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Preparation and Characterization of Nano Cu_2S Starting from Nano CdS

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Abstract: ***Nanoparticles (NP) have emerged as useful building blocks for various Semiconductor devices as well as processes. Currently, large attention is gained by Cadmium Sulfide (CdS) nanoparticles when weighed against others due to remarkable electrical, optical, and surface properties. Also, Cu_2S is an inexpensive and attractive photovoltaic material because of its large minority carrier diffusion length as well as lower sheet resistivity. These characteristics make Cu_2S a favourable candidate for usage in thin film solar cells as well as related semiconductor applications. The preparation, along with characterization of nanostructured Cu_2S from nanoCdS films attained by a Chemical Bath Deposition (CBD) process is presented in this work. This material has been characterized with a wide range of analysis methodologies like X-ray diffraction study (XRD), absorption spectrum studies, along with Fourier Transform InfraRed (FTIR) spectroscopy. The Cu_2S nano-films' optical band gap was determined from the absorbance versus energy graph, employing UV-VIS-NIR spectra. Study of the effect of various experimental conditions, like number of dips as well as time period of immersion in $CuCl_2$ solution, were also made.***

Keywords: Cadmium Sulfide (CdS), Chemical Bath Deposition (CBD), Copper Sulfide (Cu_2S), Nanomaterials, Semiconductors

1. Introduction

Nanotechnology, is an emerging multidisciplinary field gaining global attention. It plays a substantial role in medicine as well as pharmacology and is a cutting-edge technology. There is an excessive deal of interest as well as privileged status given to nanoparticles amongst nanostructures currently. Materials' broad category termed nanoparticles comprise particulate compounds, which have at least one dimension in the size range as 1 to 100 nm [1]. CdS crystals can be grown in two distinct structural phases: cubic (zinc blende) and hexagonal (wurtzite). CdS is widely used as an n-type buffer layer. Its profits contain momentous optical transmission, considerably low-cost synthesis options, band gap tunability, together with compact crystallographic cell structures due to its straight band gap (2.42 eV) along with a higher absorption coefficient of 104 cm^{-1}[2]- [3]. Cu_2S have gained interest owing to its special properties along with latent applications. It has a straight band gap of 1.2 eV and it could be used in solar cells, optoelectronic devices and as photocatalyst [4]. Cu_2S (Cu_xS, $1 \leq x \leq 2$) are stimulating materials due to their semiconducting properties. Also, they are p-type defect semiconductors with shallow Cu vacancy acceptors. Actually, in x, $1 \leq x \leq 2$, the variation could offer distinct crystalline phases dependent on the temperature, manufacturing noteworthy variation in the electrical conductivity. Also, their optical properties depend on Cu_2S size as well as shape. The chalcocite as well as dolerite's structure is hexagonal with alternative layers of copper along with sulphur ions. The covellite comprises six formula units in the unit cell with four copper ions tetrahedrally synchronized along with two triangular coordinates with a hexagonal crystal structure [5]-[6].

Sahare et al., reported that CdS nanoparticles have good adsorbing properties [7]. Mitkari et al., reported the growth of nanocrystalline hexagonal CuS film, by economic Successive Ionic Layered Adsorption Reaction technique (SILAR) and the deposition parameters were optimized [8]. As per the outcome, deposited CuS film contained of nano-sized grains; also, the grain mass augmented with growing film width. More et al., studied compact ZnO layers' synthesis employing CdS sensitized on ZnO as a photoanode with Cu_2S as well as carbon as a Counter Electrode [9]. Various parameters like the current density, fill factor, voltage, as well as efficiency, were gauged by employing the J-V characteristics. The uppermost efficiency (0.85%) was attained by employing the ZnO compact film with 30 SILAR cycles meant for the Cu_2S counter electrode.

