Wet chemical synthesis of Ru, In, and Tl doped CdSe thin films for Electrochemical and electric conductivity study

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Abstract

A systematic investigate has done to chemically deposited pristine and doped (Ruthenium, Indium and Thallium)CdSe nanostructured thin films. The deposition has been carried out in an at 323 K for about 7 hours. Complete analysis of these pristine and doped CdSe thin films were studied by using X-ray diffraction (XRD), scanning electron microscope (SEM), Energy dispersive X-ray analysis (EDX), optical absorption (by UV-*vis* analysis), cyclic voltammetry (CV), and electrical conductivity techniques. From XRD analysis it is clear that all the peaks matches with JCPDS Card No 77-2307 which confirms the films are of CdSe as deposited as well corresponding elemental doping peaks is observed which further confirms with EDX analysis. Increase in optical absorption in UV-Vis spectra. This study reveals that, from CV analysis we find specific capacitance of all samples. Specific capacitance of CdSe thin film increased from 9.5 F $g^{-1}$to 18.5 F g^{-1}. Highest specific capacitance observed for Ru doped CdSe. The electrical conductivity is in the order of 6.14 mho-cm^{-2} is obtained for Ru doped CdSe thin film.

Keywords: Doping, conductivity, chemical bath deposition, electrochemical study

1. Introduction

In last few decades, research based on nano structured materials growing rapidly in the field of science. Where the efforts of chemists, physicists, materials scientists, biologist, and engineers have merged. Now-a-days, the study of various semiconductors nanostructures has attracted a majestic attention for its wide range of applications. The II–VI semiconductor compounds, particularly cadmium sulphite (CdS), cadmiumSelenide (CdSe), cadmiumteleride (CdTe), are of great concern because they are probable candidates in many practical applications. Amongst them CdSe is a one of the most adaptable material which having band gap (1.7 eV) near to visible spectrum maxima (300nm-700nm). It has earned distinguishable attention of researchers due to high absorption coefficient, direct band gap, size dependent physical and chemical properties. These properties encourage use of CdSe in various applications such as solar cell [1–5], thin film transistor [6], light emitting diode [7-9], various electronic and optoelectronic devices [10-13] etc. Different CdSe nanostructures have been grown by various physical and chemical techniques such as thermal, chemical bath deposition (CBD) [14,15], hydrothermal [16], electro deposition [17], electron beam evaporation [18], thermal

evaporation [19], spray pyrolysis [20], successive ionic layer adsorption and reaction (SILAR) [21,22] methods etc. In order to improve the range of applications for CdSe nanostructures scientists and researchers studying to change the physical and chemical properties of CdSe nanostructures by using various synthesis techniques to explore CdSe potential. Amongst various techniques doping is one of the effective techniques to modify the optical and electrical properties of semiconductor materials. The performance of the CdSe thin film has been improved in various applications via doping it with suitable dopant materials. Doping can change the structural parameters and properties of nano materials.

In present investigation, CdSe nanostructure thin films as deposited (pristine) and various elements like Ru, In, and Tl doped CdSe thin films were synthesized by using simple and cost effective wet chemical deposition method generally named as chemical deposition method was employed to get these films. Structural, morphological, and electrochemical properties for all films were investigated. Then find out conductivity of these films by using 4-probe setup.

2. Experimental Details

2.1 Chemicals

Cadmium Sulphate ($CdSO_4$), sodium selenosulfate (Na_2SeSO_3) solution, ammonia solution (NH_3), fluorine doped-tin oxide (FTO) glass substrates, indium trichloride ($InCl_3$), Ruthenium trichloride ($RuCl_3$), Thallium trichloride $TlCl_3$, double distilled water were used. All the chemicals used to synthesis of pristine and doped CdSe were of analytical grade used without purifications having highest purity. All the used solutions were freshly prepared with double distilled water.

2.2 Method used for synthesis

Chemical Bath Deposition (CBD) method was used to synthesis of pristine and doped CdSe nanostructures. CBD is expedient and low cost method for production of large area thin film for semiconducting materials, used to deposit on various substrates like glass, FTO, indium doped-tin oxide (ITO), etc. The CBD deposition is frequently carried out in an aqueous solution which consists of specific chemicals. In the CBD method, the precipitation of compound semiconductor is controlled through the use of suitable complexing agents and the amount of ions. For synthesis of nanostructures in present work a simple CBD set-up was fabricated. This is an inexpensive technique at low deposition temperatures.

