STM JOURNALS

Journal of
Thin Films, Coating Science
Technology and Application

ISSN: 2455-3344
Volume 11, Issue 3, 2024
September–December
DOI (Journal): 10.37591/JoTCSTA

https://journals.stmjournals.com/jotcsta

Review JoTCSTA

Bismuth-Doped Cugas$_2$ Thin Films for Enhanced Photovoltaic and Electrocatalytic Performance

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Abstract

This study presents the development and application of bismuth (Bi)-doped $CuGaS_2$ thin films for enhanced performance in photovoltaic and electrocatalytic systems. Using a cost-effective all-solution processing method, Bi-doped $CuGaS_2$ chalcopyrite nanocrystals were synthesized and spray-deposited onto molybdenum substrates. The resulting films, with a thickness of approximately 730 nm and grain sizes larger than 400 nm, exhibited superior optical properties and a lower band gap compared to undoped films, making them ideal candidates for absorber layers in thin-film solar cells. In the realm of photovoltaics, Bi-doped $CuGaS_2$ showed promising results as a non-toxic, lead-free alternative to conventional materials like lead halide perovskites. These materials showed appropriate band gaps and good absorption coefficients in spite of their decreased current efficiency. Furthermore, the study explored the antioxidative stability of Bi_2Se_3 nanosheets, improving the material's potential for use in electronic devices by incorporating halide anions as passivation agents. Beyond photovoltaics, the study also highlights the potential of bismuth vanadate (BVO)-modified electrodes for electrocatalysis. The BVO@C (BVO/graphite) electrodes demonstrated remarkable efficiency in degrading organic pollutants such as Rhodamine B, with degradation rates significantly improved through photo electrocatalysis (PEC). This work underscores the potential of Bi-doped thin films and composites in advancing both solar energy harvesting and environmental remediation technologies, offering cost-effective, scalable solutions for future sustainable applications.

Keywords: Bismuth-doped $CuGaS_2$, thin films, photovoltaics, electrocatalysis, chalcopyrite nanocrystals, solar cells, photo electrocatalysis (PEC)

INTRODUCTION

The increasing demand for clean energy and efficient environmental remediation has driven extensive research into advanced materials for applications in photovoltaics and electrocatalysis. Among the materials being explored, copper-based ternary chalcogenides such as $CuGaS_2$ have gained attention due to their favorable properties, including high optical absorption and structural similarity to Cu (In,Ga)Se_2 (CIGS), a leading material in thin-film solar cells. However, the relatively wide band gap of $CuGaS_2$ (2.4 eV) limits its effectiveness in absorbing visible light. Recent efforts have focused on enhancing its optical properties through doping with elements like bismuth (Bi), which has shown promise in reducing the band gap and improving light absorption. This study explores the synthesis of Bi-doped $CuGaS_2$ thin films via an all-solution processing method and evaluates their potential for photovoltaic and electrocatalytic applications.

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Received Date: October 24, 2024
Accepted Date: November 06, 2024
Published Date: November 13, 2024

Citation Bangshidhar Goswami. Bismuth-Doped $CuGaS_2$ Thin Films for Enhanced Photovoltaic and Electrocatalytic Performance. Journal of Thin Films, Coating Science Technology and Application. 2024; 11(3): 1–7p.

Nano Bismuth Composes: Dopant

An all solution-processed method for creating bismuth (Bi)-doped $CuGaS_2$ chalcopyrite nanocrystal ink that has enhanced optical properties and a lower band gap energy than undoped

