

The Fabrication of the Infrared CdSe Doped With Cu Photodetector

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Received: April 24, 2016 Accepted: May 3, 2016 Online Published: May 7, 2016

doi:10.5539/apr.v8n3p96

URL: <http://dx.doi.org/10.5539/apr.v8n3p96>

Abstract

In this work, the implementation method of the CdSe doped with Cu (CdSe: Cu) photodetector is presented. This detector is prepared by vacuum evaporation of CdSe films on glass substrate followed by vacuum annealing under an argon atmosphere for doping with copper. This detector is found, for the first time, to cover a wide range of the infrared besides the visible region of the electromagnetic spectrum. This finding of the wavelength tuning is due to the localized energy states of copper atoms inside the band gap of the CdSe. This tuning is compared with recent work in the corresponding colloidal CdSe-ZnS core shell quantum dots and with the quantum well (QWIR) and quantum dots (QDIR) infrared detectors. The major significance of this developed detector is in its synthesis simplicity and its fabrication processes costs in comparison with that of the (QWIR) and (QDIR) detectors. The structural analysis results demonstrated that the vacuum annealing in competition with the doping concentration improves significantly the film structure. Better crystalline structure was reported at 5 wt% of Cu concentration and at annealing temperature of 350 °C. Besides the measured detectivity at room temperature is $D^*=2.31 \times 10^8 \text{ cm Hz}^{1/2}\text{W}^{-1}$. This value approaches the detectivity of the state of art mercury cadmium telluride (MCT). This result paves the way for further investigations and improvements.

Keywords: CdSe:Cu, Photodetector, Infrared, Tuning range, detectivity

1. Introduction

In the last two decades there are great potential interests in the design and implementation of photodetectors. The motivation of such interests is the expansion of absorption spectrum and increase of detectivity at room temperature. Expansion of electromagnetic spectrum provides a wide range of applications including high speed data communication Zhang et al. (2015), medical diagnosis Maiti et al. (2013), solar cells in the visible range Kashyout et al. (2012), while the infrared (IR) detectors are used in thermal imaging, night vision, heat seekers. In the present work we have found that the bulk CdSe semiconductor material when doped with Cu impurity leads to the electromagnetic spectrum expansion. Besides, the implementation of this material as a photoconductive detector could reach a detectivity value comparable with that of the state of art mercury cadmium telluride (MCT) at room temperature. Recently CdSe quantum dots detector is developed in the visible region of the electromagnetic spectrum (400-700 nm) with detectivity $D^*=10^8 \text{ cm Hz}^{1/2}\text{W}^{-1}$. The quantum dots infrared photodetector (QDIP) have emerged as a potential alternative to MCT and QWIP (Oertel et al., 2005). Asgari and Razi (2010) have designed a novel infrared quantum photodetector using a cubic shaped 6nm GaN quantum dots capped with AlGaIn. The D^* of this detector was calculated and found to be $3 \times 10^8 \text{ cmHz}^{1/2}\text{W}^{-1}$ at room temperature. Diedenhofen et al. (2015) have demonstrated that the integration of colloidal quantum dot photodetector with color tunable plasmonic nanofocussing lenses offer a significant color selectivity. Such lenses facilitate light concentration at the nanoscale and enhance light matter-interactions. The aim of the present work is to investigate an alternative approach for wavelength tuning extending from the visible to the IR spectrum region. For this purpose, we focus in particular on the CdSe doped with different concentrations of Cu atoms in which photoconductive detector plays a major role. This detector has found for the first time to cover a wide spectral range and operating at room temperature.