A study by Mousavi-Kamazani et al., demonstrated numerous Cu_2S nanostructures' synthesis via coprecipitation as well as hydrothermal routes [10]. Particle size, along with morphology, had a salient result on solar cell efficiency. Cu_2S quantum's utilization as a barrier layer in Dye-Sensitized Solar Cells (DSSCs) offered an amazing surge in solar cells' efficiency as of 6.08% to 8.34% (~37% expansion). Patil et al., discussed Cu_2S thin film's synthesis as well as characterization deposited by the CBD method [11]. The depositions were carried out for 40min in the pH range 10-11; also, the arranged thin films were characterised by UV-Vis absorption spectroscopy along with electrical characterization. For the Cu_2S thin film prepared by the CBD, the energy band gap obtained was 1.94 eV.

Numerous methods are used for obtaining Cu_XS thin films. The common methods are solvothermal technique, hydrothermal, atomic layer deposition, photochemical deposition, microwave aided reaction, Sono chemical, solid state reaction, vacuum evaporation, metal-organic deposition, spray pyrolysis, CBD, along with elemental stacked layer deposition. Among these, CBD is a low cost as well as simple method for making thin film materials at atmospheric pressure, at moderately lower temperature (< 95°C). Several studies have reported that understanding Cu_xS remains a long-standing challenge, particularly in computational investigations, owing to the complex behaviour of copper atoms in Cu_2S. However, the exact nature of these has not yet been clearly identified. The copper vacancies are unavoidable in Cu_2S. Therefore, a comprehensive understanding and

detailed phase map of Cu_2S based on copper vacancy concentrations is essential for its effective utilization as a solar absorber material [12]. Hence, it is important to investigate Cu_xS compounds with different possible structures and compositions close to x = 2 in order to develop strategies for stabilizing such phases.

In the present work, nano-sized Cu_2S is synthesized through the topotaxial conversion of chemically bath-deposited CdS nanoparticles. The fabrication of Cu_2S in nanostructured form is of significant interest due to its latent applications in solar energy conversion, along with optoelectronic devices. The prepared samples are characterized employing UV–Vis–NIR spectroscopy, FTIR spectroscopy, and XRD analysis. Further, this study examines the possibility of fabrication of nanostructured Cu_2S/CdS solar cell.

The paper is structured as: The material, along with methods, is provided in Section 2. Section 3 presents the study findings' detailed analysis. Finally, Section 4 summarizes the conclusion of this research.

2. Materials and Methods

2.1 Preparation of Nano CdS

By using the CBD, CdS nanofilms were deposited on cleaned glass substrates. Aqueous solutions of cadmium chloride ($CdCl_2$) along with thiourea ($CS(NH_2)_2$), each of concentration 0.1 M and volume 10 ml, were used as the sources of cadmium and sulphur, respectively. Firstly, a $CdCl_2$ 10 ml solution was taken in a small beaker, to which triethanolamine (TEA) was added as a complexing agent. TEA formed a cadmium complex that released Cd^{2+} ions meant for succeeding reaction with S^{2-} ions. Ammonia was added dropwise to the $CdCl_2$ solution in vigorous stirring till the pH reached approximately 10.5, resulting in a colourless solution. The entire deposition process was done at room temperature, with the temperature maintained around 27 °C during film growth. In Figure 1, the experimental setup is shown.

The deposition was permissible to ensue for one day, during which the solution's colour gradually altered to yellow. Next, the samples were detached as of the bath, washed with distilled water, along with dried in air. The obtained CdS nanofilms were homogeneous, uniform, and exhibited decent adhesion to the glass substrate.

2.2 Preparation of Nano Cu_2S

A nano-scale layer of Cu_2S was produced on the CdS surface by immersing the CdS film in a solution containing cuprous chloride. This is commonly referred to as the wet Clevite process.

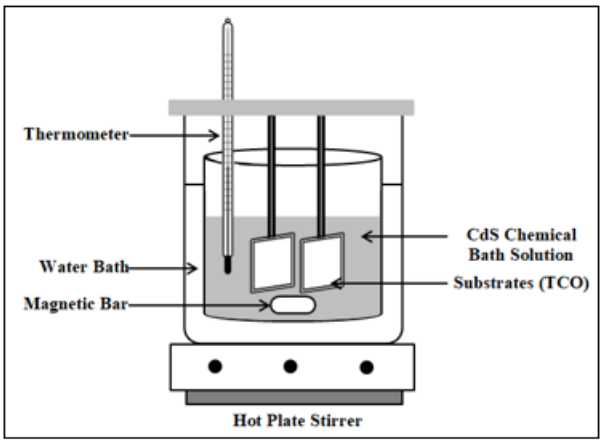

Figure 1: Experimental Setup of the CBD Technique

In the present study, the nano CdS films were immersed in 0.5 M $CuCl_2$ for different time intervals of 5s, 10s, 15s, and 30s. The films were then dried. The films appeared black in colour, indicating the formation of a nano Cu_2S layer over the nano CdS films. The prepared samples are shown in Figure 2.