semiconductor films can be used to create films with a thickness of about 730 nm. When chalcogenide nanocrystal ink is sprayed onto molybdenum substrates, the coalescence of bi-doped nanocrystals produces microcrystalline films with grains bigger than 400 nm.. This method of low-cost deposition is used to create these films. Thin film solar cells can make use of bi-doped $CuGaS_2$ microcrystalline films as an absorber layer. Introduction Chalcopyrite $Cu(In,Ga)Se_2$ (CIGS)-based thin-film solar cells are formidable rivals for silicon-based devices' high energy conversion efficiency. Due to their low band gap, high absorptivity coefficient into the visible and near-infrared (IR) ranges, high tolerance to defects and impurities, and extensive research over the past three decades, these copper-based ternary chalcogenides are among the promising materials to be applied as absorber layers in solar cells. Nonetheless, attempts have been made to identify novel absorber materials that will allow for the scalable and reasonably priced commercialization of chalcopyrite-based devices. Wide band gap (2.4 eV) ternary chalcogenide $CuGaS_2$ is structurally identical to CIGS and has a low level of toxicity. The $CuGaS_2$ is made up of elements that are more abundant than those found in chalcogenides based on In, Cd, Se, and Te, such as Ga (16.9 ppm), Se (0.05 ppm), and Te (160 ppb). However, the ideal band gap energy of a single band gap device was determined to be approximately 1.4 eV based on the Shockley-Queisser limit. Although $CuGaS_2$ does not have a band gap that is suitable for acting as a light absorption layer in single junction solar cells, the band gap can be modified by intermediate band formation or decreased by metal doping. $CuGaS_2$ doped with transition metals (Ti, Cr, Ce, and Fe), post-transition (Sn), and 15 group elements (N, P, As, and Sb), as compared to the undoped semiconductor, exhibits a higher optical absorption intensity. $CuGaS_2$ thin films have been produced using a variety of physical techniques, including spray pyrolysis, Metalorganic Vapor Phase Deposition (MVPD), and electron beam physical vapor deposition (EBPVD) [1]. Due to the use of vacuum equipment, these procedures are relatively expensive and may have throughput restrictions. In this study, we present a solvothermal technique for producing bismuth (Bi)-doped $CuGaS_2$ nanocrystal ink and use it to create microcrystalline films with improved optical properties compared to undoped semiconductor films using an all-solution processing method. The low-cost deposition method consists of spraying the chalcogenide nanocrystal ink onto the molybdenum (Mo) substrates. In addition, we go over the composition, structure, and optical characteristics of the metal-doped $CuGaS_2$ films. [1].

PHOTOVOLTAICS

Materials containing bismuth have been researched for use in photovoltaic solar cells. The descriptive article concentrated on bismuth-based perovskites, bismuth halides, and bismuth-based sulfides (Bi_2S_3, $Cu_xBi_yS_z$, and $AgBiS_2$) as substitutes for lead sulfide quantum dots and lead halide perovskites, respectively. These materials meet the criteria for being made of numerous, non-toxic elements. Additionally, they display suitable bandgaps and high absorption coefficients for photovoltaics, along with other desirable qualities like robustness and stability. Their efficiencies, however, are still far below those reported for their toxic counterparts because they have not been thoroughly studied. Here, we compile a few of the most encouraging findings, identify some potential bottlenecks, and offer some recommendations for performance enhancement.

Perovskites and inorganic quantum dot solar cells are the most efficient of the state-of-the-art PV technologies.. In comparison to conventional or other emerging technologies, they may also be more adaptable, less expensive, thinner, and efficient over a wider range of light intensities. They may also contain abundant elements, which is crucial for lowering costs and ensuring future production. The best performing devices, however, have been made from materials that contain lead (Pb): PbS or $CsPbI_3$ in quantum dot solar cells, or $APbI_3$ (A = methylammonium or formamidinium) in perovskite solar cells. The World Health Organization (WHO) lists lead as one of the chemicals of major public health concern, and its use is restricted by numerous laws around the world. This puts the future commercialization of solar cells made from these materials in jeopardy, even though the concept and extent of toxicity can be debated. [2] In this regard, materials based on bismuth can make interesting replacements for compounds that contain lead. The abundance of bismuth in the earth's crust, its status as a by-product of the refinement of Pb, Cu, and Sn, and the fact that it has few important economic

uses all contribute to its relatively low and constant price. Furthermore, despite being a heavy metal, bismuth is thought to be non-toxic and is even a component of well-known medications like Pepto-Bismol. Additionally, Bi3+ has been hailed as a leading candidate for defect-tolerant compounds, or materials that exhibit favorable optoelectronic characteristics despite defects. According to theory, defects are restricted to shallow states at the band edges because the active ns^2 lone pair tends to produce antibonding interactions at the valence band maximum [2].

