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STRUCTURAL AND OPTICAL CHARACTERIZATION OF NANOCRYSTALLINE CDS THIN FILMS SYNTHESIZED BY CHEMICAL BATH DEPOSITION

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ABSTRACT

Cadmium sulfide (CdS) is a significant II-VI semiconductor material that is utilized in thin film solar cells, optoelectronic devices such as photodetectors, sensors, and other optoelectronic devices. It can be used in CdTe and CIGS photovoltaic devices as a window or buffer layer due to its direct band gap, good response to visible light, and n-type conductivity. One of the most popular techniques for the preparation of CdS thin films is a chemical bath deposition (CBD) as it is low cost, simple, scaleable and low temperature process. A research discussion based on the literature is presented in this paper about the structural and optical characteristics of the nanocrystalline CdS thin films obtained by CBD process. Structural characterization is performed primarily by X-ray diffraction, scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy-dispersive X-ray spectroscopy (EDXS). Typical methods for optical characterisation include UV–visible spectroscopy and the Tauc plot analysis. It is found from published work that the CBD-deposited CdS films have generally been nanocrystalline and polycrystalline in nature, and their crystal structure has been found to be cubic, hexagonal or mixed crystal structure, depending on the deposition time, bath temperature, pH, concentration of the CdS precursors, complexing agents, and the annealing conditions. The optical band gap values typically range within 2.1–2.5 eV, which is close to the visible band, and are often related to the grain size, thickness, strain, defects, and stoichiometry. The review shows that the method of forming CdS thin films using CBD is still a viable and viable method for low-cost PV and OE devices.

KEYWORDS: CdS Thin Film, Chemical Bath Deposition, Nanocrystalline Semiconductor, X-ray Diffraction, UV-Vi's Spectroscopy And Optical Band Gap

1. INTRODUCTION

Nanocrystalline semiconductor thin films are significant in the recent field of materials science due to their tunable optical, electrical and structural characteristics as a function of synthesis conditions. Cadmium sulfide (CdS) is a well-known II-VI compound semiconductor having a direct band gap close to the visible region. Because of its n-type conductivity, optical transparency over a portion of the visible spectrum, and its ability to form junctions with good quality, CdS is extensively used as the buffer or window layer in thin film solar cells (TFSCs) (Mahanty et al., 1999). CdS can be utilized in photoelectrochemical systems, photocatalysis, light-emitting devices, gas sensors and photodetectors (Al-Hussam & Jassim, 2012).

The methods that have been employed to deposit CdS thin films are Sputtering, Thermal Evaporation, Spray Pyrolysis, Pulsed Laser Deposition (PLD), Successive ionic layer adsorption and reaction (SIR), Electrodeposition and Chemical bath deposition. The methods mentioned above are all attractive, but particularly CBD, which does not need high vacuum, costly instruments or extremely high processing temperature. It can be used for coating glass and other substrates with uniform coatings, from aqueous precursor solutions. CBD is particularly useful for the laboratories of developing countries like Bangladesh and India, where it enables thin-film research to be done with relatively simple equipment.

In CBD, the film growth takes place under low reaction rate of metal and sulfur ions that are close to the substrate surface. For CdS, a cadmium salt is employed as the source of Cd^{2}+, and thiourea or some other sulfur-containing compound is used as the source of S. The complexing agent slows down the release of Cd^{2+} ions and alkaline pH encourage thiourea to decompose and release thioureas (Najm et al., 2022). A controlled reaction is needed to promote the growth of CdS on the substrate and not fast precipitation in the solution.

Structural and optical quality play a crucial role in the performance of CdS thin film. The choice of whether to use the film as a solar cell or an optoelectronic depends on the crystal phase, crystallite size, surface compactness, stoichiometry, film thickness and optical band gap. Hence, structural and optical characterisation is a must. The synthesis process of the CBD, characterization techniques of the synthesized nanocrystalline CdS thin films, structural properties, optical properties, applications, challenges, and future scope of nanocrystalline CdS thin films are discussed.

