

Making Cu₂s Thin Film and Studying its Structural and Photoelectric

Abbood Falih Hasan, Sajjad Karim Rahman Abbas, Malik Jamal Abdal,
Nidhal Kadham Turkey, Zainab Mohammed Nama
Hillah University College/Applied Medical Physics

Abstract:

This review is provided a detailed overview of the synthesis, properties and applications of nanoparticles (NPs) exist in different forms. NPs are tiny materials having size ranges from 1 to 100 nm. They can be classified into different classes based on their properties, shapes or sizes. The different groups include fullerenes, metal NPs, ceramic NPs, and polymeric NPs. NPs possess unique physical and chemical properties due to their high surface area and nanoscale size. Their optical properties are reported to be dependent on the size, which imparts different colors due to absorption in the visible region. Their reactivity, toughness and other properties are also dependent on their unique size, shape and structure. Due to these characteristics, they are suitable candidates for various commercial and domestic applications, which include catalysis, imaging, medical applications, energy-based research, and environmental applications. Heavy metal NPs of lead, mercury and tin are reported to be so rigid and stable that their degradation is not easily achievable, which can lead to many environmental toxicities.[1].

Introduction

There has been a rapid increase in interest in nanotechnology and the use of nanoparticles in commercial applications. However, there is little known of the fate and behaviour of engineered nanoparticles in the environment. The properties of nanoparticles differ remarkably from small molecules and their chemistry and synthesis necessitates that they be considered more like complex mixtures than small molecules. The ability of the molecules to attach to the surface of nanoparticles and exchange with other molecules already placed there indicates that careful consideration of the chemistry of nanoparticles and how it relates to their fate in surface waters and sediments is key to predicting their final fate. We have set out to briefly introduce at a basic level the properties and synthesis of nanoparticles and then review the state of current understanding

relating to the fate and behaviour of nanoparticles in the environments with particular focus on engineered nanoparticles.

Properties of nanoparticles.

One particular subset of nanoparticles is the quantum dot. These are generally particles with diameters of less than 10 nm, although in some cases the particle size may be as large as 50 nm. They have perhaps the most distinctive size-related properties of all nanoparticles. Quantum dots are semiconducting nanoparticles where their dimensions are so small the size of the particle affects the intrinsic band gap of the semiconductor. A simple way to understand this is to consider a semiconductor as consisting of a valence and conduction band which are the result of the bonding and antibonding configuration of the crystal lattice. A simple diatomic system will have a single bonding and a single antibonding orbital. As more atoms are added to the lattice the new bonds will have slightly different bonding and antibonding energies. For a large lattice these orbitals will begin to form a continuum which is considered as the band in the final bulk material. It is therefore clear that at some point the number of bonds in the semiconductor particle will not be a good approximation to an infinite lattice and the band structure will begin to change. This results in a widening of the bandgap of the semiconductor. Most quantum dots exhibit photoluminescent properties. A photon of incident light can excite an electron from the valence band of the semiconductor to the conduction band leaving a hole in the valence band. This photon then has various possible fates: recombination of the electron and hole with the emission of light, trapping of the electron/hole in a defect in the crystal, reaction with the capping agent resulting in the formation of a radical, reaction with the solvent to form a radical. Many of these processes will also occur in particles which do not exhibit quantum confinement; however the minimum energy required to form the excited state will increase as the particle size decreases in a quantum-confined system. This minimum energy is the bandgap of the particle. This is a small but important area of nanotechnology.[2]

Studies on nanomaterials have recently been carried out widely and intensively in many fields in order to explore the new era of the nanoscopic world and to overcome the limitation of typicalness of the bulk materials. Nanomaterials with the enhanced mechanical, electrical, and optical properties distinctively different from the bulk material properties allow us to surmount many areas that the conventional technology could not address. Nowadays, such properties of the nanomaterials may be characterized electrically and mechanically by direct contact with the nanomaterials. Meanwhile, the optical methods take advantage of observing the essential characteristics of the nanomaterials without significantly modifying or permanently damaging them due to their noncontact and noninvasive nature. Common optical characterization methods include absorbance/transmittance, photoluminescence, and Raman scattering measurement.

