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Capacitance and Dielectric Properties of Mn Doped CdO Photodetectors

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CdO solution was produced using sol-gel technique and doped with Mn in 0.2 %, 6 % and 10 % molar concentrations, respectively. Mn doped and undoped CdO solutions were coated on Si substrates and glass surfaces for characterization. Capacitance -Time (C-T) characterizations were performed to assess the photo capacitance properties of detectors where good photo capacitance properties were confirmed. Photo capacitance properties revealed that photodetectors give good photoresponse and show increasing capacitance trend with increasing illumination intensities. The highest capacitance was observed at 100mW/cm2 illumination. Dielectric properties were investigated as a function of AC signal frequency. Dielectric permittivity (ε′) and dielectric loss (ε″) were assessed. It was seen that both dielectric permittivity constant (ε′) decreases with increasing AC frequency. Dielectric loss (ε″) shows totally different behavior than that of dielectric constant. Dielectric loss (ε″) values were found to increase with diminishing AC frequency.

Key Words: *CdO Thin Films, Photodetectors, Dielectric Constant, Dielectric Loss*.

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1. Introduction

Researchers from different fields such as Physics, Chemistry, Biology, Material Science, etc. interest in nanotechnology [1]. Thin films are one of the most popular topics in the field, since it coves many different applications. Thin films have been used for different purposes such as decorative and/or protective coating, optical coating, electrical and electronic device fabrication [2]. Sensors, solar cells, detectors, diodes and transistors are electronic devices where thin film technologies are vastly used [3–6]. Organic and inorganic materials are used in the fabrication of such technologies [7, 8]. While inorganic materials are preferable, organic materials are still in development due to their unstable characteristic. Due to their stable characteristics and well known properties metal oxide thin films attract the interest of the researchers who works on thin film device technologies. While ZnO, PtO, MnO, LiO, BiO, CdO films are investigated due to their electric, optic and photovoltaic properties, Cr, NiO, FeO and CoO films are researched due to their magnetic and magneto-optic (MO) properties [3, 5, 9–14]. Metal oxide films are vastly researched, since they are stable, and the properties of the metal oxide thin films can be adjusted easily. Therefore, metal oxide thin films find applications in device applications such as LEDs, sensors, detectors which require the materials in unique electrical, optical and magnetic properties. With 2,5 eV bandgap energy, cadmium oxide (CdO) is an important metal oxide due to its structural and electronical properties [15, 16]. Device properties of the cadmium oxide thin films were previously illustrated where different detectors and devices were fabricated using cadmium oxide based thin films [17–21]. It was known fact that doping metal oxides with different materials alter their electric, electronic, magnetic and optic properties [22, 23]. Previous researches illustrated that cadmium oxide thin films were also doped with different metals and elements such as Bi, Al, Ni, Cr, Pb, etc and alteration in the physical properties of CdO thin films were seen [24–28]. For instance, Dugan et al. assessed Mn dopant effect on structural, electrical and optical properties on cadmium oxide thin films [29], the group evidenced that Mn dopant enhanced the optical, electrical and electronical properties of CdO thin films. Other studies also illustrate similar results when CdO films doped with Al optical band gap enhances [23]. On contrary, doping the cadmium oxide thin films with fluorine decreases the measured bandgap [30].

Cadmium oxide films has good transmittance, outstanding conductance and low electric resistance properties. Therefore, cadmium oxide thin films has strong potential as photodetector, photodiode and photovoltaics [31–33]. Metal oxide thin films can be produced using variety of different techniques, such case is also valid for cadmium oxide thin films [17, 23, 26, 89, 34, 35]. Different production technique can alter the quality and the properties of both metal oxide and cadmium oxide thin films. Production methods may provide certain advantages or disadvantages. For example, production methods performed in UHV conditions may be expensive but better control in thickness and quality of thin films can be achieved. On the other hand, techniques using chemical methods such as sol gel method and electrochemical deposition may be cheaper. Moreover, good thin film quality can also be achieved using such techniques.

In this report, sol gel technique was used in the preparation of the CdO and Mn doped CdO solutions where pure CdO, 0.2 % Mn doped CdO, 6 % Mn doped CdO and 10 % Mn doped CdO solutions were prepared, respectively. Prepared chemical solutions were drop cast on p type silicon wafer and spin coated. Al contact on CdO film was produced using DC magnetron sputter. It was aimed to investigate the Mn dopant effect on capacitance and dielectric properties of cadmium oxide thin films. Therefore, Capacitance–time (C-t) properties of the photodiodes in different illumination degrees and dielectric properties of the photodiodes in different voltage were characterized using FYTRONIX solar simulator.

