Production and Electrical Properties of a CuZnAlMn(SMA)/p-Si Diode

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Research Article

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Production and Electrical Properties of a CuZnAlMn(SMA)/p-Si Diode

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Abstract

In this study, the Cu-23.37%Zn-13.73%Al-2.92%Mn (at.%) alloy was used. Phase identification was performed with the Scanning electron microscope (SEM), and energy-dispersive X-ray (EDX). We observed in the austenite phase in Cu-23.37%Zn-13.73%Al-2.92%Mn (at.%) alloy. To produce a new Schottky diode, CuZnAlMn alloy was exploited as a Schottky contact on p-type semiconductor silicon substrate. To calculate the characteristics of the produced diode, current-voltage (I-V), capacitance-voltage (C-V) and conductance-voltage (G-V) analyzes were taken at room temperature (300 K), in the dark and under various lights. Using electrical measurements, the diode's ideality factor (n), barrier height ($\Phi_b$), and other diode parameters were calculated. Besides, the conductance / capacitance-voltage (G/C-V) characteristics of the diode were studied and in a wide frequency interval at room temperature. Also, the capacitance and conductance values strongly rely on the frequency. From the present experimental results, the obtained diode can be used for optoelectronic devices.

Keywords: CuZnAlMn, Schottky diode, I-V characteristics, C-V characteristics, Illumination, frequency effect.

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1. Introduction

The existing SMAs (Shape Memory Alloys) are NiTi-, copper-, and ferrous-based SMAs. Cu-based SMAs are simple to fabricate, handle and are cheaper than NiTi alloys. They also have superior superelasticity and shape memory effect compared to Fe-based SMAs. Copper-based SMAs, owing to their excellent properties and low cost, have been highly attractive to various industries such as aerospace, automotive, and defense industries. Recently, the Cu-based SMAs have been more widely utilized due to their suitability for sensing, impact absorption, and vibration damping applications [1-5]. In copper-based SMAs, the atomic arrangement of the parent-phase change with the composition of the alloy and the applied effect. The Cu-based shape memory alloys (SMAs), a martensite transformation usually refers to a transformation from the disorder b.c.c. structure to the martensite phases. According to the different conditions and chemical composition, the three types of martensite can be acquired. These phases have structures of 6R, 18R and 2H, respectively [6-12]. Which phase prevails is dependent upon the electronic concentration e/a: for the e/a around 1.48, the 9R or 18R structure prevails; for the e/a below 1.48 (around 1.4), the 6R or 12R structure prevails; and for the e/a above 1.5, the 2H structure prevails [6, 7, 13].

Circuit elements based on metal-semiconductor contacts are produced from semiconductor materials of higher quality day by day and search for new materials are still going on. Making contacts of metals and alloys on semiconductor materials with advanced technological methods has facilitated the control of circuit element production. Metal-semiconductor contacts in semiconductor technology have a major role in the production of electronic circuit elements. Metal-semiconductor contacts are used in the production of field-effect transistors, solar cells, Schottky diodes, semiconductor detectors, switching elements, and microwave mixers. [14-18].
At first, the Cu-based SMAs were used as actuators and sensors in household appliances and electrical equipment. In recent years, the biomedical industry, transportation industry, and micro-electrical devices [19]. Even Schottky type semiconducting diodes and photodiodes can be fabricated from Cu-based SMAs with advanced technological methods. Some other researchers also investigated these properties with different compositions in CuAl based alloys [20-25].

In this survey, we produced a Schottky device based on a CuZnAlMn SMA. Nowadays, no such works have been reported for CuZn based alloys. So, a CuZn based alloy is used for the first time. For this reason, this study will make significant contributions to the literature. So our main aim was to produce a new Schottky diode by using the mentioned materials for modern optoelectronics.