DEVICE STABILITY

Although the topological insulator 2D Bi2Se3 has unique electrical properties that make it a potential material for electronic devices, antioxidative nanosheet preparation is challenging due to Bi2Se3's susceptibility to oxidation. In situ passivation of the Bi2Se3 surface requires a passivation agent that remains stable under a strongly biased potential. After Bi2Se3 exfoliation, surface passivation using ligand agents protects the surface effectively, but it is a laborious and technically challenging procedure. In this study, the antioxidation capacity of synthetic Bi_2Se_3 nanosheets was determined by examining the effects of halide anions (Cl^-, Br^-, and I^-) on their chemical properties during electrochemical intercalated exfoliation. Bi_2Se_3 nanosheets made in a tetrabutylammonium chloride solution (TBA^+ and Cl^-) were discovered to have the best oxidation resistance due to the surface bonding of Bi with Cl, which supports achieving better device stability. This work opens up the possibility of modifying the electrolyte's constituent parts to further enhance the stability of 2D Bi_2Se_3 -nanosheet-based electronic devices.

Two-dimensional (2D) semiconductors have significantly advanced the development of electronic and optoelectronic devices because of their remarkable charge transport capabilities and robust mechanical attributes. Among the 2D material family, 2D Bi2Se3 is a potential material for electronic devices because of its unique electronic properties as a topological insulator, which implies that its bulk is an insulator while the surface displays metallic behavior. The topologically protected surface states that give rise to the surface conductivity give rise to distinctive electronic characteristics like high carrier mobility and resistance to scattering by non-magnetic impurities. 2D Bi_2Se_3 is perfect for low-power, high-speed electronic devices thanks to its distinct electronic properties, especially those being researched as Field-Effect Transistor (FET). [3] Theoretical studies have predicted the behavior of 2D Bi2Se3 FETs with a thickness regime of 1-6 nm. Transistors can operate at room temperature in this regime with just a tiny gap created by hybridization between the top and bottom surfaces. The primary objective of research on two-dimensional Bi2Se3-based FETs is to improve the electrical performance and reliability for application by improving the fabrication process or altering the device architectures. One of the challenging problems with Bi2Se3 nanosheets is their susceptibility to oxidation and air sensitivity, which lowers device performance. To combat this issue, researchers have proposed a variety of strategies to stop Bi2Se3 nanosheets from oxidizing, including passivating the nanosheet surface with certain organic or inorganic compounds or encapsulating the material to protect it from the air. These strategies can be applied after the Bi2Se3 nanosheet has been created by chemical vapor deposition, molecular beam epitaxy, or pulsed laser deposition. The rigorous reaction conditions and challenging transferring processes required to move the thin films from the growth substrate to the target substrate, however, limit these approaches. These transfers are time-consuming, technically challenging, and, when taking into account possible oxidation during the transfer, they may cause irreversible harm to the device's functionality. [3, 4].

PRESSURE SENSOR

Investigation and comparison are done on the pressure-sensitive characteristics of pure multi-walled carbon nanotubes and the composite of multi-walled carbon nanotubes and bismuth sulfide. Each ingredient made up 50% of the composite. By using the Mortar and Pestle/Hydraulic Press technique, sandwich-type pressure-sensitive pellets (Ag/CNT/Ag and Ag/CNT-Bi_2S_3/Ag) with a 2 mm thickness and 15 mm diameter were created. To establish low resistance electrical connections, silver paste was added to the prepared samples' two surfaces. As the applied pressure was increased (0-16.9 kNm^{-2}), direct current resistance decreased in both samples. However, compared to pure carbon nanotubes, the

resistance of the multi-walled carbon nanotube/bismuth sulfide composite decreased by 1.2 times, and its sensitivity increased by 1.07 times. Simulated results and experimental results showed excellent agreement when they were compared.

