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Adsorption of Se on Cu(100) and formation of two-dimensional copper selenide layer

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ABSTRACT

In order to understand the adsorption process of selenium (Se) and Se-based molecules on noble metal surfaces, we report here on the properties of a thin film of Se on Cu(100) substrate. The deposition was carried out by incubating of a clean Cu(100) surface into Na₂Se solution under controlled conditions. The film properties were analysed as a function of the annealing temperature of the sample, using Low Energy Electron Diffraction (LEED) and photoemission techniques. A progressive structural transition from disordered thick layer to a two-dimensional Copper Selenide CuSe thin layer is obtained upon the thermal treatment. Our study proves that a large scale, well-ordered, and highly-stabilized metal chalcogenide layer can be produced for promising use in potential applications.

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1. Introduction

Self-assembled monolayers (SAMs) have been a popular topic that has received a lot of attention in the recent years due to their exceptional properties. The concept of self-assembly was first put forward in 1983, when the poly-functional SAMs were made by solution phase method, which ensures spontaneous film formation in contrast to the well-known Langmuir-Blodgett deposition [1]. In fact, ordered SAM films on noble metal surfaces form by self-assembly of organic molecules with the chalcogen atom as the head group that allows the bonding to the substrate [2]. The first applications of the SAMs were in the field of surface protection such as anti-wetting, anti-corrosion, anti-oxidation or anti-friction. The SAMs were also introduced into electronic devices because of their promising electronic and photo-electronic properties. On the other hand, intriguing physical and chemical properties of transition metal dichalcogenide (TMD) systems were the subject of considerable research and have led to a revolution in

the development of promising elements for high-tech electronic devices.

In this context, much interest has been paid to deposition of sulphur (S) based molecules on metal surfaces, inducing the formation of SAMs or TMD films. It ranges from atomic S to molecules with chain structure (alkane) or aromatic molecules (thiols, dithiols, thiophene, etc) [3–5]. The interaction between the S head-group and metal surfaces is proved to play an important role in determining the characteristics of the organic-metal hybrid system, including film structure, orientation, bonding state. As a counterpart element in the same group of the periodic table, selenium (Se) was also of high interest as alternative to the thiolate SAMs in the field of molecular devices [6–13]. In recent years, self-assembled monolayers of Se and Se-based molecules have displayed a rapid development due to their involvement in the surface chemistry and catalysis. Se is a semiconductor element used commercially in manufacture of glass, pigments and acts as additive in the stainless steel. In addition, the Se-based compounds have been introduced in the energy storage devices, detectors and lasers [14]. It has been reported that Se has a higher theoretical specific capacity and better conductivity than its analogue sulphur, making it a prosperity candidate as cathode material for high performance lithium-ion batteries (LIBs) [15].

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In the case of copper substrate, SAMs is first explored as a protection against oxidation or corrosion, especially for the ultrathin copper contacts. The formation of well-ordered SAMs of alkane and aromatic thiol SAMs on copper have been proved [16–19] with the possibility that the dissociation of the molecules through the S-C bond could happen [20,21]. In addition, it is known that adsorption of atomic S leads to a well-ordered sulphur-copper phase on the surface [22–24]. The formation of 2D material is also revealed when Te is adsorbed on Cu substrate [25]. Here we present a study on the formation of an ordered CuSe film on Cu(100) substrate. It has been demonstrated that deposition of Se on Cu(111) and Au (111) induces the formation of two dimensional CuSe and AuSe overlayers, respectively [26,27]. In our study, the adsorption of Se was carried out by simply immersing the Cu(100) substrate in aqueous Na₂Se water solution for certain time [28]. Using surface science techniques, i.e. (Low Energy Electron Diffraction (LEED) and X-ray Photoelectron Spectroscopy (XPS), we monitored the evolution of the Se film characteristics upon an annealing process at different temperatures.

