CDZNS/CUALO₂ TEMPERATURE DEPENDENCE OF CURRENT-VOLTAGE CHARACTERISTICS OF CDZNS/CUALO₂ HETEROJUNCTION DIODE

Thitinai Gaewdang¹, Ngamnit Wongcharoen¹, Atthaporn Ariyarit¹, Adison Nopparuchikun¹, Tiparatana Wongcharoen¹, Chaisingh Poo-Rakkiat³

¹School of Physics, Faculty of Science, King Mongkut’s Institute of Technology Ladkrabang.
²Department of Electrical Engineering, School of Engineering, Bangkok University.
³Department of Physics, Faculty of Science, Chulalongkorn University.

บทคัดย่อ

ในงานวิจัยนี้ได้ทำการประยุกต์รูปแบบต่อวิธีพื้นฐาน CdZnS/CuAl₂O₄ โดยการระดับฟิล์มบาง CdZnS ด้วยความร้อนเคลือบแบบแผ่นอะตอมที่เป็นเชิงมิติกของ CuAl₂O₄ การแพร่พื้นในรอบรุ่น กิจวัสดุในตรวจสอบอุณหภูมิ 350 องศาเซลเซียสเป็นเวลา 60 นาทีจะทำให้ได้ระยะต่อวิธีพื้นฐาน ที่มีสมบัติได้ทำการศึกษาลักษณะเฉพาะของกระแส-แรงดันไฟฟ้าของระยะต่อวิธีพื้นฐาน CdZnS/CuAl₂O₄ ภายใต้สภาพในอุณหภูมิในช่วง 20–300 เคลขวิน และได้ทำการคำนวณหา พร้อมทั้งอิเล็กทรอนิกส์ที่สำคัญของระยะต่ออินเดีย ค่าความสูงของก้าวที่ซีด แปลงจุดอุณหภูมิ และความ ถ้านมอนภูมิเป็นต้น ความสูงของก้าวที่ซีด และพร้อมทั้งอิเล็กทรอนิกส์ที่สำคัญโดยอาศัยทฤษฎี เทคโนโลยีอิเล็กทรอนิกส์สับสนว่ามีค่าเท่ากับอุณหภูมิอย่างมาก จากข้อมูลการทดลองยังพบอีกว่าเมื่อ อุณหภูมิมีผลต่อความสูงของก้าวที่ซีดที่แรงดันในอัตราส่วนกับชายจะมีค่าลดลง แต่พร้อมทั้ง อุณหภูมิมีค่าเท่าที่จะมีความหนาแน่นของพอลิอิิเธอร์ของฟิล์มบาง CdZnS คำนวณได้จากการวัดความจุ- แรงดันไฟฟ้าในช่วงอุณหภูมิ 20–300 เคลวิน อีกทั้งยังทำบรรยายคำนวณหาค่าความหนาแน่นของ สถานะระหว่างระยะต่อของโลหะจากลักษณะเฉพาะของความจุ-ความถี่ไฟพัดกรณ์ได้สภาวะ ในอุณหภูมิที่อุณหภูมิหนึ่ง

คำสำคัญ: ฟิล์มบาง CdZnS, โดโลโมหิตต่อวิธีพื้นฐาน CdZnS/CuAl₂O₄, ลักษณะเฉพาะกระแส- แรงดันไฟฟ้า, ลักษณะเฉพาะความจุ-แรงดันไฟฟ้า
CdZnS/CuAlO$_2$ heterojunction diode was prepared by thermal evaporating CdZnS thin films on CuAlO$_2$ ceramic substrate. Successful heterojunction was obtained by annealing in a pure nitrogen atmosphere at 350°C for 60 min. The forward current–voltage characteristics of CdZnS/CuAlO$_2$ heterojunction was studies in a temperature range of 20–300 K. We have tried to determine some important parameters such as barrier height, ideality factor and series resistance values. The apparent barrier height and ideality factor calculated by using thermionic emission (TE) theory were found to be strong temperature dependence. Evaluation of forward I–V data reveals a decrease in the zero-bias barrier height, but an increase in the ideality factor with decrease in temperature. The variation of carrier concentration in CdZnS thin films evaluated from C–V measurements in a temperature range of 20–300 K. The interface state density of diode has also been calculated from the forward bias capacitance–frequency characteristics at room temperature.

