SYNTHESIS AND CHARACTERIZATION OF CdS/CuAlO$_2$/ITO NANO-HETEROSTRUCTURES: A NOVEL LED FOR OPTOELECTRONIC APPLICATIONS

SÍNTESIS Y CARACTERIZACIÓN DE LA NANOHETEROESTRUCTURA CdS/CuAlO$_2$/ITO: UN NUEVO LED PARA APLICACIONES OPTOELECTRÓNICAS

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(Recibido: Sep./2023. Aceptado: Nov./2023)

Abstract

Nano-heterostructures (NHs) are drawing attention due to their fascinating properties as materials for constructing nano-electronic devices. CdS and CuAlO$_2$ were prepared using the co-precipitation method and deposited, respectively, on Indium Tin Oxide (ITO) substrate to study their characteristics and effectiveness for light-emitting diode (LED) applications and photodetectors. Investigations were made on the morphological, optical, and electrical characteristics. According to the X-ray diffraction pattern, CdS nanoparticles have a cubic phase structure and diffraction peaks at 26.3°, 43.8°, and 51.8°. UV-visible optical studies were used to characterize the absorbance of CdS, CuAlO$_2$, and CdS/CuAlO$_2$/ITO with redshift around 400 nm for the nanoparticles. Using the Tauc plot, the band gap energy of the prepared heterostructure showed a value of 3.1 eV. The Scanning Electron Microscopy (FESEM) images show homogeneous morphology with little agglomeration. I-V characterization reveals good properties with high forward current power. CdS/CuAlO$_2$/ITO shows high

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doi: https://doi.org./10.15446/mo.n68.110999

responsivity of 0.45 A/W, which indicates a straightforward, low-cost, and effective fabrication technique for the fabrication of light-emitting diodes and a promising heterostructure for manufacturing photo detectors.

Keywords: cadmium sulphide, delafossite, heterostructure, nanoparticles, light emitting diodes, optoelectronics.

Resumen

Las nano heteroestructuras (NH) están llamando la atención debido a sus fascinantes propiedades como materiales para la construcción de dispositivos nanoelectrónicos. El CdS y el $CuAlO_2$ se prepararon mediante el método de coprecipitación y se depositaron, respectivamente, sobre sustrato de óxido de indio y estaño (ITO) para estudiar sus características y efectividad en aplicaciones de diodos emisores de luz (LED) y fotodetectores. Se investigaron las características morfológicas, ópticas y eléctricas. De acuerdo con el patrón de difracción de rayos X, las nanopartículas de CdS tienen una estructura de fase cúbica y picos de difracción a 26.3°, 43.8°, y 51.8°. Se utilizaron estudios ópticos UV-visibles para caracterizar la absorbancia de CdS, $CuAlO_2$, y CdS/$CuAlO_2$/ITO con un desplazamiento al rojo de alrededor de 400 nm para las nanopartículas. Utilizando la gráfica de Tauc, la energía de banda prohibida de la heteroestructura preparada mostró un valor de 3.1 eV. Las imágenes de Microscopía Electrónica de Barrido (FESEM) muestran una morfología homogénea con poca aglomeración. La caracterización I-V revela buenas propiedades con una alta potencia de corriente directa. El CdS/$CuAlO_2$/ITO muestra una alta respuesta de 0.45 A/W, lo que supone una técnica de fabricación sencilla, económica y eficaz para la fabricación de diodos emisores de luz y una heteroestructura prometedora para la fabricación de fotodetectores.

Palabras clave: sulfuro de cadmio, delafosita, heteroestructura, nanopartículas, diodos emisores de luz, optoelectrónica.

Introduction

Attention is paid to nano-heterostructures (NH) based on solids and their solutions, and alloys containing such NHs are incredibly intriguing and essential as building materials for optoelectronic devices [1].
II-VI Nano crystalline semiconductors are characterized by nanoparticles that exhibit compelling unique properties that are lacking in bulk materials, such as having more surface atoms [1–4]. Because of their unique features, researchers examined the structural properties using scanning electron microscopy (SEM), X-ray diffraction (XRD), and photoluminescence (PL) spectroscopy to investigate the materialsóptical characteristics. Plasmonic compound nanoparticles (NPs) have attracted a lot of attention because of their inexpensive cost of preparation and distinctive optical characteristics [5]. Transparent conducting oxides (TCOs) are electrically conductive materials that have a comparable low light absorption. Thin-film methods are often used in the development of opto-electrical devices, such as solar cells, displays, opto-electrical interfaces, and circuitry. In opto-electrical devices, including solar cells, screens, opto-electrical interfaces, and circuits, thin-film techniques are utilized. Cadmium sulphide (CdS) is promising.