Chemical Bath Deposition Process

The chemical bath deposition technique is a solution chemistry based thin film growth technique. A cleaned substrate is dipped in a solution of cadmium ions, sulfur source, complexing agent, and pH control chemicals in an aqueous solution. Cadmium can be found in many cadmium compounds, such as cadmium chloride, cadmium nitrate, cadmium acetate, and cadmium sulfate. Often, thiourea is used as the source of sulfur, since it releases the sulfate slowly under alkaline conditions. The Cd^{2+} can be complexed by ammonia, triethanolamine, sodium citrate or other similar agents to control the reaction rate (Najm et al., 2022).

Figure 1. Representative Chemical Bath Deposition Setup for CdS Thin Film.

The glass substrate was placed in the chemical bath of cadmium precursor (Cd2+), sulphur source (S2-), complexing agent and alkaline medium at controlled temperature and time as shown in the figure.

Growth of film in CBD can occur through ion by ion, cluster by cluster or mixed mechanisms. The ion-ion mechanism involves direct interaction between Cd2+ and S- ions in the vicinity of the substrate surface to form CdS nuclei. The cluster-by-cluster mechanism is a mechanism where clusters of CdS particles are initially formed in solution and subsequently deposited on the substrate. The final film quality will be determined by which mechanism prevails. The films tend to be more compact and uniform when the growth is controlled by an ion-by-ions process, and if the clusters grow too large, the resulting roughness, agglomeration, and weak adhesion can occur (Najm et al., 2022).

Substrates need to be carefully cleaned prior to deposition. Dust, oil and surface contamination may result in poor adhesion and/or non-uniform growth. Glass substrates are typically washed with detergent, distilled water, acetone or ethanol and then dried before use. The thickness and morphology of the film are affected by the bath temperature, pH, deposition time and stirring during deposition. Film(s) can be rinsed, dried and annealed after deposition. Annealing can increase crystallinity but also may incorporate sulfur vacancies or alter the composition of the film (Agrawal et al., 2013).

Characterization Techniques

The main technique for the study of the crystalline structure of CdS thin films is X-ray diffraction. It determines the type of film (amorphous, cubic, hexagonal or mixed phase). The positions of the diffraction peaks show the crystal structure, and the width of the diffraction peaks yields an insight into the nanocrystalline size. Average crystallite size can be estimated from the full width at half maximum of the XRD peaks by using the Debye–Scherrer equation (Cullity & Stock, 2001).

The surface morphology is typically analyzed using the scanning electron microscopy and atomic force microscopy. SEM provides information on grain distribution, cracks, pinholes, porosity and agglomeration. AFM gives surface roughness and three-dimensional surface topography. The elemental composition is checked by energy-dispersive X-ray spectroscopy, and the presence of cadmium and sulfur is confirmed. Stoichiometric balance is crucial as sulfur deficiency can affect band gap and electrical properties (Mahanty et al., 1999).

The typical technique used for optical characterization is the UV-visible spectroscopy. Use of absorbance and transmittance spectra to determine absorption edge and transparency. CdS is a direct band gap semiconductor, and typically, the optical band gap is obtained by analyzing the data of this semiconductor using the Tauc plot method. In the case of direct transitions, ((\alpha h\nu) ^2) is plotted as a function of photon energy (h\nu) and the linear portion is extrapolated to the photon energy axis (Tauc et al., 1966). This approach is common for the preparation of CBD CdS films.

Structural Characterization

Typical XRD patterns of the CdS thin films deposited by CBD technique display a typically nanocrystalline and polycrystalline nature. CdS may exist in cubic zinc blende, hexagonal wurtzite or mixed crystal forms. Cubic CdS was reported for CBD films in some studies, while hexagonal structure in the films was reported depending on the bath temperature, deposition time, pH, and annealing (Al-Hussam & Jassim, 2012; Mahanty et al., 1999). This difference indicates that the synthesis conditions strongly affect the phase formation of CdS.

Figure 2. The XRD Pattern of the CBD CdS Thin Film is shown in the figure below:

The graph shows typical CdS diffraction peaks such as (100), (002)/(111), (101), (110), and related reflections. The broadening of the peaks suggests the formation of nanocrystals.

Crystallite size is one of the most important structural parameters. The size of crystallites in nanocrystalline CdS films can be from a few nanometres to several tens of nanometres depending upon the deposition conditions. Al-Hussam and Jassim (2012) reported the formation of nanocrystalline CdS films with cubic structure and nanoscale particle formation by CBD at a high bath temperature. Increasing the deposition time led to an increase in film thickness and decrease in the optical band gap which revealed structural changes due to growth (Agrawal et al., 2013).