**Keywords**: CdZnS thin films, CdZnS/CuAlO$_2$ heterojunction diode, I–V characteristics, C–V characteristics

**Introduction**

Transparent p–n junctions are of great interest in realization transparent electronics. Some studies on transparent p–n junctions such as p–SrCu$_2$O$_2$/n–ZnO, CuCrO$_2$/ZnO, CuYO$_2$/ZnO and CuAlO$_2$/ZnO have been reported [1]. It is considered that their performance is restricted by the p–type material. The report of p–type conductivity in transparent CuAlO$_2$ compound has attracted much attention. Several similar compounds, which have the delafossite structure like CuAlO$_2$, have been recently reported [2]. Transparent p–n heterojunction diodes exhibiting a rectifying I–V characteristics were fabricated using a combination of p–CuAlO$_2$/n–Zn$_{1-x}$Al$_x$O [2]. Cd$_{0.6}$Zn$_{0.4}$S thin films are considered at present one of the most promising material for photovoltaic device applications. It has high absorption coefficient in the visible range of solar spectrum and its band gap around 2.8 eV is closed to the optimum value for efficient solar energy conversion [3].
Aims

In this article, we fabricated a new heterojunction diode composed of p-CuAlO$_2$ and n-Cd$_{0.6}$Zn$_{0.4}$S semiconductor compounds. The electrical properties and rectifying behavior of CdZnS films on CuAlO$_2$ ceramic substrate will be discussed, using the thermionic emission (TE) theory and tunneling enhanced recombination mechanisms at various temperatures, in an attempt to obtain information on the transport mechanisms of the device.

Materials and Methods

Polycrystalline of CuAlO$_2$ were prepared by a conventional solid state reaction. The starting materials, CuO (99.9%) and Al$_2$O$_3$ (99.9%) were mixed in agate mortar and pressed into pellet form with 1 mm thickness and sintered at 1423 K in air for 48 h. The crystal structure of samples was confirmed by reading X-ray diffraction patterns on a powder X-ray diffractometer using CuK$_{\alpha}$ radiation ($\lambda = 1.5418\,\text{Å}$) at room temperature. Cd$_{0.6}$Zn$_{0.4}$S thin films, abbreviated as CdZnS thin films, have been deposited by thermal evaporation of stoichiometric mixture of high purity CdS and ZnS powder in vacuum better than $5 \times 10^{-5}$ mbar without heating CuAlO$_2$ ceramic substrate. The film thickness with 500 nm was monitored by a quartz crystal thickness monitor (Edward type FTM6). Successful heterojunction was obtained by annealing in a pure nitrogen atmosphere at 350°C for 60 min. Ohmic contact was made of silver paste on the surface of CdZnS and on the back surface of CuAlO$_2$. The I–V characteristic curve was measured by using a computer interfaced Keithley 236 current/voltage source. The C–V measurements were carried out by Agilent E4980A Precision LCR Meter with reverse bias from −1.2–0 V at various temperatures and frequency fixed at 750 kHz.

Results

In the literature reviews, CdZnS compound has a higher resistivity than CuAlO$_2$ and carrier concentration of CdZnS ($<10^{14}$ cm$^{-3}$) is lower than CuAlO$_2$ ($>10^{16}$ cm$^{-3}$) about 3 order. Therefore, in the view of large different carrier concentration between CdZnS and CuAlO$_2$, it may be assumed that this heterojunction act as nearly a step junction. Therefore, it may assumed
that the current through a diode at a forward bias $V$, based on the thermionic emission (TE) theory, is given by the relation [4]

$$I = I_s \left[ \exp \left( \frac{qV}{nKT} \right) - 1 \right]$$

and

$$I_s = A^* A^* T^2 \exp \left( -\frac{q \phi_{BO}}{kT} \right)$$

where $I_s$ is the saturation current derived from the straight line intercept of the semilogarithmic $I$-$V$ plot at $V=0$, $V$ is forward bias voltage, $R_s$ is series resistance, $T$ is the absolute temperature, $q$ is the electronic charge, $k$ is Boltzmann constant, $A$ is the effective area, $A^* = \frac{4\pi q m_e k^2}{\hbar^3}$ is the effective Richardson constant of $20 \text{ A cm}^{-2}\text{K}^{-2}$ for n-CdZnS, where $m^* = 0.16 m_e$ is the effective mass of the electrons, $\phi_{BO}$ is the apparent barrier height at zero bias voltage and $n$ is the ideality factor. From Eq. (1), the ideality factor $n$ which is given by