2.3 Substrate cleaning

Along with the synthesis method the Substrate cleaning plays very important role in the deposition process. Therefore before deposition, FTO substrates were initially cleaned with liquid detergent after that boiled in chromic acid and ultrasonically cleaned for 15 min and finally etched in 5 % H2SO4 for 5 min and finally ultrasonically cleaned. After all this procedure FTO substrate is ready to used for CBD deposition process.

2.4 Pristine and doped CdSe film deposition

Pristine and doped CdSe thin films were deposited by the CBD method onto FTO substrates. For deposition pristine CdSe nanostructures use analytical grade $CdSO_4$, NH_4OH, and freshly prepared Na_2SeSO_3 solution. Take 30 ml of 0.1M $CdSO_4$ solution in 100 ml capacity glass beaker. Add ammonia solution slowly added with constant stirring in to $CdSO_4$ solution. Initially, when we start to add ammonia solution the solution became milky and turbid due to the formation of $Cd(OH)_2$, if we go on adding ammonia solution further addition of excess ammonia dissolved the turbidity and made the solution clear and transparent. To this, 30 ml freshly prepared 0.1 M Na_2SeSO_3 solution was added slowly with constant stirring. The resultant pH of the final solution was 11.5.

Various doped CdSe nanostructures like ruthenium doped, thallium doped and indium doped was synthesised by following process to prepare 30ml $CdSO_4$ clear solution. 0.1 M Na_2SeSO_3 solution was added slowly in to $CdSO_4$ solution with constant stirring pH of final solution become 11.5. Finally add respective chlorides in to each solution like 0.03 mM $RuCl_3$, 0.03 mM $InCl_3$, and 0.03 mM Thallium chloride in order to synthesis of Ru doped, CdSe nanostructures. All the solutions were stirred for few seconds and then beaker is placed under cleaned FTO substrates inclined vertically to the substrate holder made of Bakelite. The FTO are making 90° angle with each other. The holder is attached to remi rotor with controlled speed. The bath solution was kept at 323 K. The substrates were removed after 90 min, rinsed in double distilled water, and dried in air to get pristine and doped (Ru, In, Tl) CdSe nanostructured films

3. Result and discussion

3.1 XRD study

The X-ray diffraction spectra (XRD) were recorded by using Philips X-ray diffractometer with CuKα (λ=1.54045 mm) radiation.XRD analysis for all samples/nanostructures was carried out to check the crystal structures of the pure and doped CdSe nanostructures. Figure 1 shows the XRD patterns of pristine and doped CdSe nanostructures.

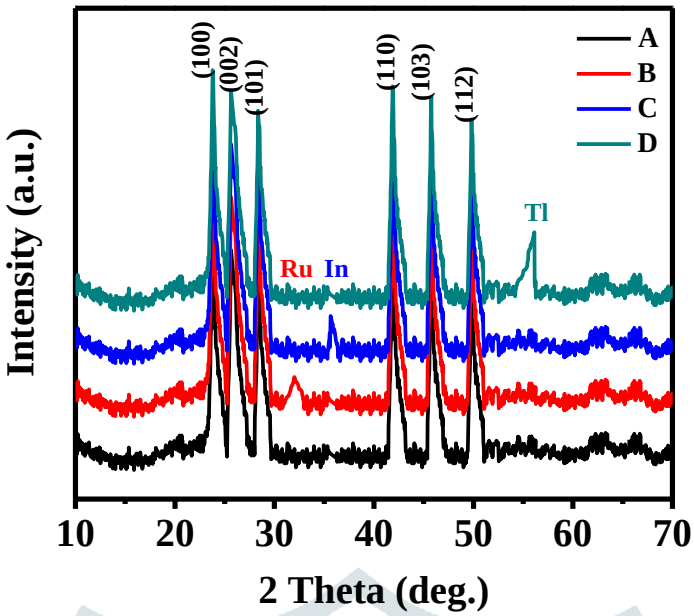

Fig. 1 XRD spectra of pristine and doped CdSe thin films

All the diffraction peaks of pristine and doped CdSe were indexed according to JCPDS files. Diffraction peaks corresponding to (100), (002), (101), (110), (103), and (112) planes were matches to JCPDS Card No 77-2307 which indicate that the samples are polycrystalline. Along with these peaks due to CdSe other peaks also seen in case of doped nanostructures (from film B to D) like Ru in sample B, Tl in sample C and In peak in sample D. This indicates evidence of respected doping in CdSe. From XRD pattern the grain size is calculated by using Debye Scherrer's formula with the help of full width at half maxima (FWHM). The crystallite grain size D, was calculated by using the Scherrer's formula [24]:

