



Electrical properties of Al/CZTSe nanocrystal Schottky diode

Z. Kişnişçi^{1,*} , F. Özel², S. Karadeniz³, N. Tuğluoğlu³, S. S. Özel⁴, and Ö. F. Yüksel¹

¹ Department of Physics, Faculty of Science, Selçuk University, Campus, 42075 Konya, Turkey

² Department of Metallurgical and Materials Engineering, Faculty of Engineering, Karamanoğlu Mehmetbey University, 70200 Karaman, Turkey

³ Department of Energy Systems Engineering, Faculty of Engineering, Giresun University, Güre Campus, 28100 Giresun, Turkey

⁴ Central Research Laboratory (BUMER), Bayburt University, 69000 Bayburt, Turkey

Received: 16 February 2024

Accepted: 1 April 2024

Published online:
15 April 2024

© The Author(s), 2024

ABSTRACT

In this study, electrical changes in diode parameters of Schottky diodes that made of a kesterite semiconductor were examined under different temperatures. For this aim, $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanocrystals were fabricated using the hot injection technique, and it was covered by spin coating on an ITO glass substrate. We was introduced the physical and structural analyses using scanning electron microscopy and X-ray spectroscopy. Current–voltage measurements were fulfilled at different temperature (from 100 to 325 K) under dark environment. It was observed that its electrical parameters were strongly affected by temperature.

1 Introduction

Due to their interesting properties and application potential, kesterite semiconductors are used in supercapacitors, light emitting diodes and memory circuits [1, 2]. Moreover, nanocrystalline kesterite semiconductors are frequently used in solar cells due to their low costs. $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) is an important kesterite material and is widely used in opto-electronic device fabrication because it is inexpensive [3], stable [4], non-toxic [5], has a suitable band gap of 1.13 eV [6, 7], and has a high light absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$) [8, 9], especially in the visible range. Moreover, $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS) thin film, created using Cu, In, Ga and Se elements is also frequently used in solar cell applications. CIGS is the highest efficiency (with 20%) in thin film solar cells [10, 11].

But, Ga and In are expensive materials that are not very common in nature. Environmentally friendly alternative materials for thin film photovoltaic systems are also being intensively researched. In recent years $\text{I}_2\text{--II--IV--VI}_4$ group quaternary semiconductors have been used as an alternative to $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ (CIGS) and CdTe materials. Because these quaternary semiconductors are plentiful, inexpensive and non-toxic [12, 13]. Among this group $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) material is promising, just like CZTSe, thanks to its cheap production, suitable band gap of 1.5 eV [14, 15] and high absorption coefficient [16–18]. Thin film solar cell (CZTS/CZTSe) produced using copper, zinc, tin and sulfur/selenium elements has lower efficiency values than silicon-based solar cell with 12.6% conversion efficiency [19]. However, $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ thin films are more advantageous

Address correspondence to E-mail: zncalcigil@selcuk.edu.tr

because the elements they contain are abundant in nature.

CZTS and CZTSe materials are employed as absorbers in a solar cell with their p-type properties [20]. For example, the band gap of CZTS is between 1.4 and 1.6 eV, and it has very high absorption coefficient. Thanks to this feature, the cells in the absorber layer of the structure absorb the most of the light. Such compound semiconductors have good material properties and are environmentally friendly [19, 21–23].

Many researchers have used different methods to produce CZTS and CZTSe thin films. For example, it is possible to prepare this material in vacuum or non-vacuum environments. Deposition parameters can be controlled in films produced using the vacuum method, and thus the desired crystal quality and stoichiometric ratio can be obtained. In addition to this method, CZTS and CZTSe nanocrystalline compound semiconductor films are also grown using many other methods such as thermal evaporation [24–26], sputtering [27–29], sol gel method [30, 31], laser evaporation [32] and spin coating [33]. Among these, the coating technique is spin coating, which is simple, safe, easy, less expensive and suitable for large scale production. One advantage of spin coating is obtaining a smooth film. Thus, a homogeneous film thickness is obtained. Therefore this technique makes it more uniform than other techniques. Furthermore, maximum conversion efficiency with 12.6% has been reported for kesterite structured thin films solar cells [19], and this has produced using spin coating technology.

In the literature, studies on Schottky-based CZTSe or similar structures have generally been carried out using a separate semiconductor substrate, and Schottky structures in which itself is used as a semiconductor substrate have not been encountered. In this study, Schottky diodes have been produced using $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanocrystal obtained with hot injection technique, and this thin film have coated onto the glass substratum using spin coater method. Electrical change in diode parameters of these devices has then studied using I-V characteristics depending on temperatures. It has been observed that diode performance parameters have strongly affected by temperature changes. The authors expect that the results obtained will be useful in the production of CZTSe-based electronic devices. Because the selection of interfacial layers play significant role in many optoelectronic applications.