Due to their improved chemical, electrical, physical, mechanical, optical, and biological properties, nanomaterials and their composites have attracted a lot of interest recently in a variety of applications. By using controlled and size-selective synthesis methods, it is possible to modify the properties of nanomaterials to suit a particular application. Due to the distinctive behavior of nanostructured materials and their composites, the field of nanotechnology has recently advanced, which has made it possible to study its pressure-sensitive properties. [4] The two most promising nanostructured materials to be used in the field of sensing technology are carbon nanotubes (CNTs) and bismuth sulfide (Bi_2S_3). Although CNTs are six times lighter than steel, their tensile strength of 60 GPa is 100 times higher than steel's. Nearly 1 TPa, or five times more than steel, can be achieved by the CNTs in terms of elasticity. Since CNTs have such exceptional qualities as high flexibility, low weight, and high gauge factor, they are a perfect material for use in sensing technology [5].

Electrode

The treatment of water contaminated by harmful organic compounds using electrocatalysis is a promising method. Degradation is made possible by the combination of nanoparticles held in place by a conductive substrate. In this study, the impact of Bismuth Vanadate (BVO) particle deposition on pencil-shaped graphite electrodes was assessed. By using coprecipitation and ultrasonic irradiation, BVO particles were produced. They were then deposited onto a graphite electrode using the impregnation technique. The fabrication of electrodes was optimized using a 23-design. Characterization methods included Dynamic Light Scattering (DLS), X-Ray Diffraction (XRD), and Matter Dispersion Spectroscopy (SEM/EDS). The electrochemistry was characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The BVO@C (BVO/graphite) synthesis was supported by the results. Additionally, compared to the electrode without any modification, BVO@C significantly increased the electrode's electroactive surface area, decreased its electron transfer resistance, and increased its electron transfer rate. To show that BVO@C performs better than the pure electrode, photoelectron catalysis (PEC) and electrocatalysis (EC) were performed in a rhodamine B (RhB) solution. According to the results, after 5 minutes of treatment with the unmodified electrode, BVO@C EC system, and BVO@C PEC system, the degradation rates were 31.53%, 46.09%, and 58.17%, respectively. After 30 minutes, the degradation rates were 95%, 98%, and 99.64%, respectively. The calculated reaction rate constants for the unmodified graphite, the BVO@C EC System, and the BVO@C PEC System were found to be $k = 0.10272\ m^{-1}$, $k = 0.12221\ m^{-1}$, and $k = 0.15022\ m^{-1}$, respectively. These results demonstrate the effectiveness of the BVO@C electrodes for usage in a range of treatments, including the treatment of organic contaminants. Recently, various materials, especially semiconductors, have drawn attention to electrode modification due to their promissory reagent properties, which include low cost, quick response, portability, increased sensitivity, reduction of overpotentials, and resistance to surface fouling. These tools have a wide range of uses, including clinical diagnosis and monitoring, water and wastewater treatment, biological research, and health monitoring.