$$n = \frac{q}{kT} \left( \frac{dV}{d(\ln I)} \right)$$

The measured $I$-$V$ plot of CdZnS/CuAlO$_2$ diode at different temperatures are shown in Figure 1. We have performed least square fits of Eq. (1) to the linear part of the measured semilogarithmic $I$-$V$ plots (Fig. 2) within bias voltage about $0.2-0.5$ V. From these fits, the experimental values of $I_s$ and $\phi_{BO}$ were determined at different temperatures. Once $I_s$ is known, the zero bias barrier height ($\phi_{BO}$) can also be computed with the help of Eq. (2). Using Eqs. (2) and (3), the experimental values of the ideality factor and the barrier height were determined and tabulated in Table 1. The CdZnS/CuAlO$_2$ diode with a large value of $n$ is far from ideal due to the presence of a thick interfacial layer and the interface states [4]. The non-linearity of $I$-$V$ characteristics at high bias value indicated a continuum of interface states, which equilibrated with the bulk of semiconductor. The current curve in forward bias quickly becomes dominated by series resistance from contact wires or bulk resistance of the semiconductor, giving rise to the curvature at high current in the semilogarithmic $I$-$V$ plot.
Table 1  Important parameters determined from I–V characteristics of CdZnS/CuAlO₂ diode at various temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Iₛ (A)</th>
<th>Ideality Factor (n)</th>
<th>Barrier Height (φₓ) (eV)</th>
<th>Series Resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I-V</td>
<td>dV/dln(I)-V</td>
<td>I-V</td>
</tr>
<tr>
<td>20</td>
<td>2.89E-07</td>
<td>127.90</td>
<td>250.02</td>
<td>0.035</td>
</tr>
<tr>
<td>60</td>
<td>2.81E-07</td>
<td>41.00</td>
<td>80.69</td>
<td>0.117</td>
</tr>
<tr>
<td>100</td>
<td>2.84E-07</td>
<td>26.64</td>
<td>48.24</td>
<td>0.201</td>
</tr>
<tr>
<td>140</td>
<td>2.35E-07</td>
<td>18.22</td>
<td>34.38</td>
<td>0.292</td>
</tr>
<tr>
<td>180</td>
<td>3.20E-07</td>
<td>15.89</td>
<td>26.69</td>
<td>0.379</td>
</tr>
<tr>
<td>220</td>
<td>2.64E-07</td>
<td>11.17</td>
<td>21.44</td>
<td>0.475</td>
</tr>
<tr>
<td>260</td>
<td>3.30E-07</td>
<td>10.10</td>
<td>17.96</td>
<td>0.563</td>
</tr>
<tr>
<td>280</td>
<td>3.42E-07</td>
<td>9.30</td>
<td>16.41</td>
<td>0.609</td>
</tr>
<tr>
<td>300</td>
<td>4.23E-07</td>
<td>8.87</td>
<td>14.69</td>
<td>0.651</td>
</tr>
</tbody>
</table>

Figure 1  The measured I–V plot of CdZnS/CuAlO₂ diode at various temperatures.
The series resistance $R_s$ is an important parameter in the electrical characteristics of diode. This parameter is significant in the downward curvature (non linear region) of the forward bias I–V characteristics, but the other two parameters ($n$ and $\phi_{BO}$) are significant in both the linear and non linear regions of the I–V characteristics. An efficient technique to determine $R_s$, $n$ and $\phi_{BO}$ has been proposed by Cheung [4]. From Eq. (1) the following functions can be written as

$$dV/d(ln I) = \frac{nkT}{q} + IR_s \quad (4)$$

$$H(I) = V - n \left(\frac{kT}{q}\right) \ln \left(\frac{I}{AA'T^2}\right) \quad (5)$$

And $H(I)$ is given as follows:

$$H(I) = n\phi_{BO} - IR_s \quad (6)$$

where $\phi_{BO}$ is the barrier height obtained from data of downward curvature region in the forward bias I–V characteristics. Experimental $dV/d(lnI)$–I and $H(I)$–I plots at various temperatures are presented in Figure 2.
3 and Figure 4, respectively. Eq. (4) should give a straight line for the data of downward curvature region in the forward bias I–V characteristics. Thus, a plot of \( \frac{dV}{d(\ln I)} - I \) will give \( R_s \) as the slope and \( nkT/q \) as the \( y \)-axis intercept. Using the \( n \) value determined from Eq. (4) and the data of the downward curvature region in the forward bias I–V characteristics in Eq. (5), a plot of \( H(I) - I \) will also lead to a straight line with the \( y \)-axis intercept equal to \( n\phi_{BO} \). The slope of this plot also determines \( R_s \), which can be used to check the consistency of this approach. Furthermore, the values of \( R_s \) obtained from \( \frac{dV}{d(\ln I)} - I \) and \( H(I) - I \) plots are in good agreement with each other as seen in Table 1. This case shows the consistency of Cheung’s approach. As seen from Table 1, the calculated \( n, \phi_{BO} \) and \( R_s \) were found to be as strongly temperature dependent. Ideality factor greater than 1 has been attributed to particular distribution of interfacial layer and interface states between CdZnS and CuAlO\(_2\). This value of \( \phi_{BO} \) calculated from forward bias I–V characteristics have shown an unusual behavior such that it increases with increasing temperature. As can be seen from Figure 5, the value of ideality factor \( n \) decreases while the \( f_{BO} \) increases with increasing temperature.

