Structural and Optical properties of Brominated Cu thin films

Desapogu Rajesh, C S Sunandana and M Ghanashyam Krishna
School of Physics, University of Hyderabad – 500046, A.P; INDIA

rajesh.desapogu@gmail.com; sunandana@gmail.com; mgksp@uohyd.ernet.in

Abstract. We describe and discuss XRD, FESEM - EDS and optical absorption behavior of nanostructured 50 nm Cu thin films obtained by thermal evaporation and subsequently exposed to bromine vapours. XRD patterns show quasi-amorphous structure due to the nanocrystalline nature of cupper particles. As bromination time increases there is a subtle broadening of the peak that hints at a possible increase in quantities such as particle size. At ambient temperature, bromination time could be used to tune surface morphology, and optical properties of nanostructured Cu thin films. During the short term bromination we observed small Cu Nanoparticles with large density, which exhibit surface plasmon resonance (SPR). Increase of bromination time yields larger Cu Nanoparticles with small density of particles, the particle size and elemental composition assessed by FESEM-EDS. These results offer a promising strategy for situ characterization and monitoring of nanopaticl and for the engineering of Cu nanoparticle with new plasmonic properties even as Cu and brominated Cu films could be promising candidates for plasmonic and nanophotonic applications.

1. Introduction
As micro-electronic devices get smaller and faster, copper interconnects, with their higher conductivity, have replaced other metals such as aluminum to enhance the performance of the devices. Recently, therefore, many researchers have begun to investigate the properties of copper especially in the form of thin films. Copper is considered as a promising material for fabrication of interconnections in integrated circuits based on planar thin films as an alternative to aluminum. Interfacial interactions underpin a range of fundamental phenomena and applications in chemical, biological, and material sciences consequently; significant attention has been directed toward strategies to precisely tune the surface interactions of materials [1]. The reasons are mainly the excellent physical properties of copper and its straightforward and quite cheap deposition using the thermal evaporation process. Film thickness, deposition rate, and method of coating play important role on microstructure as well as macroscopic properties of films [2, 3]. The bromination of Cu thin films opens up the possibility of modifying their optical, structural properties and also strong absorption in the visible to near infrared region thus making them not only feasible for gas sensors, but also as promising organic electro photographic materials, nonlinear optical materials and optical recording media [4–6]. Chemical SPR sensors are based on the measurements of the variations due to adsorption or a chemical reaction of an analyte with the active layer which results in changes of its optical properties. In this paper we reported our work on preparing Cu thin films via thermal evaporation method to study the influence of bromination on the optical, structural properties of Cu thin films. Structure is the most important factor to determine the
morphological characteristics of a material. Microstructure properties and grain size were also characterized by using FESEM.

2. Experimental part
The Cu powder purchased from Sigma Aldrich was used as obtained without further purification. Prior to the deposition of Cu thin films, the substrates were thoroughly cleaned by immersing them in soap solution for 15 min and subsequently putting them in the solution of acetone and ethanol sequentially. The pressure during deposition process was upheld at 4.5*10^{-6} m bar. The Cu films were sublimed on carefully cleaned glass substrates at room temperature. The thickness of the deposited Cu films and the rate of deposition were maintained at 60nm and 0.01 nm/sec respectively, using DTM quartz-crystal thickness monitor. Thin films of Cu were formed on the cleaned glass substrates by thermal evaporation techniques. The Cu coated films are selected for further bromination treatment and are referred as pristine film. The pristine samples were taken as a reference in comparative experiments. The structural properties of thin films were investigated by X-ray diffraction (XRD) using CuKα (λ = 0.15418 nm) radiation. The optical absorption of the films was measured using JASCO model 7800 spectrophotometer. The Field emission scanning electron microscopic studies were carried out using ZEISS model ULTR 55. Elemental analysis was carried out with an EDAX using energy dispersive X-ray spectrophotometer (EDS).