2. Experiment

The surface of Cu(100) single crystal was cleaned with multiple cycles of Ar⁺ sputtering and annealing at 500 °C under ultra-high vacuum (UHV). The crystallinity and the cleanliness of the surface were checked by the LEED and XPS, respectively. For the Se film deposition, commercial Na₂Se powder was purchased from Sigma Aldrich and was used as received without further purification. Na₂Se solution is prepared in a 0.1 M NaOH aqueous liquid. The concentration is 0.1mMol/litter and the solution is directly utilized for the deposition within a short time. The cleaned crystal is taken out from the UHV and immediately immersed into the prepared solution, under controlled N₂ atmosphere. The immersion time was about 2 min. The sample was then well rinsed with water, dried with N₂ flow and reintroduced rapidly into the UHV chamber. All the preparation process is performed under room temperature.

The high-resolution photoemission experiments were performed at TEMPO beamline in synchrotron SOLEIL. The characteristics of the beamline are described in [29]. Briefly the XPS measurements were made at room temperature with an overall energy resolution (beamline and spectrometer) better than

50 meV at photon energy of 260 eV and about 250 meV for 1150 eV excitation energy. The LEED measurements were carried out at the Surface Laboratory of synchrotron SOLEIL.

3. Results and discussion

3.1. XPS analysis

The XPS overview data at the different preparation steps are given in Fig. 1. The spectrum of clean Cu(100) shows strong Cu2p features at 953 eV and 933 eV, relatively weak Cu3s at 123 eV, Cu3p at 76 eV, as well as the valence band close to the Fermi level. Moreover, characteristic Auger structures of Cu are seen in the region between 500 and 200 eV. Note that, no O1s and C1s features are observed, proving the cleanliness of the substrate.

After selenization of the Cu(100) surface, Se3d and Se3p core level peaks appear at binding energies of about 54 eV and 162 eV, respectively. The spectroscopic feature of O1s level is also seen in the spectrum, which is mainly due to the exposure to the air during the transfer of the sample and also from the residual dissolved oxygen in the incubation solution. The intensity of this O1s peak decreases rapidly after annealing of the sample until quasi-disappearing at 500 °C. Also, the Se spectroscopic features become significantly weak, indicating a transition from thick to thin layer of Se.

Detailed analysis of the Cu2p peaks is shown in Fig. 2. The changes in the position and width of the copper Cu2p features before and after annealing can be analysed by decomposing into bulk CuB at 932.4 eV and surface CuSe at 933 eV components. In fact, we show in Fig. 2c fits of the Cu2p peak using two components: the bulk CuB (black line) obtained from the clean Cu profile and the surface component CuSe (red line) resulting from the reaction between Se and Cu atoms. We observe that the intensity of CuB component increases after heating, at the expense of the CuSe peak. This result indicates that after selenisation, Se reacts efficiently with the Cu surface. Heating of the sample induces desorption of Se atoms, leading to a decrease of the CuSe spectral weight and an increase of that of CuB.

Fig. 3 displays XPS spectra of the Se3d core levels recorded before and after annealing of the sample at 300 °C and 500 °C. The superposition of these spectra, shown in Fig. 3(a), permits to