The thickness of the film and its compactness are strongly influenced by deposition time. For short deposition time the nuclei of CdS may be incomplete thus resulting in discontinuous films. As the time passes, the nuclei grow larger and merge together, thus forming a more uniform film. But, too long of deposition time can result in particle agglomeration and rough morphology. Likewise, increasing the temperature of the bath increases the rate of release of ions and the rate of reaction. The flowability is improved with increase in temperature; however, the increase in temperature too much may cause precipitation and rough film.

Morphology is also a parameter that plays a role in the device performance. Ideal CdS film is a smooth, compact and pinhole-free film. The surface may have cracks or pinholes, and the junction may be defective resulting in recombination losses and poor device performance. All recent research on CdS and doped CdS films still points towards the significance of homogeneity, control of roughness and compactness for flexible photovoltaic applications, as mentioned by Molina-Jiménez et al., 2025.

Figure 5. Representative Morphology image for Nanocrystalline CBD CdS.

The illustration morphology image is a granular nanocrystalline surface typical of chemically deposited thin films of CdS.

Optical Characterization

Applications of CdS thin films heavily depend on their optical properties. There is usually strong absorption in the visible region that can be seen in UV-visible spectroscopy. The absorption edge is usually at 500–520 nm wavelength related to the direct band gap of CdS. The absorption edge can be shifted from the film thickness, crystallite size, defect density, and the stoichiometry.

Figure 3. Representative UV–Visible Absorbance of CBD CdS Thin Films.

The graph depicts the increase in absorbance with the increase of deposition time because thicker CdS films will have more absorption of light.

The CdS films should have suitable transparency and thickness for solar cell buffer layers. If the CdS layer is very thick, it will absorb a large number of photons before they reach the absorber layer, thus diminishing photocurrent. A very thin film can be broken up into separate segments in such a way that it does not create a suitable connection. Thus, optimizing CBD parameters for achieving both transparency and compactness, along with electronic function, is required.

The optical band gap of the CdS film of CBD is generally reported in the vicinity of 2.4 eV but the band gap has been reported to have varying values. Direct band gaps between 2.180 and 2.448 eV were reported by Mahanty et al., and they attributed these changes to composition and annealing effects (Mahanty et al., 1999). The band gap of the product decreased from 2.43 eV to 2.32 eV with increase in deposition time, which was correlated by the increased thickness and crystallite growth of the resulting product (Agrawal et al., 2013). Al-Hussam and Jassim found that a blue shift is observed in the absorption spectra, which means that there is the formation of nanoparticles and quantum size effects are present (Al-Hussam & Jassim, 2012).

Figure 4. The following plots, labeled Representative Tauc Plots, show a comparison of a direct band gap CdS with other semiconductors.

The representative Tauc plot shows an illustrative direct optical band gap of about 2.41 eV, close to the typical band gap of CdS.

There are several reasons for the variation in band gaps of CdS thin films. Band gap may be increased by the effect of quantum confinement due to smaller crystallites. Increasing the size of grains and film thickness decreases the band gap, which can be attributed to decreasing the confinement and increasing the ordering of structure. The absorption edge can also be modified by the presence of defect states, sulfur deficiency, strain and incorporation of impurities. However, in recent years, CdS:Ag has been found to be capable of shifting the band gap and increasing transmittance under well-controlled conditions (Molina-Jiménez et al., 2025).

Table 1: Summary of Typical Structural and Optical Features of CBD CdS Thin Films+

Feature	Typical CBD CdS Observation	Characterization Method
Growth medium	Cadmium salt, sulfur source, complexing agent, alkaline pH	CBD process control
Growth mechanism	Ion-by-ion and/or cluster-by-cluster deposition	XRD/SEM/kinetic analysis
Crystal structure	Cubic, hexagonal, or mixed CdS	XRD
Major XRD peaks	(100), (002), (101), (110), (103), (112), or cubic reflections	XRD
Morphology	Granular, compact, or agglomerated nanocrystalline surface	SEM/AFM
Optical edge	Visible absorption edge near 500–520 nm	UV–Vis spectroscopy
Band gap	Commonly about 2.1–2.5 eV	Tauc plot
Key variables	Temperature, pH, time, concentration, complexing agent, annealing	Combined analysis
Applications	Solar-cell buffer/window layer, photodetectors, sensors	Device testing

