Conductance and Density of Interface State Characteristics of Mn Doped CdO Photodiodes

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ABSTRACT

Sol-gel technique was used to fabricate cadmium oxide and manganese doped cadmium oxide solutions which were used to produce thin films. 10% manganese doped, %6 manganese doped, %0.2 manganese doped and undoped cadmium oxide solutions were spin-coated on Si wafers to fabricate photodiodes. Conductance – voltage (G – V) measurements were performed. Mn doping enhances the conductance properties of the CdO diodes. Increased conductance characteristics were obtained with increasing AC signal frequency. Corrective conductance – voltage (G adj – V) graphs were obtained using conductance voltage graphs. Increased corrective conductance (G adj) values were obtained with increasing AC signal frequency. Using corrective conductance – voltage (G adj – V) and conductance – voltage (G - V) data density of interface states (Dit) characteristics of the diodes were assessed. Different density of state values was obtained for the different photodiodes. The density of state values was found to increase with increased Mn doping.

Key Words: CdO Thin Films, Mn Doping, Photodiodes, G - V, G adj - V, Density of Interface States

Mn Katkıtı CdO Fotodiyotların İletkenlik ve Arayüz Durumu Karakteristikleri

ÖZET

İnce film üretiminde kullanılan CdO ve Mn katkıtı CdO çözeltiler Sol-gel yöntemi kullanılarak üretildı. Katkısız, %0.2 Mn katkıtı, %6 Mn katkıtı ve %10 Mn katkıtı CdO çözeltileri spin kaplama yöntemi kullanılarak silisyum tabakalar üzerine fotofiyot üretim amacı ile kaplandı. İletkenlik – voltaj (G - V) ölçümleri gerçekleştirilirdi. Mn katkısının CdO fotodiyotlarının iletkenlik özelliklerini iyileştirdiği görüldü. Artan AC sinyal frekansı ile iletkenlik karakteristiğini de artış gösterdiği tespit edildi. Düzeltilmiş iletkenlik – voltaj (G adj – V)ografikleri, iletkenlik – voltaj grafikleri kullanılarak elde edildi. Artan AC sinyal frekansı ile düzeltilmiş iletkenlik değerlerini de artış gösterdiği analiz edildi. Düzeltilmiş iletkenlik – voltaj ve iletkenlik – voltaj grafikleri kullanılarak arayüz durum yoğunluğu değerleri elde edildi. Üretilen farklı fotodiyotlar için farklı arayüz durum yoğunluğu değerleri var olduğu anlaşıldı. Arayüz durum yoğunluğu değerlerinin Mn katkısını ile arttığı keşfedildi.

Anahtar Kelimeler: CdO İnce Filmler, Mn Katkıtı, Fotodiyotlar, G - V, G adj - V, Arayüz Durum Yoğunluğu
I. INTRODUCTION

Nanotechnology is an essential part of developing technology where scientists from different fields such as Physics, Biology, Material Science, and Engineering use nanotechnology for various applications [1], [2]. Nanoparticles and nanostructures are the driving force of nanoscience and nanotechnology [1], [3], [4]. Thin films are vastly used in different electric and electronic applications such as detector, sensor, display, and nanoelectronics technologies regarding their electronic, optic and magnetic properties [5]–[14]. Moreover, thin films can also be used as decorative and protective purposes [15], [16]. Depending on their chemical and physical properties organic and inorganic films may find an application on different subjects [17]–[19]. Metal-oxide (MO) thin films are an essential research field, since characteristics of metal oxide thin films are well known [20]. Moreover, magnetic electric and electronic properties of the metal-oxide films can easily be tuned [21], [22]. Different metal-oxide films were used for different applications, for example, Zn and Pt-based thin films provide good electric and optoelectronic properties; on the other hand, Fe, Co, Ni and Cr based thin films provide good magnetic and magneto-optic properties [13], [14], [23]–[28]. In addition, electric, electronic and magnetic behaviours of metal-oxide films can be tuned by doping them with materials and/or producing alloy and composite structures [26], [29]–[33]. Cd based thin films have an important role among metal and metal-oxide thin films where they are frequently used in detector, sensor and photodetector, solar cell and LED applications [28], [34]–[43]. Mechanic, electric, electronic and optoelectric properties of the Cd are well studied [44]–[46]. Moreover, previously tuning the electric electronic and optoelectric structures and properties of the CdO (cadmium oxide) thin films were reported. For example, various elements like F, B, Au, Ag, Bi, Cr, Pb, etc were used in the doping procedure [39], [47]–[54]. Reports indicate that doping the CdO based thin films with different atoms enhances the electric electronic and physical properties of the thin films. For example, in our previous study doping CdO thin films with Mn significantly improve the electric and photoresponsive properties of thin films [55]. Other studies showed that doping CdO thin films with F decreased the bandgap energy, Al doping decreased the optical bandgap [39], [48].