2. Experimental

Sol-gel technique was used to produce the solution used in the preparation of CdO and Mn doped CdO thin films. Four different cadmium acetate solution were prepared by dissolving 0.5M cadmium acetate in the 10 ml isopropanol. Manganese acetate with 0.2 %, 6 % and 10 % molar ratios were added to the prepared cadmium acetate solutions. Result product was stirred using magnetic stirrer at 500 rpm till manganese acetate was totally dissolved. When manganese solution was totally dissolved, aminoethanol was added to the solutions. Aminoethanol works as stabilizer in the solutions. Result products were stirred using magnetic stirrer for 1 hour. Solutions, which were prepared using sol-gel technique, were coated on p type silicon wafers using spin coating method. Cleaning procedure is essential to obtain high quality thin film [36]. Hence, cleaning procedure was applied to Si wafers, before the application of spin coating. P type silicon wafers were sonicated in alcohol for 5 mins and in deionized water for 5 mins, respectively. Wafers then dried with Nitrogen gas. Cleaned wafers were placed on spin coater where CdO, 0.2 % Mn doped CdO, 6 % Mn doped CdO, 10 %Mn doped CdO solutions were drop cast on wafers. Drop cast mixtures were spin coated on 3000 rpm for 3s and thin films in CdO, 0.2 % Mn doped CdO, 6 % Mn doped CdO, 10 %Mn doped CdO structures were produced. Thin films were dried for 5 mins at room temperature then annealed at 450 °C. Al contacts were prepared by using PVD -HANDY/2S-TE (Vaksis Company) vacuum thermal evaporation in the pressure of 4.5×10^{-5} Torr. Result products in Al/CdO/p-Si/Al and Al/Mn:CdO/p-Si/Al were obtained. Preparation method was reported in our previous work please see the work for the details [29]. Electric and optoelectronic properties of photodiodes were investigated using FYTRONIX FY-7000 Solar Simulator I–V characterization system.

3. Results and Discussion

Surface, optical and some of electrical properties of CdO and Mn doped CdO thin films were discussed in our previous report please see the report for the details [29]. To sum up, both CdO and Mn doped CdO consist of flake like structures. However, it should be noted that 6 % Mn doped CdO films has slightly different surface characteristics which altered the electrical and optoelectric properties of the diodes. Structure, size and orientation of the flakes alters with different dopant rates. Transmittance of the thin films were found high for all samples. Energy bandgap of the CdO thin films showed decreasing trend with increasing Mn dopant rate. I-V characteristics show that diodes have rectifying behaviours. Ion/Ioff rates of the detectors were calculated no correlation between Mn dopant effect and Ion/Ioff rates. However, increased I_{on} /I_{off} rates were obtained with increased illumination intensity. In this report, capacitance and dielectric properties of the diodes were discussed.

Capacitance –time characteristics of the photodiodes investigated where illumination was turned on and off with 5 seconds intervals. Different degrees of illuminations changing from 20mW/cm^2 to 100mW/cm^2 were applied to the photodiodes. Application of illumination to the photodiodes increased measured capacitance rapidly when the illumination was shut off measured capacitance dropped suddenly. Capacitance–time (C-t) characteristics were found to be coherent with the current – time (I – t) characteristics. Both undoped and Mn doped CdO thin films respond to the illumination where capacitance of the photodetectors alters with changing illumination. For all samples, the highest capacitance obtained in the 100 mW/cm2 illumination where the lowest capacitance was found at 20 mW/cm2 illumination. In figure 1, capacitance – time characteristics of the 0.2 % Mn doped CdO photodetectors was assessed. Minimum capacitance degree was obtained for the 20 mW/cm^2 and maximum capacitance was obtained for 100 mW/cm^2 illumination. Increasing capacitance was seen for increasing illumination. Minimum capacitance was measured around 4.9 nF at 20 mW/cm^2 and maximum capacitance was measured around 5.8 nF. Figure 2 illustrates the capacitance – time characteristics of the 6 % Mn doped CdO photodiodes. Increasing capacitance was measured for increasing illumination intensities. Minimum capacitance measured at 20 mW/cm^2 as 3.8 nF, maximum capacitance was measured at 100 mW/cm^2 at around 5 nF. Figure 3 shows C - t curves of 10 % Mn doped CdO photodetectors. Enhanced capacitance measured for the increased illumination where minimum capacitance measured at 20 mW/cm^2 as 3.8 nF and maximum capacitance measured at 100mW/cm^2 as 5.8 nF. Capacitance values of doped photodiodes for different illumination intensities were presented in table 1. Capacitance of 6 % Mn doped CdO photodiodes were found slightly lower than that of other Mn doped CdO photodiodes. No correlation between measured capacitance and Mn doping rate was obtained.