Advanced Oxidative Process (AOP) are effective technologies for treating industrial and sanitary effluents in environmental treatment processes. The most prevalent of these techniques is photoelectron catalysis with semiconductors because of its practical applicability in a wide variety of organic molecules. However, only 4% of sunlight falls within the UV spectral range, which is where the majority of semiconductor photocatalysts are active. There have been numerous attempts to create visible photoconductors (VLD) in order to get around the limitations of UV radiation. Doping remains a crucial tactic with semiconductors, sensitizing dyes, and the heterojunction of several semiconductors, which requires the electrodeposition of metals and their oxides on the semiconductor surface. Due to improved charge transfer and decreased electron-hole recombination, mixed bismuth oxide systems, such as BVO, Bi_2WO_6, Bi_2MoO_6, $BiFeO_3$, and $Bi_2Fe_4O_9$, have demonstrated high photocatalytic efficiency. Because of its modest band gap (2.3 eV), low toxicity, strong dispersibility, and high

corrosion resistance, bismuth vanadate (BVO) has garnered a lot of interest for its ability to degrade organic contaminants when exposed to visible light. BVO displays strong photocatalytic activity when exposed to visible light at wavelengths under 520 nm. Only the monoclinic phase of the three main scheelite polymorphs that BVO can exhibit, tetragonal zirconia, tetragonal, and tetragonal—shows photocatalytic activity when exposed to visible light. Because of its semiconductor qualities, which lower the electron hole in the semiconductor material employed as a photoelectrode, BVO can also be utilized in PEC and EC. This semiconductor can greatly improve the photoelectron catalyst performance of BVO-based materials when combined with carbon nanoparticles. This happens as a result of the carbon nanoparticles' large electron storage capacity, which makes nanocomposites' PEC action superior to that of conventional semiconductors. As a result of the transfer of photogenerated electrons from semiconductors to carbon nanoparticles in this instance, a large number of photogenerated holes have been amassed on the semiconductor surface. The photocatalytic capabilities of m-BVO powder and m-BVO supported on carbon fiber were examined in order to destroy dye. Although the cycling properties of m-BVO in powder showed poor performance, the photocatalytic action of m-BVO supported on carbon fibers did not demonstrate performance degradation following repeated use in four cycles. Based on the theoretical synergy between BVO and carbon, the study assessed the synthesis, optimization, characterisation, and application of a graphite pencil electrode modified with BVO particles (BVO@C). For the efficiency investigations of the resulting electrode, rhodamine B (RhB) degradation was performed utilizing BVO@C and unmodified electrodes. [5] The coprecipitation method was used to create semiconductor nanoparticles, which were then deposited on a pencil graphite surface that served as the carbon support. The process used to make photoelectrocatalysts is inexpensive. By using 23 factorial planning, better conditions for m-BVO nanoparticle synthesis were achieved. In this study, the electrode produced by BVO deposition on pencil graphite will be called BVO@C. For electrochemical characterisation, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were also employed. It has been noted that the properties of the two materials combine synergistically when nanocomposites made of graphite and BVO are formed. By reducing overvoltage, enhancing the kinetics of the electrode redox processes, having a progressive effect on mass transfer, and raising the sensitivity of the modified electrode, this semiconductor demonstrates the great potential of using it to modify electrodes that can be used in a variety of studies. BVO@C and unmodified electrodes were used to degrade Rhodamine B (RhB) for electrode efficiency studies. (RhB) was selected because it is a cationic industrial dye that, in addition to being neurotoxic and carcinogenic, can irritate the skin, eyes, and respiratory system when consumed by both people and animals. It is important to develop materials that can stop this class of compounds from ending up in aquatic effluents because of their harmful characteristics. This will improve the quality of the water that we can drink. Reverse osmosis, electrodialysis, and adsorption with activated carbon, for example, are more focused effluent treatment techniques that remove persistent compounds but are also more expensive, time-consuming, and difficult to implement. Since this semiconductor can be activated by visible light rather than UV light, recent studies have shown interest in its use in photocatalysis and electro-photo catalysis. This enables activation by sunlight and speeds up the breakdown of newly discovered pollutants. [6,7].

