Influence of Annealing Times on the Structural and Optical Dispersion Parameters Properties of Thermally Cadmium Telluride Films

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Abstract
Thin CdTe films had been prepared by thermal evaporation technique on glass substrate under vacuum of about 10^{-5} mbar. The thicknesses of the films were 900±5 nm. The films were annealed at different duration (60, 90, and 180) minute. The X-ray pattern showed that the prepared and annealed films were polycrystalline structure cubic phase with preferred orientation at (111) plane. Absorbance spectra of the films indicates that the films had high absorption at the visible region. The optical studies revealed that the transition was direct with band gap value decreased from 1.47 eV to 1.36 eV with increasing the duration of annealing. Also, the optical constant such as refractive index, extinction coefficient and real and imaginary parts of dielectric constant were determined. The refractive index dispersion curves obeyed to the single oscillator's model. The dispersion energy and single-oscillator energy varied with the duration of annealing. The moments of optical spectra had been studied. The infinite refractive index increased from 2.60 to 3.84 with increasing the duration of annealing.

Key Word: CdTe Film, Thermal Evaporation, XRD, UV-VIS Spectrum, Single Oscillator Model

1. Introduction
Semiconductors of II-VI thin films are mostly used in many semiconductor photoelectronic devices such as photo-electrochemical cells, photodetectors, field effect transistors (FETDs), photodiodes, and photovoltaic solar cells [Hernandez et al. 2004; Fritsche et al. 2003; Romeo et al. 2000]. Cadmium telluride (CdTe) semiconductor is one of the most promising polycrystalline materials for photovoltaic devices such as solar cells thin film due its optical and electrical properties. It has a direct band gap that can be varied in the range of 1.5 to 2.1 eV which is covering the most range of the peak emission power of the solar spectrum, therefore such materials were suitable for photovoltaic and photoelectronic applications [Gur et al. 2005; Morales 2006]. They are also excellent using in the thermoelectric applications, because these materials have very low thermal conductivity [Bao et al. 2005]. Also, CdTe thin films have very high absorption coefficient more than 10^{5} cm^{-1} in the wavelength of 700 nm makes even it absorbs more than 90% of light energy which is corresponding to the energy gap of CdTe thin films. [Morgan, 2002] thus making it useful for solar cell applications.
There are many methods which are used to prepare CdTe films such as vacuum deposition [Khairnar et al., 2003; Bakr, 2002; Sathyamoorthy et al., 2003], electro deposition [Mathew et al. 2004], molecular beam epitaxy [Ringel et al. 1991], metal-organic chemical vapor deposition [Chu, et al., 1992], closed-space sublimation [Hernandez et al., 2004], and screen-printing [Nakano et al. 1986]. The vacuum evaporation technique is the most one used because it has some advantages such as: the amount of impurities included in the growing layer will be minimized, the tendency to form oxides will be considerably reduced and finally straight line propagation will occur from the source to substrate. The method has been employed by us for preparation of the CdTe thin films is thermal evaporation technique. Because of the recrystallization, the lattice parameter of the CdTe sample shall be different from the commonly grown ones Consequently, one can expect the band parameters to differ from the commonly used ones.

In the present work, the structural optical and dispersion characteristics of CdTe thin films deposit on glass substrates are investigated as a function of the duration annealing under vacuum. The aim of the present work is to study the behavior of the films obey to which dispersion curve.

2. Experimental

Thin CdTe films have been deposited by thermal evaporation method using Edward E306A vacuum system under high vacuum of about 10^{-5} mbar on 7059 corning glass slides substrate which kept at room temperature. Molybdenum boat has been used as a source. Prior to deposit on glass substrates, it should be cleaned ultrasonically with acetone, demonized water, and finally dried by air blower. The thicknesses (t) of the prepared films are measured using fizue method which is 900±5 nm. The crystalline structure of CdTe films is analyzed using (SHIMADZU 6000 X-ray diffractometer system) which records the intensity as a function of Bragg’s angle. The source of radiation is CuKα with wavelength (λ=1.5406Å), current (30 mA) and voltage (40 kV). The scanning angle 2θ is varied in the range of (20–50) degree with a speed of 4 deg/min. The optical properties have measured by using a double beam UV-VIS spectrophotometer type Perkin-Elmer Lambda 900. Transmittance and Reflectance spectra have been recorded in the wavelength range 300-900 nm. The effect of duration times on the optical properties and dispersion parameters of CdTe thin films have been studied. The optical absorption has been measured after each annealing process.