Direct band gap semiconductor has multiple applications in a variety of fields [6, 7], including photo detectors [8], solar cells [9], photo catalysts [10], nonlinear optical materials [11], and antibacterial properties [12, 13]. Sol-gel templates were one of the techniques used to create CdS nanoparticles [14]. Manufacturing p-type TCO with high conductivity and exceptional transparency is difficult, and this has limited the use of TCO materials in devices. $CuAlO_2$ and Cu_2O are two metal oxide compounds that exhibit p-type conductivity, but $CuAlO_2$ thin films produced by pulsed laser deposition by Kawazoe et al., in 1997, were discovered to be p-type and delafossite-structured with a wide band gap. $CuAlO_2$ films have a 3.5 eV optical band gap and a higher responsivity [15, 16], whereas Cu_2O has a shorter band gap, allowing it to be transparent. Major structural, physical, and technical nano-heterostructure parameters may be used to assess the fundamental elements that influence their quality, such as current-voltage (I-V) characteristics, the quantum efficiency (QE) of radiation, and their dependency on the current density [17].

This research aims to prepare a novel heterostructure of $CdS/CuAlO_2/ITO$ by enhancement of optical properties to fabricate a low-cost, promising heterostructure, suitable for light-emitting diodes, and photo detectors applications with maximum quantum efficiency.

Materials and Methods:

Cu(II) nitrate trihydrate or aluminum (Al) nitrate enneahydrate (0.4 M) were dissolved in 2-methoxyethanol and stirred for 12 h at room temperature to create Cu and Al source solutions. A thin blue solution was created by stirring the two solutions in a 1:1 Cu/Al ratio for 12 hours at room temperature.

Cadmium sulphide (CdS) nanoparticles were produced by precipitation using water as the solvent, cadmium chloride ($CdCl_2$), sodium sulphide (Na_2S), and temperatures ranging from 20-80 °C. The prepared CdS nanoparticles were deposited on the prepared $CuAlO_2/ITO$ film and washed to prepare them for measurement.

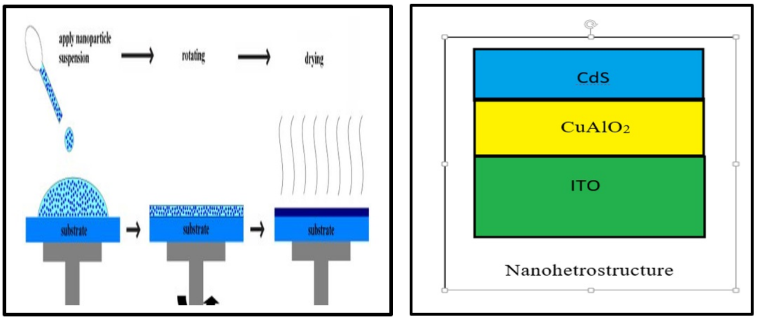

FIGURE 1. *Spin coating for multilayer deposition*

Nano-heterostructure was prepared using the spin coating method for multilayer deposition (Figure 1). The prepared film of $CuAlO_2$

was deposited on an ITO substrate. After deposition, the samples were dried, cleaned with deionized water, and placed in a tube furnace at room temperature with ambient air present for 1 hour. Subsequently, the furnace temperature was raised to 700 °C, followed by the deposition of CdS nanoparticle suspension to create the final layer.

Results and Discussion

Film thickness is measured using the Angstrom Sun Technologies Inc., USA device and a spectroscopic reflectometer. Light must be able to pass through the film and be reflected back from the film/substrate contact for these optical techniques.

X-ray diffraction (XRD) Bruker analysis with CuKα was used to examine the films' structural characteristics (diffracto grams). Thickness of each layer was tested using a spectroscopic reflectometer of approximately 150 nm. $CuAlO_2$ has broad peaks at $2\theta = 38.52°$, while other peaks were at $2\theta = 16.32°, 32.56°, 37.46°, 42.41°, 48.07°, 53.37°, 57.61°, 65.74°$, as shown in Figure 2.

The pure phase of the rhombohedra structure is used to index all of the reflections (003, 006, 101, 012, 104, 009, 107, and 018) (JCPDS Card N° 075-2356) [17].