APPLICATIONS

CdS thin films deposited by CBD are very popular buffer or window layers of thin film solar cells. CdS plays a role in heterojunction formation and in the separation of carriers in CdTe and CIGS solar cells. The wide band gap results in partial light transmission and the n-type conductivity facilitates device operation (Mahanty et al., 1999). As the material is inexpensive and easily scaled, it has been a widely used technique to prepare CdS buffer layers. The visibilities of CdS thin films make them also suitable for use in photodetectors. They are nanocrystalline and have a high surface area that may be beneficial for gas sensing or photoelectrochemical applications. Optical response, conductivity and device performance can be further enhanced with the introduction of doped CdS and heterostructures based on CdS. For instance, CdS with ZnO or graphene-based materials can facilitate enhanced charge transfer and light harvesting.

CBD is extremely useful in the research laboratories of developing countries. It is also used to study the growth of thin film, XRD, SEM, UV-visible spectroscopy and estimation of the band gap without any expensive vacuum system. Cadmium is toxic, however, so safety precautions must be taken. Gloves, lab coat, using a fume hood, labelled waste bottles, and disposal in a safe manner are key.

CHALLENGES AND FUTURE SCOPE

CBD products are cheap and easy to make, but there are some drawbacks. Bath pH, bath temperature, bath stirring, precursor concentration and substrate cleanliness are among the factors that can cause small changes to film reproducibility. In cases where the reaction is too rapid, CdS could precipitate in the solution instead of forming a uniform film. If the reaction is too slow, the film is thin, discontinuous. This means careful optimization should be done.

Another big problem is Cadmium toxicity. The use of CdS-based films is beneficial; however, the use of cadmium requires careful environmental and laboratory safety control. Reducing chemical waste, increasing re-use of the bath, and finding alternatives to deposition techniques should be the subject of future studies. Meanwhile, other buffer layers like CdS, ZnS, In_2S_3 and Zn (O, S) are also in study and CdS is still significant for its performance.

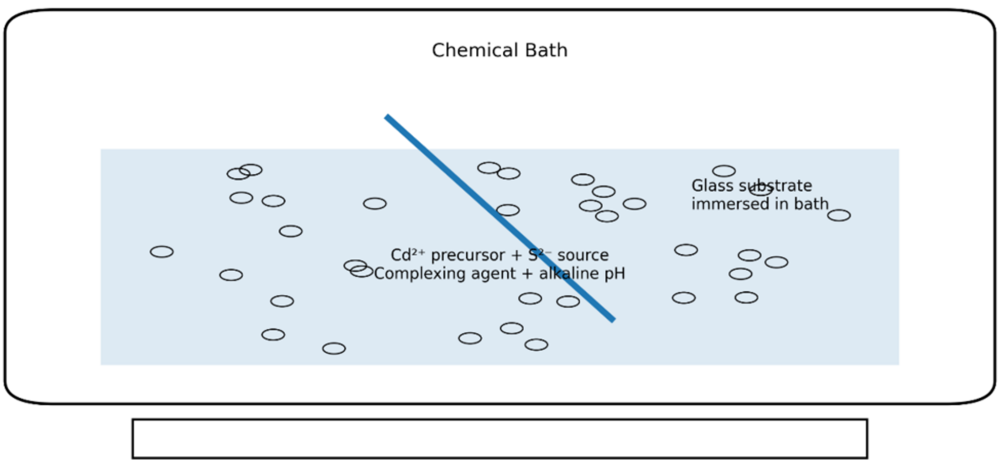
Advanced characterization should also be a focus of future studies. Defects, carrier concentration, chemical state and recombination can be understood better by Raman spectroscopy, photoluminescence, Hall measurement, impedance spectroscopy and XPS. Machine learning and statistical optimization can also be utilized to determine the most optimal CBD conditions to produce high-quality CdS films.

CONCLUSION

The CdS thin films prepared by chemical bath deposition technique are of great importance in optoelectronic and photovoltaic applications, as they are nanocrystalline. CBD is simple, low cost, low temperature and applicable to large area deposition. Generally, the structural characterization confirms that CBD CdS films are nanocrystalline and polycrystalline and their phase depends on the CBD parameters used. They are controlled by bath temperature, deposition time, pH, precursor concentration, complexing agent and annealing.