3 Results and Discussion

3.1 X-ray Diffraction Studies

X-ray diffraction (XRD) pattern of thin CdTe film prepared at RT and annealed to different duration of times (60, 120, 180) minutes with thickness of 900 nm is illustrated in Fig.1. From the figure, it can be noticed that XRD pattern of the CdTe films exhibits polycrystalline consists of mixture of cubic (C) and hexagonal (H) phases according to ASTM cards with display strong reflections at (111)C, (102)H and (311) Planes with the preferred diffraction peak is observed at 2θ = 23.7° which corresponds to the cubic (111) orientation. The direction of (111) plane is coincided packing direction of the zinc blende structure and it is know that this type of textured growth has often been noticed in the polycrystalline CdTe thin films deposited on amorphous substrates [Gordillo et al. 1995]. This result is in agreement with many researches [Heiba et al., 2003; Arizpe et al. 1999; Pandey et al. 2005; Hyeong et al. 2003; Al Dhafiri, 2001, De Morure; et al.2012]. Also, it can be obtained that there is
not peak of diffraction corresponding to metallic Cd, Te, or other compounds are noticed.

![Image: X-ray diffraction pattern of a deposited and annealed thin CdTe films at different duration times.](image)

**Fig. (1):** The X-ray diffraction pattern of a deposited and annealed thin CdTe films at different duration times.

For all cases of deposit films, one can be noticed that the preferred orientation growth along the (111). Also, it has cleared from the figure that the intensities of the peaks increase when the duration times of annealing increase. This can be attributed to increase in the concentration when the duration times of annealing increase and then the crystallite size increases. The crystallite size dimensions (D) can be calculated from the Debye Scherer equation [Osuwa *et al.*, 2009]:

$$D = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where \(k\) is the shape factor, which is approximately 0.9 and \(\beta\) is the line broadening of pure diffraction profile on 20 in radius and equal to the full width at half maximum intensity (FWHM) of the peak and \(\lambda\) is the wavelength. Such crystallinity improvements with increasing the time of annealing have been observed by Al-Dhafiri [Al Dhafiri, 2001], Enriquez and Mathew [Enriquez and Mathew, 2004]. The improvement of crystal structure may be due to that the annealing produce an excess of Te atoms, which they are usually not bounded in the CdTe site. This lead to enhance the density of Te vacancies, then the Cd and Te atoms will be rearranged in the CdTe crystallites [Al Dhafiri, 2001; Rusu and Rush, 2000]. Also it can be observed that the formation of Te oxides as TeO$_3$ and TeO$_2$ oxides, which may due to evaporate of the highly volatile Te, then the vacancies have been created in the lattice and provide possible way for oxygen to diffuse into the lattice [Heiba *et al*. 2003]. The thermally grown oxides begun to disappear with increasing the duration times of annealing. One can be observed that there is no diffraction peaks observed corresponding to any oxides after annealed for 180 minutes. Oxygen diffusion into II-VI semiconductors up on annealing was assumed by many authors Heiba [Heiba *et al.*, 2003], Enriquez and Mathew [Enriquez and Mathew, 2004], Sundari *et al* [Sundari *et al.*, 2000] and Pérez *et al* [Bartoo *et al.*, 2001]. The incorporation of oxygen into the CdTe lattice site has no preferential substitution for Cd or Te atoms, as the radius of oxygen atom of $65\times10^{-12}$ m is smaller than Cd atom of $169\times10^{-12}$ m and Te atom of $207\times10^{-12}$ m [Heiba *et al.*, 2003; Moutinho *et al*. 1995], the oxygen atoms substitution may shrink the lattice which it finally distorted. However, the increasing of duration times of annealing produces an increase in the crystallite size of
CdTe films, as given in Table 1, this agree with Kokate et al [Kokate et al., 2007]. The lattice constant (a) of the films are approximately 5.89Å. This value of lattice constant is very near from the bulk value of CdTe and this is indicated that films deposited on the glass substrate without stresses at the interface. The values of interplaner distance (d) nearly agree with that of ICCD cards. Also, from the results of XRD, it can be determined the micro strain (S), dislocation density (δ) and the numbers of crystalline per unit area (N), respectively using the following relations [Jenkis and Snyder, 1996]

$$S = \beta \cos\theta / 4$$  \hspace{1cm} (2)

$$\delta = 1 / D^2$$  \hspace{1cm} (3)

$$N = t / D^3$$  \hspace{1cm} (4)