The observed lattice characteristics for both materials nearly match those previously published. XRD analysis of CdS NPs revealed three featured peaks with lattice planes at 2h of 26.3° (111), 43.8° (220), and 51.8° (311), which are unique identifiers for CdS's cubic crystal structure (JCPDS: 10-0454) [18] (Figure 2).

Scherer's equation was used to calculate crystallite size:

$$D = 0.9\lambda/\beta\cos\theta \quad [19] \qquad (1)$$

Where β is the Full Width at Half Maximum (FWHM) in radians, and λ is the Wavelength (1.5 A), as stated in Table 1.

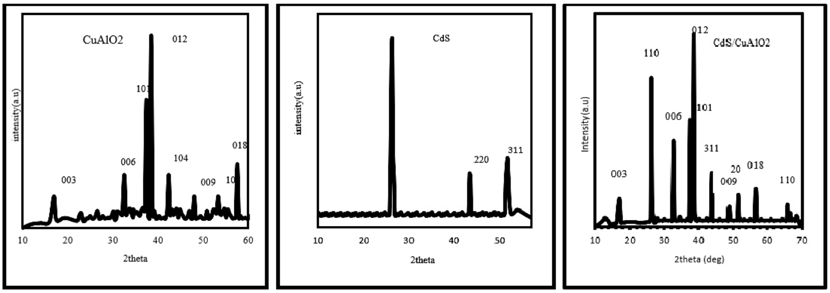

FIGURE 2. *X-ray patterns of samples*

Strain in hetero structure may be caused by lattice parameters difference between films and substrate can be calculated from equation:

$$\varepsilon = \frac{\beta cos\Theta}{4} \tag{2}$$

The number of dislocations of a crystalline material is measured by the dislocation density. The sample's dislocation lines across unit area are plotted:

$$\delta = \frac{1}{D^2} \tag{3}$$

Parameter	CdS Np	$CuAlO_2$ Np	CdS/ $CuAlO_2$
hkl	111, 220, 311	003, 006, 101, 012, 104, 009, 107, 018	110, 006, 101, 012, 311, 009, 018, 200
β(rad)	0.0123	0.0139	0.0348
D(nm)	11.5	12.05	50
ε (10^{-3}lines^{-2}·m^{-4})	72.6	47.29	6.8
δ(1/nm^2)	0.0074	0.0069	0.0004

TABLE 1. *XRD parameters for samples*

Absorption spectra were investigated using Shimadzu spectrophotometers in the range between 300-1000 nm. Nano-sized Cadmium Sulphide (CdS) exhibits distinct electrical characteristics that depend on its size and form. As the size of CdS particles decreases to the nano scale (typically less than 10 nanometers), the energy gap increases. This phenomenon is known as the quantum confinement effect. The band gap energy (Eg) may be calculated using:

$$\alpha h\upsilon = [A(h\upsilon - E_g]^{\frac{1}{2}} \quad [20] \tag{4}$$

Where $h\upsilon$ represents photon energy, E_g represents the energy gap, and α represents the absorption coefficient. Figure 3 illustrates the energy gap of CdS nanoparticles (2.99 eV) compared to bulk. Smaller nanoparticles have a larger band gap, requiring more energy to move electrons from the valence band to the conduction band. The size-dependent energy gap of CdS nanoparticles makes them suitable for a variety of uses such as optoelectronic devices.

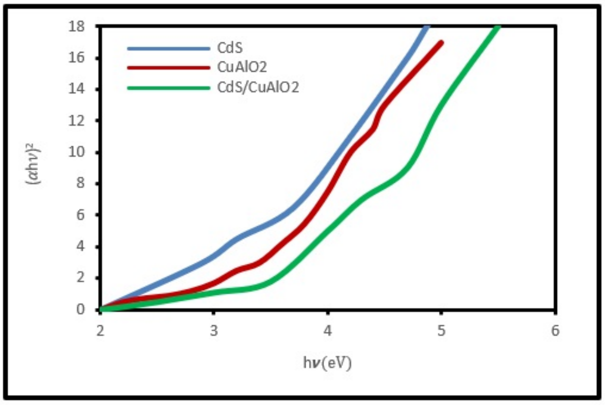

FIGURE 3. *Energy gap of samples*

Bulk $CuAlO_2$ belongs to wide-band gap materials in the range between 2.99 and 3 eV. However, the quantum confinement effects for $CuAlO_2$ nanoparticles increased the band gap value to 3.35 eV. The energy band gap for CdS/$CuAlO_2$ is estimated from Figure 3. It was discovered to be approximately 3.1 eV. The existence of delafossite in the heterostructure as a p-type conducting oxide modifies its energy band structure, leading to a better understanding of the relationship between the electronic structure and the characteristics of oxide materials. In semiconductors, a smaller band gap energy can absorb longer wavelengths.