The optical characterization reveals that thin films of the semiconductor CdS exhibit high absorption in the visible region of the spectrum and a direct optical band gap typically of the order of 2.1–2.5 eV. The thickness, grain size, stoichiometry, strain, and defect states all affect the band gap. For the use as a solar-cell buffer, it is desirable that the CdS is compact, uniform and well-crystallized. Despite the problems of film defects, reproducibility and cadmium toxicity, CBD is still one of the most convenient ways to prepare CdS thin films. By optimizing, CBD deposited CdS films can be used in the applications of solar cell, photodetector, sensor, and semiconductor research.

Figure 1. Representative Chemical Bath Deposition Setup for CdS Thin Films



Controlled temperature, time and stirring regulate CdS film growth

Figure 2. Representative XRD Pattern of CBD CdS Thin Film

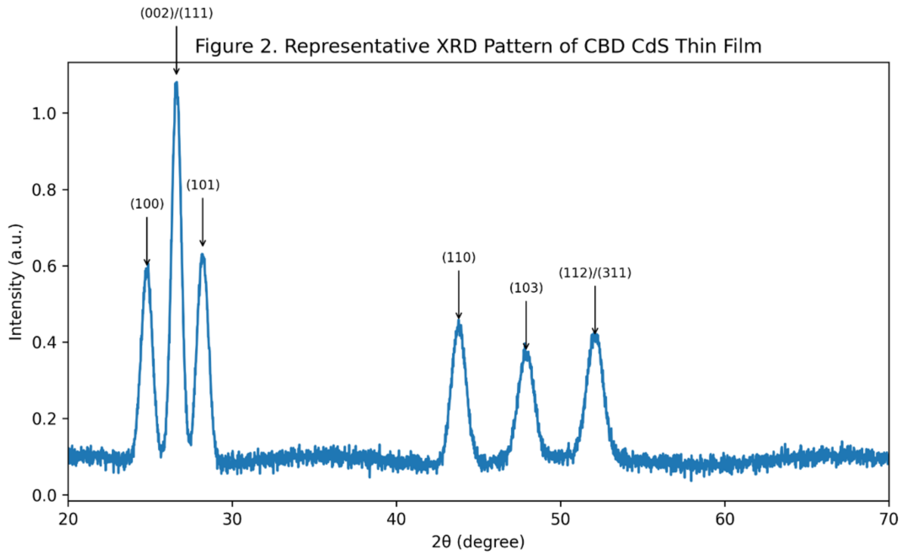


Figure 3. Representative UV–Vis Absorbance of CBD CdS Thin Films

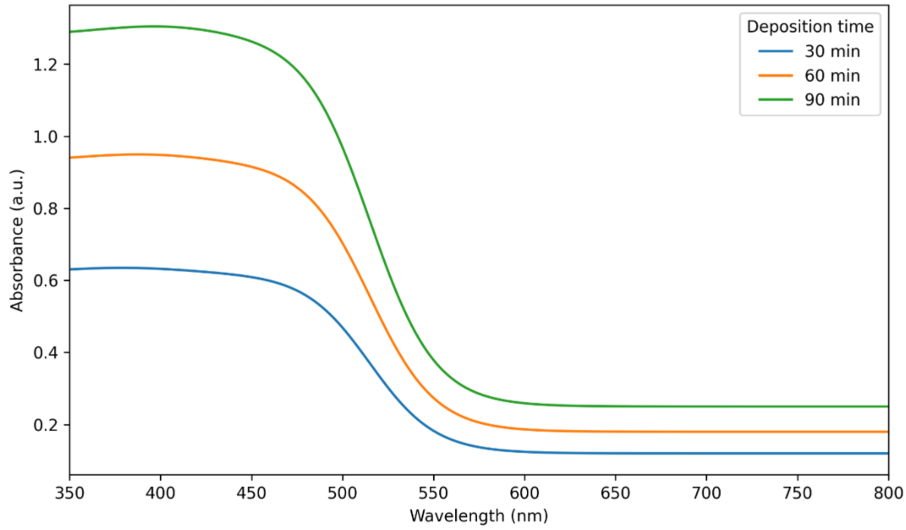


Figure 4. Representative Tauc Plot for Direct Band Gap CBD CdS

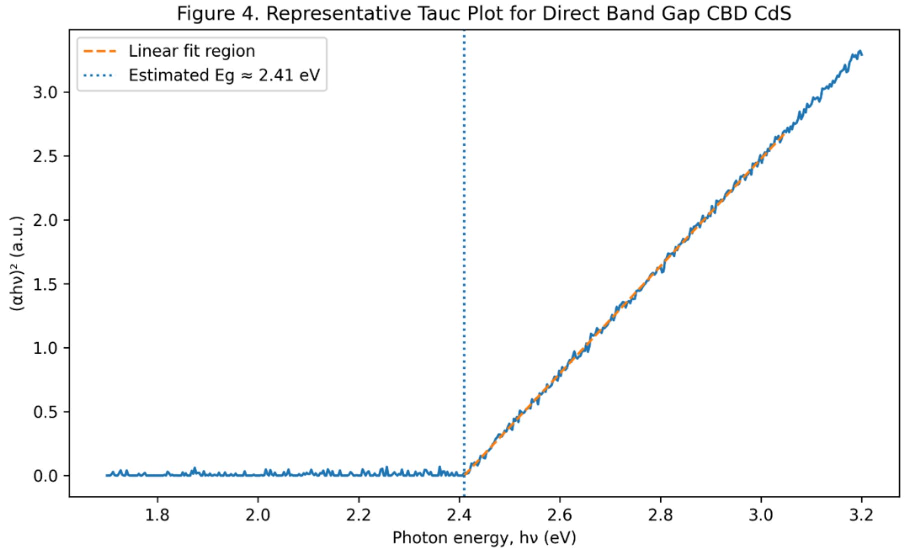