2 Experimental details

2.1 Synthesis

The hot injection method used to produce CZTSe solution allows controlling important parameters such as phase, particle size distribution and composition. Essentially, this technique does not use step-by-step annealing processes as in electrolysis, sputtering and molecular deposition techniques. On the other hand, it allows the production of crystals from nanometer to micrometer sizes. Synthesis of nanocrystal structures was carried out based on previously used procedures [34–36]. For this, 0.25 mmol tin(II) acetate dihydrate, 0.25 mmol zinc(II) acetate, 0.5 mmol copper(II) acetate, 1 g TOPO and 20 mL OLA (> 70%) were added to make a mixture. This mixture was placed in a 25 mL three-neck flask and heated up to 200 °C in a stream of N_2 gas. When a reddish-brown solution was obtained, 1 mL of OLA containing 1 mmol of diphenyl diselenide was added to the reaction flask. Afterwards, the reaction temperature was increased up to 280 °C with stirring and kept for 30 min. The solution was then cooled to room temperature. After this process, a 1:3 mixture of toluene and 2-propanol was added to the CZTSe crystals and centrifugation was performed. Finally, CZTSe nanocrystals were washed abundantly with ethanol and dried at 70° for 2 h.

2.2 Device fabrication

Indium tin oxide plated glass (10–12 Ω/sq) was used as substrates in fabrication of nanocrystal Schottky diodes. The substrate was cleaned by washing first with acetone and then with isopropanol for 10 min. An ultrasonic cleaner was used at each stage during cleaning. The cleaned substrates were dried in an oven and then cured in a UV/ O_3 chamber. On the other hand, a 20 mg/mL solution was prepared by adding the synthesized CZTSe nanocrystals into chlorobenzene solution. This solution was coated onto ITO layers using a spin coating device. The coating process continued for 1 min using a rotation speed of 1500 rpm. 1000 Å thick rectifier contacts were formed on the obtained CZTSe thin films by evaporating 99.999% purity of Aluminum (Al) material with a diameter of 2 mm in vacuum environment. Likewise, 1000 Å thick ohmic contacts were formed on ITO in a vacuum environment. During the evaporation process, a pressure value of 1.5×10^{-6} Torr was used. The schematic diagram of fabricated

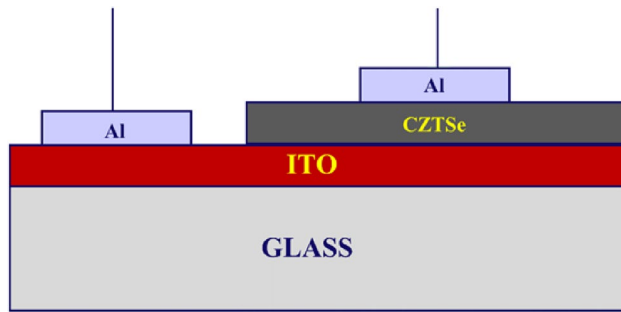


Fig. 1 Schematic diagram of Al/CZTSe device

Al/CZTSe nanocrystal Schottky device was illustrated in Fig. 1.

2.3 Characterization

XRD graph for CZTSe nanocrystals were recorded on a Bruker D8 Advance with Cu- α radiation source ($\lambda = 1.5406 \text{ \AA}$) to analyze the structural properties. Zeiss Evo model scanning electron microscope was used to obtain the surface images. Electrical measurements of fabricated diodes were realized at different temperatures (100–325 K) using cryostat system and Keithley 2400 source meter.

3 Results and discussion

Figure 2 illustrates the crystal structure of CZTSe nanocrystals that characterized with X-Ray Diffractometer. Owing to the random nature of powdered materials, one can get all lattice diffractions by scanning the sample across a 2θ range across orientations ranging from 20° to 70° . The identified peak serves as the basis for the XRD analysis. The surface is amorphous if no obvious peak is visible; if one doesn't, the surface may be crystalline. Using the peak data, Scherrer's equation can be used to determine the particle size in crystalline formations [37]. As seen from Fig. 2a, CZTSe thin film represents good crystallinity and shows three broad peaks that can be associated with the three main peaks of the kesterite bulk (JCPDS No. 70-8930). Figure 2c shows the elemental analysis (EDX) of the CZTSe structure. EDX results of CZTSe thin films confirmed the presence of copper (Cu), selenium (Se), tin (Sn), copper (Cu) and zinc (Zn) elements (Fig. 2b). Atomic percentages obtained from elemental analysis results