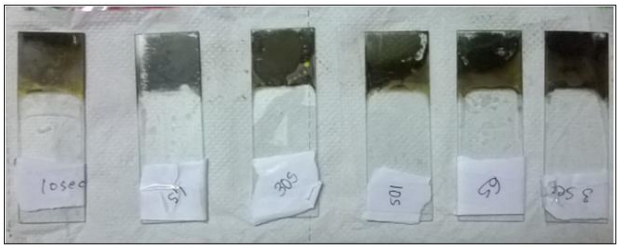

Figure 2: Nano Cu_2S Films with Varying Time

2.3 Material Characterization

The prepared materials were characterized using XRD, absorption spectroscopy and FTIR. Absorption spectroscopy is an effective analytical tool, especially in studying dilute colloids and solutions of nanoparticles. Absorption spectra of CdS were recorded by employing a UV-VIS-NIR spectrophotometer (JASCO V670). XRD was used to study the crystal structure and crystallite size. Diffraction peak broadening contained information about the sample's microstructure. FTIR was used to recognize the chemical bonds in a molecule by generating an infrared absorption spectrum.

3. Result and Discussion

3.1. Absorption Studies of Nano CdS Samples

3.1.1 UV-VIS-NIR of CdS Samples Prepared by Varying Amount of TEA

The optical properties of CdS thin films prepared with different amounts of TEA were studied using UV–Vis–NIR spectroscopy. Figure 3(a) represents the absorption spectrum of the CdS samples prepared at room temperature by varying amounts of TEA, and Figure 3(b) represents the corresponding $(\alpha h\nu)^2$ versus $h\nu$ plot.

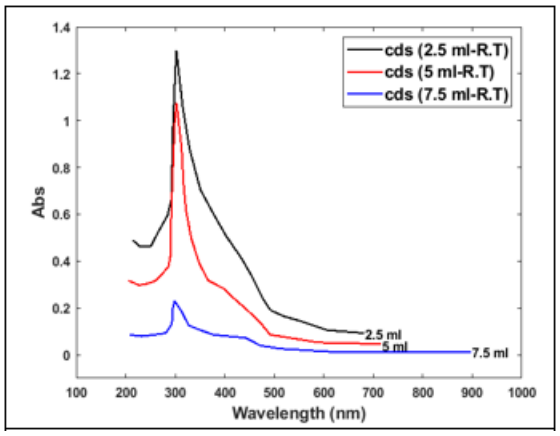

Figure 3 (a): Absorption Spectra of CdS

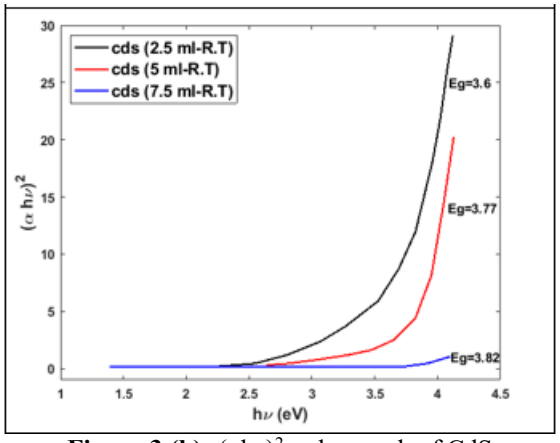

Figure 3 (b): $(\alpha h\nu)^2$ vs hν graph of CdS

The energy band gap (Eg) of the prepared nano CdS films were greater than the bulk CdS (2.42 eV), as reported earlier [13]. This increase in band gap can be accredited to the size quantization effect of the samples. As the particle size decreases, the band gap is increased and there is a shift of the emission wavelength toward higher energies (lower wavelengths). Thus, the blue shift witnessed in the optical absorption edge clearly specified nano-sized CdS particles' formation. Furthermore, it was found that the band gap gradually increased with increase in the amount of TEA. The band gap values obtained for these samples are illustrated in Table 1.