$$D = K\lambda/\beta \cos\theta$$

Where, λ = X-ray wavelength, θ = Bragg diffraction angle and B = is the full width at half maximum (FWHM) of the XRD peak. The grain size calculates for pristine and doped CdSe thin films by using (100) peak in the range of 25.5nm to 36.7 nm.

In XRD analysis minor peaks are appear other than CdSe peaks in spectra. In sample B to D these minor peaks are due respective doping but peak intensity was not more. So for better understanding of the doping EDX analysis of all the thin films are carried out. EDX gives clear idea about compositional analysis of all films. Fig. 2 a-d represents results which are obtain from EDX analysis

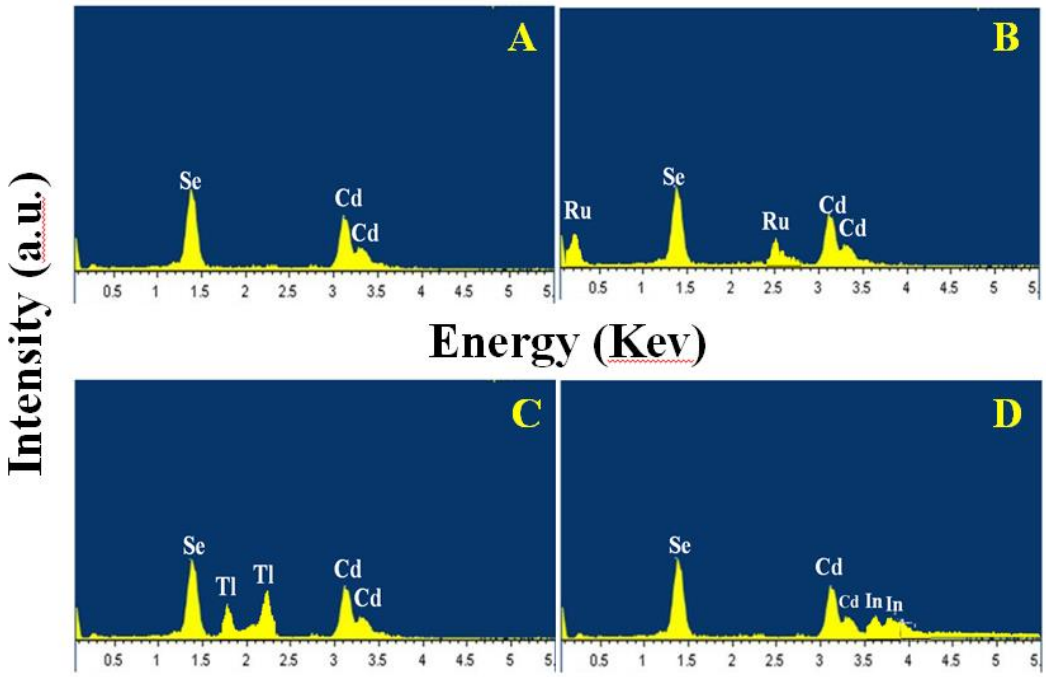

Fig.2 EDX spectra of the of A) pristine, B) Ru doped, C) Tl doped, and D) In doped CdSe thin film

EDX measurement on individual thin film surface was carried and Cd, Se, Ru, Tl and In elements were scanned shown in Fig. 2 A-D and results obtained were tabulated in Table 1. In Pristine CdSe thin film (Fig. 2 A) only Cd and Se elements are detected. Whereas its weight percentage (wt.%) is decreased in doped thin films. In case doped films doping was confirm as respective elements were detected in respective thin film like Ru element is detected in B film, Tl was detect in C film, similarly In element is detected in film D.