Where t is film thickness. It is notice that the duration of annealing decreases the strain, dislocation density and the number of crystallites the in the films. The increasing of crystallite size leads to increase the surface area of each grain, which leads to increase the pores among the grains and reduce the pore per unit area on each two adjacent grains, i.e. reduce the strain, then improves relaxed media as given in Table 1. Thus, the number of crystallites increases and the dislocation density decreases with increasing the annealing of duration times.

Table (1): X-ray diffraction parameters of (111) plane of a deposited and annealed CdTe films at different annealing of duration times.

<table>
<thead>
<tr>
<th>Films</th>
<th>D (nm)</th>
<th>S×10^4</th>
<th>δ×10^13 (Lines/m²)</th>
<th>N×10^14 (m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>as deposited</td>
<td>165.75</td>
<td>19.08</td>
<td>3.64</td>
<td>1.98</td>
</tr>
<tr>
<td>60 min</td>
<td>240.35</td>
<td>13.16</td>
<td>1.73</td>
<td>0.65</td>
</tr>
<tr>
<td>120 min</td>
<td>282.76</td>
<td>11.18</td>
<td>1.25</td>
<td>0.39</td>
</tr>
<tr>
<td>180 min</td>
<td>436.99</td>
<td>07.24</td>
<td>0.52</td>
<td>0.11</td>
</tr>
</tbody>
</table>

The results of XRD are quantified by defining the texture coefficient $T_c(hkl)$ . We can calculate the degree of preferred orientation of CdTe films from the intensities of preferred peaks using the of Harris method for polycrystalline texture analysis [Harris, 1952]. This factor can be calculated for each orientation using the following equation [Harris, 1952]:

$$T_c(hkl) = \frac{n I_{(hkl)} / I_{(hkl)}}{\sum_n I_{(hkl)} / I_{(hkl)}}$$  \hspace{1cm} (5)

Where, $I_{(hkl)}$ is the measured peak intensity of (khl), $I_{0(hkl)}$ is the relative corresponding peak intensity of a powder reference and n is the number of peaks (here n =5). When $T_c(111) = n$, which interrupted all the films grain of CdTe which are oriented in the (111) plane, and lower values of $T_c(111)$, mean random orientation. Figure 2 shows the variation of texture coefficient as a function of duration times. It can be noticed that the reduction of time duration, leads to decrease $T_c(111)$ and become close to 2.
3.2 Optical Properties

The absorbance and transmittance spectra of a deposited and annealed CdTe films measured in the range 0.34-0.9 µm at different annealing of duration times as have been shown in Figure 3. It is noticed that the prepared films display high absorption at wavelength range (0.58 -0.62 ) µm known as absorbing region.

The absorption coefficient (α) of thin CdTe films can be calculated from the following relation [Neamen, 1992]:

\[ \alpha = \frac{1}{t} \ln \left( \frac{I_0}{I} \right) \]  

Where \( I_0 \) and \( I \) are the incident and transmitted intensities beam, respectively. Fig. 4 shows the variation of \( \alpha \) as a function of photon energy for CdTe films at different duration of annealing. In general, it can be observed from this figure that the absorption coefficient exhibits high values >10⁴ cm⁻¹ in the shorter wavelength gives an indication that the transition allows direct transition [Brodsky et al. 1997]. Also, from Figure 4 it is clear that the value of absorption coefficient decreases with increasing the duration of times and this leads to the shifts spectrum of absorption coefficient to the smaller energies (i.e longer wavelength) compared to the deposited films.
The optical band gap of the films is calculated using Tauc equation [Hummel, 2011]:

$$\alpha h\nu = B (h\nu - E_g)^r$$

(7)