CdO thin films have good electric, optic, electronic properties with low resistance and 2.5 eV bandgap energy and good transmittance [49], [55]. Hence, CdO thin films can be used at the solar cell, photodetector and photodiode implications. Previously, various methods have been reported for the production of Cd based films where magnetron sputtering, epitaxial methods, electrochemical deposition techniques were used [43], [47], [56]. It was a known fact that different deposition techniques provide different advantages and disadvantages. In this report, we used the sol-gel technique to produce Cd solutions where spin coating techniques were used to coat Cd solutions to Si wafers. Undoped and manganese doped cadmium oxide thin films were manufactured for photodiode purposes. Mn dopant effect upon conductance and corrective conductance characteristics were studied. Such characteristics affect the behaviour of the photodiodes where photocapacitance, photovoltaic, electric, electronic and optical properties of the photodiodes can be changed. The density of interface states plays an important role in such properties where charges trapped interface states alter overall characteristics of the thin films and diodes. Therefore, the density of interface states was calculated using the data obtained from conductance, and corrective conductance characteristics. Conductance characteristics of the photodiodes for altering AC signal frequency were obtained using Fytronix FY-7000 solar and electrical characterization device.
II. MATERIALS AND METHODS

A. PRODUCTION OF PHOTODIODES

Prior to thin film production procedure, undoped cadmium oxide and manganese doped cadmium oxide solutions were produced. Solutions were prepared via sol-gel method where cadmium acetate was dissolved in deionized water. Mn acetate in 0.2%, 6%, 10% of molar concentrations was added to three different cadmium oxide solutions to obtain manganese doped cadmium oxide solutions. Manganese doped and undoped cadmium oxide solutions were stirred until dissolved at 500 rpm. Aminoethanol was added to the solution as a stabilizer. Solutions were mixed using a magnetic stirrer for 1 hour. Before the coating procedure, p-type silicon wafers were cleaned. Sonication was applied to silicon wafers in alcohol for 5 mins and then wafers rinsed in deionized water for 5 mins. Silicon substrates were dried with nitrogen gas. Clean wafers were placed on spin coater and result products (Mn doped and undoped CdO solutions) were drop cast on different p-type Si wafers. Drop cast solution was spin coated for 3000 rpm for 3 sec where CdO 0.2% Mn doped CdO, 6% Mn doped CdO and 10% Mn doped CdO thin films were obtained. Films were dried at room temperature and 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. Al/CdO/p-Si/Al and Al/Mn:CdO/p-Si/Al photodiodes were obtained. Electric and optoelectronic properties of photodiodes were investigated using FYTRONIX FY-7000 Solar Simulator I – V characterization system.

