

ลักษณะเฉพาะของกระแส-แรงดันไฟฟ้าที่ขึ้นกับอุณหภูมิของไดโอด รอยต่ออวิวิธพันธ์

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

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บทคัดย่อ

ในงานวิจัยนี้ได้ทำการประดิษฐ์รอยต่ออวิวิธพันธ์ CdZnS/CuAlO₂ โดยการระเหยฟิล์มบาง CdZnS ด้วยความร้อนเคลือบบนแผ่นรองรับที่เป็นเซรามิกส์ของ CuAlO₂ การแอนนีสในบรรยากาศ ก๊าซไนโตรเจนบริสุทธิ์ที่อุณหภูมิ 350 องศาเซลเซียสเป็นเวลา 60 นาทีจะทำให้ได้รอยต่ออวิวิธพันธ์ ที่มีสมบัติดี ได้ทำการศึกษาลักษณะเฉพาะของกระแส-แรงดันไฟฟ้าของรอยต่ออวิวิธพันธ์ CdZnS/CuAlO₂ ภายใต้สภาวะไบแอสตรงที่อุณหภูมิในช่วง 20-300 เคลวิน และได้ทำการคำนวณหา พารามิเตอร์ที่สำคัญของรอยต่ออันได้แก่ ค่าความสูงของกำแพงศักย์ แพลกเตอร์อุดมคติ และความต้านทานอนุกรมเป็นต้น ความสูงของกำแพงศักย์ และแพลกเตอร์อุดมคติคำนวณโดยอาศัยทฤษฎี เทอร์มิออนิกส์อิมิสชันพบว่าค่าขึ้นกับอุณหภูมิอย่างมาก จากข้อมูลการทดลองยังพบอีกว่าเมื่อ อุณหภูมิลดลงความสูงของกำแพงศักย์ที่แรงดันไบแอสเท่ากับศูนย์จะมีค่าลดลง แต่แพลกเตอร์ อุดมคติมีค่าเพิ่มขึ้น ความหนาแน่นของพาหะอิสระของฟิล์มบาง CdZnS คำนวณได้จากการวัดความจุ-แรงดันไฟฟ้าในช่วงอุณหภูมิ 20-300 เคลวิน อีกทั้งยังทำการคำนวณหาค่าความหนาแน่นของ สถานะระหว่างรอยต่อของไดโอดจากลักษณะเฉพาะของความจุ-ความถี่ฟอสลับภายใต้สภาวะ ไบแอสตรงที่อุณหภูมิห้อง

คำสำคัญ: ฟิล์มบาง CdZnS, ไดโอดรอยต่ออวิวิธพันธ์ CdZnS/CuAlO₂, ลักษณะเฉพาะกระแส-แรงดันไฟฟ้า, ลักษณะเฉพาะความจุ-แรงดันไฟฟ้า

Abstract

CdZnS/CuAlO₂ heterojunction diode was prepared by thermal evaporating CdZnS thin films on CuAlO₂ 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/CuAlO₂ heterojunction was studied 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/CuAlO₂ 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–SrCu₂O₂/n–ZnO, CuCrO₂/ZnO, CuYO₂/ZnO and CuAlO₂/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 CuAlO₂ compound has attracted much attention. Several similar compounds, which have the delafossite structure like

CuAlO₂, have been recently reported [2]. Transparent p–n heterojunction diodes exhibiting a rectifying I–V characteristics were fabricated using a combination of p–CuAlO₂/n–Zn_{1–x}Al_xO [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-CuAlO₂ and n-Cd_{0.6}Zn_{0.4}S semiconductor compounds. The electrical properties and rectifying behavior of CdZnS films on CuAlO₂ 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 CuAlO₂ were prepared by a conventional solid state reaction. The starting materials, CuO (99.9%) and Al₂O₃ (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_α radiation ($\lambda = 1.5418 \text{ \AA}$) 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 5×10^{-5} mbar without heating CuAlO₂ 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 CuAlO₂. 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 CuAlO₂ and carrier concentration of CdZnS ($< 10^{14} \text{ cm}^{-3}$) is lower than CuAlO₂ ($> 10^{16} \text{ cm}^{-3}$) about 3 order. Therefore, in the view of large different carrier concentration between CdZnS and CuAlO₂, 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]

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

$$\text{and } I_s = AA^*T^2 \exp(-q\phi_{BO}/kT) \quad (2)$$

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, $A^* = \frac{4\pi q m_e k^2}{h^3}$ is the effective Richardson constant of $20 \text{ A cm}^{-2} \text{ K}^{-2}$ for n-CdZnS, where $m^* = 0.16m_0$ is the effective mass of the electrons, ϕ_{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

$$n = \left(\frac{q}{kT} \right) \left(\frac{dV}{d(\ln I)} \right) \quad (3)$$

The measured I-V plot of CdZnS/CuAlO₂ 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 ϕ_{BO} were determined at different temperatures. Once I_s is known, the zero bias barrier height (ϕ_{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/CuAlO₂ 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.

