OPTICAL PROPERTIES AND BAND OFFSETS OF CdS/ZnS SUPERLATTICE DEPOSITED BY CHEMICAL BATH

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CdS/ZnS superlattice (SL) were deposited on glass microscope slides at 300K using chemical bath deposition. X-ray diffractometry method was used to obtain structural characterization. Micrographs of the deposited films were taken using an Olumpus optical microscope. A Janway 6405 UV/VIS spectrophotometer was used to obtain the spectra absorbance data. Other optical properties of the films which include reflectance, transmittance, refractive index, dielectric constant, optical conductivity and extinction coefficient where obtained by calculations based on the data. A valence band offset of 0.02eV and conduction band offset of 1.29eV at CdS/ZnS interface was determined by optical method. The band alignment was found to be type 1.

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Keywords: Band offset, Superlattice, Chemical bath

1. Introduction

Semiconductor superlattices (SLS) were proposed about 40 years ago by [1]. They are synthetic crystals, which consist either of a periodic sequence of ultrahigh layers of two different semiconductors (compositional superlattices) or of a single homogeneous semiconductor, which is periodically n-and p-doped.

In the simplest case, they consist of a periodic arrangement of two semiconductors A and B with different energy gaps [2]. The difference in their energy gaps leads to discontinuities in both the conduction and valence band and a set of square potential wells separated by potential barriers forms. Infact, they are fascinating model system for electrons in a periodic potential [3]. The existence of the superlattice potential substantially alters the energy spectrum, as a result of which superlattices have a number of interesting properties which ordinary semiconductors do not have. It is found that an extremely wide spectrum of possibilities results from the fact the properties of superlattices can be tailored for a given goal. Superlattices offer a unique possibility for altering their band structure practically arbitrarily.

The flexibility introduced by this design possibility makes superlattices useful in several technological applications, including semiconductor diode lazers [4], electro – optic modulators [5,6], nonlinear optical materials [7], infra detectors [8] and multi -layer applications in p – i – n solar cells [9].

The first attempt to grow superlattices used the chemical vapour deposition technique in $GaAs/GaAs_{1-x}P_x$ ($0.1 \leq x \geq 0.5$) material system [1, 10]. Other methods such as molecular beam epitaxy, metal organic vapour deposition, glow discharge process , chemical bath deposition, spray pyrolysis, hydrothermal synthesis, electrochemical atomic layer epitaxy, etc., have been used to grow superlattices. [11] fabricated μC-Si:H/a-Si multilayers using the glow discharge method. [12] fabricated CdS/ZnSe/BeTe superlattice using molecular beam epitaxy [13] synthesized CdS/ZnS

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using hydrothermal synthesis, [14] also synthesized CdS/ZnS multilayer using chemical bath method. [15] prepared CdS/ZnS superlattice using the electrochemical atomic layer epitaxy. [16] deposited PbS - CdS multilayer using spray pyrolysis. Here we report the synthesis of CdS/ZnS superlattice using a simple and low cost technique called the chemical bath deposition [17].

2. Materials and methods

A very attractive method for producing films with large area deposition is the so-called chemical bath deposition (CBD) method. We synthesized all the films for this experiment using chemical bath deposition (CBD). Chemicals, pH meter, thermometer, digital weighing meter, beakers, glass microscope substrate, stirrers, synthetic foam covers were utilized in the course of deposition. Single films of CdS and ZnS were first fabricated before the superlattices were made.

The deposition of CdS thin film was based on the reaction between cadmium bromide ($CdBr_2$) thiourea ($CS(NH_2)_2$, using TEA ($N(CH_2CH_2OH)_3$ as a complexing agent and ammonia solution as a pH adjuster. Thiourea is used as our sulphide ion source and $CdBr_2$ as our Cadmium ion source. The deposition process is based on slow release of Cd^{2+} and S^{2-} ions in the solution which condensed on the substrate. The solution for deposition of cadmium sulphide thin film using a glass substrate (glass microscope slide) were constituted from solution of 1.0 mole of $CdBr_2$, 1.0 mole of thiourea and 1.0 mole of TEA.
The reaction mechanism is of the form:

$$CdBr_2 .4H_20 + TEA \rightleftharpoons Cd(TEA)^{2+} + 2HOBr + 2H_30$$
$$Cd(TEA)^{2+} \rightleftharpoons Cd^{2+} + TEA$$
$$(NH_2)_2CS + OH^- \rightleftharpoons CH_2N_2 + H_20 + HS^-$$
$$HS^- + OH^- \rightleftharpoons H_20 + S^{2-}$$
$$Cd^{2+} + S^{2-} \longrightarrow CdS$$