2. Experiment

Thin films of CdSe (purity= 99.999%) are prepared by vacuum evaporation on a glass substrate ($7.6 \times 2.6 \text{ cm}^2$) using Balzers-OE-8 evaporation unit. High purity (99.999%) aluminum is deposited on the CdSe film to act as

ohmic contacts. Copper atoms of a different weight percentage are also introduced into the CdSe lattice by dipping the films in a CuCl solution, complemented by annealing using a vacuum furnace and flowing argon gas. The experimental layout is shown in Figure 1. The sample is annealed at variable temperature between 100 and 350°C for a period of 2.5 hours. It has been found that a better film structure was obtained at the temperature of 350°C. The doped CdSe films prepared by this method have enjoyed characteristics similar to the CdSe single crystal doped with impurity atoms. The mask was fabricated from Mo material using a CNC cutting machine. The shape and dimensions of the mask are given in Figure 2. The photocurrent and spectral response were measured by the detector test bench DSR-500 supplied by Optronic laboratories. For lasers wavelength response test, the mounted test bench shown in Figure 3a was used. This test bench consists of the laser source, mechanical chopper for chopping the CW CO₂ laser, CdSe:Cu detector and storage oscilloscope. The detector bias circuit is shown in Figure 3b which presents a DC power supply (100V, 5 mA) and a load resistor. In the present experiment a bias voltage of 20V was used. For responsivity measurements, the power incident on the detector area is measured by a calibrated thermopile.

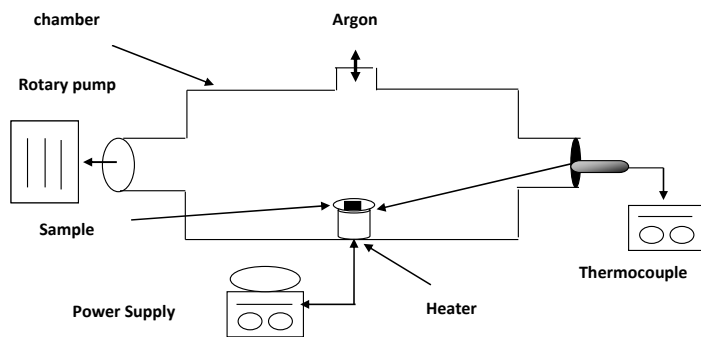


Figure 1. Film annealing setup

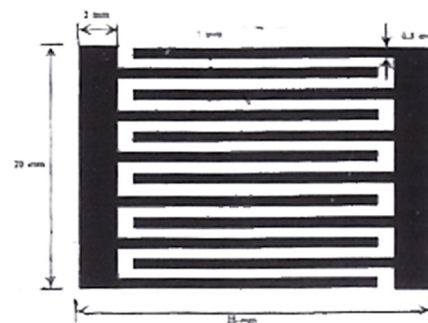


Figure 2. The detector mask

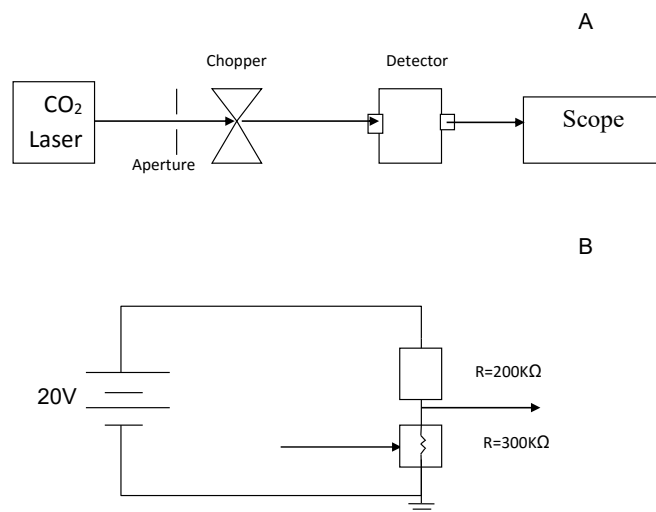


Figure 3. (A) Detector response test bench, (B) Detector bias circuit

3. Results and Discussion

3.1 Structural Properties

The doping of pure CdSe with Cu at different concentrations (film thickness= 1 μ m) improves significantly the structure. Better crystalline is reported at 5wt% Cu concentration. The X-ray diffraction of Cu doped samples depicts that only reflection from the (100) plane appeared and indicated that a single crystal grew on this plane. Figure 4 shows the diffraction pattern of CdSe doped with 5 wt% of Cu and at 2wt% for comparison. The results of the X-ray diffraction pattern are confirmed by the SEM morphology which indicates the single crystalline

