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Mapping of Copper Oxidation State Using High Pressure X-Ray Photoelectron Spectroscopy

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The interaction of O₂ with polycrystalline foil of Cu, from ultra high vacuum to 1 mbar and up to 773 K has been investigated. The study were performed by using the high pressure X-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis) ultraviolet photoelectron spectroscopy system. In this work the results of mapping copper oxidation states as a function of temperature at 1 mbar O₂ have been presented.

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1. Introduction

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces. XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, medical implants, bio-materials, viscous oils, glues, ion modified materials and many others. From XPS measurements we can obtain information about identification of elements near the surface, local chemical environments, valence band electronic structure, morphology of thin layers and oxidation states of transition metals. Generally, the identity of the element and the orbital electron binding energies depend both on the local chemical environmental and the formal oxidation state of the atom. An increase in oxidation state causes the binding energy to increase due to a decrease in the screening of the bound electron from the ion core. The ability of XPS to determine oxidation states is used extensively in many research works.

In this article we would like to present the results of mapping copper oxidation states as a function of temperature at 1 mbar O₂. For these study the high pressure XPS (ESCA)/ ultraviolet photoelectron spectroscopy (UPS) system was used.

In particular, the XPS (ESCA)/UPS system is dedicated for ambient pressure 1–10⁻¹⁰ mbar (Fig. 1) photoelectron spectroscopy experiments with controllable sample temperature from 100 K to 850 K in analysis chamber. The high precision and repeatability of the chemical analysis are guaranteed by using both the full PLC (Programmable Logic Controller) protection as the software control.

Especially, the software (Fig. 2) provides control of the system, visualisation of machine state, data acquisition and possibility to control other devices connected to the

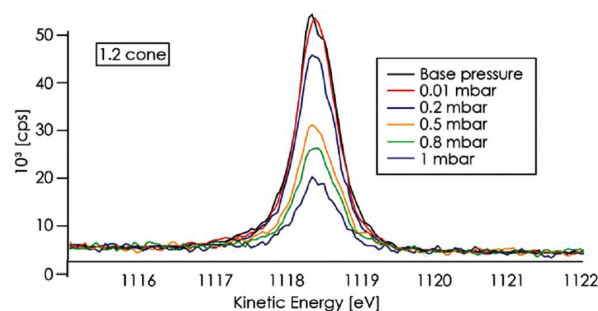


Fig. 1. Ag 3d_{5/2} XPS recorded under different pressure of N₂.

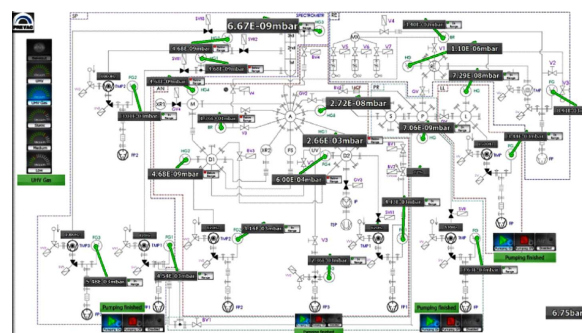


Fig. 2. The scheme of software in XPS (ESCA)/UPS system.

system like UV power supply, etc. The XPS (ESCA)/UPS system is equipped with VG Scienta R3000 HP analyser and three differentially pumped components: the X-ray monochromator, the double anode X-ray source and the UV source. The high vacuum quality is ensured by the four pumping stages for main chamber and analyser. The unique laser heating method using the laser and resistive heating of sample holder, allows to make analysis in a wide temperature range 100–2200 K.

The XPS (ESCA)/UPS system is equipped with a high pressure reactor (up to $p = 20$ bar and $T = 650$ °C) and gas dosing system with ability of heating and thermal sta-

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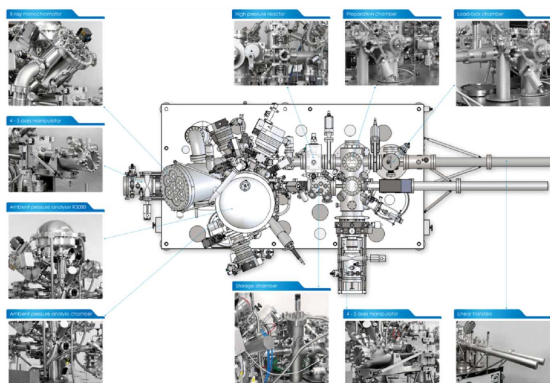


Fig. 3. The scheme of XPS (ESCA)/UPS system.

bilisation. The special sample preparation chamber with 5 sample holders makes this system easy, friendly and economic to operate. Additionally, thanks to the special heating and temperature control systems, the thermal desorption spectroscopy (TDS) measurements can be successfully realised. Simultaneous XPS and reaction kinetic measurements on solid surfaces make this system an important tool to measure the dynamic electronic structure changes on material surfaces under reaction conditions. The complete scheme of the XPS (ESCA)/UPS system with the main components is presented in Fig. 3. This system was designed and completely made by PRE-VAC.