The existence of $CuAlO_2$ increases the band gap energy in this heterostructure to the visible or near-infrared (NIR) range [21]. Finding such a substance in technology enhances the use of CdS/$CuAlO_2$/ITO heterostructure for new applications like UV-emitting LEDs [22].

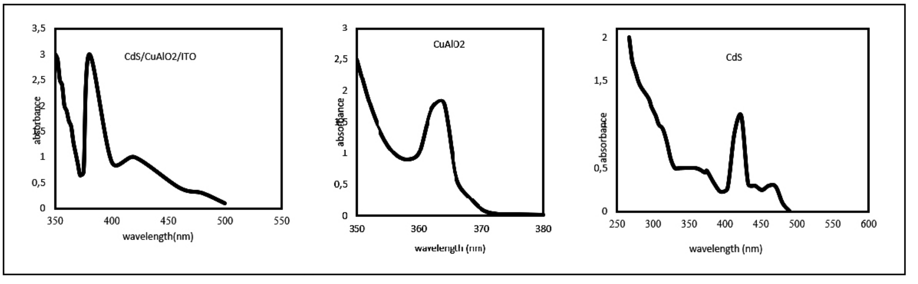

FIGURE 4. *Absorbance for samples*

Figure 4 illustrates CdS NPs absorption peak at (420 nm) which is blue-shifted in comparison to the usual absorption of CdS in bulk (512 nm). This might be due to a particle size distribution of CdS centered around 420 nm (peak broadening).

For $CuAlO_2$, the optical absorption found to be (365) nm, in the near-visible region (see Fig 4). While optical absorption of the prepared heterostructure was about 400 nm with red shift and an energy gap of about 3.1 eV. A semiconductor's sensitivity to higher energy photon of the electromagnetic spectrum increases with a greater band gap because it can absorb photons of higher energy. It can be noticed that the band gap decreases as the particle size increases, and the emission wavelength shifts towards lower energies (higher wavelengths). CdS/$CuAlO_2$/ITO heterostructure makes enhancement in optical properties in order to fabricate low-cost, promising hetero structure suitable for light emitting diode, and photo detectors applications with maximum quantum efficiency.

Field Emission Scanning Electron Microscope analysis (FESEM) of CdS samples demonstrated presence of nano clusters and holes in the sample with crystallite size about 25 nm. It has a homogeneous morphology with little agglomeration as a result of production using Co-precipitation method. However, single phase -Al_2O_3 and $CuAlO_2$ were produced following decomposition of as-prepared $Al(OH)_3$ and $CuAl_2O_4$ generated after high temperature annealing; this might explain the grain agglomeration seen in the FESEM and found to be 35 nm (crystallite size) (see Fig 5).

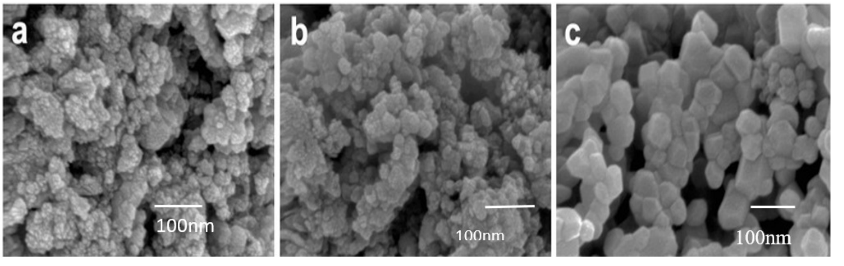

FIGURE 5. *FESEM images for a-CdS b-$CuAlO_2$ c-CdS/$CuAlO_2$*

The heterostructure has regular distribution conglomerates with side branches and a uniform crystal structure. The smaller nanoparticles combine and form larger particles for both CdS and $CuAlO_2$ (55nm). Its high roughness, which is a heterostructure feature, makes it a candidate for LED and optoelectronic applications (see Figure 6).