Table 1: Obtained Band Gap Values

The amount of TEA (ml)	pH scale	Deposition Temperature			
		27^{0}C	50^{0}C	70^{0}C	90^{0}C
2.5	10.5	3.61	3.60	3.35	3.31
5	10.5	3.78	3.51	3.38	3.35
7.5	10.5	3.82	3.47	3.41	3.38

Findings indicated that the particle size decreased with increase in the amount of the capping agent, TEA. This was confirmed by the gradual increase in the band gap as the TEA concentration is increased. A similar trend was observed for the samples prepared at 27 °C , 50 °C, 70 °C, as well as 90 °C.

3.1.2 Variation in Band Gap with Deposition Temperature

The optical band gap of CdS thin films varies with deposition temperature. It was observed that changes in deposition temperature significantly affects the optical properties of the films. Figure 4 depicts band gap variation with deposition temperature of the prepared samples. As the deposition temperature is increased, a gradual decrease in the band gap was noted. This indicated an increase in particle size with increase in deposition temperature. The reduction in band gap is due to the decrease in quantum confinement effects as the particles grow larger at higher temperatures.

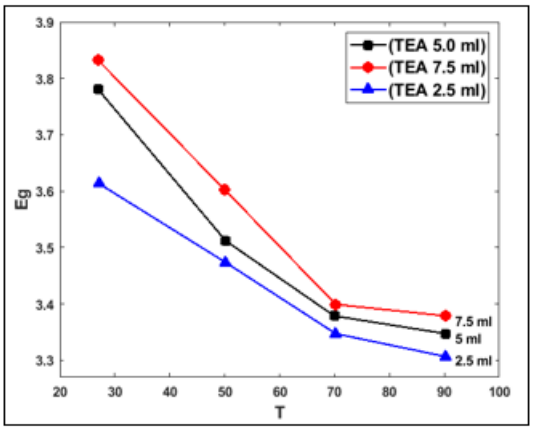

Figure 4: Variation of Band Gap with Deposition Temperature

3.2 Absorption Studies of nano Cu_2S Samples

Absorption spectra of the Cu_2S samples were recorded in the wavelength range 200nm-800nm. The corresponding absorption spectra and $(\alpha h\nu)^2$vs hν plots are shown in Figure 5(a) and 5(b) respectively. The obtained band gap values ranged between 2.5–2.74 eV, matching with the reported band gap values of Cu_2S. Bandgap energy increased with increasing film thickness.