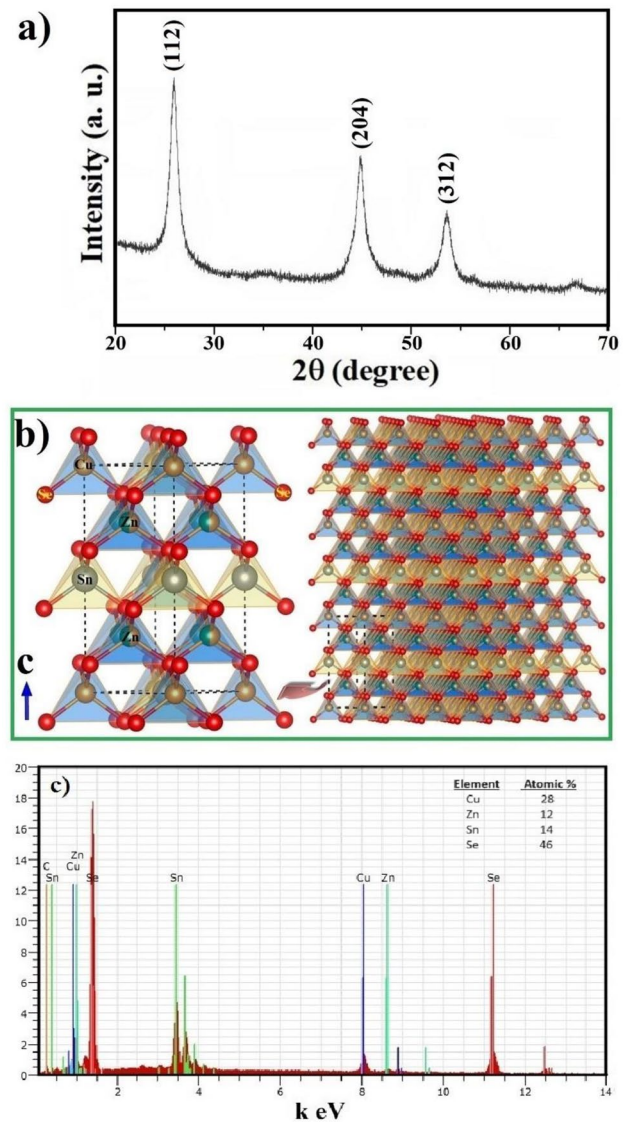


Fig. 2 XRD characterizations of CZTSe nanocrystals: **a** diffraction patterns, **b** 3D crystal structure, and **c** EDX elemental analysis results

are also given as an inset in Fig. 2c. The carbon formation is due to the carbon band used in the previous imaging.

Surface images of CZTSe structure have analyzed using scanning electron microscopy (SEM). Figure 3a and b represents the surface morphologies with different area sizes. When we see at the morphology, a homogeneous surface distribution of nanoparticles has obtained (Fig. 3a). Moreover, what stands out in the transmission electron microscopy (TEM) images (Fig. 3b) is the nanocrystals have been perfectly crystallized as small particles. Furthermore, the average size

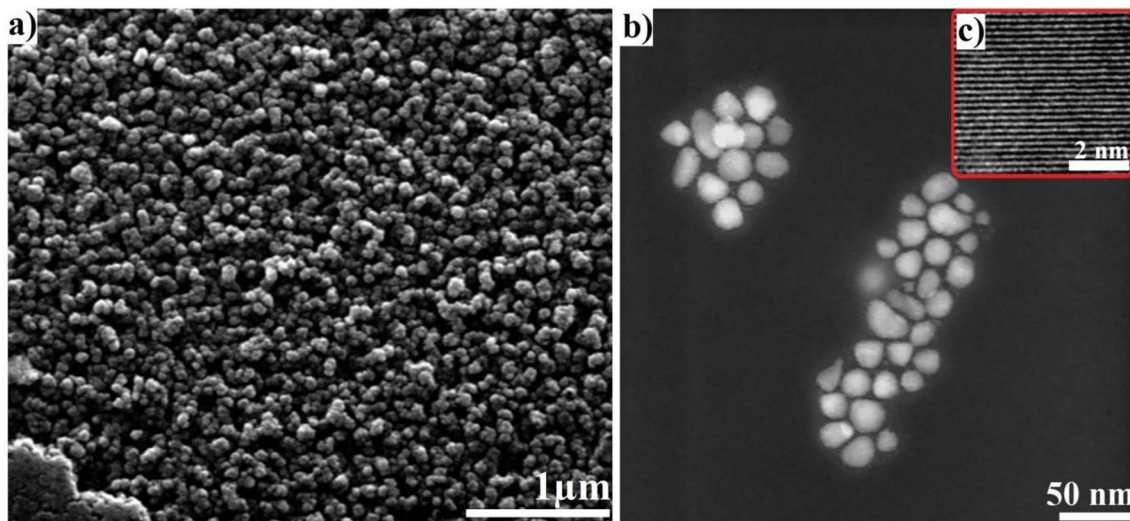


Fig. 3 **a** SEM, **b** TEM and **c** HR-TEM images of the CZTSe nanoparticles

of nanocrystals is found to be around 15–17 nm and their standard deviation is 5 nm. Due to the small size of CZTSe nanocrystals, the sample showed broad X-ray diffraction peaks. The lattice fringes of the nanoparticles were measured as 0.32 nm, which corresponds to the crystallographic (122) planes.

Figure 4a and b depicts the I–V plots for all voltages and forward voltage semi-log I–V plots, respectively, of prepared Al/CZTSe device at various (from 100 to 325 K) temperatures. As seen in figure, the device exhibits a rectification behavior at all temperature values. The current exhibited an exponentially increasing behavior with the increase of the forward bias. On the other hand, a linear behavior is observed in

the middle part of the forward region of plots. These linear regions represent the current produced by the majority charge carriers. However, as the voltage applied in the positive direction increases, a declination from linearity is observed owing to the serial resistance effects [38]. The rectification characteristics of the device have been determined at each temperature by calculating the rectification ratio (RR) which is the ratio of forward current to reverse current at constant bias voltage (± 1 V) calculated as two orders of magnitude, and are listed in Table 1. The obtained ratios tended to first increase and then decrease with increasing temperature. These changes in RR values depending on temperature can be attributed to the

Table 1 Diode parameters obtained depending on temperature using different methods for Al/CZTSe Schottky device