This study explores the effects of bismuth (Bi) doping on $CuGaS_2$ thin films, synthesized via a solution-based method. Bismuth doping enhances the optical properties of the films, reducing the band gap and increasing light absorption. The resulting microcrystalline films show larger grain sizes and improved charge transport, making them suitable for use as absorber layers in photovoltaic applications. These advancements offer a potential low-cost, non-toxic alternative for thin-film solar cells. Figure 1

Methodology

Bi-doped $CuGaS_2$ nanocrystals were synthesized using a solvothermal method to create an ink, which was then spray-deposited onto molybdenum substrates to form microcrystalline thin films with thicknesses of approximately 730 nm. To evaluate the films' optical characteristics and structure, X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical spectroscopy were used. For electrocatalysis, bismuth vanadate (BVO) particles were synthesized and deposited on graphite electrodes (BVO@C), and their performance was tested in the degradation of Rhodamine B under photo electrocatalytic (PEC) and electrocatalytic (EC) conditions.

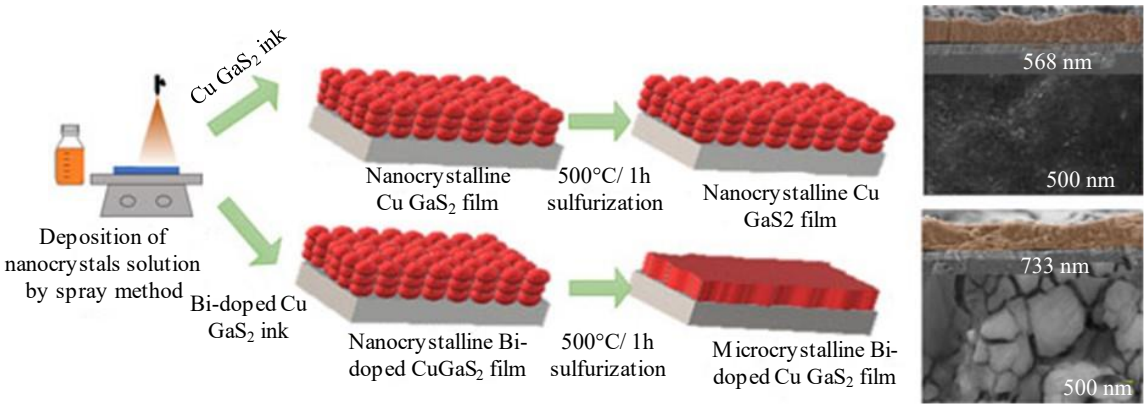

Figure 1. Bismuth doping on $CuGaS_2$ thin films: structural and optical properties.

DISCUSSION

The Bi-doped $CuGaS_2$ films demonstrated improved optical properties, such as a reduced band gap, compared to undoped films, making them suitable for photovoltaic applications as an absorber layer. The increased grain size in the microcrystalline films, resulting from bismuth doping, also contributed to enhanced charge transport, a key factor in solar cell efficiency. While the photovoltaic efficiency of Bi-doped $CuGaS_2$ is still under investigation, the material's non-toxic nature and scalability make it a promising alternative to lead-based solar cell materials.

In the electrocatalytic study, BVO-modified graphite electrodes (BVO@C) exhibited superior performance in the degradation of Rhodamine B compared to unmodified electrodes. The synergistic effects of BVO and carbon nanoparticles enhanced the charge transfer rate and reduced electron-hole recombination, leading to higher degradation efficiency. The PEC system, in particular, showed near-complete degradation of Rhodamine B in just 30 minutes, demonstrating the potential of these materials for environmental applications [8-10].

CONCLUSION

This study demonstrates that Bi-doped $CuGaS_2$ thin films and BVO@C electrodes offer significant improvements in both photovoltaic and electrocatalytic performance. The reduction in band gap energy and enhanced optical properties of the Bi-doped films make them promising candidates for use in thin-film solar cells, while the BVO-modified electrodes show great potential for use in environmental remediation through the efficient degradation of organic pollutants. These results open the door to the creation of scalable, reasonably priced solutions for environmental and renewable energy applications.

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