Where B is energy independent constant and r is used to find the type transition to allow indirect or direct transitions by plotting the relations \((\alpha h\nu)^{1/2}\), \((\alpha h\nu)^{1/3}\), \((\alpha h\nu)^{2/3}\), and \((\alpha h\nu)^2\) versus photon energy \((h\nu)\). It is found that the relation for \(r=1/2\) yields linear dependence, which describes the allowed direct transition in this transition process, the total energy and momentum of the electron–photon system must be conserved [Neamen, 1992]. \(E_g\) is then determined by the extrapolation of the portion at \((\alpha =0)\). The values of the direct optical band gap \((E_g)\) values of the CdTe thin films are obtained from the intercept of \((\alpha h\nu)^2\) as function of photon energy \((h\nu)\) curves plotted as shown in Fig.5 and their values are given in Table 2. It is cleared from this figure that the values of \(E_g\) have decreased with increasing duration of times of annealing, this may explained on the basis of the fact that the heat treatment makes CdTe samples more transparent or less absorbing to the incident light. Also it can be attributed this behavior to decrease disorder present in the structure, which occurring by annealing, then redistribution of tails from band to tail .Thus, allows a great number of possible band to tail and from tail to tail transitions, which lead to decrease optical energy gap [Mott and Davis, 1979]. The energy independent constant \((B)\) has been obtained from the root square of the straight line in Tauc slope \(((\alpha h\nu)^2\ vs.\ photon\ energy)\). The \(B\) values have tabulated in Table 1. Our results show that \(E_g\) decreased with increasing the annealing temperature. \(B\) is inversely proportional to non-crystallinity and width of tail states [Mott and Davis, 1979]. The decreasing of \(B\) suggests an increasing of non-crystallinity.
Fig. (5): The variation of \((\alpha h\nu)^2\) with photon energy and the absorption coefficient as a function of wavelength of deposited and annealed thin CdTe films at different duration times.

We know that the extinction coefficient depends mainly on absorption coefficient according to the relation \((k = \alpha \lambda / 4\pi)\). Figure 6 shows the variation of extinction coefficient as a function of wavelength for CdTe as a function of duration of times of annealing. The behavior of extinction coefficient \((k)\) is nearly similar to the corresponding absorption coefficient. The rapid increasing in the extinction coefficient at the wavelengths below nearly 0.7 µm is due to the rapid change in the absorption coefficient in the vicinity of the absorption edge (i.e. high absorbance) of CdTe films in that region and in the visible range, extinction coefficient is decreasing slightly with increasing wavelength for all samples.

Fig. 6: The variation of extinction coefficient as a function of wavelength of as deposited and annealed thin CdTe films at different duration times.

The variation of refractive index \((n)\) as a function of the wavelength for CdTe films at different duration times of annealing is shown in Figure 7. In general the figures show two regions: in the first region the refractive index of the films increases with increasing wavelength up to a certain values depended on annealing times, after that wavelength (second region), exceeding the wavelength which associated a slightly decreased in the refractive index of the films. This may be due to the increase of pores when films are annealed at high annealing time. Also, figures depict
systematic shift of the refractive index peak towards higher wavelength i.e lower energy gap as the annealing time increases.

**Fig.(7): The variation of refractive index as a function of wavelength of as deposited and annealed thin CdTe films at different duration times.**

The variation of the real ($\varepsilon_r$) and imaginary part ($\varepsilon_i$) of dielectric constant versus wavelength in the range (0.34- 0.9) $\mu$m at different annealing times for CdTe films are shown in the Figure.8 and Figure.9, respectively. The variation of $\varepsilon_r$ and $\varepsilon_i$ with the increase of the wavelength of the incident radiation is due to the change of reflectance and absorbance . In general, it is observed that both $\varepsilon_r$ and $\varepsilon_i$ increase rapidly with increasing wavelength from 0.34 $\mu$m to a certain value depended on the annealing process and then decreased slightly with increasing wavelength.