The deposition of ZnS thin film by CBD was based on the reaction between zinc acetate ($Zn(CH_3COOH)_2$) and thiourea $SC(NH_2)_2$ using ammonia solution (NH_4OH) as a complexing agent at 300K bath temperature. Thiourea is used as our sulphide ion source and $Zn(CH_3COO)_2$ as our zinc ion source. The deposition process is based on slow release of Zn^{2+} and S^{2-} ions in the solution which condensed on the substrate. The solution for deposition of zinc sulphide thin film using a glass substrate (glass microscope slide) were constituted from solution of 1.0 mole of $Zn(CH_3COO)_2$ and 1.0 mole of thiourea.
The reaction mechanism is of the form:
Zinc acetate dissociates as:

$$Zn(CH_3COO)_2 \longrightarrow Zn^{2+} + 2CH_3\,COO^-$$

Ammonia hydrolyses in water to give OH^- according to:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$$

Thiourea dissociates as:

$$\rightleftharpoons SC(NH_2)_2 + OH^- \qquad SH^- + CH_2N_2 + H_2O$$
$$SH^- + OH \rightleftharpoons S^2 + H_2O$$
$$Zn(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \longrightarrow$$
$$ZnS + 4NH_3 + C_2H_2 + 2H_2O$$

After the deposition of the single layer films were achieved, CdS/ZnS superlattice was fabricated by dipping a glass substrate already coated with CdS thin film into a bath containing zinc acetate, thiourea and ammonia solution and left to stand for 24 hour at a pH value of ~11.

The optical absorbance spectra were obtained by means of UV/VIS Janway 6405 spectrophotometer. Surface morphology of the thin films deposited on glass substrate was examined by an Olumpus optical microscope. The structure of this films were checked by X-ray diffraction measurement with Cukα radiation. From the spectrophotometer, the absorbance in arbitrary units was measured. Parameters such as transmittance, reflectance, refractive index, extinction coefficient, dielectric constant, band offset and optical conductivity were then calculated.

3. Results and discussion

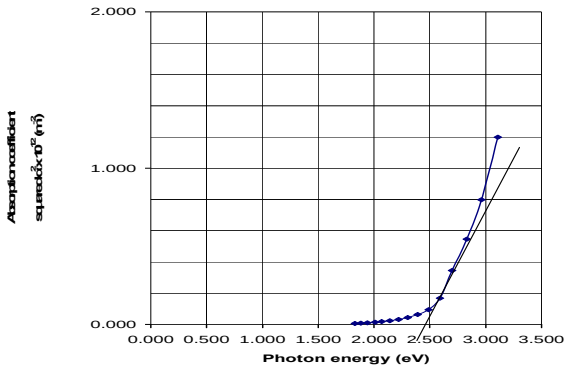


Fig. 1: Plot of Absorption coefficient squared (α^2) against Photon energy for CdS thin film

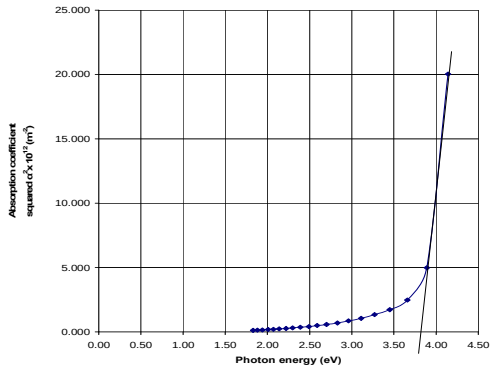


Fig. 2: Plot of Absorption coefficient squared (α^2) against Photon energy for ZnS thin film