Table- 1 Parameters obtained in EDX analysis of Pristine and doped CdSe thin films

Samples	Element	Weight %	Atomic %
A	Cd	67.60	61.20
	Se	32.40	34.40
B	Cd	62.56	61.20
	Se	28.48	26.38
	Ru	8.96	12.42
C	Cd	64.17	61.98
	Se	24.43	25.32
	Tl	11.40	12.70
D	Cd	65.31	67.35
	Se	25.12	23.56
	In	9.57	9.09

3.2 Surface morphology study

Surface morphology of as-deposited/pristine CdSe and doped (Ru, In, and Tl) CdSe thin films investigated by FE-SEM images as shown in fig.3 (a-d).

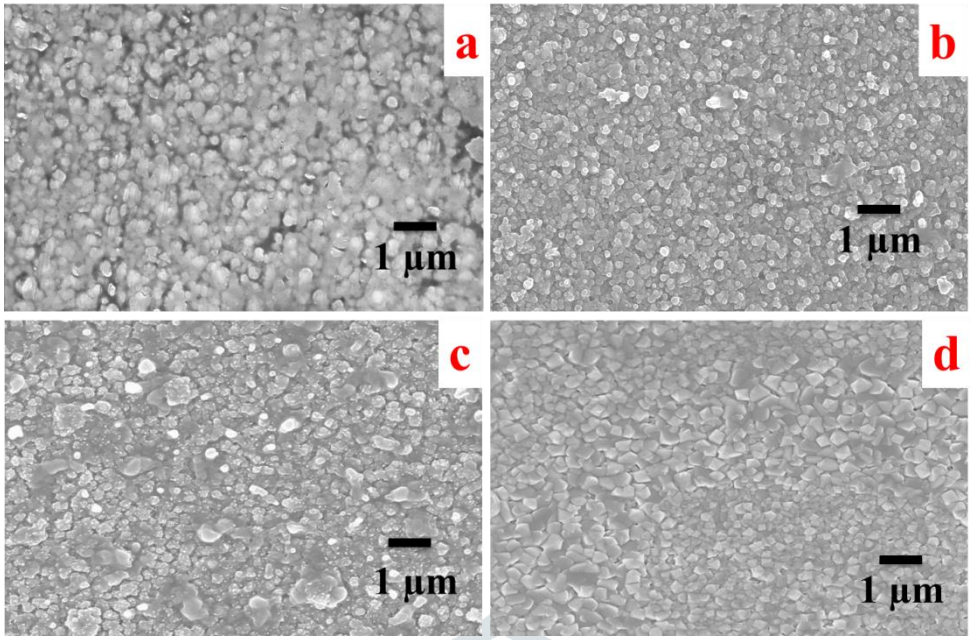

Fig. 3 FE-SEM images of a) pristine CdSe, b) Ru doped CdSe, c) Tl, and d)In doped CdSe Thin film

In fig. 3 a) in case of pristine CdSe nanostructured film found to possess slightly agglomerated structure. In case of Ru as dopant in CdSe (fig. 3 b) changes the morphology entirely as well as it starts to grow cube like particles. After Tl doping as shown in fig. 3 c the CdSe surface morphology shows formation of cubic structures along with these structures some agglomerated structures also form some of the places on the surface. From fig. 3 d) it is clear that after In doped in CdSe the surface morphology shows cubes are well linked with each other which form compact structures on CdSe surface.

3.3Optical absorption measurement

Fig. 4 shows the optical absorption spectra of pristine and doped CdSe thin film. It is observed that the absorption coefficient is high at lower wavelength and decreases sharply below a certain wavelength for all films.