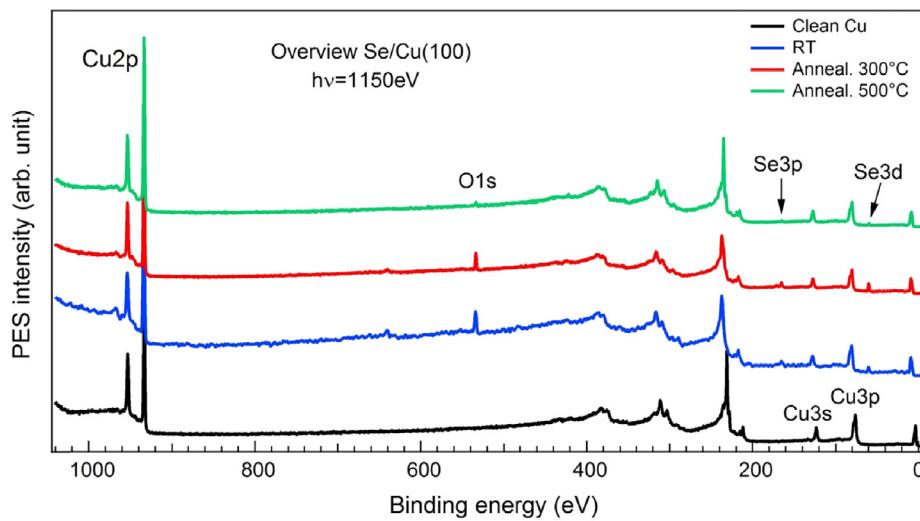


Fig. 1. Overview spectra taken at 1150 eV photon energy. The spectra were taken on the clean Cu(100) surface, after selenization, followed by annealing at 300 °C and further annealing at 500 °C.

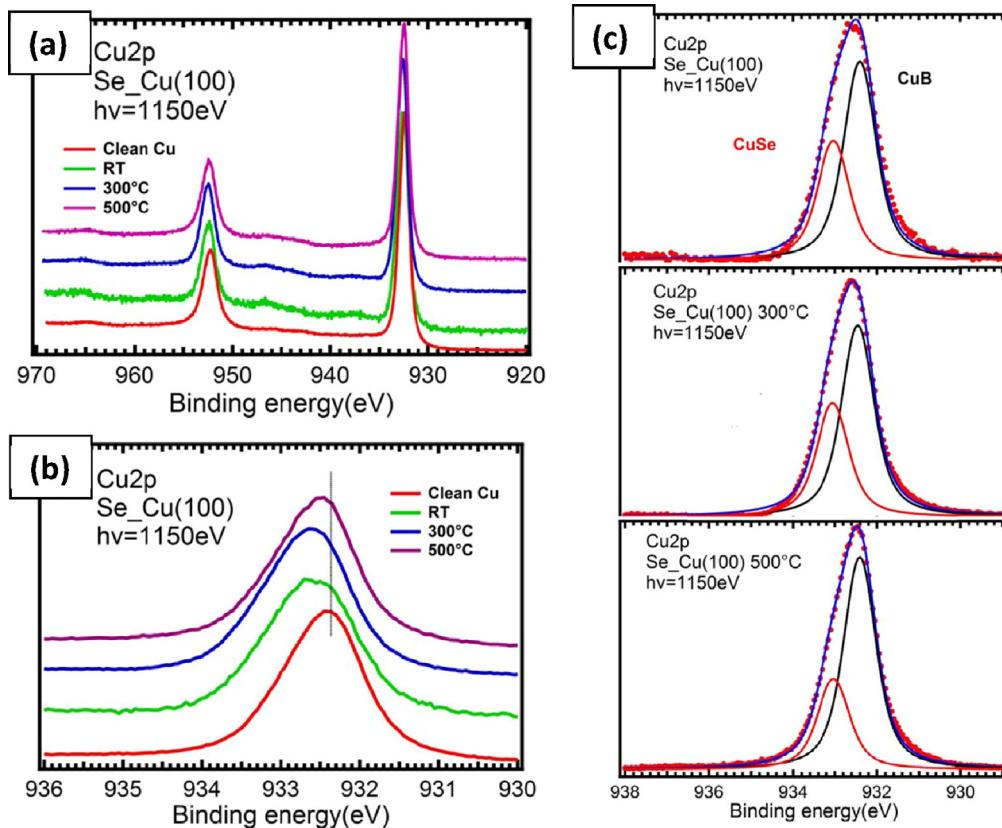


Fig. 2. Cu 2p peaks measured on clean Cu(100), after its selenisation, and after heating at different temperatures (300 °C and 500 °C): (a) Cu2p_{1/2} and Cu2p_{3/2} are shown, (b) only Cu2p_{3/2}, (c) fitting of the Cu2p_{3/2} peaks. The black and red lines refer to Cu bulk (CuB) and the CuSe surface components, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