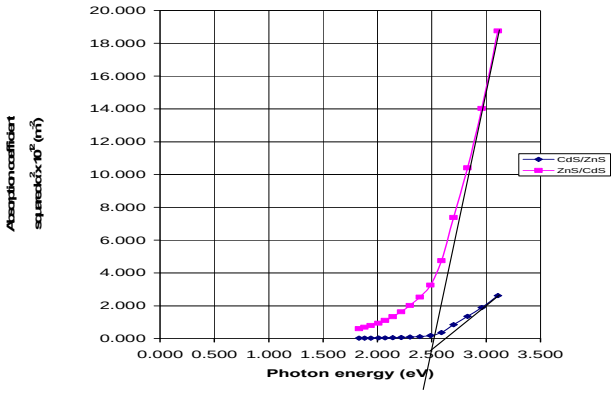


Fig. 3: Plot of Absorption coefficient squared (α^2) against Photon energy for CdS/ZnS and ZnS/CdS superlattices

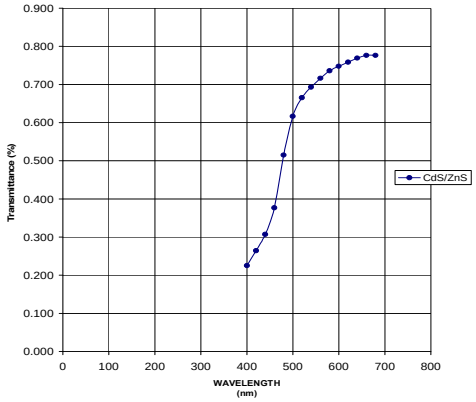


Fig. 4: Plot of Transmittance versus wavelength for CdS/ZnS superlattice

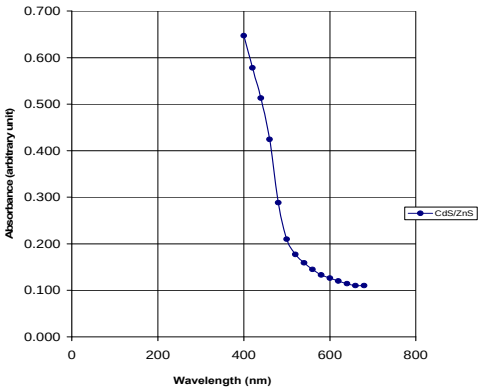


Fig. 5: Plot of Absorbance versus wavelength for CdS/ZnS superlattice

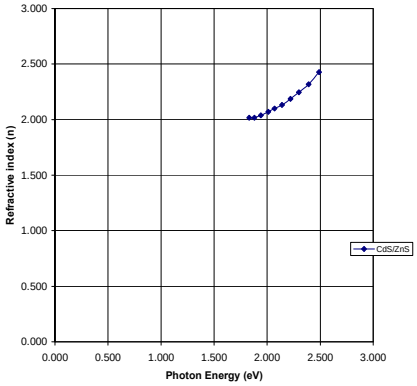


Fig. 6: Plot of Refractive Index versus Photon energy for CdS/ZnS superlattice.

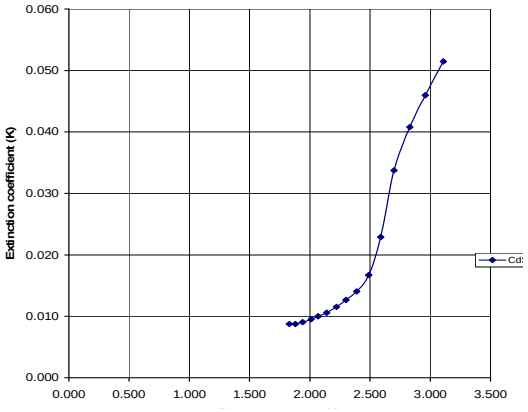


Fig. 7: Plot of Extinction coefficient versus Photon energy for CdS/ZnS superlattice