This special issue arranges a series of up-to-date articles dealing with characterizing the various nanomaterials by using such optical characterization methods. M. Benson et al. discovers, from the absorbance analysis, the metamaterial properties of silver nanorod thin film grown by oblique angle deposition, "Optical characterization of silver nanorod thin films grown using oblique angle deposition." Y. C. Choi et al. describes a purity analysis for carbon nanotubes by using Raman scattering, "Novel method of evaluating the purity of multiwall carbon nanotubes using Raman spectroscopy." N. Shanmugam et al. reports the effect of thermal process on ZnS nanocrystals synthesized by chemical precipitation by using

UV-Vis absorption and photoluminescence, "Effect of annealing on the ZnS nanocrystals prepared by chemical precipitation method." By FT-IR, absorbance, and fluorescence spectroscopy, T. L. Tan et al. observe the change in optical characteristics of Mn-doped ZnO nanoparticles synthesized by coprecipitation method while varying the manganese dopant concentration, "Tunable band gap energy of Mn-doped ZnO nanoparticles using the coprecipitation technique." F. Severiano et al.

introduces an electroluminescent device based on white light emission from ZnO:In/PS by electroluminescence and photoluminescence, “Electroluminescent devices based on junctions of indium doped zinc oxide and porous silicon.” By using photoluminescence, H.-S. Chin and L.-S. Chao investigate the thermal annealing effect on ZnO thin film grown by radio frequency sputtering, “The effect of thermal annealing processes on structural and photoluminescence of zinc oxide thin film.”

Measuring the optical transmittance, F.-H. Wang et al. analyzes the hydrogen effect on sputter-deposited Al₂O₃-doped ZnO thin films, “Effects of hydrogen on the optical and electrical characteristics of the sputter-deposited Al₂O₃-doped ZnO thin films.” T. K. Kim et al. observes the negative differential resistance from molecular nano silver chain, “Symmetric negative differential resistance in a molecular nano silver chain.” F. Q. Zhou et al. proposes single ring-shaped nanotubes, dimmers, and arrays and discuss their optical transmission properties, “Formation and evolution mechanism of plasmon resonance from single ring-shaped nanotube to dimer and arrays.”

As we have seen from the papers in this special issue, the optical characterization methods are essential in analyzing the various fundamental and functional properties of the nanomaterials. The noncontact and noninvasive nature makes the optical characterization methods one of the best ideal and at the same time practical tools to investigate and to take advantage of many different types of nanomaterials. We believe that the articles in this special issue would serve as excellent examples of how these optical methods are utilized in characterization of some of the wellknown nanomaterials.[3]

Morphology of nanoparticles

Depending on the mutual impact forces between the polymer and silicate incubator surfaces, thermodynamics accept the presence of three different types of Nanocomposites:

1. Intrusive nanocomposites: In intrusive nanocomposites, they are introduced The polymer matrix in the silicate structure is uniformly crystalline, alternating with polymer chains with a silicate layer whose distances change between them from 1 to 4 nm, at a distance within the length of the polymer chain;
2. Floping nanocomposites: These are the same as intrusive nanocomposites, except that some layers of silica are sometimes scattered by the mutual immersion between hydroxyl cliques in silicates
3. Peeled nanocomposites: In peeled nanocomposites, individual layers are formed

Minerals were randomly separated inside a continuous polymer incubator at an average distance based on the overall vegetable load, and the vegetable content in peeled nanocomposites is much lower than in the case of composite nanomaterials[4]

Properties of nanoparticles

The fate, behaviour and therefore the ecotoxicology of nanoparticles will be closely related to their intrinsic properties. There are several aspects to nanoparticles which can easily be dismissed in error due to their apparent ability to behave more like molecules than larger colloidal suspensions. We will discuss here a simple description of particles in suspension; a more detailed discussion may be found else where (Shaw 1992).

Particle mobility

The process of diffusion is controlled by several factors: gravitational forces, buoyancy and Brownian motion. These factors can all be taken into account using Einstein’s law of diffusion:

$$D = \frac{1}{4} kT \delta l^2$$

where D = diffusion coefficient, f = the frictional coefficient for the particle, k = Boltzmann constant and T = temperature.

