Research Article

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Wide Band Gap Semiconductor Alloy Nanomaterials for Potential Applications – A Future Perspective Approach

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ABSTRACT

Semiconductor alloy nanomaterials, especially metal oxide and metal sulphide semiconductors, are emerging as advanced materials in this era due to their fascinating properties. The wide bandgap of these materials makes them attractive candidates for their promising application in photocatalytic, optoelectronic, magnetic, optical, energy conversion, and storage devices. Intermediate energy levels in the binary, ternary, and quaternary alloy semiconductors nanomaterials make them useful in such applications. Tailoring a material with the desired bandgap is often a difficult task for which a wide bandgap semiconductor materials the choice of material by many researchers and these materials have a long way to go. This research article presents an overview of efficient methods to synthesis semiconductor alloy nanomaterials and their potential applications in various fields. It also covers significant advancements in these materials reported in the literature and their importance in the days to come.

Keywords: Bandgap; Quaternary alloy; Metal oxide; Metal Sulphide; Nanomaterials; Review; Semiconductor alloy.

1. INTRODUCTION

The research on group II-VI semiconductor nanostructures of metal sulphide and metal oxide has been an intensive area of research for the past many decades, yet the research on these materials has never subsided and still remains unabated. The control of the structure, morphology, optical, and electrical properties of wide bandgap semiconductor nanomaterials has always been the most fundamental and yet challenging task. This is because, properties of nanomaterials are driven essentially by their shape, crystallite size and distribution of particles. Metal sulphide and metal oxide semiconductors of group II-VI compounds are the materials of interest by many researchers and that has been widely investigated and reported owing to remarkable nanotechnology applications. The wide bandgap of these materials makes them attractive candidates for promising applications in photocatalytic, optoelectronic, magnetic, optical, energy conversion, and storage devices. (Sahai and Goswami, 2014).In addition to these applications, there are numerous attempts have been made by the researchers (Banu Priya *et al*. 2014; Sharma *et al*. 2014; Banu Priya *et al*. 2015; Gowdhaman *et al*. 2016) to use semiconductor alloy nanomaterials for sensor-specific applications. In that perspective, research on these materials has its own significance.

Wide band-gap of metal oxide and metal sulphide semiconductor nanomaterials exhibit size-dependent variation of the band-gap energy, and that makes these materials reliable for diverse applications. Numerous methods have been reported so far for the synthesis of semiconductor nanomaterials. Solvothermal reaction, colloidal methods, the solution route, ultrasonication, chemical processing, hydrothermal reaction, a vapour–solid growth method, catalyst assisted vapour deposition, a binary solution method, thermal evaporation, and RF thermal plasma are some of the methods predominantly used in the synthesis of nanomaterials (Omurzak *et al*. 2011). Among different methods, microwave-assisted preparation of nanoparticles is emerging as one of the most promising methods to synthesis semiconductor alloy nanoparticles with better control over crystallite size and morphology.

Regardless of a wealth of literature, less attention is paid to the detailed systematic study of these wide bandgap semiconductor nanomaterials, more importantly, their integration of structural and optical properties. Through this paper, an attempt has been made to provide an overview of synthesis methods and their effectiveness on the future development of semiconductor alloy nanomaterials. Also, an attempt has been made to study the structural, optical and electrical properties of these materials and their effectiveness for practical applications in the present and future.

2. SEMICONDUCTOR ALLOY NANOMATERIALS

Semiconductor alloy nanomaterials have been studied extensively owing to their relatively wide-bandgap. The usage of single semiconductor material for device applications has its own restrictions, which limits their effectiveness and practical applications. Therefore combined properties of more than two semiconductor material in the form of an alloy leads us to overcome these difficulties by altering the physical and chemical properties of those materials. Therefore, tailoring a suitable semiconductor alloy material according to the device applications can be useful to improve the device performances. Numerous efforts have been undertaken to synthesize wide bandgap semiconductor alloy nanomaterials. Compared with a single semiconductor, composite semiconductors can extend the absorption range and enhance the absorption of the solar spectrum, which makes them attractive candidates for solar cell applications. However, the toxicity and harmful effects of cadmium, lead, and their compounds to the environment and to human beings have caused them to be regulated by several regulatory control agencies. Hence, it is imperative to replace highly toxic cadmium or lead-based materials with other environmentally friendly ones (Lee and Yong, 2012).