with hexagonal (wurtzite) of the film structure at 5wt% of doping (Figure 5). This large crystalline structure change with doping indicates the incorporation of this dopant within substitutional or interstitial site in the CdSe lattice structure. It was shown that the grain size increases from 0.4 μm to 2.87 μm with an increase in Cu concentrations (Figure 6). A great improvement of the films structures was achieved at doping with 5wt% of Cu complemented by 2.5 hours of annealing at 350 $^{\circ}\text{C}$. The improvement in the crystal structure leads to a better optical sensitivity than that found in the case of the pure CdSe. The crystal structure is found to be hexagonal and cubic when Cu concentrations are below 3wt%. The increase in grain size can be related to the atoms thermal energy gained by annealing in presence of argon gas which facilitates the recrystallization. The SEM morphology results of CdSe:Cu (5wt% of Cu) and the X-ray diffraction of the same material can be considered to be identical.

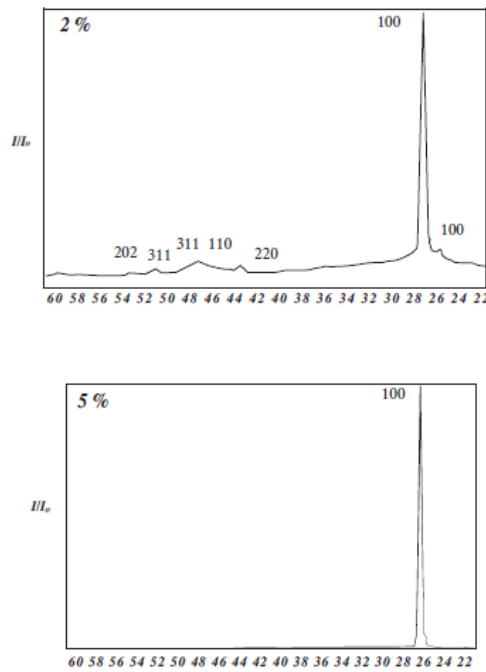


Figure 4. the diffraction pattern of CdSe doped with 5 wt% of Cu and 2 wt%

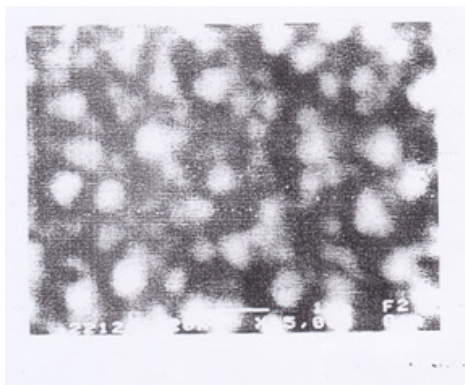


Figure 5. SEM morphology of CdSe doped with Cu at 5 wt% concentration

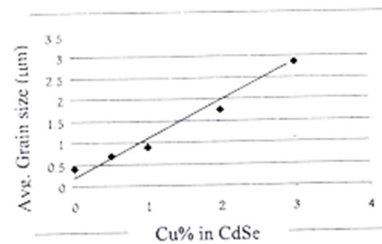


Figure 6. the average grain size as a function of Cu concentration

3.2 The Optical Properties

The absorption coefficient increases with the increase in the Cu doping concentration (Figure 7). Red shift in photon energy was found to be relative to the pure CdSe. This shift can be related to the presence of localized Cu

levels inside the band gap of CdSe. The Cu levels induced field effect that shift the band edge towards energy lower than that of the pure CdSe. The change in the absorption coefficient $\Delta\alpha = (\alpha_{\text{doped}} - \alpha_{\text{pure}})$ was calculated for various doping concentrations. Figure 8 depicts the values of $\Delta\alpha$ as a function of photon energies (hf). $\Delta\alpha$ represents the electronic transitions for various copper levels inside the band gap to the conduction band. The positions of the copper levels were estimated from the full width at Maximum (FWHM) for each doping concentrations. As predicted by Wei et al. (2000), the CdSe can easily be n-doping in consistent with observation of deep levels below the conduction band minimum. These levels were localized relative to the conduction band at (0.67, 0.825 and 1.1eV) corresponding to the Cu concentrations (1, 2 and 5wt% respectively). Other levels were detected in the near and mid infrared region of the spectrum. The first level is situated at 0.116eV just below the conduction band. The position of this level is accurately ascertained when CdSe: Cu detector is selectively excited by a modulated CO₂ laser (10.6 μm), and the output signal was detected by the storage oscilloscope (Figure 9). Another accurate determination of Cu level is by selective excitation using the GaAs semiconductor laser pulse. This pulse is shown in Figure 10 with a rise time of 0.2 μs .