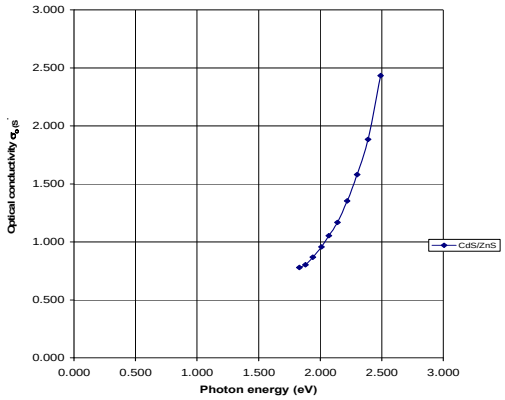


Fig. 8: Plot of Optical conductivity versus Photon energy for CdS/ZnS superlattice

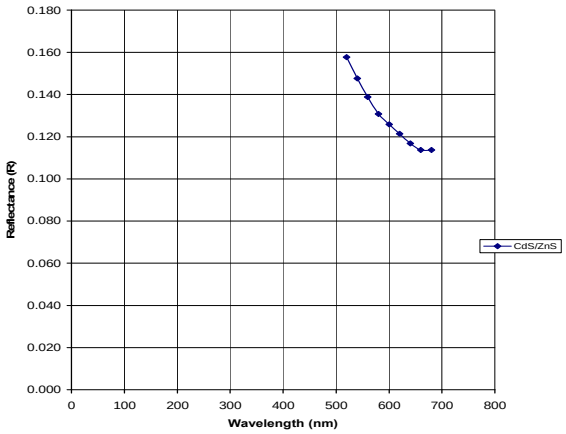


Fig. 9: Plot of Reflectance versus Photon energy for CdS/ZnS superlattice

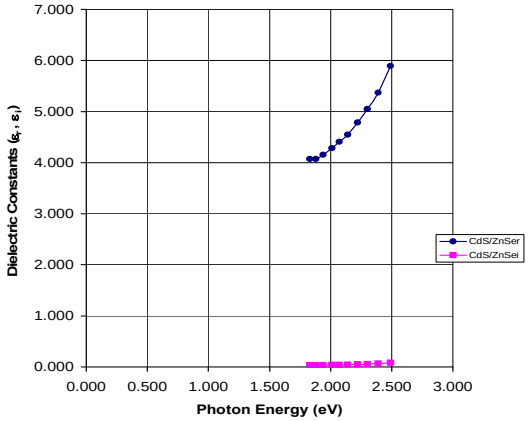


Fig. 10: Plot of Dielectric constants (ε_r, ε_i) versus Photon Energy for CdS/ZnS superlattice

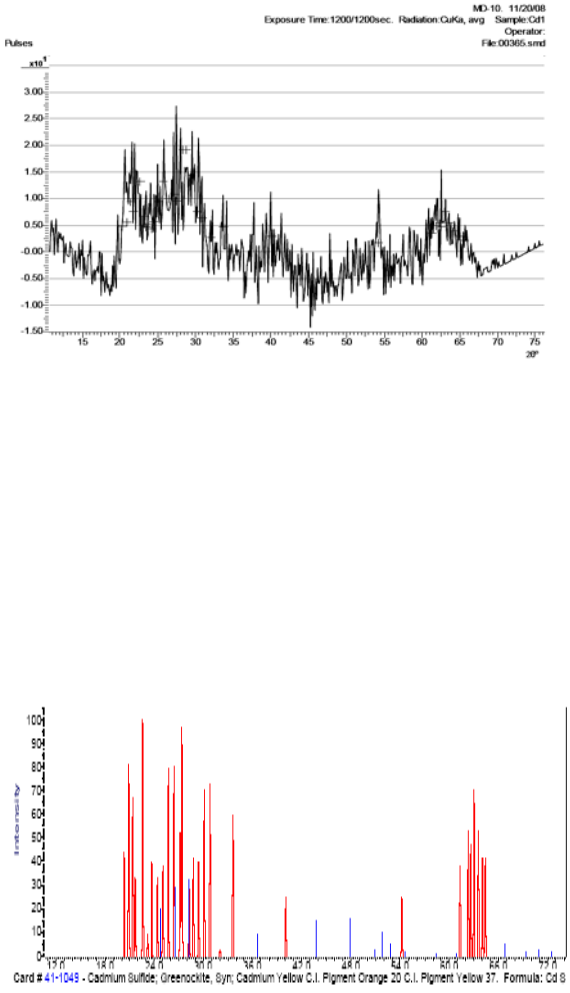
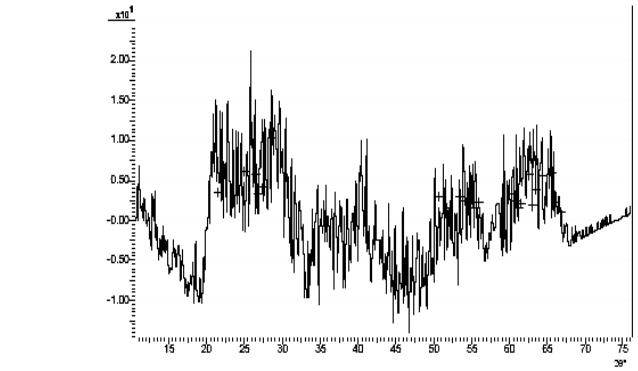