Development and optimization of binary, ternary and quaternary mixture of semiconductor nanomaterials are highly helpful to obtain a new class of materials with a wide bandgap. The combined properties of these materials make them attractive candidates with a broader scope of future research and thus has attracted the attention of many researchers for the same.

2.1 Metal oxide nanoparticles

Metal oxide semiconductor alloy nanomaterials are widely exploited due to their attractive features for specific unique applications. An overview of significant research on the binary, ternary combination of these nanomaterials synthesized is discussed here.

Hwang *et al*. 2011 and Kyung Eun Lee *et al*. 2011 have reported a transparent and flexible optoelectronic material composed of vertically aligned ZnO nanowires grown on reduced graphene-based substrates. Large-area reduced graphene films were prepared on substrates by chemical exfoliation from natural graphite via oxidative aqueous dispersion and subsequent thermal reduction. They hydrothermally grew ZnO nanowires on the reduced grapheme film substrate and maintained their structural uniformity even in highly deformed states. The electrical contact between semiconducting ZnO nanowires and the metallic graphene film was directly measured by electric force microscopy (EFM). It shows a typical metal-semiconductor ohmic contact without a contact barrier. Owing to the mechanical flexibility, transparency, and low contact barrier, the ZnO nanowires/graphene hybrids show excellent field emission properties as per their report.

Single-phase cadmium stannate (Cd_2SnO_4)thin films were deposited on glass substrates through rf magnetron sputtering by varying rf power and keeping substrates at room temperature (Sakthivel *et al*. 2018). The authors studied the effect of rf power on the physical properties of the films and their correlations. It has been found from XRD that structural phase transition occurred from amorphous to spinel structure with an increase of rf power. AFM images revealed that the deposited films show a smooth surface with nanograins. High transmittance was retained by the films in the visible region, and the bandgap was decreased from 3.05 to 2.49 eV for increasing rf power by quantum confinement effect.

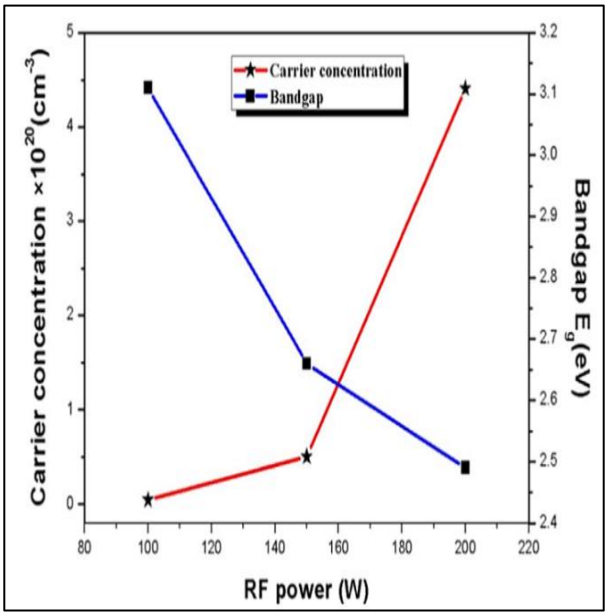

Fig. 1: Relation between carrier concentration and band gap of Cd_2SnO_4thin films with rf power [reprinted from (Sakthivel *et al*. 2018)]

The Mott-Davis model and drude model were used to evaluate the optical constants and free carrier absorption. The electrical resistivity of the films varied in three orders of magnitude as a function of rf power which could be explained by oxygen vacancy formation. From these results, the films deposited at 150 W have low resistivity of the order of $10^{-3}\Omega$cm with high optical transparency of 80%, which could be the preferred conditions to deposit high-quality films for future TCO layers for cadmium based CdTe/CdS solar cell devices as reported by them.