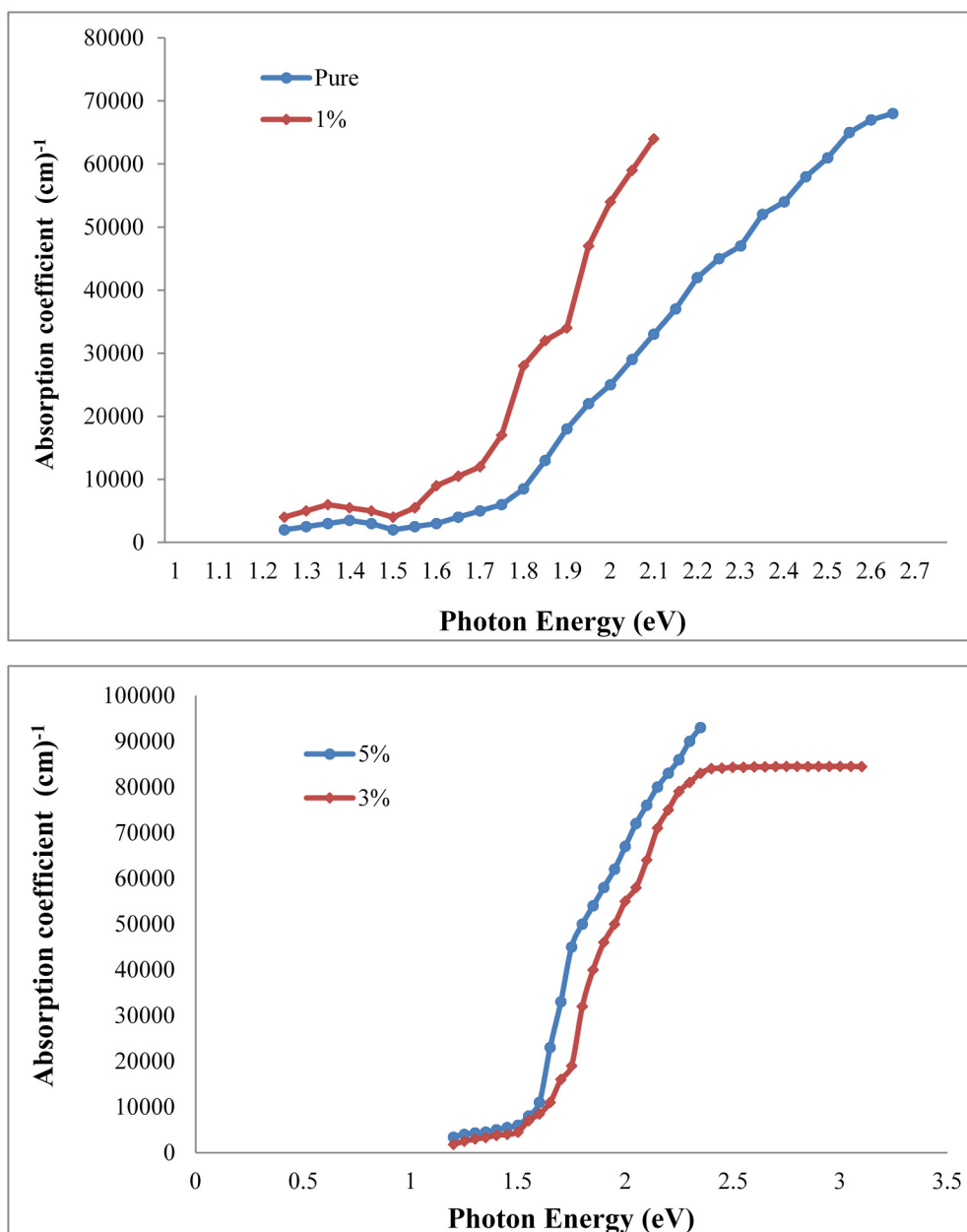


Figure 7. The absorption coefficient as a function of photon energy at different Cu wt%