2. Experimental details

The alloy with a composition of Cu-23.37\%Zn-13.73\%Al-2.92\%Mn (at.\%) was obtained melted by arc-melting and then induction melting. It was done in an argon atmosphere. The sample obtained from the alloy was exposed to homogenization at 800 °C for 1 hour followed by water quenching at room temperature. The SEM investigations, prepared samples were mechanically polished. After polishing, the sample was soaked in the FeCl₃·6H₂O methanol with HCl solution etching. Microstructural characterization analysis was carried out by SEM. The compositions of the prepared samples were analyzed by (EDX) operating within SEM. The diode was prepared using a p-type silicon (p-Si) wafer and Cu-23.37\%Zn-13.73\%Al-2.92\%Mn (at.\%) alloy. We have used consecutive chemical baths to clean a p/Si wafer. After the cleaning process, we deposited an ohmic contact to the backside of the Si wafer by thermal evaporation of the Aluminum (Al) wire. Subsequently, we performed annealing, to obtain Schottky dot contacts. The prepared CuZnAlMn SMA
was thermally evaporated on to the front of p-Si substrate. Finally, CuZnAlMn/p-Si/Al Schottky diode was fabricated. The contact area of the diode was measured as $7.85 \times 10^{-2}$ cm$^2$. The characteristic analyses I–V, C–V and G–V of diod were examined by FYTRONIX 5000 characterization system under changing frequencies. All experimental procedures were realized at room temperature.

3. Results and discussion

3.1 Microstructure of the alloy

The SEM micrographs in Fig.1 illustrate the microstructure of the Cu-23.37%Zn-13.73%Al-2.92%Mn alloy. Scanning electron micrograph (Fig. 1.a) indicates the presence of an austenite phase, which was confirmed through the EDS spectra in Fig. 1.b. In Fig.1, typical austenite grain boundaries exist for the alloy. It has been found from previous studies that quenching significantly affects the transformation properties [26-27]. For the Cu-23.37%Zn-13.73%Al-2.92%Mn alloy, the grain size of the alloy increases with the addition of Mn. Additionally, we observed that the Mn element prevents the formation of precipitation in the alloy.

3.2 Electrical Characterization

I–V measurements of the diode can be described by the thermionic emission model. According to this model, the current can be expressed as [28, 29],

$$I = I_0 \exp \left( \frac{q(V - IR_s)}{nkT} \right) \text{ for } (V \geq 3kT/q) \quad (1)$$

Here $I_0$ is given as,

$$I_0 = AA^*T^2 \exp \left( -\frac{q\Phi_b}{kT} \right) \quad (2)$$
where \( V \) is the applied voltage, \( R_s \) is the series resistance, \( q \) is the electronic charge, \( n \) is the ideality factor, \( k \) is the Boltzmann's constant, \( T \) is the temperature, where \( A \) is the Schottky contact area, \( A^* \) is the Richardson constant, and \( \Phi_0 \) is the zero-bias barrier height [30].

The \( n \) is given as,

\[
\frac{q}{kT} \left( \frac{dV}{d(\ln I)} \right)
\]  

In general, I-V graphs showing the characteristics of the contact are obtained by giving positive and negative voltages to the Schottky contacts. The forward bias part of these graphs, usually shown on the right, indicates that the contact conducts current with very little resistance. The reverse bias part, which is usually shown on the left of the graph, displays resistance increment with the relatively blocked current. Fig. 2 gives the I-V curves of the diode for conditions of dark and different solar light intensities. As seen in Figure 2, the diode reverses current changes with the light intensity. Also, the reverse current increases by the increment of light intensity. The photodiodes reverse current increases by \( 1.83 \times 10^{-3} \) A under 100 mW/cm\(^2\) (applied as the highest light intensity value). This result shows that electron-hole pairs formation in the depletion layer of a light-illuminated diode. Moreover, after photogeneration, the charge carriers contribute to the current through the diode. The current rises due to the generation of the photocurrent, and the current in the zero bias [31-34] also exists. Besides, this result suggests that the generated CuZnAlMn (SMA) / p-Si diode current changes depending on the light intensity and thus, it can be used for different applications in different optoelectronic circuits [35, 36].