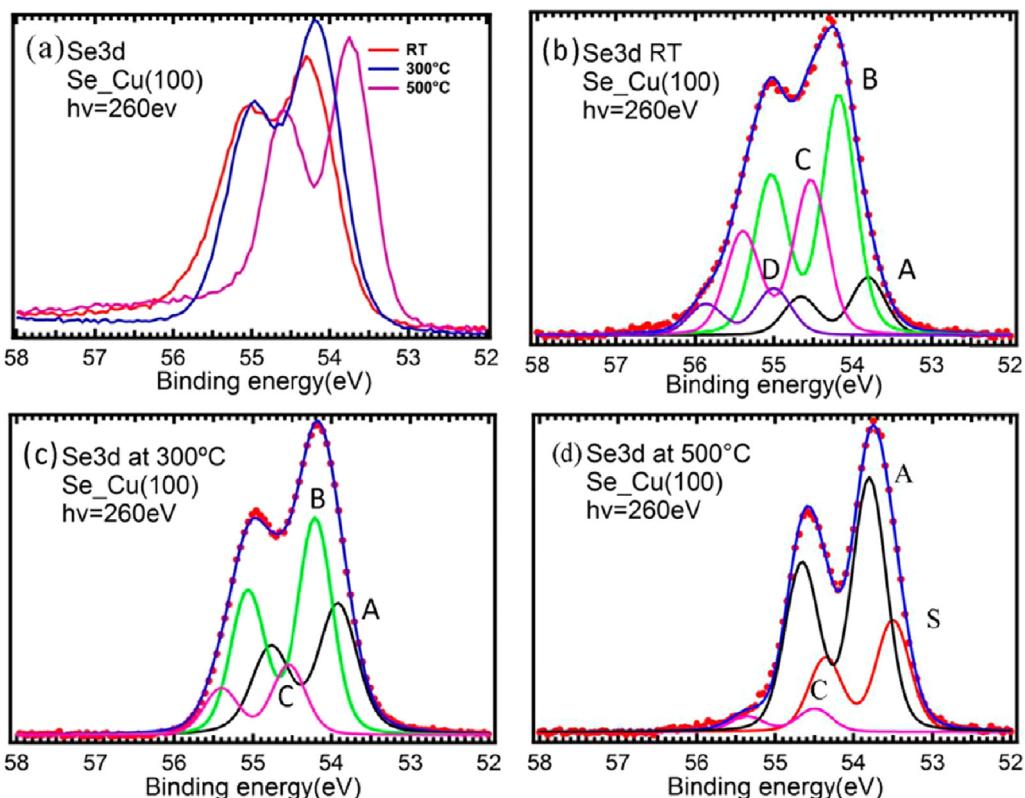


Fig. 3. (a) Comparison of the XPS spectra of Se3d core levels for Cu(100) taken at a 260 eV photon energy under different situations. (b,c,d) Fits of the spectra at room temperature, after annealing at 300 °C and 500 °C, respectively.