The frictional coefficient of a nanoparticle may be derived from Stokes law:

$f = 6\pi\eta a$ where η = the viscosity of the medium and a = particle radius.

This means that the diffusion coefficient is inversely proportional to the radius of the particle and the average displacement of a single particle in time t will be proportional to the inverse square root of the particle radius. Figure 3 shows a plot of the average distances moved after 20 time units for particles of different sizes.

Solvothermal Synthesis of Nanoparticles

Solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. The process involves the use of a solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction of precursors during synthesis. If water is used as the solvent, the method is called “hydrothermal synthesis.” The synthesis under hydrothermal conditions is usually performed below the supercritical temperature of water (374 °C). The process can be used to prepare many geometries including thin films, bulk powders, single crystals, and nanocrystals. In addition, the morphology (sphere (3D), rod (2D), or wire (1D)) of the crystals formed is controlled by manipulating the solvent supersaturation, chemical of interest concentration, and kinetic control. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic routes. Over the last decade, a majority (~80%) of the literature concerning solvothermal synthesis has focused on nanocrystals; therefore, this review will highlight some advances in nanocrystalline, solvothermal synthesis. [5,6] Interest in nanocrystals is driven by their unique properties. One example of the unique properties of nanocrystals is illustrated by the discovery of solvothermally synthesized quantum dots (QDs)[7-9] elucidate the degree to which solvothermal synthetic techniques are now an essential technique for controlling the size of the II–VI and III–V semiconductor materials. Synthesis of the QDs typically requires a cation source material that is soluble in the chosen solvent and a surfactant that caps or stabilizes the quantum dot, arresting its growth. For example, CdSe QDs are prepared by dissolving CdO in trioctylphosphine oxide (TOPO) and trioctyl phosphine (TOP), which acts as both a solvent and capping agent. The solution is heated to 300 °C, after which elemental selenium dissolved in tributylphosphine (TBP) is added. The reaction is then quenched and nanocrystals are observed.[10]





Experimental Work

The schematic diagram of experimental set-up for the deposition of thin films of copper sulfide by solution growth technique⁵ is shown in FIGURE 1. It consists of chemical reaction bath and substrate. Chemical bath consists of a 100 ml glass beaker (Borosil make) with the mixture of chemical reactants. It is placed in the constant temperature water bath whose temperature can be controlled. The chemical reactants containing solution is stirred by magnetic stirrer. The substrates used for the deposition of Cu_2S thin film were commercial microscope glass slides with the size of $75\text{mm} \times 25\text{mm} \times 1.35\text{ mm}$. Before deposition, the substrates were degreased in chromic acid solution for 24 h, cleaned by commercial detergent. Finally rinsed with deionised water and dried in air. This process is done to ensure a clean surface, which is necessary for formation of nucleation centers, required for thin film deposition.

All the calculations for molar concentrations were made for 50ml final solution. To prepare the mother solution firstly 0.025 M of CuSO_4 dissolved in 1 ml of NH_3 and 4-5 ml of Triethanolamine (TEA) in 100 ml beaker to this 25ml of DI water was added and the solution was stirred for 15 minutes, in another beaker 25ml of 0.05 M solution Thiouria were prepared and stirred for 15 minutes. Both the solutions were then added together and the pH was maintained at 10, this 50ml solution was used as mother solution. All chemicals used in the present investigation were Analytical reagent (AR) grade. Pre-cleaned glass substrates were inserted into the 100 ml beaker with mother solution with bath temperature maintained 45°C . After every 20 min the solution was changed with newly prepared mother solution until two and half hour. Thereafter substrate coated with Cu_2S was removed, rinsed with distilled water, and dried in open air at room temperature, film obtained was uniform, well adherent and then calcined at 150°C . Then studied its structural, optical and electrical properties using X-ray diffraction, UV-vis spectrophotometer and I-V system.