**Fig.(8): The variation of real part of dielectric constant as a function of wavelength of as deposited and annealed thin Cd films at different duration times.**

**Fig.(9): The variation of imaginary part of dielectric constant as a function of wavelength of as deposited and annealed thin CdTe films at different duration times.**
Table (2): Some optical parameters of as deposited and annealed thin CdTe films at different duration times measured at $\lambda=860$ nm.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_g$ (eV)</th>
<th>k</th>
<th>n</th>
<th>$\varepsilon_r$</th>
<th>$\varepsilon_i$</th>
<th>$\alpha \times 10^4$ (cm$^{-1}$)</th>
<th>$B \times 10^3$ (cm$^2$/eV)</th>
<th>$E_u$ (meV)</th>
<th>$B \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>1.47</td>
<td>0.026</td>
<td>2.21</td>
<td>4.89</td>
<td>0.12</td>
<td>0.39</td>
<td>13.53</td>
<td>242.13</td>
<td>106.80</td>
</tr>
<tr>
<td>60 min.</td>
<td>1.46</td>
<td>0.028</td>
<td>2.26</td>
<td>5.09</td>
<td>0.13</td>
<td>0.41</td>
<td>13.90</td>
<td>246.30</td>
<td>104.99</td>
</tr>
<tr>
<td>120 min.</td>
<td>1.41</td>
<td>0.034</td>
<td>2.37</td>
<td>5.63</td>
<td>0.16</td>
<td>0.49</td>
<td>9.08</td>
<td>332.23</td>
<td>77.84</td>
</tr>
<tr>
<td>180 min.</td>
<td>1.36</td>
<td>0.038</td>
<td>2.45</td>
<td>5.99</td>
<td>0.19</td>
<td>0.56</td>
<td>5.33</td>
<td>442.48</td>
<td>58.44</td>
</tr>
</tbody>
</table>

The energy width of Urbach tail in the localized states inside the optical band gap is related to the films structure disorder [Brodsky et al., 1997]. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach. The Urbach tail of the films has determined by the following relation [Urbach, 1953]:

$$\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)$$  \hspace{1cm} (8)

Where $h\nu$ is the photon energy, $\alpha_0$ is constant and $E_u$ is interpreted as the width of the tails of localized states in the gap region (Urbach energy). $\alpha_0$ and $E_u$ can be evaluated by plotting of $\alpha$ in logarithmic scale as a function of photon energy $h\nu$. The reciprocal of the slope of of Fig. 10 yields the magnitude of $E_u$. Fig. 10. shows the variation of $\ln \alpha$ as a function of photon energy for the CdTe thin films. This behavior corresponds to optical transitions between occupied states (in the valence band tail) to unoccupied states (in the conduction band edge). Urbach energy value has calculated from the reciprocal of the slope.

![Fig.(10): The variation of $\ln \alpha$ as a function of photon energy of as deposited and annealed thin CdTe films at different duration times.](image-url)
The value of Urbach energy related inversely with optical band gap $E_g$ of the films and decreases with increasing of duration times of annealing, as shown in table 2. The dependence of the optical absorption coefficient with photon energy may arise from electronic transitions between localized states [Hummel, 2011]. The density of these states falls off exponentially with energy is consistent with the theory of Tauc [Hummel, 2011], so that equation 2 can be written as the following:

$$\alpha = \alpha_0 \exp \left( \frac{\beta}{k_B T} \right)$$

(9)

Where $\beta$ is called the steepness parameter, $k_B$ is Boltzmann's constant and $T$ is the absolute temperature which is measured at room temperature. This parameters can be calculated from the relation $\beta = (k_B T/E_u)$.

If the width of the edge has related to the slope of figure 10, the value of $\beta$ is tabulated in the Table (2). It is clear from the table that the steepness parameter increases with increasing the duration of times of annealing.

The refractive index dispersion data are calculated according to the single-effective oscillator model [Didomenico and Wemple, 1969] and developed by Didomenico and Wemple. The model suggests that the refractive index, $n$, of the films could be correlated to the oscillator energy, $E_o$ and the dispersion energy $E_d$ and by the following formula:

$$n^2 - 1 = \frac{(E_o E_d)}{[(E_o)^2 - (h\nu)^2]}$$

(10)

where $E_d$ is a single oscillator constants which called dispersion energy, and measures the intensity of the inter band optical transitions, $E_o$ is the energy of the effective dispersion oscillator. The oscillator energy $E_o$ is an average of the optical band gap. Experimental verification of Eq. (5) can be obtained by plotting $(n^2-1)^{-1}$ versus $(h\nu)^2$ as illustrated in Figure. 11 which yields a straight line for normal behavior having the slope $(E_o E_d)^{-1}$ and the intercept with the vertical axis equal to $E_o/E_d$. $E_o$ and $E_d$ values are determined from the slope, $(E_o E_d)^{-1}$ and intercept $(E_o/E_d)$ on the vertical axis.

