Accurate measurements of the thickness of very thin copper oxide layers on copper

Cakir, Deniz[1], Anglaret, Eric[2], Frety, Nicole[3], **Barchiesi, Dominique**[4]

Contact email: dominique.barchiesi@utt.fr

[1] *Laboratoire Charles Coulomb Universite Montpellier CNRS;* [2] *Laboratoire Charles Coulomb, Universite Montpellier CNRS;* [3] *Institut Charles Gerhardt, Universite Montpellier CNRS;* [4] *Gamma3, Universite de technologie de Troyes INRIA*

Copper oxidizes spontaneously in air. The nature and thickness of the copper oxide layer depend on time and thermal history, and are key parameters to control some of the basic properties of copper, *eg* its electrical conductivity or its plasmonic properties. However, accurate measurements in the *nanometer* range are not straightforward since the two most widely used techniques suffer from limitations: i) the XPS signatures of Cu and Cu(I) oxide (Cu_2O) are very close and related Auger spectra only lead to semi-quantitative analyses, ii) ellipsometry analysis are very sensitive to the dielectric constants of Cu and Cu(I) which may vary significantly for very thin layers.

Here, we report on a coupled absorption/Raman spectroscopy study of thin layers of copper/copper oxide. Thin layers of copper were deposited by thermal evaporation on fused silica substrates and annealed at various time/temperatures (short/low enough to avoid the growth of Cu(II) oxide (CuO)), in order to oxidize them progressively. We show that using an adapted inverse problems resolution strategy for absorbance allows to determine accurately the thickness and dielectric constants of Cu and Cu(I) in the near-UV and visible/near-infrared (NIR) ranges, respectively. The whole UV-visible-NIR spectra can be accurately fitted by the calculations. On the other hand, we show that the Raman signal of thin copper oxide layers on copper is very sensitive to the thicknesses of both copper and copper oxide layers because of a strong variation of reflectance, and some periodic enhancement through constructive interferences, respectively. In the most favorable conditions, the Raman signal is easy to measure even for very thin layers in the *nanometer* range. In summary, an accurate measurement of the thickness of very thin layers of copper oxide on copper can be easily achieved by Raman measurements, providing accurate dielectric constants are determined independently by absorption spectroscopy.

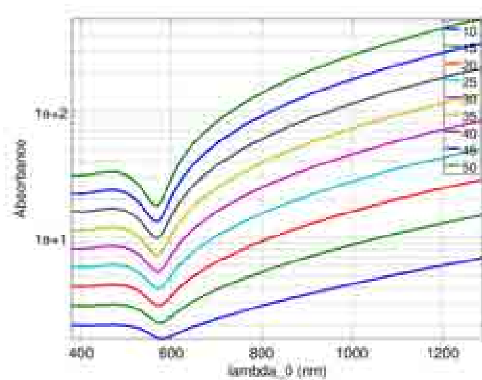

Figure 1: Absorbance of various samples of copper. The unkown thickness of Cu2O has to be determined.