T (K)	n	I_0 ($\times 10^{-6}$ A)	Φ_B (eV)	RR	N_{ss} ($\times 10^{11}$ $\text{eV}^{-1} \text{cm}^{-2}$)	$^a n$	$^a R_s$ (Ω)	$^b \Phi_B$ (eV)	$^b R_s$ (Ω)
100	11.07	2.53	0.175	4.89	18.60	11.10	26.14	0.194	28.78
125	9.41	3.20	0.222	4.97	15.52	9.44	24.86	0.241	26.39
150	8.05	4.12	0.270	5.04	13.01	7.98	24.47	0.290	25.39
175	7.14	4.57	0.318	5.02	11.33	7.03	24.05	0.336	24.49
200	6.22	5.42	0.366	5.09	9.63	6.22	23.69	0.382	23.96
225	5.64	6.57	0.414	5.07	8.56	5.68	23.22	0.427	23.34
250	4.95	7.72	0.463	4.94	7.29	5.01	22.62	0.476	23.22
275	4.55	8.26	0.512	4.82	6.55	4.57	22.56	0.526	23.45
300	4.21	9.05	0.560	4.62	5.92	4.21	22.15	0.566	23.78
325	3.87	9.68	0.610	4.56	5.28	3.63	20.44	0.624	23.31

$^a dV/d\ln(I)-I$

$^b H(I)-I$

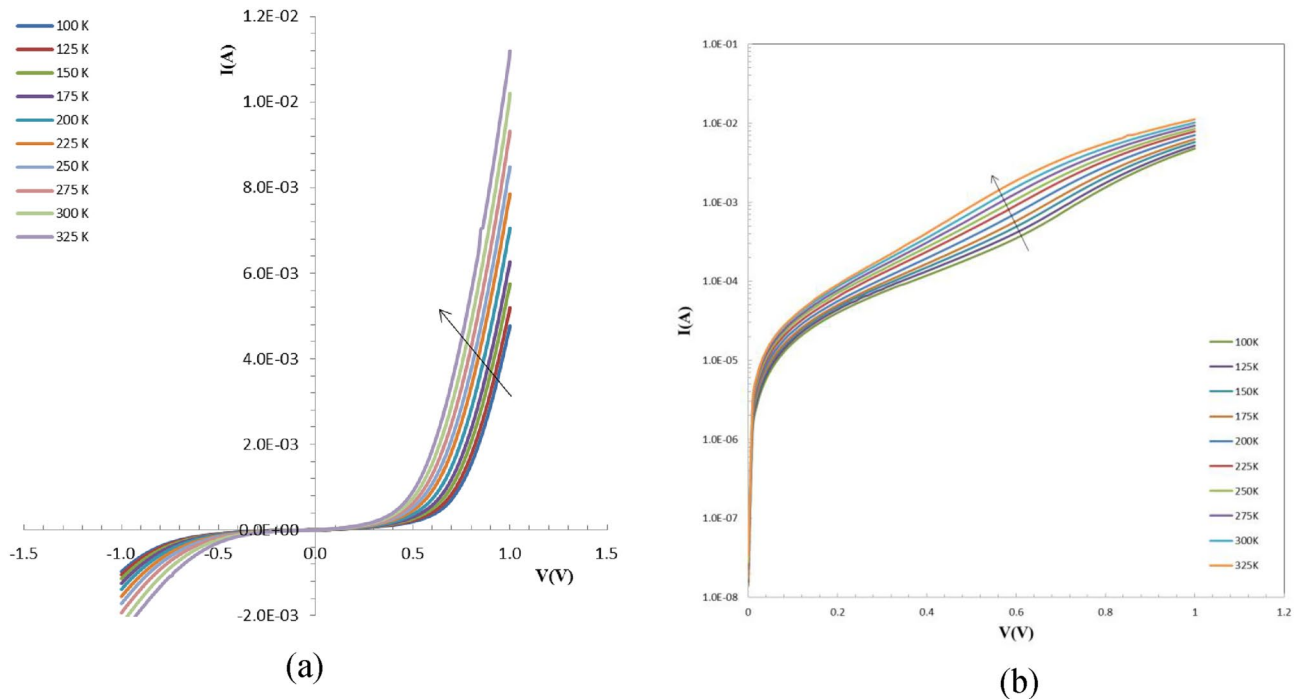


Fig. 4 **a** I–V plots with reverse voltages and **b** Forward voltage semi-log I–V plots under different temperatures

effect of inhomogeneous trap levels formed localized at the interface and, as a result, the charge carriers changing the reverse bias current [39].

Inside the diode, the depletion region affects the forward bias current and created an exponential current–voltage mechanism called Thermionic Emission (TE). This mechanism is dominant over other current–voltage mechanisms. Thus, this mechanism allows the calculation of some electrical parameters such as serial resistance (R_s), saturation current (I_0) barrier height (Φ_B) and ideality factor (n). Another important aspect is that this mechanism is used at the voltage limit of $V > 3kT/q$ to eliminate the contributions from reverse bias. Considering the Thermionic Emission mechanism, the current flowing through the Schottky contact can be described as follows: [40];

$$I = I_0 \left[\exp \left(\frac{q(V - IR_s)}{nkT} \right) - 1 \right], \quad (1)$$

where, I represents the current value obtained in response to the applied bias, q is the electronic load, k is Boltzmann constant, the expression IR_s is the voltage drop created by the resistor R_s and T is the ambient temperature in Kelvin. n represents the ideality factor associated with current transport mechanism

throughout the junction. This parameter is obtained from slope of linear region of the $\ln I$ -V graph. On the other hand, I_0 is saturation current acquired from zero bias intersection point of linear part of $\ln I$ -V curve and described as follows:

$$I_0 = AA^* T^2 \exp \left(-\frac{q\Phi_B}{kT} \right), \quad (2)$$

where A is the effective geometric area depending on the metallic rectifier part, A^* is Richardson constant ($A^* = 12.02 \text{ A/cm}^2\text{K}^2$ for CZTSe [41]) and Φ_B is effective barrier height at zero bias, and is obtained using Eq. 3. Experimentally obtained Φ_B , n and I_0 parameters are summarized in Table 1 under different temperatures.