From equation 3, the slope of the linear region of the forward-bias \( \ln(I) \)-V plot gives the \( n \) value. Table 1 lists the results of the \( \Phi_0 \) and \( n \) values obtained from the I-V method under dark and 100 mW/cm\(^2\) conditions. In their former work, the authors produced a diode and obtained the \( n \) of 3.52 and 3.31 under dark and 100 mW/cm\(^2\) respectively while
corresponding $\Phi_b$ were 0.58 and 0.59 eV [25]. In another study, the $n$ values for Au/CuAlMnFe/n-Si/Al diode were obtained to be as 3.92 ± 0.3 and 4.19 ± 0.3 and $\Phi_b$ were determined as 0.73 ± 0.2 and 0.69 ± 0.2 [21]. So, the $n$ value of our earlier p-type semiconductor (CuAlMn shape memory alloy diode) is greater than this work [23]. The $\Phi_b$ value was obtained as 0.58 eV for dark. The variety of the $\Phi_b$ values originate due to the different compositions of metallic alloys with separate work functions [21, 37]. Thus, the diodes $n$ was found to be bigger than its ideal value. A large $n$ value indicates that there is a small insulating layer (oxide, ie chemical pollution) between the metal and the semiconductor on the rectifier contact side of the diodes [38]. Also, large ideality factors are related to the magnitude of the ohmic contact resistance which is directly proportional to factors such as the density of the interfacial states and the magnitude of the series resistance ($R_s$) of the neutral zone. [39, 40]. The $n$ and $\Phi_b$ including $R_s$ are found from $dV/d(lnI)$ plot. Fig. 3 shows the plots calculated from Cheung's method and these parameters of the diode are summarized in Table 1. The plots in the graphs indicate straight lines. The uniformity of these parameters found from Cheung's method approves the $R_s$ effect.

Cheung's method can be obtained by the equation [41],

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

(4)

3.3 Photocurrent measurements of the diode

The photocurrent of CuZnAlMn/p-Si/Al Schottky diode was analyzed by equation 5 below [42, 43],

$$I_{ph} = AP^m$$

(5)

In Eq. 5, $P$ denotes the intensity of the light, $I_{ph}$ indicates the photocurrent, $A$ is a constant and $m$ represents an exponent. The $I_{ph}$ graph according to diode at -4V value is shown in
Figure 4. As in Figure 4, photocurrent varies with the intensity of light. It increases by the increasing light intensity. The slope of the linear photoconductivity graph affords the numerical m value of 1.23. The m value suggests the occurrence of photoconduction mechanism by the linear molecular recombination process [21].

The transient photocurrent-time analyses are common techniques to understand the photoconduction mechanism. Fig. 5. shows the characteristic of transient photocurrent characteristics for various illuminations. In the turned on illumination, photocurrent enhances rapidly to a definite position. In its turned off mode, the photocurrent diminishes suddenly and goes back to its initial position. In this way, this alteration in the current due to light displays that the produced photodiode has photoconductivity and can therefore be used as a photodiode or photosensor. [44-46].

3.4 C-V and G/ω-V measurements

Measurements of capacitance-voltage (C-V) and conductance-voltage (G/ω-V) for wide frequencies give valuable info about the basic electrical and dielectric properties of the prepared CuZnAlMn(SMA)/p-Si Schottky diode. Figure 6.a,b; in a wide frequency range (10 kHz-1MHz); shows the C-V and G/ω-V characteristics of the produced diode at room temperature (300 K). In both C-V and G/ω-V graphs of the diode, the measured C-V and G/ω-V are found to be frequency-dependent. As in Figure 6.a, when frequency increases, the capacity of the fabricated diode decrease. Further, it becomes almost constant in the negative voltage region. Unlike capacitance behavior, the measured G value increases after an increase in frequency (Fig. 6.b). The frequency characteristics for the C and G may be attributed to the presence of the interface states [47-51]. Because the interface states at low frequencies can follow the AC signal while they do not follow the AC signal at high frequencies [52]. So, the interface state capacitance value does not contribute to the total capacitance value which results only from the space charge capacitance.
Also, the $R_s$ of the diode was extracted from admittance measurements. The $R_s$ were calculated by using the Nicollian and Goetzberger conductance method [52, 53]. The $R_s$ was obtained from by equation 6,