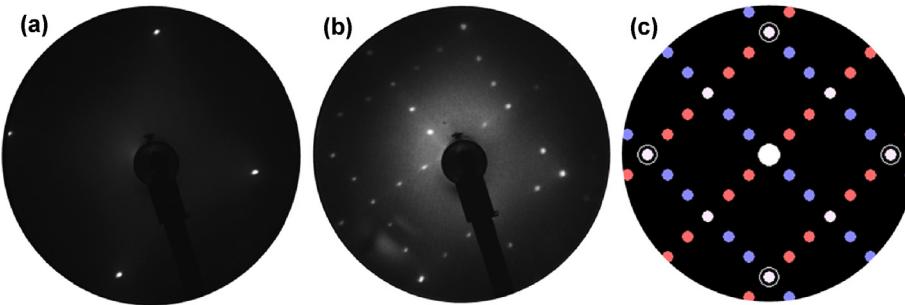


Fig. 4. LEED images obtained on (a) clean Cu(100) and (b) after adsorption of Se on Cu(100) followed by annealing at temperature above 300 °C, together with (c) simulation of the LEED pattern of (b). The patterns were measured at electron energy of 80 eV. (3x1) reconstruction forms when the Se film on Cu(100) is annealed at 300 °C.

highlight a significant change in the shape and energy position of the Se3d structures after the annealing process. All the spectra are fitted using Voigt peaks after a Shirley background subtraction, as seen in panels (a), (b) and (c) of Fig. 3. A spin orbit splitting of 0.86 eV was used. One should note that no structure due to Se oxidation is observed at 57 eV. This means that the oxygen feature observed in the XPS spectrum before annealing corresponds to physisorbed oxygen, which is easily desorbed when the sample is heated.

The Se3d spectrum measured on Cu(100) surface after being selenized at room temperature has two dominant peaks B and C at 54.15 eV and 54.5 eV, respectively. To well reproduce the spectrum, two extra peaks A and D are needed, located at 53.8 eV and 55 eV. Component D disappears after annealing at 300 °C, while the other components remain, but with a relative change in their intensities. In fact, component A increases in intensity at the expense of components B and C, even though component B remains dominant. Therefore, one can assign contributions B, C and D to the core levels of Se bulk in different configurations, while contribution A is associated with Se-Cu chemical environment. After heating at higher temperature, at about 500 °C, the spectrum shifts to lower energies and is composed of dominant component A at 53.8 eV and low intensity C contribution, together with a new feature S at 54.4 eV, which can be attributed to another adsorption configuration of Se on the Cu surface. This means that at this annealing temperature, the surface is mainly formed of CuSe layer.

3.2. LEED investigation

In order to better understand the structural change of the Se film on Cu(100), LEED measurements were performed and the corresponding results are presented in Fig. 4. The latter shows a LEED pattern of clean Cu(100) with square lattice. After adsorption of the Se film without annealing of the sample, no LEED pattern was observed, which is the signature of a large disorder on the surface and it is only after being heated at a temperature above 300 °C that a well-ordered structure occurs and this structure remains stable until an annealing temperature of 500 °C. The observed pattern is well simulated with a matrix [3 -3, 1 1], as shown in the Fig. 4c. In fact, the surface is characterized by two domains perpendicular to each other and both have a rectangular lattice with lattice parameters $a = 7.65\text{Å}$ and $b = 2.55\text{Å}$. They display a (3x1) reconstruction with respect to the Cu(100) lattice. The red and blue dots in Fig. 4c enable to distinguish the diffraction patterns of these structural domains. This structure is rather different from the one observed after adsorption of oxygen on Cu(100) [30–32]. Therefore, it is directly related to the Se that strongly reacts with the Cu substrate. It is the fingerprint of a well-ordered two-dimensional copper selenide film formed on the Cu(100) surface.

4. Conclusion

Using surface science techniques XPS and LEED, we have investigated the formation of two dimensional CuSe overlayer on Cu(100) substrate. Although the film elaboration was made using chemical deposition method, the resulting layer was of high-quality, especially after annealing the sample at a temperature above 300 °C. The XPS indicated the presence of several chemical environments associated with Se interacting with other Se atoms and with the Cu substrate, respectively. The LEED data revealed a progressive structural transition from an unordered film to a highly-organized and crystalized layer. We observed the formation of two domains perpendicular to each other that present a (3x1) reconstruction. In conclusion, we have produced here large scale, well-ordered, and highly-stabilized metal chalcogenide CuSe layer, which can be very promising for future technological applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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