$$\Phi_B = \frac{kT}{q} \ln \left(\frac{AA^* T^2}{I_0} \right). \quad (3)$$

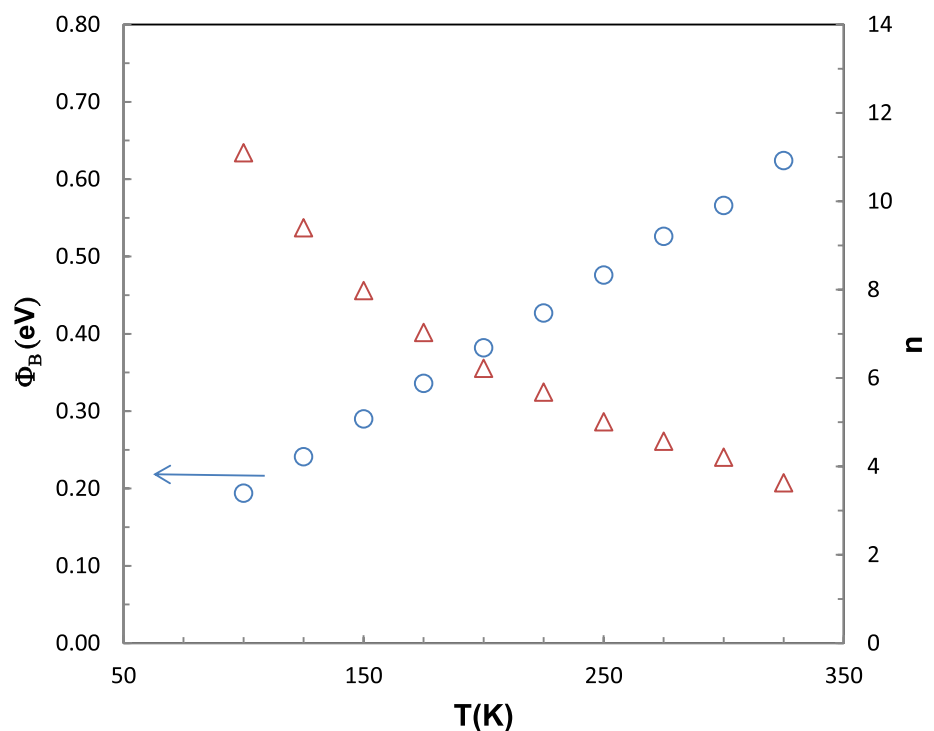
It can be seen from Table 1 that Φ_B and n are strongly dependent on temperature. The values of Φ_B increased as the temperature increased, whereas the value of n decreased. The experimental values of Φ_B and n obtained to be 0.175 eV and 11.07 at 100 K, and 0.610 eV and 3.87 at 325 K, respectively. Similar behaviors of Φ_B and n have been reported at the literature [42,

[43]. For example, Ashery et al. have been found the Φ_B and n for Al/n-Si/CZTSe₄/Ag structure 0.520 and 2.61, respectively, at 330 K [44], Terlemozoglu et al. have been found the Φ_B and n for CZTSSe/n-Si structure 0.710 and 3.29, respectively, at 330 K [39], Ashery et al. have been found the Φ_B and n for CZTSe/n-Si structure 0.510 and 2.75, respectively, at 330 K [45]. This increase in Φ_B values can be attributed to the improvement in the Al/CZTSe junction with increasing temperature [39]. Moreover, this temperature dependence shows that there is a current at the metal-semiconductor interface that can be activated by temperature. When temperature increases, the carriers that gain sufficient energy can overcome high barrier heights. They also have the ability to overcome low barriers heights at low temperatures. Therefore, the current conduction mechanism must be evaluated by taking into account the effect of localized barrier potential patches [42, 46]. On the other hand, for an ideal diode characteristic n is approximately unity. It can be seen from here that the structure does not have ideal characteristics. The fact that ideality factor values are high and inversely proportional to changes in temperature can be attributed to existence of interface states at junction area and inhomogeneities in the barrier height [47, 48].

Figure 5 depicts the variation of Φ_B to n parameters depending on temperature. As shown in Fig. 5, both

parameters have a strongly temperature dependent. Experimental values of n have decreased as the temperature increased. This kind of attitude of the n can be referable to the interfacial states and a special dispersion of the interface layer [49–52]. Meanwhile, Φ_B values have increased with increasing temperature. It was observed that Φ_B obtained from these results exhibited abnormal behavior. The form of this behavior is incompatible with known negative temperature coefficient of the barrier height in Schottky diodes. On the other hand, when the figure is examined, it is seen that the value of n increases as Φ_B decreases at low temperatures. The amount of current is affected by temperature along the metal-semiconductor interface, and therefore low-temperature electrons can overcome lower barrier levels. That is, with increasing temperature and applied external bias, many electrons will have higher energy and overcome the barrier height. Thus, the current mechanism will be dominated by a current flowing within a low barrier, resulting in large ideality factor [53–56]. Moreover, even if TE mechanism is dominant, a large increase in the expected unity value of the ideality factor can be observed as a result of decrease in image force or laterally inhomogeneous diode structure [57–59]. Moreover, a possible decrease in Φ_B and a significant increase in n values at low temperatures are owing

Fig. 5 Temperature dependent n and Φ_B of Al/CZTSe Schottky diode



to formation of inhomogeneous barrier heights [60]. However, the TE mechanism is based on formation of homogeneous barrier height in the junction. For this purpose, the changes of Φ_B to n have investigated to determine the homogeneous barrier height of fabricated device (Fig. 6). The relationship between Φ_B and n in Fig. 6 has analyzed with a linear fitting process. With this linear fitting process, the homogeneous barrier height has found to be approximately 0.721 eV with $n = 1$ extrapolation [61].