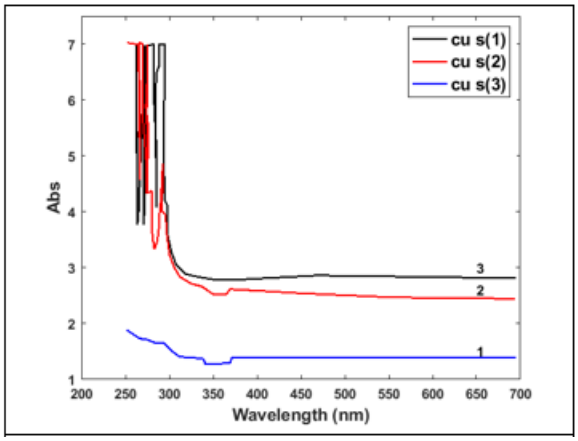

Figure 5(a): The Absorption Spectra of Cu_2S

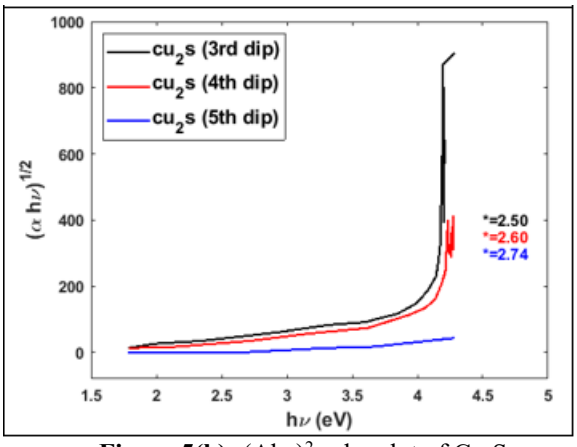

Figure 5(b): $(Ah\nu)^2$vs hν plot of Cu_2S

By utilizing second-dip nano CdS films, the Cu_2S samples were prepared at room temperature. The immersion time in cuprous chloride solution was varied for the three samples. The CdS films were dipped in 0.5 M $CuCl_2$ solution for 3 s, 10 s, and 30 s. The films were then removed and dried at 80°C. As per Table 2, the bandgap value diminished with growing dipping time. This decrease in bandgap might be attributed to an increase in particle size along with Cu_2S layer's improved growth with longer immersion durations.

Table 2: Band Gap Values

No. of Dips	Time of Immersion (s)	pH Scale	Temperature	Band Gap (eV)
2	3	10.5	27°C	2.74
2	10	10.5	27°C	2.20
2	30	10.5	27°C	1.75

3.3 XRD Analysis

3.3.1 XRD Pattern of Nano CdS

XRD is a sturdy non-destructive technique to characterize crystalline materials. Information regarding the structures, phases, desired crystal orientations (texture), as well as other structural data like average grain size, crystallinity, strain etc can be obtained. Figure 6 indicates the XRD pattern of nano CdS films. XRD peaks were very broad, which indicated the very fine size of the grain. The XRD pattern exhibited broad peaks at 2θ values of 28.33 (002), 43.75 (110), and 51.85^0 (112), which were indexed to the (002), (110), as well as (112) crystallographic planes.

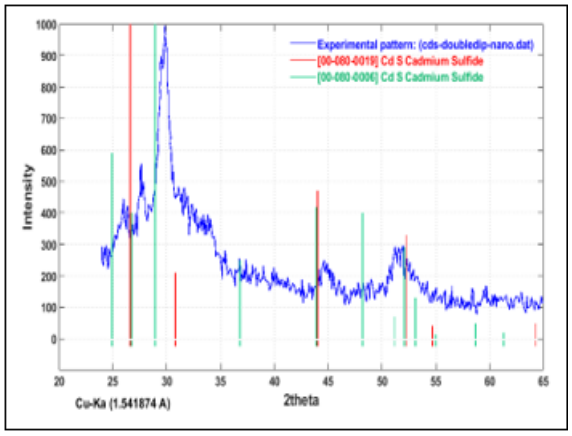

Figure 6: XRD of Nano CdS

3.3.2 XRD Pattern of Nano Cu_2S

In the present work, two samples: sample1 immersed in $CuCl_2$ solution for 5 seconds and sample 2 immersed for 15 seconds, were studied by XRD and the XRD patterns are shown in Figures 7(a) and 7(b) respectively. it clearly indicated the formation of Cu_2-xS. In Sample 1, the peaks detected at 2θ values of 32.92° as well as 40.28° resemble to the preferred orientations of (006) and (106) planes, respectively. The XRD of the as-prepared films of sample 2 contained various diffraction lines with a broad hump at 2θ: 32.92° and 40.28° corresponding to the same crystallographic planes. The broadening of the peaks indicated the nanocrystalline nature of the particles. The XRD analysis demonstrated that the nanoparticles possessed a hexagonal crystal structure, and the particle size increased with increasing immersion time in $CuCl_2$ solution.