T (K)	I _s (A)	Ideality Factor (n)		Barrier Height (ϕ_{BO}) (eV)		Series Resistance(k Ω)	
		I-V	dV/dln(I)-V	I-V	H(I)-I	d(V)/dln(I)-V	H(I)-I
20	2.89E-07	127.90	250.02	0.035	0.036	19.92	20.18
60	2.81E-07	41.00	80.69	0.117	0.120	17.36	20.17
100	2.84E-07	26.64	48.24	0.201	0.205	17.14	18.97
140	2.35E-07	18.22	34.38	0.292	0.300	16.43	18.36
180	3.20E-07	15.89	26.69	0.379	0.346	15.59	18.15
220	2.64E-07	11.17	21.44	0.475	0.516	14.93	16.75
260	3.30E-07	10.10	17.96	0.563	0.577	14.67	15.58
280	3.42E-07	9.30	16.41	0.609	0.640	9.36	12.27
300	4.23E-07	8.87	14.69	0.651	0.692	7.29	10.29

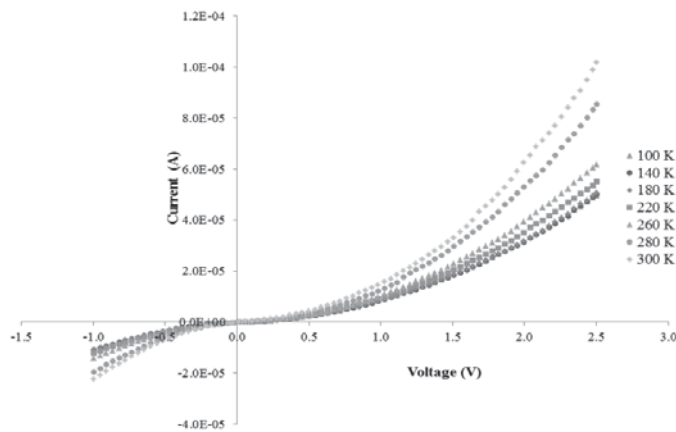


Figure 1 The measured I-V plot of CdZnS/CuAlO₂ diode at various temperatures.

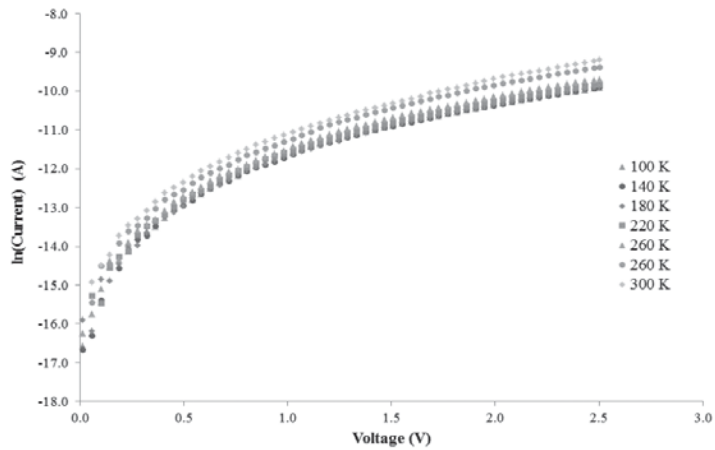


Figure 2 The semilogarithmic forward bias I-V plots of CdZnS/CuAlO₂ diode at various temperatures.

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 ϕ_{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 ϕ_{BO} has been proposed by Cheung [4]. From Eq. (1) the following functions can be written as

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

$$H(I) = V - n \left[\frac{kT}{q} \right] \ln \left[\frac{I}{AA^*T^2} \right] \quad (5)$$

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

$$H(I) = n\phi_B - IR_s \quad (6)$$

where ϕ_{BO} is the barrier height obtained from data of downward curvature region in the forward bias I-V characteristics. Experimental $dV/d(\ln I)$ -I and $H(I)$ -I plots at various temperatures are presented in Figure

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 $dV/d(\ln I) - I$ 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 $dV/d(\ln I) - I$ 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 , ϕ_{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 ϕ_{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.

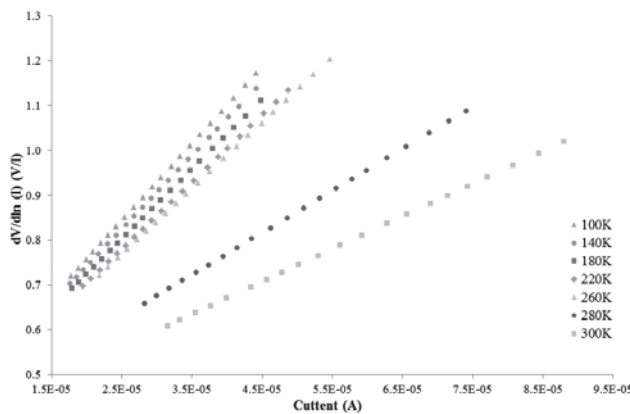


Figure 3 $dV/d(\ln I) - I$ plots of CdZnS/ $CuAlO_2$ diode at various temperatures.