Series resistance (R_s) values of Al/CZTSe device have obtained using the Cheung technique with the help of the following defined expressions [62]:

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

$$H(I) = V - \left(\frac{nkT}{q} \right) \ln \left(\frac{I}{AA^*T^2} \right) = n\phi_B + IR_s. \quad (5)$$

This technique is an effective method for calculating R_s and also allows the determination of Φ_B and n parameters. Figure 7 shows the curves of the Cheung functions at a temperature of 325 K. As can be seen from the figure, the $dV/d \ln(I)$ vs. I plot has given a straight line in the bending zone of semi-log I–V plot. n and R_s parameters are determined

from slope of this straight line and the point where it intercepts y -axis, respectively. Likewise, $H(I)$ vs. I plot exhibited a straight line in series resistance region of the semi-logarithmic I–V curve. The slope of this straight line gives a second R_s value, which confirms the consistency of the technique used. All these parameters obtained from Cheung functions are represented in Table 1 as a function of temperature, and R_s values were found to be in agreement with each other.

As seen in Fig. 7, as the temperature increases, the R_s value decreases. A similar behavior of R_s has been reported at the literature [45]. The reason for this decrease is due to the increase in the ideality factor and can also be attributed to the factors that cause the increase in free carrier concentration at low temperatures [63, 64]. Furthermore, the improvement in diode conductivity with increasing temperature also causes this decrease [45, 65]. It can be clearly seen from the Table 1 that the value of n varies between 11.1 and 3.63 with temperature. At 100 K, the value of Φ_B has initially found to be 0.194 eV, and it has reached 0.624 eV at 325 K.

In Fig. 8, the density of interface states (N_{ss}) of Al/CZTSe structure are given as a function of energy. Interface states are the impurity levels between the

Fig. 6 The correlation between Φ_B to n for Al/CZTSe Schottky diode

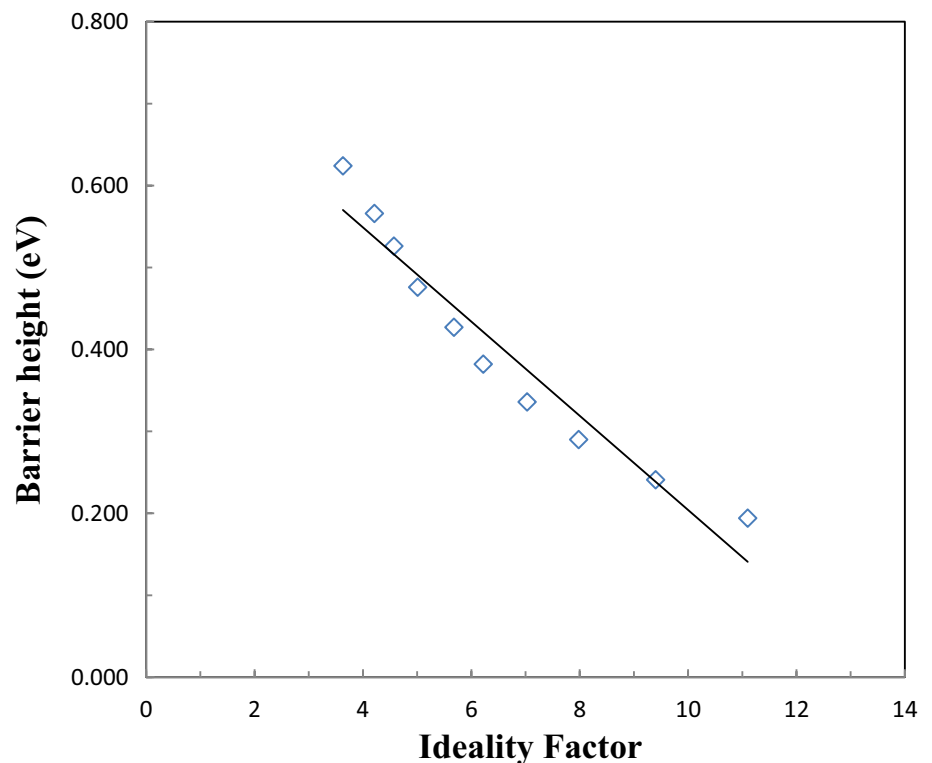


Fig. 7 $dV/d\ln I$ vs. I and $H(I)$ vs. I plots of Al/CZTSe Schottky device at 325 K