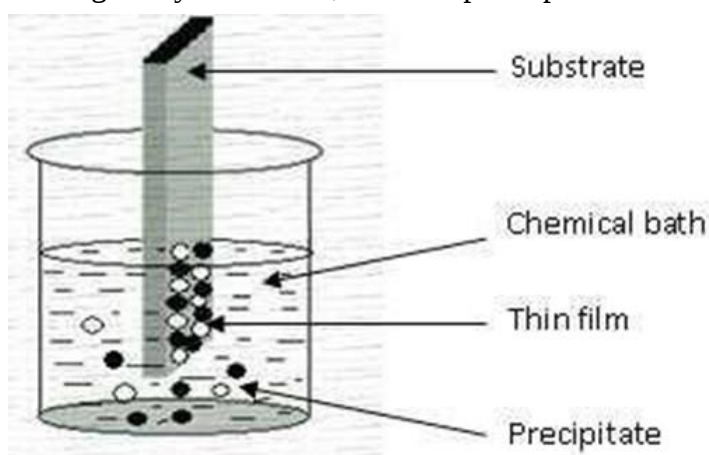


FIGURE 1. Schematic of Chemical Bath Deposition

Results And Discussion

1. Structural Analysis

The crystal structure of Cu₂S thin films was determined by XRD. XRD patterns were recorded with (Make: Rigaku, Model C/max-2500) using

CuK α radiation ($\lambda=1.54056$ Å) operated at 40Kv and 30 ma in the wide Angle region from 10 to 80. The PH value of the Cu₂S thin films was maintained as 9.5. Their crystalline structure exhibits peaks corresponding to (002), (100), (110), and (112) planes. The average size of crystallite is estimated by Scherrer formula:

$$D = k\lambda / \beta \cos\theta$$

Where λ is the wavelength of CuK α radiation (0.154nm), $k = 0.9$ is the shape factor, θ is the Bragg angle and β is the experimental full-width at half maximum on the respective diffraction peak. The average grain size for the Cu₂S orientation is about 1.45 nm. The typical XRD patterns of Cu₂S thin films with different Concentrations (0.1, 0.2 and 0.3 M) and different conditions such as deposited and pre-heated precursor at elevated temperature are shown in Fig1. The broad hump in the 2θ range of 230- 300 is mainly observed due to amorphous Glass substrate and similar result was observed in the literature. Fig 1a and 1b show that the data are fitted with a long (002), (100), (101), (110) and (112) planes. The micro-strain was calculated using the formula (16).

$$\varepsilon = \beta \cos\theta \div 4$$

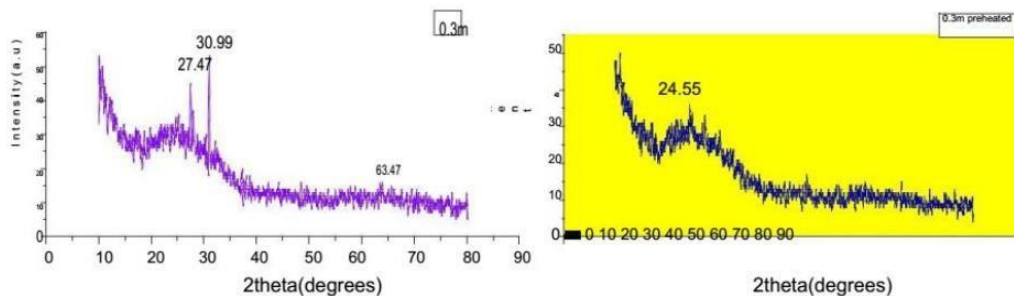


Fig1(a). 0.3M XRD GRAPH

Fig1(b). 0.3 M Pre-heated Graphs

FIGURE 2. shows the annealing effect on Cu₂S thin film. Before annealing Cu₂S nanoparticles are haphazardly arranged on the surface of substrate and after annealing at 150°C these nanoparticles rearrange themselves and forms linear arrangement. Thus crystalline nature was observed of annealed Cu₂S thin film which decreased the film resistance.