We know that the oscillator energy is related to the optical energy gap by an empirical formula [Cody, 1984]. It is clear from the tables that the value of $E_o$ increases as the energy gap increases when increasing of duration times of annealing means. These results are very important because they show that the optical and dispersion parameters changed with annealing temperature.
Fig.(11): The variation of \((n^2 - 1)^{-1}\) as a function of the square of photon energy of as deposited and annealed thin CdTe films at different duration times.

The single-oscillator model suggested that the single oscillator parameters \(E_0\) and \(E_d\) are related to the imaginary part of the dielectric constant, these moments \(M^{-1}\) and \(M^{-3}\) can be derived from the following relations [Wemple and Didomenico, 1969]:

\[
E_d^2 = \frac{M^{-1}}{M^{-3}} \quad (11)
\]
\[
E_0^2 = \frac{M^{-3}}{M^{-2}} \quad (12)
\]

From table 3, it can be observed that the values of \(M^{-1}\) and \(M^{-3}\) moments increase with increasing of duration times of annealing. For the definition of the dependence of the refractive index \(n\) on the light wavelength \(\lambda\), the single-term Sellmeier relation can be used [Wolaton and Moss, 1963]:

\[
\frac{n_{\infty}^2 - 1}{n_{\infty}^2} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2
\]

(13)

Where \(\lambda_0\) is the average oscillator position and \((n_{\infty})\) is refractive index at infinite wavelength which is determined by plotting of \((n^2 - 1)\) vs. \(\lambda^2\). The values of \(n_{\infty}\) have been found within the range 2.60 - 3.84, which is deceased with increasing of duration times, as given in Table 3.

Table (3): Dispersion parameters of as deposited and annealed Thin CdTe films at different duration times.

<table>
<thead>
<tr>
<th>Samples</th>
<th>(E_0) (eV)</th>
<th>(E_d) (eV)</th>
<th>(M^{-1})</th>
<th>(M^{-3}) (eV)(^2)</th>
<th>(n_{\infty})</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>1.84</td>
<td>1.22</td>
<td>0.66</td>
<td>0.19</td>
<td>2.60</td>
</tr>
<tr>
<td>60 min.</td>
<td>1.84</td>
<td>1.15</td>
<td>0.62</td>
<td>0.18</td>
<td>2.66</td>
</tr>
<tr>
<td>120 min.</td>
<td>1.79</td>
<td>0.62</td>
<td>0.35</td>
<td>0.11</td>
<td>3.27</td>
</tr>
<tr>
<td>180 min.</td>
<td>2.18</td>
<td>0.78</td>
<td>0.36</td>
<td>0.07</td>
<td>3.84</td>
</tr>
</tbody>
</table>
4 Conclusions

CdTe films are prepared on glass substrate using thermal evaporation technique. The results of the optical properties suggest that the films have direct optical band gap, which decreased as duration of times of annealing increased. Urbach energy of the films changes inversely with optical band gap. The refractive index dispersion curve of CdTe thin film obeys the single-oscillator model. The single oscillator parameters $E_o$ and $E_d$ are calculated by applying the Wemple DiDomenico (WDD) model. The calculated optical band gaps increase with increasing of annealing times. The increase of energy gap may be attributing to the increase in crystallites size. The increase of grain size with annealing process can be attributed to the improved crystallinity of the film because of the annealing process which led to it more homogeneous films. It minimizes the number of defects and localized states, and thus the optical band gap increases. The dispersion energy and single-oscillator energy for as deposited films are found to be 1.94 eV and 1.91 eV respectively and changed to 0.81 eV and 1.29 eV respectively with increasing the duration times of annealing.

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