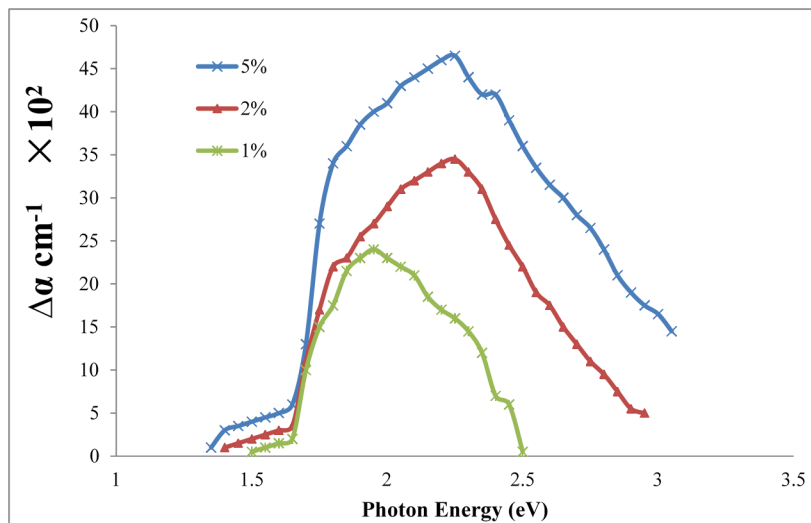


Figure 8. The change in absorption coefficient for various doping concentrations as a function of photon energies