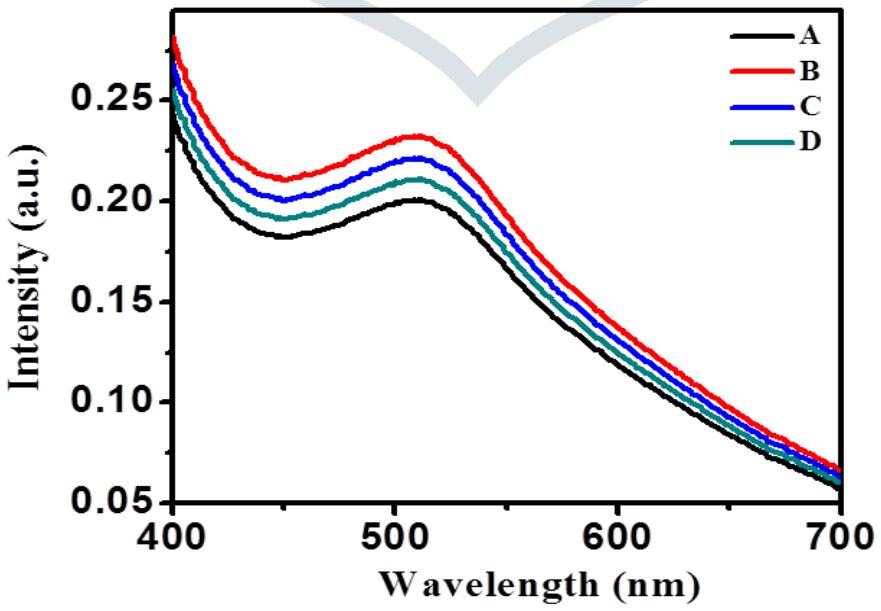

Fig. 4 Optical absorbance spectra of pristine and doped CdSe thin film

UV-*vis* absorption spectra show absorption peak nearly in equal position at 520 nm which is characteristic peak due to CdSe. It is observed the absorption intensity increases for various doping in to CdSe, amongst all we get highest absorption intensity for Ru doped CdSe where as absorption intensity of remaining two is lower as compared to Ru doped CdSe.

3.4 Electrochemical Measurement

Electrochemical properties such as cyclic voltammetry (CV) of as deposited CdSe (Sample A) and doped CdSe films (Samples B to D) as working electrodes were performed in 0.1 M H_2SO_4 electrolyte for super capacitor application. Fig. 5 shows (CV) characteristic of pristine and doped CdSe nanostructure.

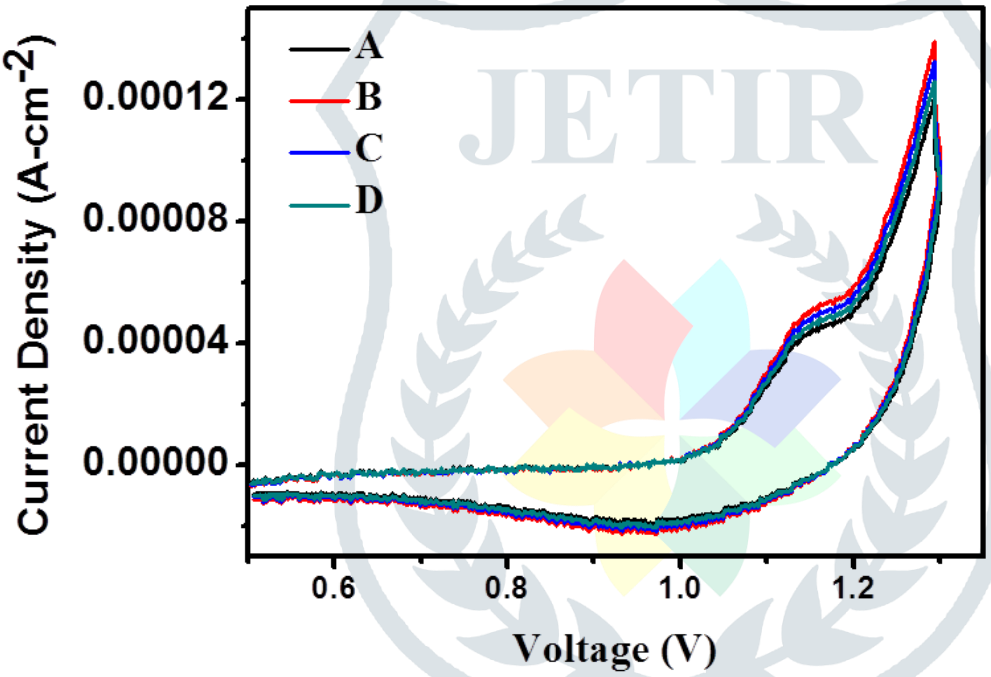

Fig. 5 cyclic voltammetry (C-V) characteristic of pristine and doped CdSe nanostructure.

The CV measurement was operated for pristine and doped films of different doping elements (Ru, In and Tl sample B to D respectively) in 0.1 M H_2SO_4 electrolyte within the fixed potential window of 0.5 V to 1.3 V and were collected for 10 mV s^{-1}scan rates.