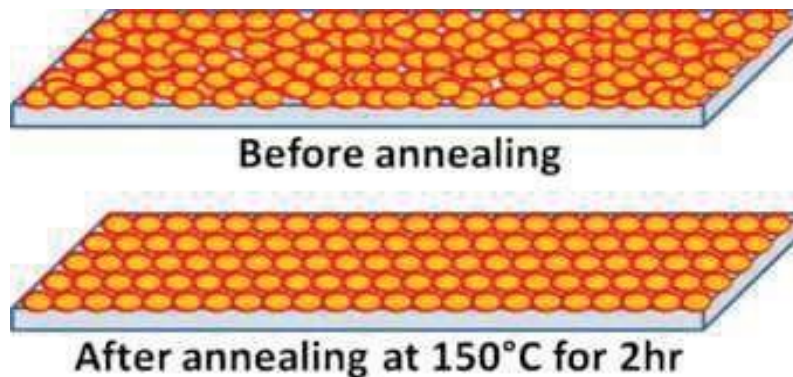


FIGURE 2. Schematic of effect of annealing on Cu₂S thin film.

The XRD pattern of a Cu₂S film shows in FIGURE 3 it gives peaks at 21.96°, 29.96°, and 45° corresponding to (222), (142), and (562) planes, respectively. These results are in agreement with

the literature reported earlier⁶. The grain size of copper sulfide thin films is calculated by using the Scherer's relation. The grain size was found to be averaged 13 nm Cu₂S films.

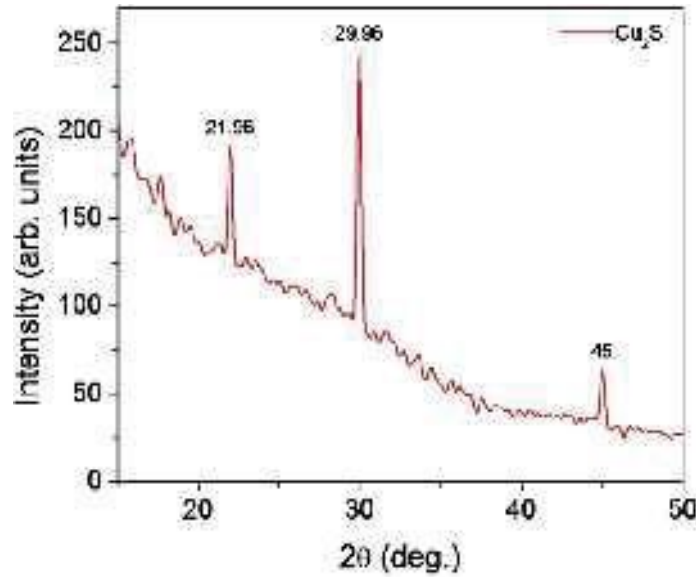
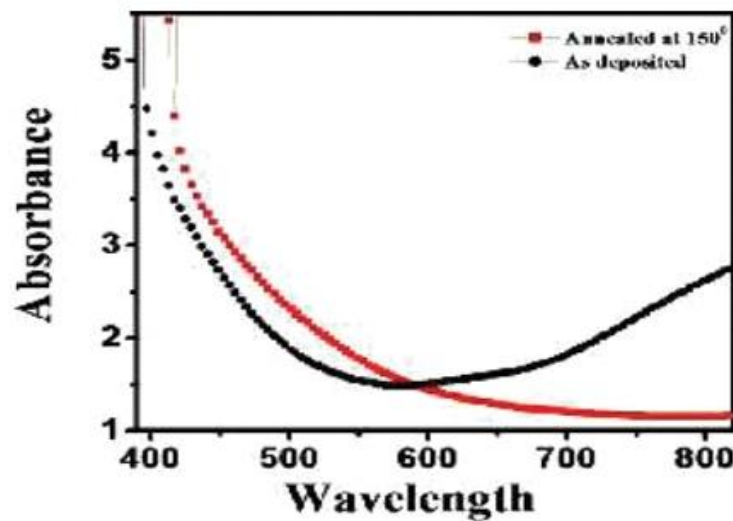


FIGURE 3. X-ray diffraction pattern of 150°C annealed Cu₂S thin film.