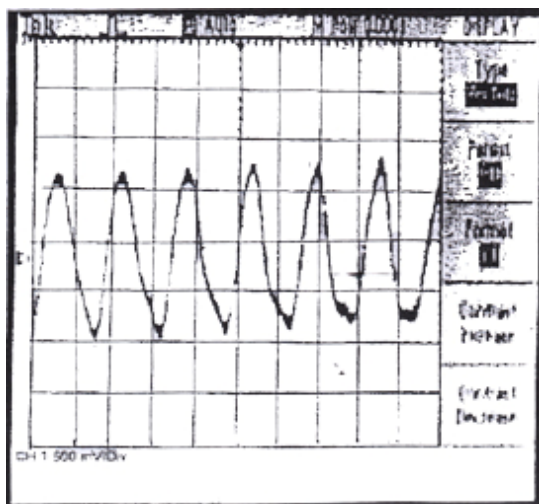


Figure 9. The output signal of the modulated CO₂ Laser

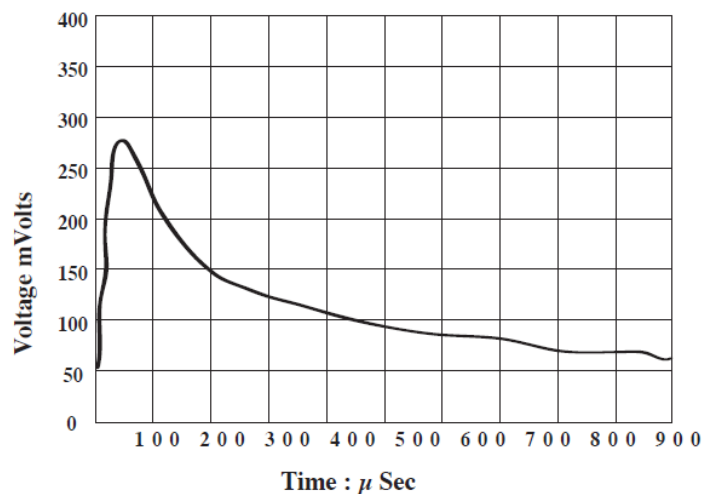


Figure 10. The output signal of the GaAs semiconductor laser

Figure 11a depicts the energy levels involved in the absorption of CdSe:Cu film. This schematic diagram shows a wide wavelength tuning range extending from the visible to the infrared spectrum. This tuning spectrum of the copper doped bulk CdSe can be compared with colloidal CdSe- ZnS core-shell quantum dots (Figure 11b). The common index of the bulk CdSe:Cu and the colloidal CdSe core-shell quantum dots is the single crystalline structure. As a matter of fact the bulk crystal covers the micorscale range, whereas the quantum dots is in the nanoscale. However, this tuning spectrum was detected by using a surface Plasmon's technique. Five distinguishable transitions were detected by the absorption and fluorescence spectra of the CdSe quantum dots (Mohammed, 2013). The populations of these levels were explained by the multiple exciton generation (MEG), in full agreement with the theoretical predictions. It can be remarked that the traditional bulk CdSe doped Cu and the CdSe -ZnS quantum dots are manifested in wavelength tuning. The advantages of the bulk CdSe over the size dependent confinement energy of the same semiconductor material are easier to prepare and at much less fabrication cost than the corresponding size confinement quantum dots. Besides, the CdSe quantum dots tuning range never extends over the visible region of the spectrum, whereas this reported tuning of the bulk CdSe:Cu does extend to the infrared region. Recently, researchs were done in the synthesis and characterization of CdSe doped Cu nanoparticles. Raj et al. (2014) were observed that the increase in the concentration of copper shifts the emission towards the higher wavelength. They explained such blue shift was caused by strong confinement effect. Meulenberg et al. (2004) have studied the structure and composition of Cu doped CdSe nanocrystals using soft X-ray absorption near edge spectroscopy (XANES). They indicated changes in the Se density of states with Cu doping, due to a local bonding environmental effect. Bear et al. (2014) were studied copper doped CdSe-ZnS core-shell quantum dots (QD) and have shown that doping small amounts of Cu into the ZnS shell partially quenches the QD core luminescence and a blue shifts in luminescence peak with respect to pure ZnS shell was detected. This is in contrast to a pure ZnS shell, where a significant increase in quantum yield and a red shift in luminescence were observed. The pioneer work of Türe et al. (1986) have investigated by photoconductivity and space-charge region capacitance technique multiple levels of copper centers in single crystal of CdSe. They demonstrated that the only center referring to copper was situated at 1eV with respect to the valence band. Photoluminescence blinking dynamics for $\text{Cu}^+:\text{CdSe}$ was analyzed by Whitham et al. (2015) and compared to undoped CdSe nanocrystal. They identified the effect of Cu^+ , which selectively traps photogenerated holes and revealed that the $\text{Cu}^+:\text{CdSe}$ nanocrystal off state dynamics are statistically identical. A theoretical and experimental studies implemented by Wright and Meulenberg (2013) have demonstrated the effect of dopant into the CdSe quantum dots. They predicted that the dopant concentration causes a lowering of band energy as compared to the bulk band gap energy. This red shift was explained in terms of the contribution of both the hybridization energy and the confinement energy. They demonstrated that the dopant can affect not only the electronic structure but also the optical properties.

It can be concluded from the previous studies in CdSe:Cu as a bulk or a nanostructure, no evidences were reported for the existence of Cu localized levels with an accurate determination of their positions in the band gap of CdSe, particularly, in the infrared region of the spectrum.