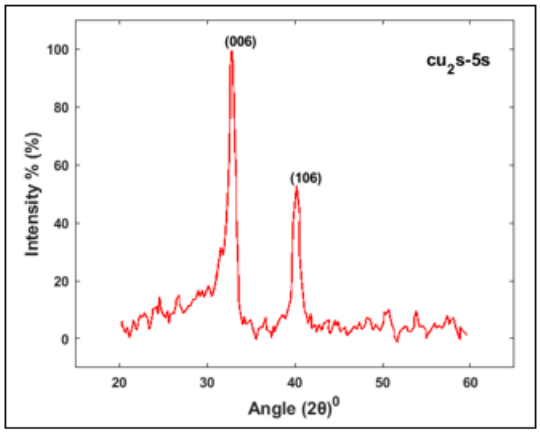

Figure 7(a): XRD Analysis of Nano Cu_2S film immersed for 5sec

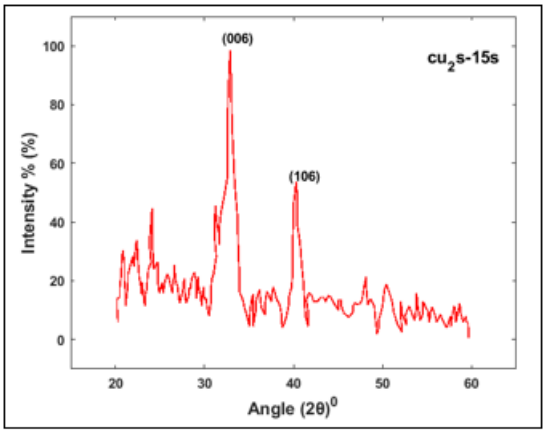

Figure 7(b): XRD Analysis of Nano Cu_2S film immersed for 15sec

3.4 FTIR Spectrum Analysis

3.4.1 Nano CdS and Cu_2S

FTIR analysis of nano CdS and Cu_2S primarily focused on identifying the metal-chalcogen bonds and detecting any surface-adsorbed species or capping agents. Figures 8(a) and 8(b) represent the results of the FTIR spectrum of nano CdS as well as Cu_2S, respectively. CdS sample was synthesized at room temperature with 2.5 ml TEA. Its spectrum exhibited absorption bands corresponding to different vibrational modes. The major characteristic peaks of CdS could be observed at 409.79 cm^{-1},988.33 cm^{-1}, and1641.12 cm^{-1}, which were in decent agreement with those reported earlier [14]. For nano Cu_2S, the characteristic peaks were at 501.40 cm^{-1}, 981.59 cm^{-1}, as well as 1158.04 cm^{-1}, which were in decent agreement with those reported in by Soliman et al.,[15]. The FTIR outcomes showed that the complexes were well-shaped.