2. Optical Analysis

The calculated thickness of the as deposited Cu₂S thin films by weight difference method was found to be ~435nm. The optical properties of Cu₂S thin films are determined from absorbance measurements in the range 200-1100nm (UV-VIS-IR) by spectrophotometer. FIGURE 4. a) shows absorbance and b) shows energy band gap plot of the Cu₂S thin-films grown by solution growth technique at 45°C. Absorbance spectrum shows high absorbance in the visible region and the relation between the absorption coefficient and the incident photon energy (h) can be written as, $(h)^{1/n} = A(h - E_g)$, Where A is constant, E_g is optical band gap of the material, and the exponent ' n ' depends upon the type of transition. The band gap was obtained from the $(h)^2$ versus h plot (FIGURE 4.) and it is found to be 2.38 eV^{7, 8} and 2.3 eV for as deposited and 150°C annealed thin film respectively. This band gap value of the thin film is close to the optimum band gap required for a solar cell. It indicates that Cu₂S is a promising material for thin film solar cell.



(a)

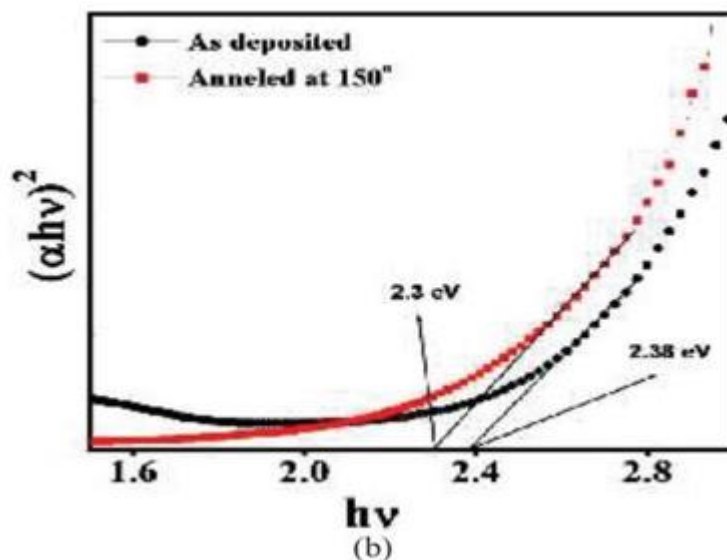


FIGURE 4. a) UV-absorption and b) band gap calculation for as deposited and annealed Cu₂S thin film

3. Morphology Analysis

Scanning electron microscope (SEM) is one of the promising techniques for the topography study of the samples and it gives important information regarding the surface morphology, shape and size of the particles in the film. The surface morphology of the as-deposited, post and pre heated precursor Cu₂S films are shown in Fig. 2a–c, respectively. Figure 5 shows the uniform distribution of particles with the size less than 60 nm. Some well agglomerated grains spread out over the surface with nonuniform size more than several ten nano meters. These grains are loosely bounded and thus most of the larger size grain are absent in post heat-treated thin film as shown in Fig. 5. Figure 5 also shows the uniform distribution of particles with few nano meter dimension throughout the surface. Figure 2c shows the uniform distribution over the surface with smaller particle size compare to other films for pre heated precursor thin film. Figure 2d shows the surface morphology of pre heated precursors Cu₂S thin film with high resolution. All the films have almost compact globular structures composed of hierarchical spherical particles. The noticed morphologies are well agreed with our previous theoretical results from XRD.