3. Results and discussion
3.1 XRD
Representative XRD patterns of as-deposited Cu thin films are shown in Fig. 1. It is apparent that thin films in the thickness 50 nm are by and large amorphous-possessing only short range order which is in keeping with the islanded nanostructured quasi-continuous films XRD patterns show quasi-amorphous structure due to the nanocrystalline nature of cupper particles. As bromination time increases there is a subtle broadening of the peak that hints at a possible increase in quantities such as particle size which could be conveniently probed by FESEM to be described later.

3.2 Optical properties
The optical properties of the copper thin films were measured immediately after the preparation process, and then followed as a function of the exposure time to bromine vapors at room temperature. Figure 2 shows the optical absorption spectra of the films at the different times that elapsed after the reduction.
process as compared with the spectrum of the film in bromine vapors at room temperature. It was found that the optical density of these samples increase with the increase in bromination time (<5min). The absorption peak centered at about 780 nm is due to SPR absorption of the metallic copper nanoparticles embedded in the glass substrate. After 20, 60min bromination, the optical density spectrum of the reduced film showed stabilized behaviour with no SPR peak similar to the spectrum of the Cu film at 300 \( ^\circ \text{C} \). The optical absorption of the Cu thin films exposed to Br for 20, 60 min did not present any significant absorption feature. We observed that, at ambient temperature, leveraging bromination time it is possible to tune the surface morphology and optical properties of nanostructured Cu thin films.

![Absorption spectrum of Cu thin films](image)

**Figure 2.** Absorption spectrum of Cu thin films at different bromination times (a) pure Cu film (b) 1min bromine (c) 3min bromination (d) 5min bromination (e) 20min bromination (f) 60min bromination

3.3 FESEM

Surface morphology of the Cu thin films containing copper nanoparticles was studied by FESEM, as presented in fig. 3 for the Cu thin films brominated at room temperature and as compared to the pure Cu films. In fig3.a the growing accumulated Cu Nanoparticles are observed at before bromination, after 5min bromination some quite uniform nano-sized particle features are clearly observed in the fig3.b, the size of the surface particles was in the range of \(-10\text{–}40\text{ nm}\) (with average size of about 20 nm). Based on the absorption, morphology analysis it was shown that the copper nanoparticles initially accumulated on surface of the films, when we bombard with bromine vapors it could substantially penetrate into the film after 5, 20min bromination we got the different morphologies shown in the fig3.b, fig3.c. Especially in 20min bromination case we got the Cu nano rods, this is we found new observation in thermal evaporation and followed by bromination method. Hence, the particle features observed on the film surfaces could be attributed to the copper nanoparticles, nano rods. Fig3.d shows the elemental analysis of brominated Cu thin films.
4. Conclusions

We describe and discuss XRD, FESEM - EDS and optical absorption behavior of nanostructured 50 nm Cu thin films obtained by thermal evaporation. XRD patterns show quasi-amorphous structure due to the nanocrystalline nature of cupper particles. As bromination time increases there is a subtle broadening of the peak that hints at a possible increase in quantities such as particle size. These results are useful indications for in situ characterization and monitoring of nanopaticle preparation and for the engineering of Cu nanoparticle with new plasmonic properties. These Cu and Cu brominated films could be promising candidates for plasmonic and nanophotonic applications.

Acknowledgement
D Rajesh thanks the University of Hyderabad for providing UGC-BSR fellowship.

References

[1] Chilkoti A and Hubbell J A, 2005 MRS Bull 30 175
[2] Raymond E K, Donald F O, Martin G and David E 1979 Kirk- Othmer Encyclopedia of chemical technology third edition 6 826
[3] Kundu S 1998 J. Phys. D. Appl. Phys. 31 L73-L77.
[4] Capone S, Rella R, Siciliano P, Valli L and Troisi L 1998 Thin Solid Films 465 327
[5] Chen Q, Gu D, Shu J, Tang X and Gan 1994 J. Mater. Sci. Eng. B 25 171
[6] Qian S and Wang G, 2001 *Nonlinear Optics – Principles and Developments*, Fudan Univ. Press, Shanghai

[7] Rajesh D and Sunandana C S 2012 *Results in Physics* **2** 22