III. RESULTS AND DISCUSSION

A. CONDUCTANCE CHARACTERISTICS

Optic, surface and electric properties of the Mn (manganese) doped cadmium oxide photodiodes were reported in our previous study [55]. Surface characteristics were assessed using AFM. Surfaces of both CdO and Mn doped CdO photodiodes were covered with flake like structures where the structures at the surface of 6% Mn doped CdO photodiodes were found to be slightly bigger than others. It was believed that such characteristics alter the electrical and optoelectronic characteristics of the photodiodes. Bandgap energies were calculated using transmittance data. It found out that increasing the manganese dopant rate decreased the bandgap energy of the CdO photodiodes. Photodiodes show rectifying characteristics. Ion/Ioff rates were calculated and no effect of Mn dopant was observed where enhanced illumination makes an increasing effect on Ion/Ioff rates. In this report, manganese dopant effect on conductance – voltage (G-V), corrective conductance – voltage (Gadj - V) were assessed for varying AC signal frequency. Using conductance and corrective conductance density of interface states of cadmium oxide and manganese doped cadmium oxide diodes were assessed.

(G – V) characteristics of the undoped cadmium oxide and manganese doped cadmium oxide photodiodes were investigated between -5 V and 5 V. Characteristics of the photodiodes were obtained for different AC signal frequency in the range between 10 kHZ and 1 MHz. Effect of voltage and AC signal frequency on G (conductance) were illustrated in figure 1, 2, 3 and 4 for undoped cadmium oxide 0.2% manganese doped cadmium oxide, 6% manganese doped cadmium oxide and 10% manganese doped cadmium oxide, respectively. In the backward bias region, no significant effect of AC signal frequency was observed where measured conductance stayed almost stable for both undoped and manganese doped cadmium oxide photodiodes. For the forward bias region, the conductance of the diodes shows a dramatic increase between 0.5 V and 2 V. A separation can be
observed on conductance characteristics depending on the AC signal frequency. Increased conductance was observed for increasing AC signal frequency, especially on forward bias region. Increased conductance characteristics with increased AC signal frequency indicate that frequency excites the charges and helps them to transport in the diode. Low conductance at low AC signal frequencies can be attributed to the interface states where charges may be trapped. The results indicate that the conductance characteristics of the CdO photodiodes were slightly enhanced with Mn doping. However, no relation was found between increased Mn dopant and enhanced conductance characteristics.

Figure 1: $G - V$ characteristics of undoped cadmium oxide photodiodes.
Figure 2: $G - V$ characteristics of 0.2% Mn doped cadmium oxide photodiodes.

Figure 3: $G - V$ characteristics of 6% Mn doped cadmium oxide photodiodes.
B. CORRECTIVE CONDUCTANCE CHARACTERISTICS

Corrective conductance – voltage (\(G_{adj} - V\)) behaviours of the undoped cadmium oxide and Mn doped cadmium oxide photodiodes were investigated between -5 V and 5 V. Corrective conductance characteristics of the photodiodes were obtained for different frequencies between 10 kHz and 1 MHz.

Corrective conductance (Gadj) were calculated using following formula

\[
G_{adj} = \frac{G_m^2 + (\omega C_m)^2}{\alpha^2 + (\omega C_m)^2} \alpha
\]

(1)

Where \(C_m\) and \(G_m\) are measured capacitance and measured conductance, respectively. \(\alpha\) is variable parameter which was defined below and \(\omega\) is angular frequency.

\(\alpha = G_m - [G_m^2 + (\omega C_m)^2]R_s\), where \(R_s\) is series resistance of photodiode. \(R_s\) was calculated by using the equation below [57]:

\[
R_s = \frac{G_{ma}}{G_{ma} + \omega^2 C_{ma}^2}
\]

(2)