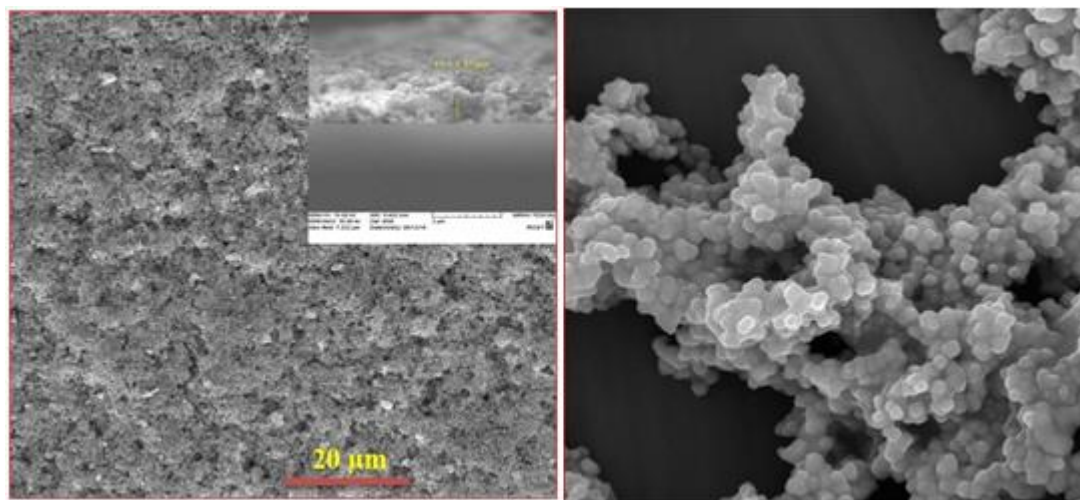


Figure 5

4. Electrical Characterizations

The electrical conductivity can be measured by using dc two- probe method. In this method, copper wires were attached to both ends of the film sample. Silver paste was applied to the surfaces of the sample to serve as electrodes. The current I, which flowed through the film samples was measured by Keithley System consisting of voltage source and current detector. The electrical conductivity (ρ), was calculated from the equation:

$$\rho = RA \div L$$

Where R is the resistance of the sample A is the surface area and L is the thickness of the sample.

FIGURE 6 shows the I-V characteristics of as deposited and 150°C annealed Cu₂S thin films. The resistance of the thin film decreases after annealing at 150 °C this may be due to the enhancement of crystalline nature of the thin film after annealing.

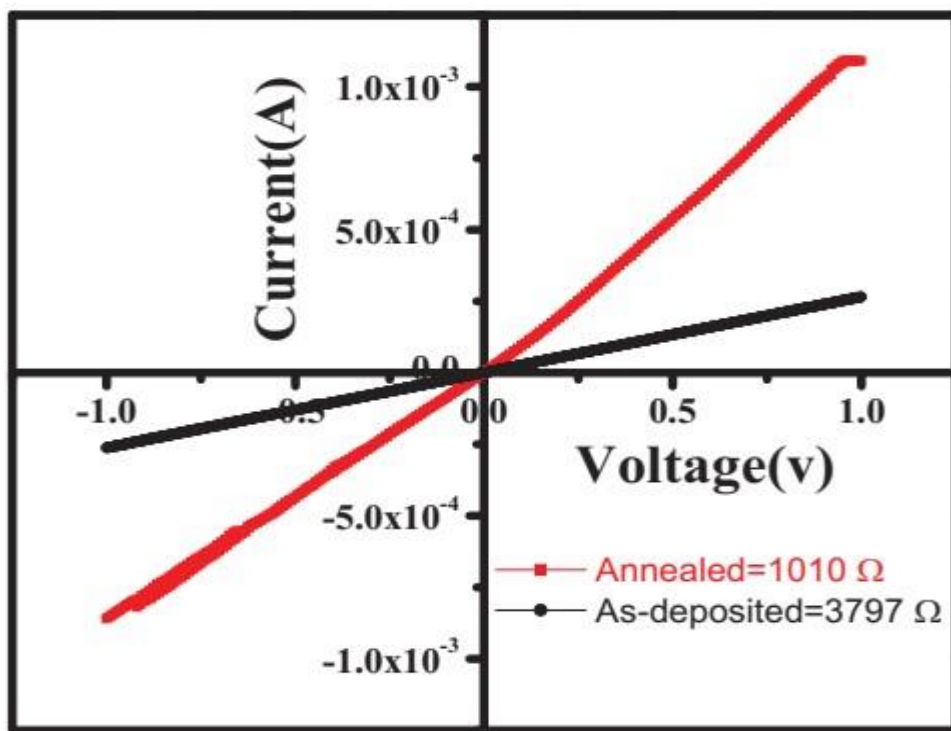


FIGURE 5. I-V of as deposited and 150 °C annealed Cu₂S thin film.

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2. P. Christian (&)School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK,e-mail: paul.christian@manchester.ac.uk F. Von der Kammer Th. Hofmann Department of Environmental Geosciences, Vienna University, Althanstrasse 14, Vienna 1090, Austria e-mail: frank.kammer@univie.ac.at M. Baalousha School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK e-mail: m.a.baalousha@bham.ac.uk

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