Fig. 11: X-ray diffraction spectra for CdS thin film



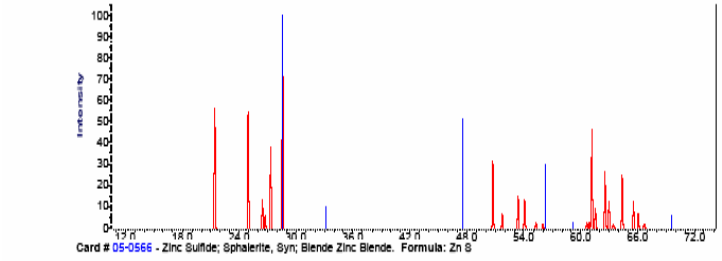


Fig. 12: X-ray diffraction spectra for ZnS thin film

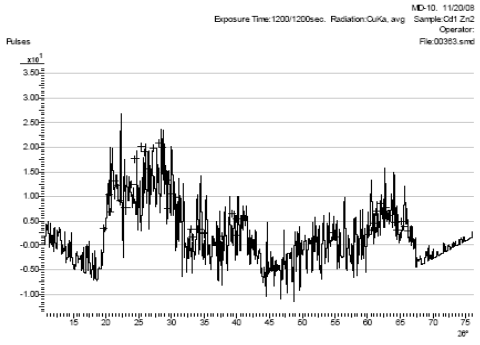


Fig. 13: X-ray diffraction spectra for CdS/ZnS

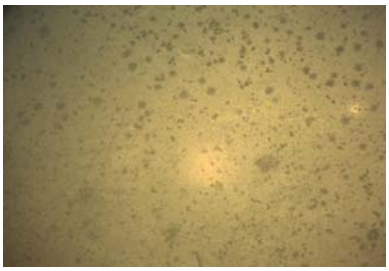


Fig. 14: Micrographs of CdS thin film

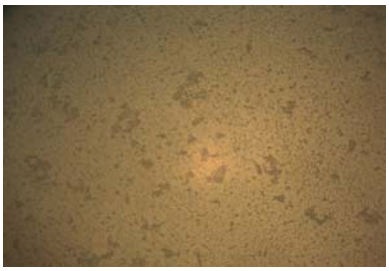


Fig. 15: Micrographs of ZnS thin film

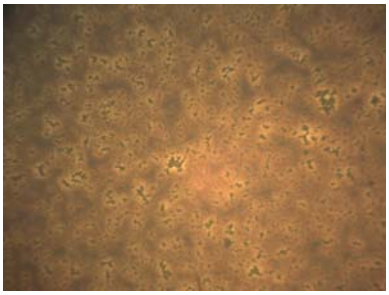


Fig. 16: Micrographs of CdS/ZnS

Figs. 1, 2 and 3 are plots of absorption coefficient squared (α^2) as a function of photon energy for CdS, ZnS, ZnS/CdS and CdS/ZnS. From this graph, the optical bandgap energy of CdS and ZnS semiconductors and CdS/ZnS superlattice were obtained. The values were found to be 2.49eV for CdS, 3.80eV for ZnS and 2.50eV for CdS/ZnS. This wide energy gaps, makes these films applicable as window layers for photocells. A valence band offset of 0.02eV and conduction band offset of 1.29eV was then calculated for CdS/ZnS superlattice (See Fig. 17). The value of bandgap for the chemically deposited ZnS thin film in this work is in close agreement with those obtained by [18, 19, 20]. For CdS thin film, our bandgap compares favourably with those obtained by [21, 22]. Our C_{BO} value compares favourably with 1.1eV reported by [23]. The band alignment in CdS/ZnS superlattice was found to be type 1 (see fig. 17). This compares favourably with results obtained by [24].

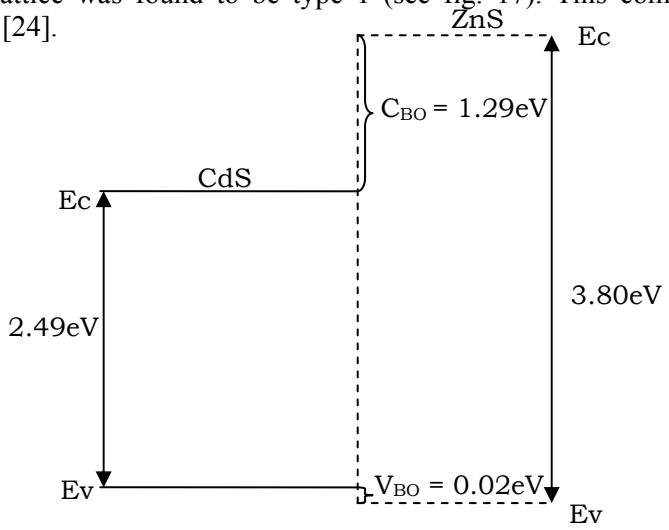


Fig. 17: Schematic diagram for Band alignment of CdS/ZnS superlattice

Fig. 4 is a plot of transmittance versus wavelength for CdS/ZnS superlattice. It has a high transmittance in the vis-region with a range of 23%-78% at a wavelength range of (400-680) nm. This high transmittance makes this material useful as buffer layer for CGS Solar Cells.

