Formation processes of copper sulfide thin films

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The deposition of thin films using chemical bath deposition (CBD) techniques has been previously studied by a number of researchers [1]. In this current research, the CBD process is further investigated using Raman spectroscopy, infrared spectroscopy, electron microscopy, and neutron reflectance.

The preparation of chalcogenide thin films by CBD has attracted much attention because of its simplicity, low cost, low deposition temperatures and availability of starting materials. Starting materials are generally metal salts used in the presence of a complexing agent, and a chalcogenide source such as thiourea or thioacetamide. Deposition generally occurs at temperatures ranging from ~25 °C to 80 °C, depending on the film being prepared.

Copper sulfide is of specific interest because of its many established and prospective applications in photovoltaics, solar control coatings and in other electronic devices [2]. The binary Cu/S system is a complex one, with five distinct equilibrium phases: chalcocite [Cu_2S], djurleite [$Cu_{1.96}S$] digenite [$Cu_{1.8}S$], anilite [$Cu_{1.75}S$] and covellite [CuS] with numerous polymorphs and metastable phases.

The deposition of thin copper sulfide films by CBD on to glass microscope slides, single crystal silicon or polycrystalline platinum surfaces, was undertaken in a manner similar to that outlined by Nair et al [3]. These films were then characterised using Raman spectroscopy, infrared spectroscopy, electron microscopy, and neutron reflectance.

The relationship between deposition time and film thickness is illustrated in figure 1, which presents neutron reflectivity data for two copper sulfide films deposited on silicon. This data, from films with deposition times of 35 or 40 minutes at 40 °C, indicate a 20 nm increase in thickness from 76 – 96 nm in a 5 minute period. This rapid growth after a slow growth period supports previous research which describes an induction period followed by a short deposition step. TEM images indicate that the as prepared films are composed of amorphous spherical particles (figure 2). Raman spectra of the as prepared films are characterised by a broad band at 420 cm^{-1} (figure 3a), which rapidly shifts to the covellite position of 474 cm^{-1} (figure 3b), on heating in air at 150 °C.

1. R.S. Mane and C.D. Lokhande, *Materials Chemistry and Physics*, **65** 1 (2000).
2. M.T.S. Nair, L. Guerrero and P.K. Nair, *Semiconductor Science and Technology*, **13** 1164 (1998).
3. P.K. Nair, V.M. Garcia, A.M. Fernandez, H.S. Ruiz and M.T.S. Nair, *Journal of Physics D: Applied Physics*, **24** 441 (1991).

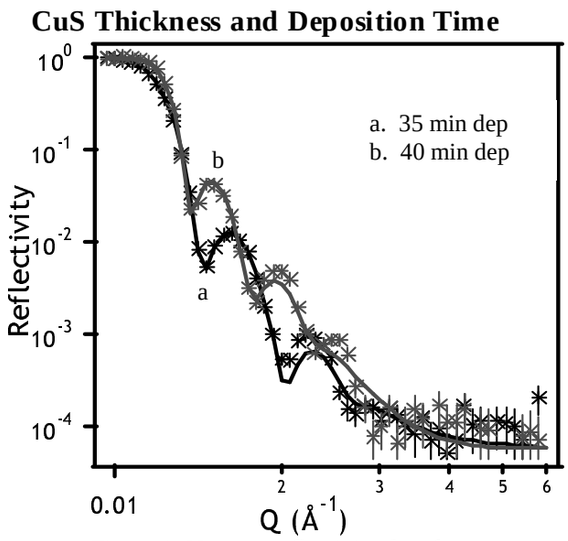

Figure 1: Neutron reflectivity data for two films deposited at 40 °C – one for 35 min and the other 40 min

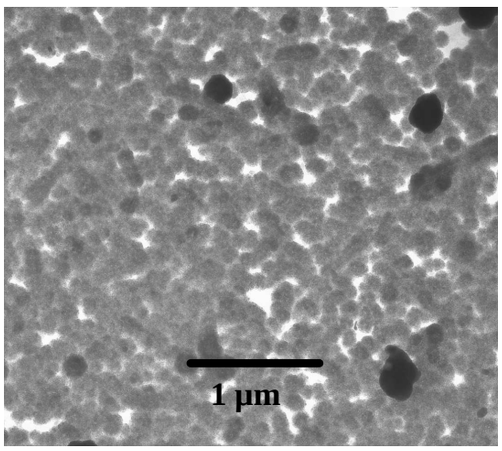

Figure 2: TEM image of an as prepared copper sulfide thin film deposited at 40 °C for 40 min.

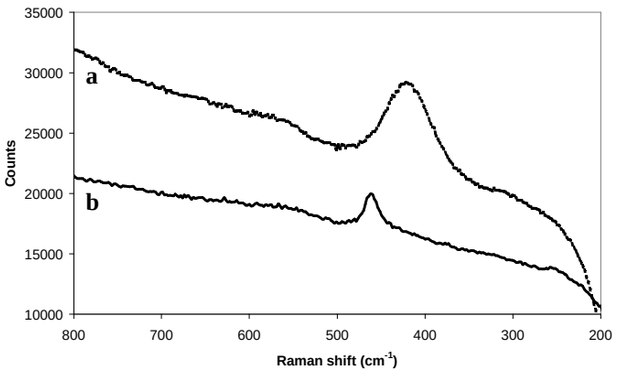

Figure 3: Raman spectra for copper sulfide thin films (a) an as prepared film and (b) after heating in air at 150 °C for 5 min.