Table 1: Capacitance values Mn doped photodiodes for different illumination.

Sample	0.2 %	6 %	10 %
Illumination	Mn CdO	Mn CdO	Mn CdO
20 mW/cm^2	4.9 nF	3.8 nF	3.8 nF
40 mW/cm^2	5.3 nF	4.4 nF	4.7 nF
60 mW/cm^2	5.5 nF	4.6 nF	5.2 nF
80 mW/cm^2	5.7 nF	4.8 nF	5.6 nF
100 mW/cm^2	5.8 nF	5 nF	5.8 nF

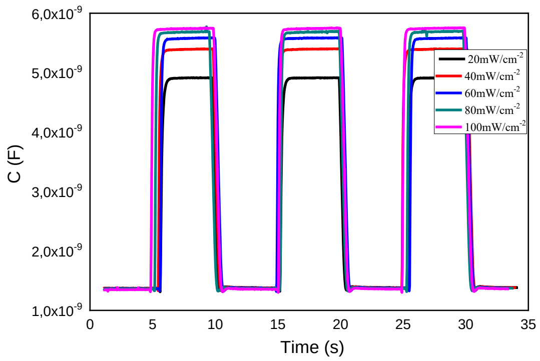

Figure 1: *Capacitance – time (C - t) characteristics of 0.2 % Mn doped CdO photodetectors.*

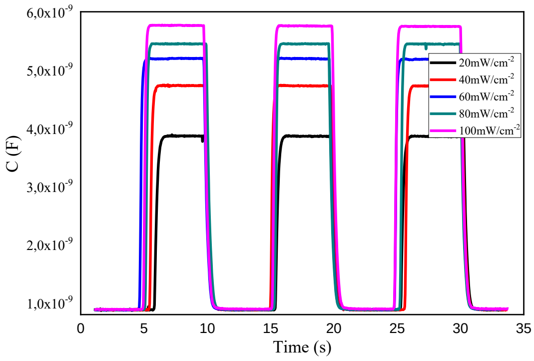

Figure 3: *Capacitance – time (C - t) characteristics of 10 % Mn doped CdO photodetectors.*

Frequency dependent dielectric permittivity–voltage graphs were obtained for undoped CdO, 0.2 % Mn doped CdO, 6 % Mn doped CdO and 10 % Mn doped CdO were presented in figure 4, 5, 6 and 7, respectively. The values of relative permittivity (ε') were calculated using the following equation

$$\varepsilon' = \frac{Ct}{\varepsilon_0 A}$$

where C is the capacitance of the sample, t is the thickness of the sample, ε0 is the dielectric permittivity of the vacuum $\varepsilon_0 = 8.856\times10^{-14}$ Fcm^{-1} and A is the area of cross-section of the sample [37].

When each graph was investigated, it was seen that Mn dopant slightly enhanced the ε’. In the backward bias, ε′ was stayed almost constant and effect of frequency change was slightly low. Significant effect of Mn dopant was not seen. All in all, decreasing ε’ was obtained for increasing frequency. For the undoped CdO photodiodes, a slight bump was seen between 1V and 1.5V. For the Mn doped CdO photodiodes, peaks in the forward bias region, becomes more apparent. Peaks were seen between 0.5 V and 1.5 V. For the low AC signal frequencies (frequencies lower than 100 KHz), separation obtained for ε’ becomes more apparent. When the AC signal frequency was increased, separation diminishes. Moreover, increased AC signal frequency result in reduced ε’ in the forward bias region. The position of the peaks alters depending on Mn dopant rate. The position of peaks obtained between 0.5 V and 1 V. For the reduced AC signal frequency, increased dielectric permeability was obtained. Such increase at low voltage and low AC signal frequencies indicates the accumulation of charges at interface states which result in interfacial polarization [38]. Such charges accumulate on the interface states, since lower AC signal frequencies at low voltage degrees cannot transport them [39].
Therefore, immobile charges become polarize and behave like a capacitor where dielectric properties of the diodes change and peaks at lower voltages at low AC signal frequencies were seen.