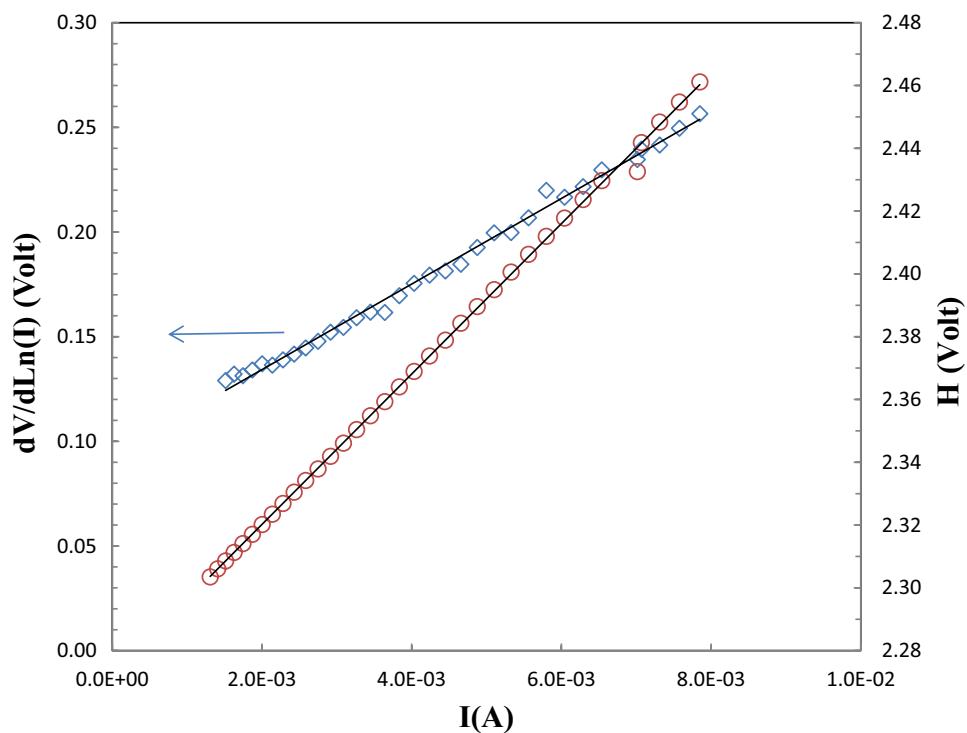
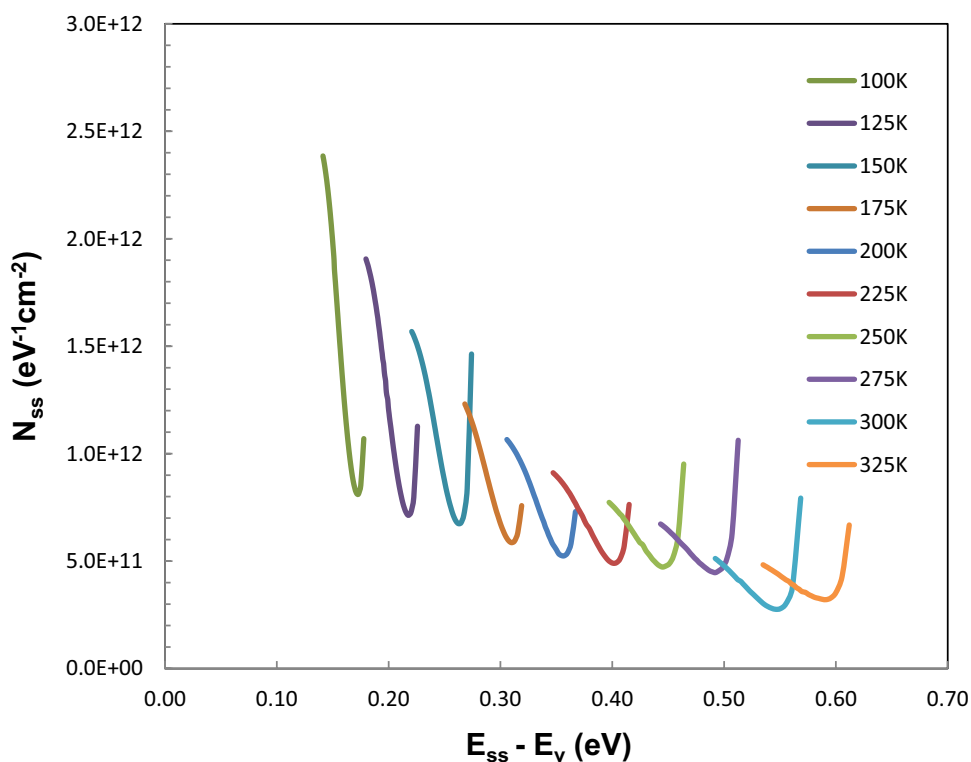


Fig. 8 The N_{ss} distribution profiles of Al/CZTSe device



valance band and the conduction band and represent states where electrons are located around crystal defects. Moreover, it can exist in different energy

states in the forbidden region between the valance and conduction bands [37]. These interfacial states may arise from foreign atoms or surface defects on

the surface and may affect the electrical characteristics of the device. As a matter of fact, it is possible to see the existence of the interfacial state density and the effect of its continuity in the forward bias region of the current-voltage graph [66]. As seen from figure, N_{ss} values have decreased with increasing temperature. Moreover, they have exhibited an exponential trend towards the bottom of conduction band at each temperature value. At 100 K, the value of N_{ss} has decreased from 53.8×10^{11} to $17.3 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$, while; at 325 K the value have decreased from 7.5×10^{11} to $4.3 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$ towards the conduction band edge. This can be associated with reconstructing and arrangement process that occurs between metal and CZTSe layer [43, 64, 67].