The obtained CVs for all the samples were almost symmetrical and shows higher area under curved for doped samples (for samples A to D) as compare to pristine CdSe sample. The specific capacitance (SC) values, obtained by using following relation,

$$\mathbf{SC = I/m \times Scan\ rate = I/ m \times (dV/dt)}$$

Where '**I**' is average of oxidation and reduction potentialcurrents, '**m**' is the mass of active electrode material, **dV/dt** is the scan rate. As high as 18.5 F g^{-1}SC value at 10 mV s^{-1}scan rate was obtained for Ru doped CdSe nanostructured thin film. Whereas lowest SC 9.5 F g^{-1} of was obtain for CdSe thin film (sample A). For In and Tl doped CdSe thin films we get 12.0 F g^{-1}and13.1 F g^{-1}respectively. It is observed that with different doping area under the curve increased as well as the redox peaks were evidently seen indicating pseudo capacitor behaviour.

3.5 Current–voltage (IV) plots

To investigate the conductivity of pristine and doped CdSe nanostructures we performed I-V characteristic measurement for samples A-D. I-V measurement was carried out in the range of 2–9 Vat 1 × 1 cm^2 sample surface area and obtained results are displayed in Fig. 6.

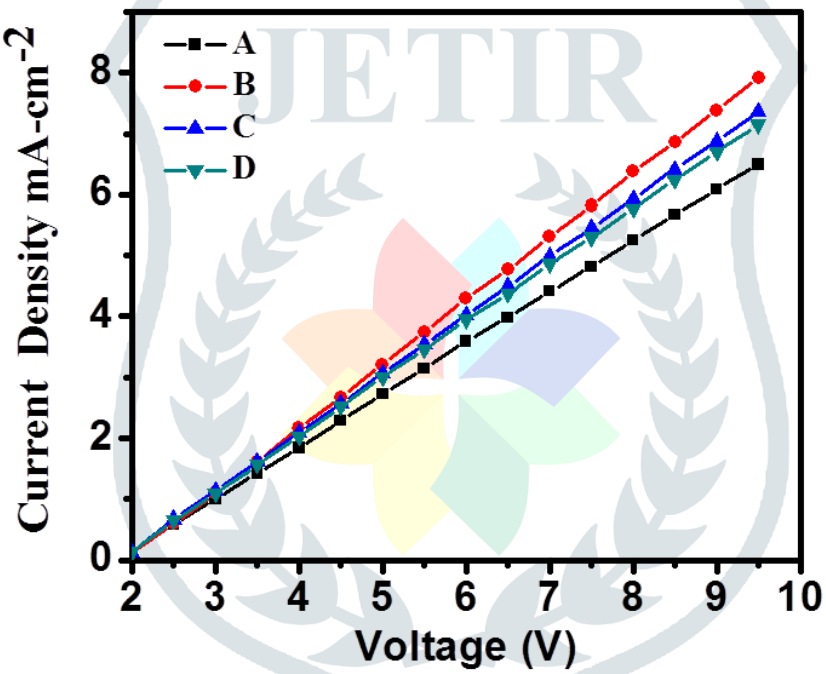

Fig. 6 I-V characteristic of pristine and doped CdSe nanostructure.

During each measurement ohmic contacts were established. All the current–voltage plots were linear demonstrating good conductivity; however, a slight change in their slopes was evidenced, indicating infinitesimal variation in conductivity as Ru, In, and Tl doping come in to picture. Surface conductivity increased from 0.57 mho-cm^{-2} to 6.14 mho-cm^{-2} with doping of various elements like Ru, In, and Tl. We believe that increase in conductivity is due to doping elements. Highest conductivity in case of sample B i.e. Ru doped CdSe films whereas, in case of smple C and D it was 5.76 mho-$cm^{-2}$and 4.37 mho-cm^{-2-} respectively.

4. Conclusions

In present work, Pristine and doped CdSe thin films were synthesized by using chemical bath deposition method. Doping of various element (Ru, In, and Tl) confirmed by characterizing films for structural, surface morphological and optical properties supported by EDX in terms of chemical elemental stoichiometric analysis. Specific capacitance of CdSe thin film increased from 9.5 F g^{-1} to 18.5 F g^{-1}. Highest specific capacitance observed for Ru doped CdSe. It is observed that conductivity is increased from 0.57 mho-cm^{-2} for as deposited (Pristine) CdSe to highest conductivity of 6.14 mho-cm^{-2} for Ru doped CdSe film.

5. Referances

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