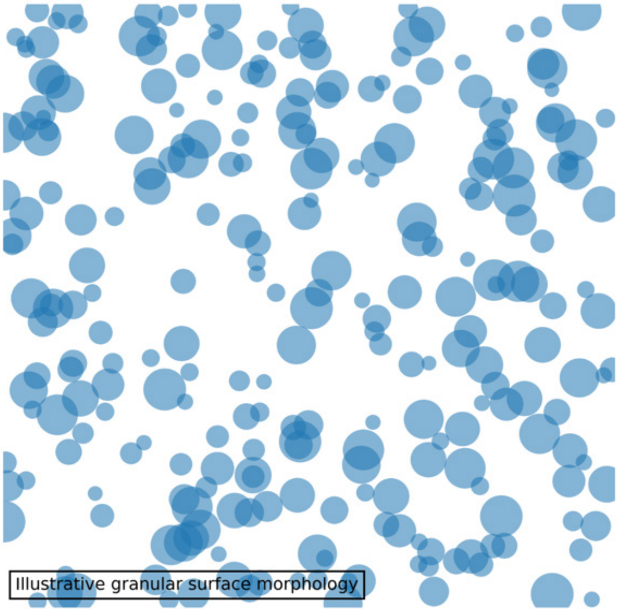


Figure 5. Representative Morphology Image of Nanocrystalline CBD CdS



Feature	Typical CBD CdS observation	Main characterization tool
Chemical bath medium	Cadmium salt + sulfur source + complexing agent in alkaline aqueous bath	CBD process control
Growth mechanism	Ion-by-ion and/or cluster-by-cluster surface deposition	XRD/SEM/kinetic analysis
Crystal structure	Cubic, hexagonal, or mixed CdS depending on temperature, pH and annealing	XRD
Main XRD indicators	(100), (002), (101), (110), (103), (112) or cubic-related reflections	XRD
Morphology	Granular, compact, nanocrystalline surface; roughness increases with time/thickness	SEM/AFM
Optical edge	Absorption edge in visible region, commonly near 500â€“520 nm	UVâ€“Vis
Band gap range	Often about 2.1â€“2.5 eV depending on thickness, stoichiometry, strain and crystallite size	Tauc plot
Major variables	Bath temperature, pH, deposition time, precursor concentration, complexing agent, annealing	Combined optimization
Application relevance	Window/buffer layer for CdTe/CIGS solar cells; photodetectors and sensors	Device testing

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