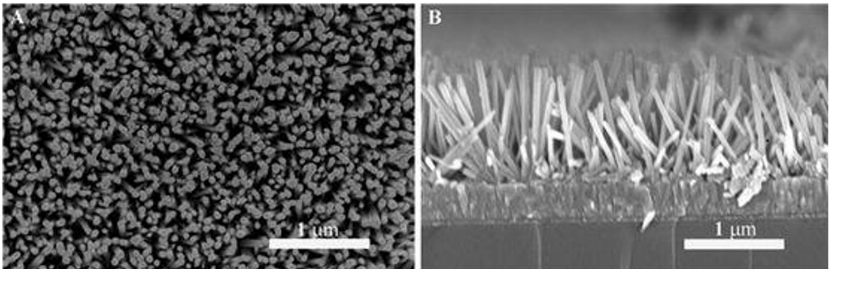

FIGURE 6. *FESEM images for nanoheterostructure*

Major structural, physical, and technological nano-heterostructure parameters can be used to estimate the fundamental characteristics that determine a material's quality for complex optoelectronic materials and devices. The optical characteristics of the thin films are mostly determined by the diameters of the NPs in the x-y plane.[22] However, it cannot be understood how the localised surface resonance occur. Such materials with nano-heterostructure are ideal for LEDs. These characteristics include the current-voltage (I-V) characteristics (see Table 2).

Parameters	CdS	$CuAlO_2$
Carrier concentration (Cm^{-3})	(n-type) $N_D=10^{18}$	(p-type) $N_A = 10^{12}$
Hall coefficient (cm^3/C)	-0.023	6.2×10^6
Mobility ($cm^2/v \cdot sec$)	4.6×10	0.25
σ $(\Omega.cm)^{-1}$	5.8×10^{-1}	1.33×10^{-2}

TABLE 2. *Nano Heterostructure electronic parameters*

Conductivity of layers can be determined using:

$$\sigma = \frac{L}{RA} \tag{5}$$

R represents the film resistance; A, the cross-section area; L, the distance between electrodes. Hall coefficient can be determined using:

$$RH = \frac{1}{Ne} \tag{6}$$

I-V characteristics and responsivity can be used to examine the sample for the light emitting diode and other optoelectronic applications. Positive or forward current travels through the diode.

Figure 7 illustrates voltage as a function of current but the forward current and voltage remain incredibly low. In near-infrared photoelectric devices, ITO is an excellent material for electrodes [22].

I-V photocurrent characterization was tested using a power supply across the $CdS/CuAlO_2/ITO$ heterostructure for a p-n junction. The diode becomes forward biased, forcing electrons to travel from n to p type. The optical sensitivity of a semiconductor refers to its ability to absorb photons and generate electron-hole pairs (excitons) when exposed to light [23]. This sensitivity is closely related to the band gap energy of the material. So the maximum band gap relates to optical sensitivity [24].

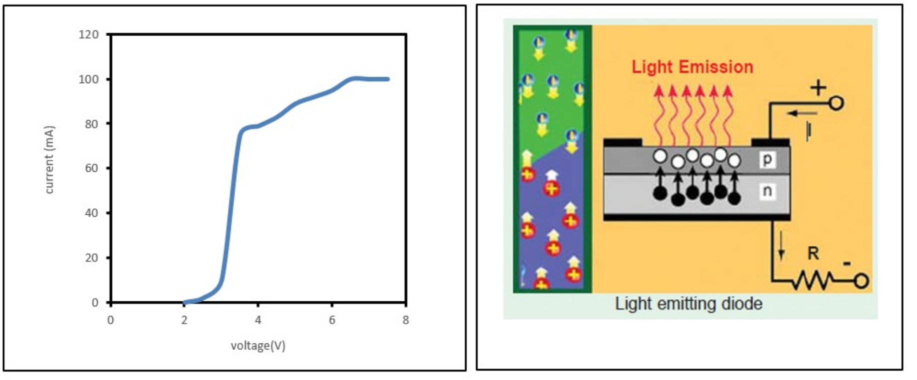

FIGURE 7. *I-V characteristics of CdS/ CuAlO$_2$/ITO*

As a result of recombination, the electrons in the conduction band move down to the valence band. The prepared heterostructure demonstrates responsiveness to CdS red-shift as well as an increase in light output. The results for photo detectors and light-emitting diodes using heterostructure are commendable (see Figure 8).