Effect of voltage and AC signal frequency on conductance were illustrated in figure 5, 6, 7 and 8 for undoped cadmium oxide, 0.2% manganese doped cadmium oxide, 6% manganese doped cadmium oxide and 10% manganese doped cadmium oxide, respectively. In the backward bias region, no
significant effect of AC signal frequency was observed where measured conductance stayed almost stable for undoped cadmium oxide photodiodes. For the manganese doped cadmium oxide photodiodes, increased corrective conductance was observed for increased AC frequency. For the forward bias zone, the conductance of the diodes gives a peak between 0.5 V and 2 V. Position and width of the peak varies for each CdO photodiodes. The effect of Mn dopant on corrective conductance characteristics was not observed in terms of the position of peaks. A separation was observed on corrective conductance characteristics especially at low AC signal frequencies (10 kHz and 50 kHz). Increased corrective conductance was observed for increasing AC signal frequencies at forward bias region. The separation observed at low AC signal frequencies may be an indication of the existence of interface states. Especially at low frequencies charges cannot be transported and stuck at interface states exiting in the structure of the thin films. Such stuck affect the electrical and electronic properties of the diodes. Increased AC signal frequencies help charges to be transported. Regarding the Conductance behaviours of the diodes the density of interface states (Dit) were calculated. Signal frequency excites the charges and helps them to transport in the diode. Low conductance at low AC signal frequencies can be attributed to the interface states where charges may be trapped. The results indicate that the conductance characteristics of the CdO photodiodes were slightly enhanced with Mn doping. However, no relation was found between increased Mn dopant and enhanced conductance characteristics.

![Graph](image_url)

*Figure 5: Gadj - V characteristics of undoped cadmium oxide photodiodes.*
Figure 6: $G_{adj}$ - $V$ characteristics of 0.2% Mn doped cadmium oxide photodiodes.

Figure 7: $G_{adj}$ - $V$ characteristics of 6% Mn doped cadmium oxide photodiodes.
C. THE DENSITY OF INTERFACE STATE CHARACTERISTICS

The density of interface states ($D_i$) of the diodes were calculated using Hill-Coleman method. Since charges at low AC signal frequency trapped by the interface states, calculated $D_i$ was expected to be found higher at low AC signal frequencies. $D_i$ was calculated using the following formula

$$D_i = \left(\frac{2}{qA}\right)\frac{G_{max}/\omega}{[G_{max}/\omega C_{ox}+(1-C_{max}/C_{ox})^2]^2}$$

In the formula, $A$ is the surface area of the photodiode, $C_m$ represents the measured capacitance, $C_{ox}$ is the insulator layer capacitance, $G_m$ shows measured conductance and $\omega$ represents the angular frequency which is equal to $2\pi f$. And the density of states characteristics for undoped cadmium oxide, 0.2% manganese doped cadmium oxide, 6% manganese doped cadmium oxide, 10% manganese doped cadmium oxide were presented at figure 9, 10, 11 and 12, respectively. No significant effect of Mn doping was observed upon the density of interface states where undoped and manganese doped cadmium oxide photodiodes showed almost similar behaviours. Overall, the density of states showed decreasing characteristics with increasing AC signal frequency.
**Figure 9:** Density of interface states of undoped cadmium oxide photodiodes.

**Figure 10:** Density of interface states of 0.2% Mn doped cadmium oxide photodiodes.
IV. CONCLUSION

In this work, Mn dopant effect on conductance and density of state characteristics of cadmium oxide photodiodes were studied. A conductance graph was obtained for doped and undoped cadmium oxide photodiodes where increasing conductance was obtained for increasing AC signal frequency. For the
backward bias zone, separations were not obtained for undoped cadmium oxide for altering AC signal frequencies. Manganese doped cadmium oxide photodetectors showed an apparent enhancing conductance trend for augmenting AC signal frequency. Corrective conductance was calculated using conductance data where apparent peaks were seen in the forward bias region. Increased corrective conductance behaviour was seen for increased AC signal frequency for both undoped and Mn doped CdO photodiodes. The density of interface states was calculated using conductance characteristics. Decreasing $D_s$ characteristics were seen for increasing AC signal frequency. Overall, the apparent positive effect of Mn dopant on conductance and density of interface states was not observed for CdO photodiodes.

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