Raman and NEXAFS study of the oxidation of Cu_3N thin films during their growth procedure

K. Mavridou, F. Pinakidou, M. Katsikini*, J. Arvanitidis, E. C. Paloura
School of Physics, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

M. Brzhezinskaya
Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany

M. Zervos
Nanostructured Materials and Devices Laboratory, School of Engineering, University of Cyprus, PO Box 20537, Nicosia, 1678, Cyprus

Cu_3N thin films were grown by annealing of Cu under NH_3:O_2 flow. The Cu layers were deposited on different substrates by sputtering. The procedure followed is the one proposed by Matsuzaki *et al.* [1], where the O_2 molecules adsorbed on the Cu surface are transformed to oxygen species that selectively cause dehydrogenation of NH_3 creating adatoms on the surface that migrate into the bulk forming Cu_3N. The annealing temperatures were ranging from 300 to 800 °C. The samples were studied by Raman and N-K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopies. Raman spectra were recorded using two different excitation wavelengths (647.1 and 514.5 nm) since resonance effects affect, to a different extent, the Raman peak intensities of copper oxides and Cu_3N, allowing for their better discrimination. Cu_2O surface oxide is formed in almost all the samples even at low annealing temperatures. On the other hand, the formation of CuO is generally observed at higher temperatures with the onset depending on the amount of O_2 in the gas mixture. However, high temperature is necessary to grow larger crystallites, as it is deduced by the narrowing of the high-frequency Raman peak (at ca. 650 cm^{-1}) of Cu_3N and SEM. N-K-edge NEXAFS spectra revealed that the formation of CuO, at elevated annealing temperatures, is accompanied by the creation of N_2 trapped in the sample. Molecular nitrogen is most probably formed by the N atoms originating from the dissociation of the Cu-N bonds.

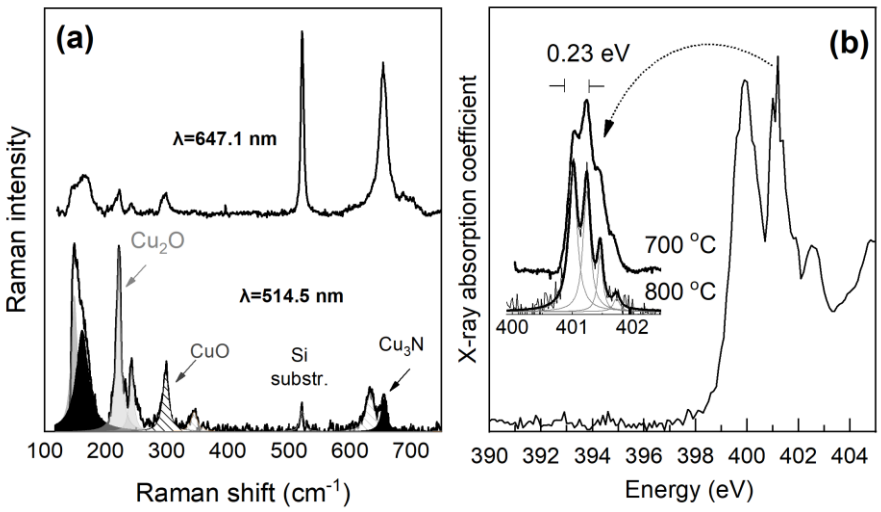

Figure 1: (a) Raman spectra of a sample annealed at 600 °C recorded using two different excitation wavelengths. (b) N-K-edge NEXAFS spectrum of a sample annealed at 700 °C. The inset shows the fine structure of the N_2 peak due to vibronic transitions.

Reference

[1] K. Matsuzaki, K. Harada, Y. Kumagai, S. Koshiya, K. Kimoto, S. Ueda, M. Sasase, A. Maeda, T. Susaki, M. Kitano, F. Oba, H. Hosono, Adv. Mater. **30,** 1801968 (2018).

* katsiki@auth.gr