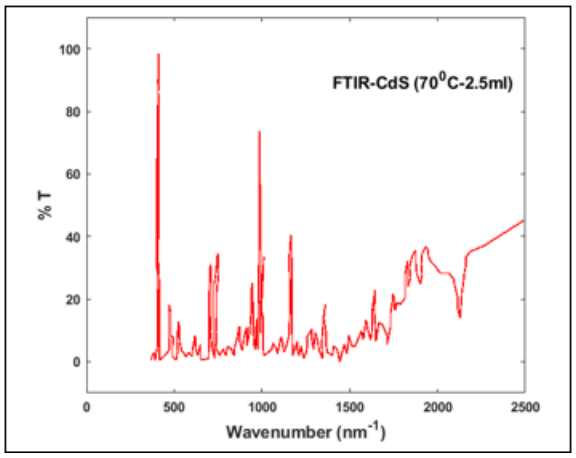

Figure 8 (a): FTIR Spectra of Nano CdS Film

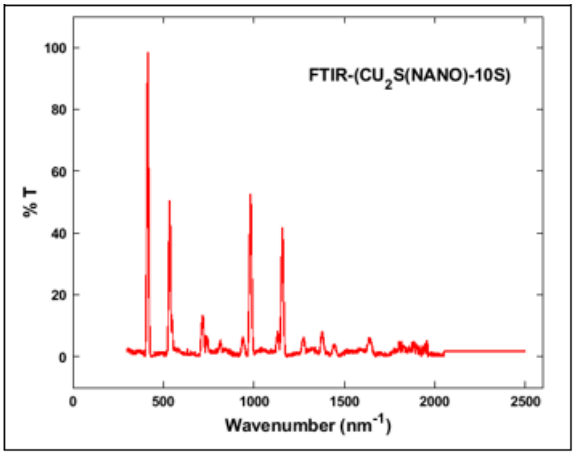

Figure 8 (b): FTIR Spectra of Nano Cu_2S Film

3.5 Hot Probe Measurement

A hot probe measurement (or hot point probe) is a simple, non-destructive technique used in semiconductor physics to check whether a material is n -type or else p- type. It worked via employing a hot probe as well as a standard multi meter, where heat drove major charge carriers (electrons or else holes) from a hot region toward a cold region, generating a measurable voltage. Thus, to determine the majority carrier type of a semiconductor, a hot probe technique can be used. In this technique, two probes (hot and cold) were brought into contact with the semiconductor sample. One probe was artificially heated (hot), while the other probe was kept at room temperature (cold). The hot probe was wired to the multimeter's positive terminal, and the cold probe was wired to the adverse terminal. While the probes were functional to an n-type semiconductor, a positive voltage reading was observed on the meter. In contrast, a negative voltage reading was gained for a p-type semiconductor. In an n-type semiconductor, the majority of the free charged carriers were electrons. When they diffused as of the hot to the cold probe, they created a positive potential at the hot probe. The multi meter displayed a positive voltage. Meanwhile, in a p-type semiconductor, the majority of the free charged carriers were holes**.** As these positively charged holes diffused away from the heated region, the hot probe was left with a negative potential, yielding negative voltage readout on the meter. On applying a probe in the case of a nano CdS film, the voltage increased, i.e., a positive current reading on the meter. Thus, it showed that the CdS sample was n-type, while in the case of nano Cu_2S films, the voltage decreased, i.e., a negative current reading on the meter. Thus, it showed that the Cu_2S sample was p-type.

3.6 Fabrication of CdS-Cu_2S Solar Cell

By using chemical bath deposition, an attempt was made to fabricate a CdS/Cu_2S solar cell. For the fabrication of CdS/Cu_2S solar cell, a CdS film was first deposited onto an Indium Tin Oxide (ITO) covered glass substrate, which served as a transparent conducting oxide owing to its high electrical conductivity along with optical transparency. The prepared CdS film was then immersed in a 0.5 M $CuCl_2$ solution for 30 seconds. After removal from the solution, the film was dried at 80 °C. The films appeared black in colour, indicating Cu_2S layer's formation over the CdS film. Thus, a p-n junction solar cell was formed with the p-type Cu_2S as well as the n-type CdS layer. The fabricated cell was subsequently annealed at 80 °C for 30 minutes. Figure 9 represents CdS/Cu_2S solar cell's preparation stages.

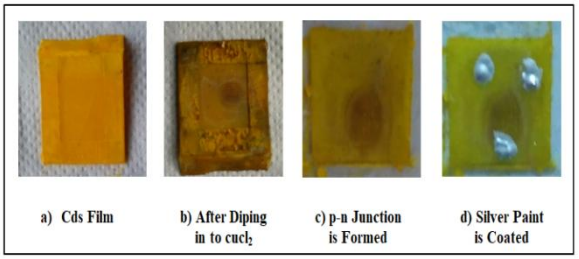

Figure 9: CdS–Cu_2S Solar Cell

Under diffused radiation, the cell's open-circuit voltage (Voc) along with short-circuit current (Isc) were measured using an ordinary multimeter. An open-circuit voltage of 164 mV was obtained, whereas the short-circuit current was found to be negligible. This might be attributed to the CdS layer's higher resistance and the fabricated cell's non-uniformity. Further studies are required to improve device efficiency.

4. Conclusion

Here, this study was aimed to prepare nano Cu_2S films from the CdS nanofilms prepared using cadmium chloride and thiourea precursors through the well-known CBD technique. Absorption studies revealed that the particle size of CdS decreased with the amount of the capping agent TEA, whereas The particle size increased with increasing reaction temperature. Structural characterization using XRD confirmed that both CdS and Cu_2S films possessed a hexagonal crystal structure. Hot probe measurements revealed that the prepared CdS nanomaterial displayed n-type semiconducting behaviour, whilst the Cu_2S film showed p-type semiconducting behaviour. Attempts were made to fabricate a CdS/Cu_2S thin film solar cell. Further study and optimization is needed to enhance the performance.

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