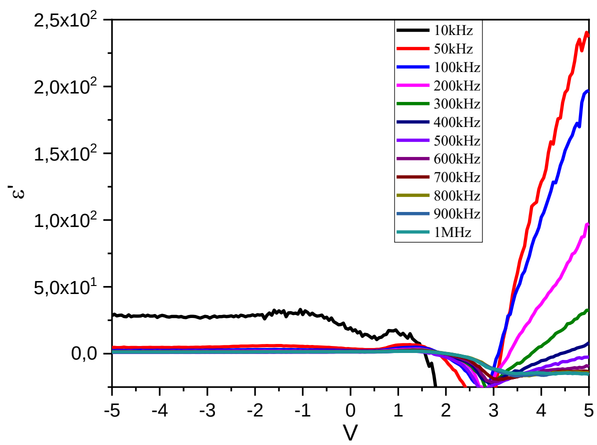

Figure 4: *ε′ -V characteristics of undoped CdO photodiode*

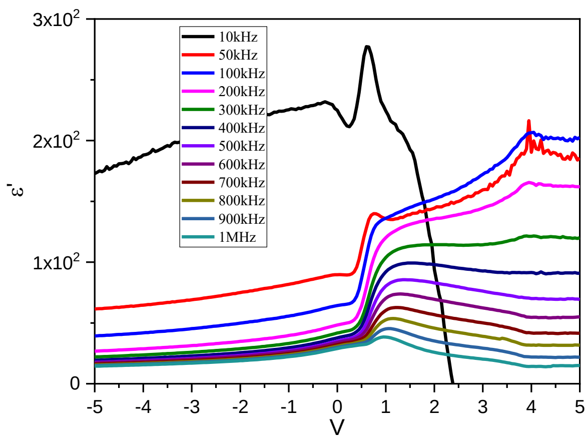

Figure 5: *ε′ -V characteristics of 0.2 % Mn doped CdO photodiode*

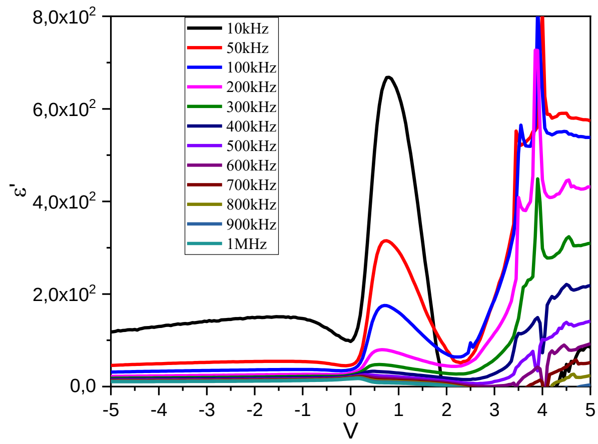

Figure 6: *ε′ -V characteristics of 6 % Mn doped CdO photodiode*

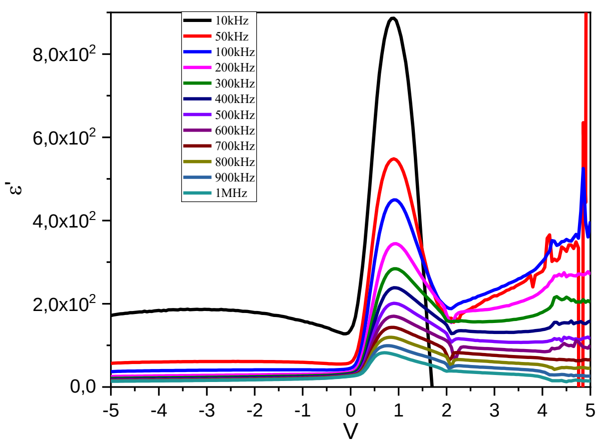

Figure 7: *ε′ -V characteristics of 10 % Mn doped CdO photodiode.*

Frequency dependent dielectric resistance – voltage (ε" -V) graphs were obtained for undoped CdO, 0.2 % Mn doped CdO, 6 % Mn doped CdO and 10 % Mn doped CdO were presented in figure 8, 9, 10 and 11, respectively.

It is well known fact that there is complex dielectric constant was known as

ε*= ε'+i ε"

where ε' and ε" are the real and imaginary part of the dielectric constant, respectively.

The values of dielectric resistance (ε") were obtained using the following equation

ε"= ε'. D.

When the graphs were investigated, it was seen that in the reverse bias region no separation was observed at ε". All in all, increased ε" were seen for increased AC signal frequency. In the forward bias region separation becomes prominent for different AC signal frequency. Mn doping slightly enhances the measured ε" in the reverse bias region. However, apparent increased ε" cannot be observed for increased Mn dopant in the reverse bias region. Dramatic ε" increase in the forward bias region was seen in the forward bias region between 0 V and 1 V. For the higher AC signal voltage, a separation occurs for different AC signal frequencies. In the forward bias region, increased ε" were observed for increased AC signal frequencies.