2.2 Metal sulphide nanoparticles

Metal sulphide semiconductor nanomaterials have promising applications in optical, electronic and optoelectronic devices. Well-aligned nanostructure arrays of these nanomaterials are highly attractive for their enhanced properties and novel applications. The general solution route and thermal evaporation under controlled conditions have been utilized for the oriented growth of various metal sulphide nanostructure arrays, and this has demonstrated their applications in energy conversion and storage (Lee and Yong, 2012).

Metal sulphide nanostructures have been synthesized by a variety of chemical or physical methods. Hydrothermal growth, solution-phase reactions, high-pressure autoclave processes, physical vapour deposition(PVD)and chemical vapour deposition (CVD). Depositionbased synthesis methods are the most popular among these methods. Thermal evaporation methods (PVD and CVD), laser-assisted growth and arc discharge are members of this group. The most common deposition based synthesis methods is PVD and CVD. In order to grow metal sulphide nanostructures at lower temperature and without using catalysts, high-pressure autoclave processes are commonly used to overcome the high interfacial energy between a substrate, liquid and particle for oriented growth of metal sulphide nanostructures, as reported by (Lee and Yong, 2012).

Zinc cadmium sulphide - a ternary II-VI semiconducting alloy material was developed by chemical bath deposition using a non-aqueous medium(Kumar *et al*. 2014; Kumar *et al*. 2015). It is important for the window material in solar cells, photoconductors, optical waveguide etc. They deposited ZnCdS films on molybdenum substrate using $CdCl_2$, $ZnCl_2$ and thiourea in ethylene glycol. The prepared ZnCdS nanofilm was annealed at 400 °C. The influence of annealing on the solid-state and optical properties of the films were studied by X-ray diffraction, Field emission microscope, Scanning electron microscope, energy dispersive X-ray analysis, Atomic force microscope, UV-Visible spectrometer, and Photoluminescence spectrometer.

The crystallite size of the as-deposited and annealed ZnCdS films is estimated to be 36nm and 41nm using Scherrer's formula. According to Tauc theory, the bandgap of ZnCdS thin films was determined. Compositional analysis peaks indicate the presence of Zn, Cd and S. The surface roughness of both the films is observed to be 127 nm and 39 nm, as reported by the authors.

Table 1. Average crystalline size, microstrain of as-deposited and annealed ZnCdS films (Kumar *et al.* 2014; Kumar *et al.* 2015)

S. No	Compound	FWHM (degree)	Average Crystalline Size(nm)	Micro-strain (10^{-3})
1.	ZnCdS (Asdeposited)	0.2378	36 nm	1.008
2.	ZnCdS (Annealed)	0.2080	41 nm	0.882

3. CONCLUSION

Presently, numerous efforts have been put forwarded by many researchers to develop new semiconductor alloy materials with better electrical, optical and structural properties. The development of new materials with a wide bandgap will be more helpful for the development of optoelectronics, energy conversion and storage devices.

Semiconductor metal oxide and metal sulfide nanomaterials developed so far become so popular due to their wide bandgap and potential applications. The formation of intermediate energy levels termed as Fermi energy levels between the conduction band and valence band of semiconductor alloy nanomaterials makes them attractive candidates with unique properties and applications.

Among several methods, the microwave radiation technique is identified to be one of the promising material methods to synthesise semiconductor alloy nanomaterials. In comparison with the performance of metal oxide and metal sulphide nanostructures, both materials have their own merits and limitations. More research on these materials will be helpful for the sustainable development of these materials for device applications. Therefore, these materials still are a great hope for various applications in the future.

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