy, 20.218 eV) photoemission spectra of MBO on Cu(100) at RT (298 K), as a function of MBO exposure.

range is similar to that observed at LT for exposure up to ~ 2 L. No further changes in the photoemission spectra are observed for exposures higher than 10 L at RT, indicating a saturation coverage. It is interesting to observe that the same spectral features are observed at RT after an exposure almost 3–5 times higher than at LT.

The comparison of the adsorption trends at LT and RT suggests that MBO is initially chemisorbed on the Cu surface at both temperatures, so that new bonding states are formed between the molecule and the metal, which give rise to the photoemission signals at -4.75 , -5.2 and -1.5 eV. The photoemission structures characteristic of this chemically bonded layer are present up to saturation coverage at RT, while they are attenuated above roughly 2 L, at LT. In fact, at higher exposures, the LT data suggest that the molecule is physisorbed on top of the chemisorbed layer (see comparison with gas phase data in Fig. 1), so that the signals characteristic of MBO chemically bonded to the metal are attenuated by the inelastic scattering within the physisorbed overlayer.

The MBO chemisorption phase on Cu(100) is stable as a function of temperature, by warming up the system up to 180°C , while at higher temperatures the above described photoemission features are modified. The MBO–Cu binding chemisorbed phase is thus stabilized at temperatures (180°C) higher than the sublimation temperature of pure MBO (115°C). This behaviour seems indicative of the formation of a chemical bond between the molecule and the substrate stronger than the intermolecular interaction. A structural investigation of MBO adsorption on the Cu(100) surface at RT has been performed by LEED, and shows the clear evidence of a self-assembled long-range ordered pattern, with a reconstructed (2×2) symmetry [8].

In the literature, formation of chemisorbed layers of alkanethiols [9] and benzenethiols [10,11] on copper has been studied by photoemission and electron-energy-loss spectroscopy: the adsorbate–substrate bonding is ascribed to $\text{Cu } 3d_{xz,yz}\text{--S } 3p_{x,y}$ and $\text{Cu } 4s/3d_{z^2}\text{--S } 3p_z$ interactions with formation of new bonding and antibonding states. In our system a similar bond formation between the molecular orbitals localized mainly on the sulphur atom in the MBO free molecule and the copper 3d-4s

orbitals of corresponding symmetry can be supposed. In fact the second peak (-2.8 eV) in the gas phase photoemission spectrum, which comes from an orbital mainly localized on the sulphur atom and with a large contribution of the S 3p atomic orbitals [7], is absent in the chemisorbed phase, while new features are detectable at lower (-4.75 and -5.2 eV) and higher (-1.5 eV) binding energies indicating the formation of bonding and antibonding states from the combination of the S 3p orbitals with the metal substrate.

More information can be obtained from the HeII spectra (40.814 eV photon energy) measured during the MBO adsorption at RT and reported in Fig. 3. By comparison with the corresponding HeI spectra, it can be observed an increase of the Cu 3d

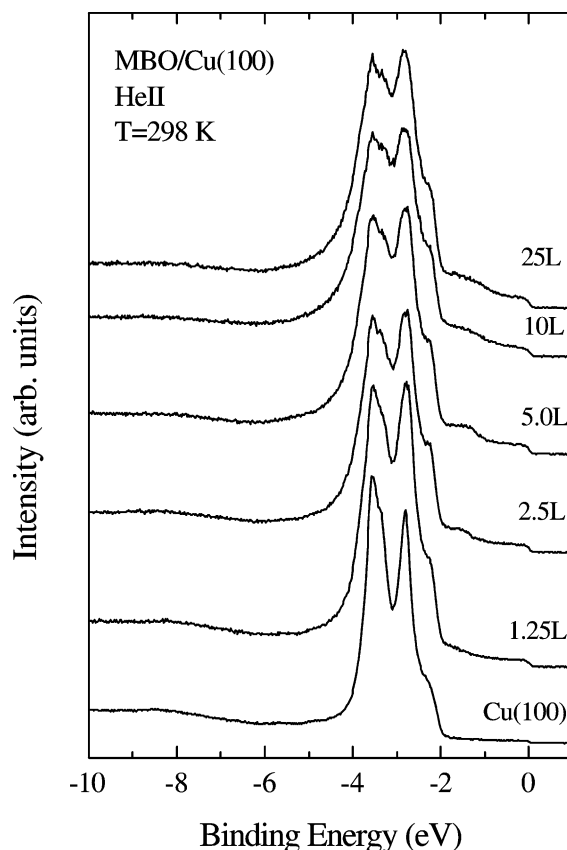


Fig. 3. High resolution UV (HeII photon energy, 40.418 eV) photoemission spectra of MBO on Cu(100) at RT (298 K), as a function of MBO exposure.

bands in the -2 to -4 eV binding energy range, of the MBO–Cu signal at -1.5 eV and of the spectral density close to the Fermi energy, while the features at -4.75 and -5.2 eV are no more detectable. The Cu 3d photoexcitation cross section increases from 7.2 to 9.9 Mb [12] upon changing the photon energy from HeI to HeII, while the S 3p cross section decreases from 4.3 to 0.6 Mb [12]. Thus, we suggest that in the formation of the MBO–Cu bond, the Cu 3d orbitals contribute mainly to the formation of the band at higher binding energy (-1.5 eV) and to the augmented spectral density just below the Fermi energy, while the S 3p atomic orbitals are more involved in the formation of the bands at lower binding energy (-4.75 and -5.2 eV).

4. Conclusions

Adsorption of MBO on Cu(100) by controlled sublimation in UHV conditions, has been studied by HRUPS, at RT and at 100 K. The valence band region presents new structures associated to a chemical interaction of MBO with Cu, that can be ascribed to a chemical bond formation between S 3p and Cu 3d orbitals. Saturation is reached at RT with the chemisorbed phase formation, while a physisorbed MBO multilayer forms on top of the interfacial chemically interacting layer at LT.

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