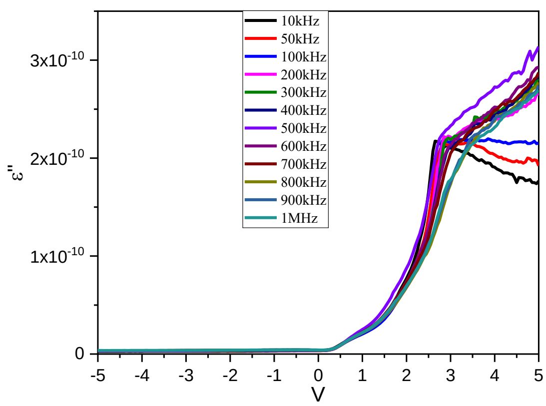

Figure 8: *ε" - V characteristics of undoped CdO photodiode.*

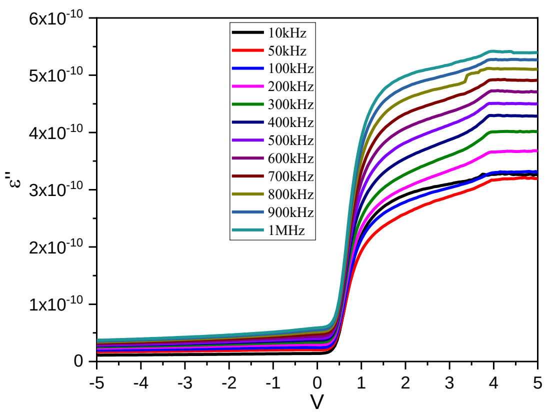

Figure 9*: ε" - V characteristics of 0.2 % Mn doped CdO photodiode.*

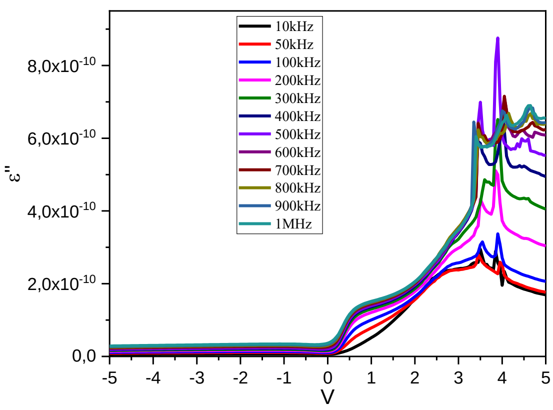

Figure 10: *ε" - V characteristics of 6 % Mn doped CdO photodiode.*

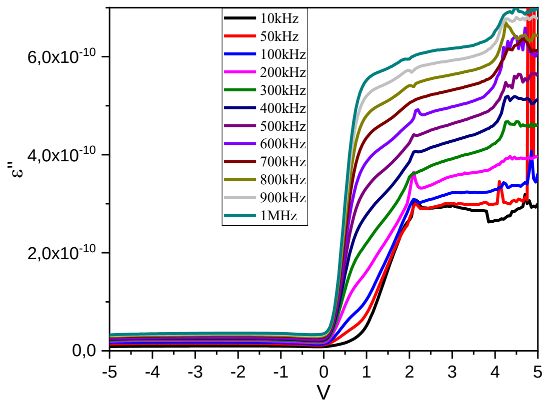

Figure 11: *ε" - V characteristics of 10 % Mn doped CdO photodiode.*

Conclusion

Mn dopant effect upon capacitance and dielectric properties of CdO photodiodes were assessed in this report. Capacitance of the photodiodes increased rapidly when illumination was applied to the diodes. When the illumination was turned off, measured capacitance drops suddenly. Capacitance – time graphs showed that photodiodes are responsive for the lights and increased capacitance were measured for increased illumination. ε' and ε'' dielectric properties were also assessed. ε' properties indicate that Mn dopant slightly increased the ε' properties where increased ε' were obtained for decreased AC signal frequency. For the forward bias, peaks were seen at low AC signal frequencies at low voltages. Such peaks indicate the existence of interfacial polarization which affects the dielectric properties of the CdO photodiodes. ε'' - V graphs show increasing ε'' trend with decreasing AC signal frequencies. Mn doing slightly enhanced the dielectric properties.

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