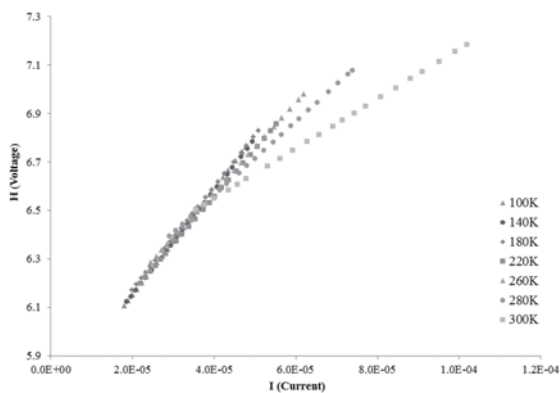


Figure 4 $H(I)$ - I plots of CdZnS/CuAlO₂ diode at various temperatures.

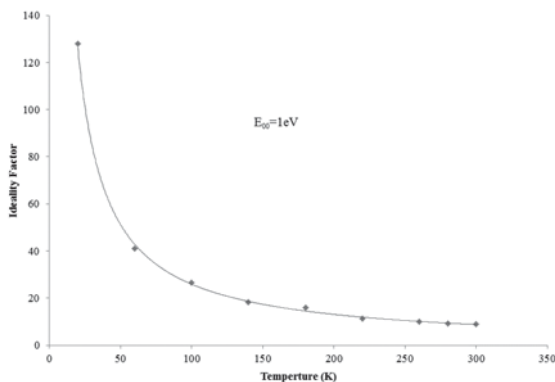


Figure 5 The variation of n as a function of temperature of CdZnS/CuAlO₂ diode.

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 CuAlO₂. Electron concentration of

CdZnS layer around $4.2 \times 10^{14} \text{ cm}^{-3}$ 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]

$$J = J_0 \exp(qV/nkT) = J_{00} \exp(-E_a/nkT) \exp(qV/nkT) \quad (7)$$

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

$$\ln(J_0) = -E_a/kT + \ln(J_{00}) \quad (9)$$

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 CuAlO_2 into the interface states and subsequent recombination with electrons available in CdZnS layer leads the temperature dependence of the diode ideality factor as

$$n = (E_{00}/kT) \coth(E_{00}/kT) \quad (10)$$

where E_{00} is the charateristic 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.

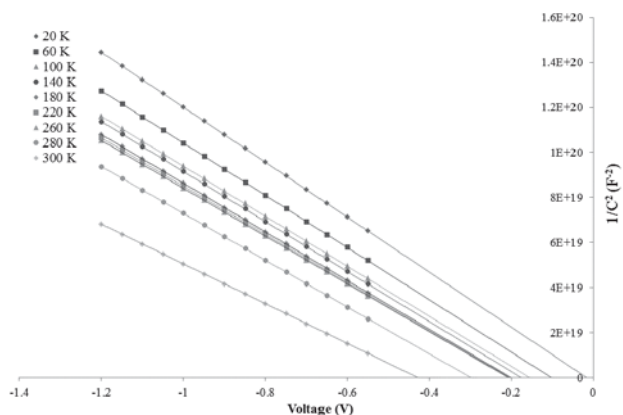


Figure 6 $1/C^2$ - V plots of CdZnS/CuAlO₂ diode at various temperatures.

The energy of interface states E_{SS} with respect to the bottom of CdZnS conduction band at the interfacial layer between CdZnS and CuAlO₂ is given by [6]

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

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].

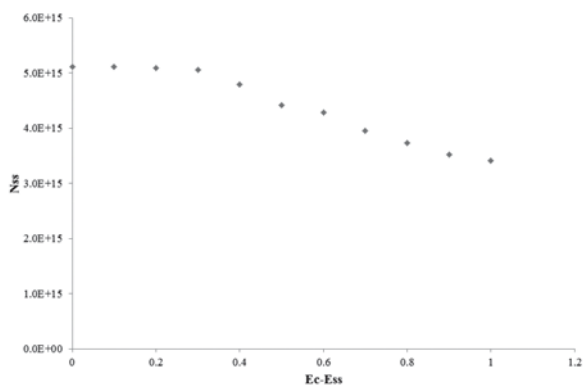


Figure 7 The energy distribution of surface states of CdZnS/CuAlO₂ diode at room temperature.

Conclusions and Discussion

The forward bias I-V characteristics of CdZnS/CuAlO₂ were measured in the temperature range 20–300 K. The obtained n and ϕ_{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 ϕ_{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 CuAlO₂. In the view of tunneling enhanced recombination mechanisms, a large E₀₀ value about 1 eV were obtained from forward bias I-V curve at low temperature.

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