Fig. 5 is a plot of absorbance versus wavelength. The absorbance decreases as wavelength increases. It has an absorbance range of (0.647-0.110) at wavelength range of (400-680) nm.

Figs. 6, 7 and 8 are plots of refractive index(n), extinction coefficient (k) and optical conductivity (σo) against photon energy for CdS/ZnS superlattice. It has a refractive index of 2.43 at 2.49eV and 2.02 at 1.83eV respectively. A peak extinction coefficient value of 5.1×10^{-2} is obtained at photon energy of 3.11eV. For optical conductivity, a value of 2.433 was obtained at 2.49eV. The optical conductivity decreases as photon energy decreases.

Figs. 9 and 10 are plots of reflectance and dielectric constant versus wavelength and photon energy respectively. It shows a low reflectance through out the Vis-region. This low reflectance value makes CdS/ZnS an important material for anti-reflection coating. It has a real dielectric constant of 5.891 at 2.49eV and 4.072 at 1.83eV.

Figs. 11, 12 and 13 shows the x-ray diffraction spectral of CdS, ZnS and CdS/ZnS while Figs. 14, 15 and 16 shows the optical micrographs. XRD measurement clearly indicates

crystallization of CdS and ZnS in the hexagonal and cubic phases respectiviely. This compares favourably with those obtained by [22]. It has been reported that both hexagonal and cubic CdS can be grown by CBD [25]. According to [25], the structure of CdS is determined by the deposition mechanism. From the micrographs, it can be seen that all the films exhibit the growth of small grains distributed across the surface of the substrate. It also shows uniform surface coverage.

We have demonstrated using chemical bath deposition technique, the synthesis of CdS/ZnS superlattice. A band offset of 0.02 eV was calculation at the CdS/ZnS interface, extinction coefficient of approximately 5.1×10^{-2} at 3.11eV and a refractive index of approximately 2.43 at 2.49eV (400 nm) was found for CdS/ZnS superlattices.

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