$$R_s = \frac{G_{ma}}{G_{ma}^2 + (\omega C_{ma})^2} \quad (6)$$

In Eq. 6, $C_{ma}$ and $G_{ma}$ hold for the measured capacitance and conductance, respectively. Fig. 7 outlines the series $R_s$-V curves for different frequencies. This variation shows that the electrical loads at the interface can follow the frequency change depending on the applied voltage.

4. Conclusions

In this survey, copper-based the Cu-23.37%Zn-13.73%Al-2.92%Mn (at.%.) alloy was handled as a Schottky contact. Then, the SMA CuZnAlMn/p-Si/Al Schottky diode was fabricated. The microstructural properties of the SMA were characterized by SEM and EDS. The electrical properties of the Schottky diode were analyzed using the data obtained from the measurements made under different illumination intensities and a wide frequency range. The usual I-V characteristics and Cheung techniques have been used to explore several electrical features of the diode in the dark and under different illuminations. Thanks to the information provided from the I-V graph, we have concluded that the CuZnAlMn/p-Si/Al Schottky diode we prepared is sensitive to light. Both the $C$ and $G$ measurements were found to be strongly dependent on bias voltage and frequency for CuZnAlMn/p-Si/Al Schottky diode structure. According to the presently obtained results, we can also conclude the photoconductivity behavior of the presently fabricated diode. Therefore, the presently fabricated Schottky diode is promising for the practical applications of recent optoelectronics. The results obtained in this study may inspire the production of other Schottky diodes including different alloying elements.
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**Figure Chapter**

**Fig 1.** (a) SEM micrographs obtained for a quenched sample of CuZnAlMn alloy (b) EDX spectra obtained from the identified region in Fig 1.a.

**Fig. 2.** I-V plots under dark and different illuminations intensity.

**Fig. 3.** The plots of dV/d(lnI) versus I for dark and 100 mW/cm².

**Fig. 4.** Plot of $I_{ph}$-P of the diode (at -4 V).

**Fig. 5.** Transient photocurrent measurements of the diode under -1V.

**Fig. 6.** As a function of frequency of the diode (a) C/V (b) G/w-V plots.

**Fig. 7.** In various frequencies of the diode $R_s$-V plots.

**Table Chapter**

**Table 1.** The diode parameters derived from I-V and Cheung's methods.
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Tables;

**Table 1.** The diode parameters derived from I-V and Cheung's methods.

<table>
<thead>
<tr>
<th>$P$ (mW/cm$^2$)</th>
<th>$n$ (I-V)</th>
<th>$\Phi_b$ (eV) (I-V)</th>
<th>$n$ (dV/dlnI)</th>
<th>$R_s$ (Ω) (dV/dlnI)</th>
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</thead>
<tbody>
<tr>
<td><strong>Dark</strong></td>
<td>2.9</td>
<td>0.54</td>
<td>2.3</td>
<td>109.23</td>
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<tr>
<td><strong>100</strong></td>
<td>2.7</td>
<td>0.47</td>
<td>1.9</td>
<td>96.06</td>
</tr>
</tbody>
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I-V plots under dark and different illuminations intensity.
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The plots of $dV/d(\ln I)$ versus $I$ for dark and 100 mW/cm².
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Plot of $I_{ph}$-P of the diode (at -4 V).
Figure 5

Transient photocurrent measurements of the diode under -1V.
Figure 6

As a function of frequency of the diode (a) C/V (b) G/w-V plots.
Figure 7

In various frequencies of the diode Rs-V plots.