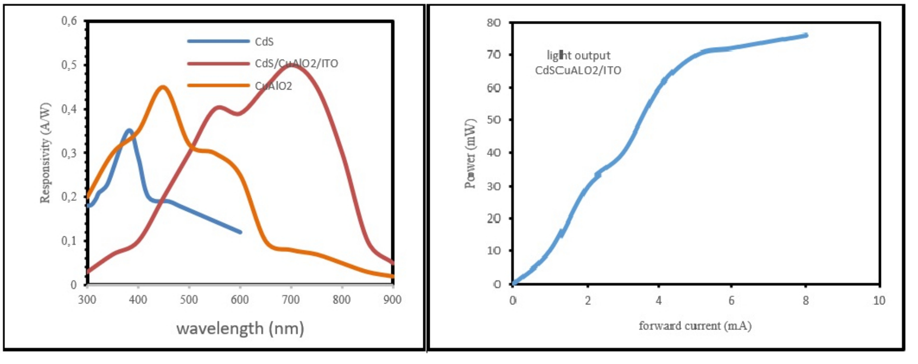

FIGURE 8. *Power and responsivity for CdS/CuAlO$_2$/ITO*

Conclusions

CdS/CuAlO$_2$/ITO heterostructure was prepared and deposited, respectively, on an ITO substrate using chemical roots to study their characteristics and suitability for LED applications. The prepared heterojunction exhibits high absorbance with a redshift, an energy gap of about 3.1 eV, and a high responsively of about 0.45 A/W therefore, the findings of structural, optical, and electrical properties suggest that this heterostructure can be employed in applications including light emitting diodes, displays, and transparent electrodes owing to the energy gap within the desired region of the spectrum.

Acknowledgments

Our thanks and respect to the Ministry of Science and Technology, especially the Solar Research Department.

References

[1] k. Saumya, S. Naskar, and T. Mukhopadhyay, Nano Futures **7**, 032005 (2023).

[2] Q. Qian, Z. Wan, and X. Duan, National Science Open **2** (2023).

[3] H. Inaya and M. Mahdi, Iraqi J. Phys. **21**, 92 (2023).

[4] M. Almamari, N. Ahmed, and et al., Heliyon **8**, e09959 (2022).

[5] N. Hullavarad and S. Hullavarad, Photonic. Nanostruct. **5**, 156 (2007).

[6] I. Ismail, K. Khashan, and A. Alwaan, Silicon **9**, 321 (2017).

[7] I. Hadi, K. Khashan, and D. Sulaiman, Mater. Today-Proc. **42**, 3054 (2021).

[8] C. Martínez, C. Rodríguez, and et al., Int. J. Photoenergy **2014**, 453747 (2014).

[9] A. Samadi and M. Sadeghi, Spectrochim. Acta A **152**, 156 (2016).

[10] S. Talwatkar, Y. Tamgadge, and et al., Solid State Sci. **38**, 42 (2014).

[11] M. Abd, H. Wasly, and K. Batoo, Appl. Phys. A **125**, 283 (2019).

[12] M. Shariati, A. Samadi, and A. Colagar, J. Hazard. Mater. **366**, 475 (2019).

[13] T. Park, K. Lee, and S. Lee, Appl. Microbiol. Biotechnol. **100**, 521 (2016).

[14] N. Hullavarad and S. Hullavarad, Photonic. Nanostruct. **5**, 156 (2007).

[15] H. Kawazoe, M. Yasukawa, and et al., Nature **389**, 939 (1997).

[16] L. Cattin, B. Reguig, and et al., App. Surf. Sci. **254**, 5814 (2008).

[17] O. Rabinovich, S. Legotin, and et al., Jpn. J. Appl. Phys. **55**, 05FJ13 (2016).

[18] T. Ehara and T. Nakanishi, MATEC Web Conf. **67**, 04012 (2016).

[19] Z. Abdul, Adv. Nat. Appl. Sci. **10**, 72 (2016).

[20] Z. Abdul, J. Compos. Adv. Mater. (RCAM) **31**, 167 (2021).

[21] C. Bouzidi, H. Bouzouita, and et al., Mat. Sci. Eng. B **118**, 259 (2005).

[22] M. Maleki, S. M., and et al., Semicond. Phys. Quantum Electron. Optoelectron. **10**, 30 (2007).

[23] J. Pellicer, A. Segura, and et al., Appl. Phys. Lett. **88**, 181904 (2006).

[24] H. Kawazoe, M. Yasukawa, and et al., Nature **389**, 939 (1997).