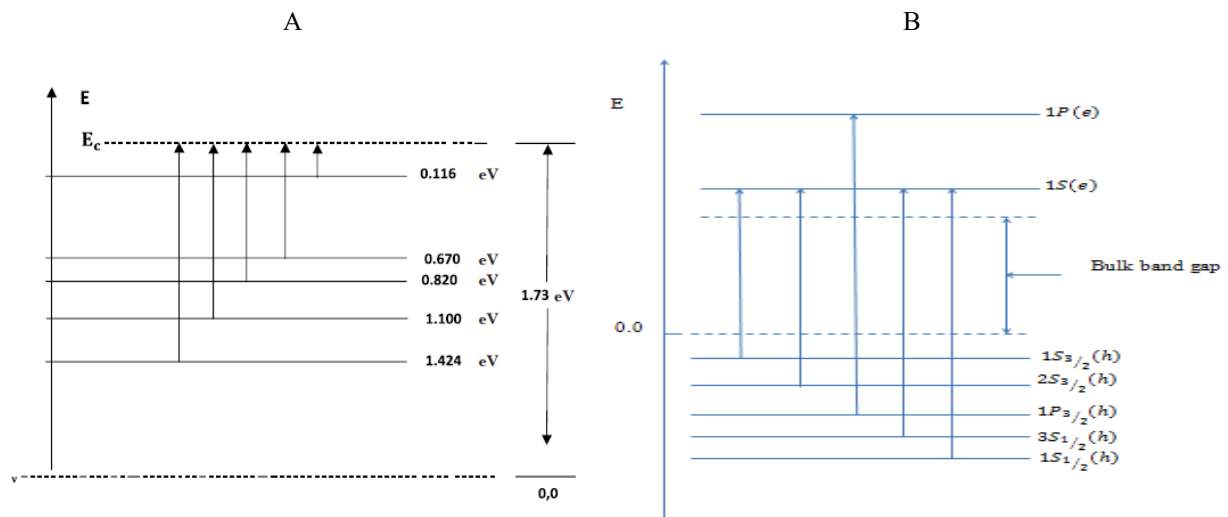


Figure 11. A) Energy levels involved in the absorption of CdSe:Cu film B) Energy Levels involved in the absorption and fluorescence of CdSe-ZnS core-shell quantum dots (Mohammed, 2013)

3.3 Detection Characteristics

Figure 12 shows that the photoconductivity of the CdSe grows exponentially with the increase in Cu wt% concentration. This growth feature is due to the improvement of the film structure. This improvement is confirmed by the increase in the crystal grain size as stated earlier. The noise voltage and the responsivity of this detector are measured and found to be $\sim 1\text{nV}$ and 0.73V/W respectively. The detectivity was calculated by using the following relationship:

$$D^* = (A \Delta f)^{1/2} R / V_n \quad (1)$$

Where A is the detector active area ($A=0.1\text{ cm}^2$), ($\Delta f=1\text{Hz}$) the electrical bandwidth, V_n is the noise voltage and R is the responsivity. Using the Eq.1, a value of $D^*=2.31 \times 10^8\text{ cm Hz}^{1/2}\text{W}^{-1}$ is obtained. Comparison of this D^* value of the CdSe bulk detector at room temperature with the specific detectivity across a different technology is reasonable. The room temperature detectivity of the state of art MCT is $2 \times 10^8\text{ cm Hz}^{1/2}\text{W}^{-1}$ (Hamamatsu 2015) which approaches the measured D^* value for the CdSe:Cu detector. However, the predicted detectivity can be increased by an optimization methodology which includes surface plasmons effect by deposition of the CdSe films into gold coated substrates. Besides, other dopant than Cu like Ag and Au can be used for comparison. The present CdSe:Cu detector paves the way for further investigations and improvements in the field of a dual range antiaircraft missile seekers.

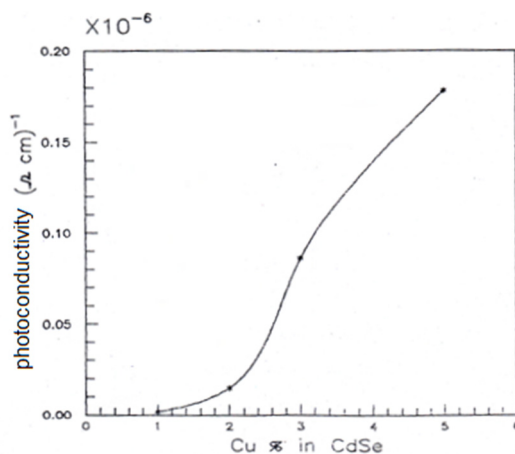


Figure 12. The photoconductivity of CdSe as a function of Cu wt% concentration

4. Conclusions

The following conclusions are drawn:

- (i) The tuning range of the bulk CdSe:Cu is found greater than the recent technological CdSe quantum dots. This may open the door for more applications, particularly in the IR region of the electromagnetic spectrum.
- (ii) The detectivity of this detector at room temperature is comparable with the corresponding state of art MCT detector and the recent designed GaN QDs. Therefore, the CdSe:Cu detector can be considered as an additional prototype to the traditional MCT as an IR detector operating at room temperature.

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