![Figure 3 dV/d(\ln I)–I plots of CdZnS/CuAlO\(_2\) diode at various temperatures.](image)
Figure 4  H(I)–I plots of CdZnS/CuAlO$_2$ diode at various temperatures.

Figure 5 The variation of $n$ as a function of temperature of CdZnS/CuAlO$_2$ diode.

The high value of the ideality factor show that there is a deviation from TE theory in the current conduction mechanism. The temperature dependence of $n$ suggests that the current conduction mechanism is controlled by the surface states are more pronounced because of the spatial distribution of the interfacial layer of CdZnS and CuAlO$_2$. Electron concentration of CdZnS layer around $4.2 \times 10^{14}$ cm$^{-3}$ at 300 K was obtained from the slope of $1/C^2$–V curve (Figure 6). This value slightly decreases when the temperature decreases.

If current transport is dominated by any of the thermally activated like injection, interface or space charge recombination, the forward current density of a heterojunction is generally determined by [5]
\[ J = J_0 \exp(\frac{qV}{nkT}) = J_{00} \exp(-\frac{E_a}{nkT}) \exp(\frac{qV}{nkT}) \quad (7) \]

where \( J_0 \) is the reverse saturation current density and \( J_{00} \) is a prefactor which depends on the transport mechanism.

For tunneling dominated current transport, the \( J-V \) relationship is generally express as

\[ J = J_0(T) \exp (AV) \quad (8) \]

The slope of the \( \ln J-V \) plot is essentially temperature independent and called as the voltage factor \( A \). At constant voltage, \( \ln J_0 \) is more nearly a linear function of temperature \( T \) than of \( T^{-1} \). Since thermally activated holes make step wise tunneling into interface states, \( J_0 \) is slightly thermally activated. A relatively new approach explaining the tunneling enhancement of recombination via deep centers in the space charge region or at heterojunction interface provides analytical expression for the forward current transport in CIGS based solar cells [5]. This model namely tunneling enhanced recombination in the bulk of the absorber or at the buffer–interface, assumes that the forward current of the heterojunction is also determined by Eq. (7). The value of the activation energy \( E_a \) can be deduced from experimental data by reorganizing Eq. (7) as

\[ \ln(J_0) = -\frac{E_a}{kT} + n\ln(J_{00}) \quad (9) \]

Thus, the activation energy \( E_a \) of the process can be calculated from the slope of a linear plot of \( \ln(J_0) \) versus \( 1/T \).

According to this model, \( E_a \) represents the interface barrier height for holes in the case of interface recombination. Tunneling of holes from the bulk of \( \text{CuAlO}_2 \) into the interface states and subsequent recombination with electrons available in \( \text{CdZnS} \) layer leads the temperature dependence of the diode ideality factor as

\[ n = \frac{(E_{00}/kT) \coth(E_{00}/kT)}{1} \quad (10) \]

where \( E_{00} \) is the characteristic tunneling energy measuring the amount of tunneling contribution to the recombination process. From Figure 5, the large value of \( E_{00} \) about 1 eV suggests that tunneling enhancement of recombination via deep centers at heterojunction interface provides analytical expression for the forward current transport in our diode.
The energy of interface states $E_{ss}$ with respect to the bottom of CdZnS conduction band at the interfacial layer between CdZnS and CuAlO$_2$ is given by [6]

$$E_c - E_{ss} = q (\phi_{BO} - V)$$ (11)

The density distribution curves of the interface states were obtained from experimental data of this region of forward bias I–V and given in Figure 7. As can be seen in Figure 7, slow growth of the interface state density towards the bottom of conduction band is apparent. This state agrees with distribution obtained in I–V characteristics [4].

Figure 6 $1/C^2$–V plots of CdZnS/CuAlO$_2$ diode at various temperatures.

Figure 7 The energy distribution of surface states of CdZnS/CuAlO$_2$ diode at room temperature.
Conclusions and Discussion

The forward bias I–V characteristics of CdZnS/CuAlO\textsubscript{2} were measured in the temperature range 20–300 K. The obtained n and $\Phi_{BO}$ determined by using TE theory were found to be a strong dependence of temperature. Using the evaluation of experimental I–V measurements reveals a decrease in n and an increase in $\Phi_{BO}$ with increasing temperature. The temperature dependence of n suggests that the current conduction mechanism is controlled by the surface states are more pronounced because of the spatial distribution of the interfacial layer of CdZnS and CuAlO\textsubscript{2}. In the view of tunneling enhanced recombination mechanisms, a large $E_{00}$ value about 1 eV were obtained from forward bias I–V curve at low temperature.

References