2. Results

The Cu $2p$, Cu LMM Auger level and valence band (VB) spectra recorded in the presence 1 mbar O_2 from room temperature (RT) to 675 K are shown in Figs. 4–6 [1]. The Cu $2p$ spectrum from a clean Cu

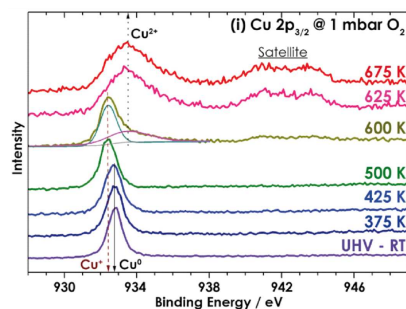


Fig. 4. XPS Cu $2p$ core level spectra measured while exposing a polycrystalline Cu foil to 1 mbar O_2 at various temperatures.

surface obtained under UHV conditions and at RT immediately after Ar^+ sputtering and annealing is shown for reference (bottom-most trace in all figures). The Cu $2p_{3/2}$ core level spectrum centred at 932.8 eV (grey solid arrow) which is characteristic of metallic Cu remains unchanged until 425 K indicating that the metallic nature of Cu surface is retained until this temperature. Cu LMM also shows corresponding feature at 918.8 eV.

On increasing the temperature to 500 K, a dramatic change in oxidation state to Cu^+ (i.e. Cu_2O) is evident

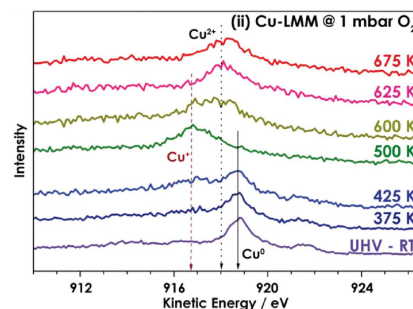


Fig. 5. XPS Cu LMM core level spectra measured while exposing a polycrystalline Cu foil to 1 mbar O_2 at various temperatures.

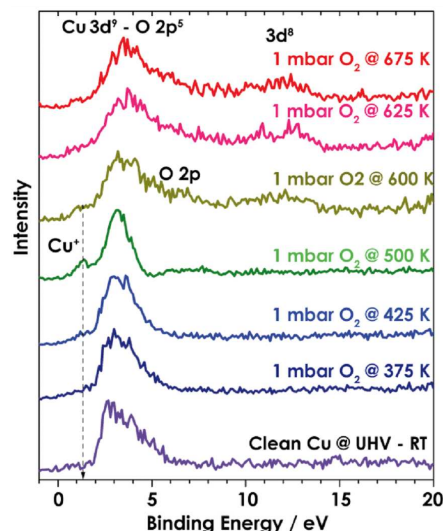


Fig. 6. High pressure valence band spectra recorded at 1 mbar O_2 and at different temperatures. Systematic conversion of Cu metal at UHV RT to Cu_2O (at 500 K) and CuO above 500 K is observed in 1 mbar O_2 .

from the shift observed in Cu $2p$ (to 932.4 eV), Cu LMM (to 916.7 eV) compared to metallic Cu features. A distinct feature appears at 1.2 eV with a narrowing of VB feature.

Further increase in temperature to 600 K shows features due to Cu_2O as well as CuO . This marks the beginning of oxidation of Cu_2O to CuO . A prominent satellite feature, typical for CuO (Cu^{2+} oxidation state), begins to appear along with a shift in Cu LMM feature. Broadening of VB with O $2p$ features confirms the oxidation of Cu_2O to CuO . Spectra recorded at 625 and 675 K fully support the complete oxidation of Cu surfaces to CuO , and sufficiently thick CuO layers observed suggest the beginning of bulk oxidation towards CuO . Features typical for CuO were observed in all three spectra, such as $3d^8$ satellites in Cu $2p$ core level.

References

- [1] Kanak Roy, C.P. Vinod, Chinnakonda S. Gopinath, *J. Phys. Chem. C* **117**, 4717 (2013).