4 Conclusions

In the present work, $\text{I}_2\text{-II-IV-VI}_4$ compound semiconductor $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) nanocrystalline thin films have been fabricated by hot injection method and used in construction of a Schottky diode. For this aim, CZTSe nanoparticle film has coated using spin coating technique on ITO Corning glass. The CZTS films have grown in nanocrystallized form and exhibit kesterite structure.

From the current-voltage measurements obtained, it has been seen that the characteristic currents of Al/CZTSe structures have compatible with the thermionic emission mechanism. The effect of temperature on diode parameters of the structures has determined using the current-voltage plots. The measurement results showed us that n and Φ_B are strongly dependent on temperature. The fact that n values decrease with increasing temperature can be associated with a special dispersion of interfacial states. The increase in Φ_B values with increased temperature are owing to inhomogeneities of barrier heights within device, and the homogeneous barrier height for the device has found to be 0.721 eV.

Author contributions

ZK: Experimental, Methodology, Data collection and Writing—original draft. FÖ: Materials synthesis and Formal analysis. SK: Data collection and Writing—original draft. NT: Discussion and Writing—review &

editing. SSÖ: Materials synthesis and Formal analysis. ÖFY: Supervision, Sample preparation, Investigation and Discussion.

Funding

Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK). The authors declare that no funds were received during the preparation of this manuscript.

Data availability

All data generated and analyzed during this study are included in this publication.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

1. S.C. A. Walsh, S.-H. Wei, X.-G. Gong, Kesterite thin-film solar cells: advances in materials modeling of $\text{Cu}_2\text{ZnSnS}_4$. *Adv. Energy Mater.* **2**, 400–409 (2012)
2. S. Siebentritt, Kesterites a challenging material for solar cells. *Prog. Photovolt. Res. Appl.* **20**, 512–519 (2012)
3. G. Chen, C. Yuan, J. Liu, Y. Deng, G. Jiang, W. Liu, C. Zhu, Low-cost preparation of $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSn}(\text{SxSe}_{1-x})_4$ from binary sulfide nanoparticles for solar cell application. *J. Power Sources.* **262**, 201–206 (2014)
4. M. Nakashima, T. Yamaguchi, S. Yukawa, J. Sasano, M. Izaki, Effect of annealing on the morphology and compositions of $\text{Cu}_2\text{ZnSnSe}_4$ thin films fabricated by thermal evaporation for solar cells. *Thin Solid Films.* **621**, 47–51 (2016)
5. K. Woo, K. Kim, Z. Zhong, I. Kim, Y. Oh, S. Jeong, J. Moon, Non-toxic ethanol based particulate inks for low temperature processed $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ solar cells without S/Se treatment. *Sol. Energy Mater. Sol. Cells* **128**, 362–368 (2014)
6. B. Pani, S. Padhy, A comparative study of kesterite thin films prepared from different ball milled precursors. *Mater. Today Proc.* **4**, 2536–12544 (2017)
7. T.S. Shyju., S. Anandhi, R. Suriakarthick, R. Gopalakrishnan, P. Kuppusami, Mechano-synthesis, deposition and characterization of CZTS and CZTSe materials for solar cell applications. *J. Solid State Chem.* **227**, 165–177 (2015)
8. S.M. Lee, Characteristics of $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSn}(\text{Se, S})_4$ absorber thin films prepared by post selenization and sequential sulfurization of co-evaporated Cu–Zn–Sn precursors. *J. Alloys Compd.* **579**, 279–283 (2013)
9. P.M.P. Salome, J. Malaquias, P.A. Fernandes, M.S. Ferreira, A.F. da Cunha, J.P. Leitao, J.C. Gonzalez, F.M. Matinaga, Growth and characterization of $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ thin films for solar cells. *Sol. Energy Mater. Sol. Cells* **101**, 147–153 (2012)
10. P. Jackson, D. Hariskos, R. Wuerz, W. Wischmann, M. Powalla, Compositional investigation of potassium doped $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells with efficiencies up to 20.8% physica status solidi (RRL) –. *Rapid Res. Lett.* **8**(3), 219–222 (2014)
11. P. Jackson, D. Hariskos, E. Lotter, S. Paetel, R. Wuerz, R. Menner, W. Wischmann, M. Powalla, New world record efficiency for $\text{Cu}(\text{In,Ga})\text{Se}_2$ thin-film solar cells beyond 20%Progress. *Photovolt. Res. Appl.* **19**(7), 894–897 (2011)
12. H. Katagiri, K. Jimbo, W.S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, Development of CZTS-based thin film solar cells. *Thin Solid Films.* **517**(7), 2455–2460 (2009)
13. D. Dumcenco, Y.-S. Huang, The vibrational properties study of kesterite $\text{Cu}_2\text{ZnSnS}_4$ single crystals by using polarization dependent Raman spectroscopy. *Opt. Mater.* **35**(3), 419–425 (2013)
14. X. Jiang, L.-X. Shao, J. Zhang, D. Li, W. Xie, C.-W. Zou, J.-M. Chen, Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of metallic precursors evaporated with a single source. *Surf. Coat. Technol.* **228**, S408–S411 (2013)
15. W. Liu, B. Guo, C. Mak, A. Li, X. Wu, F. Zhang, Facile synthesis of ultrafine $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals by hydrothermal method for use in solar cells. *Thin Solid Films.* **535**, 39–43 (2013)
16. B.-S. Ko, D.-H. Kim, D.-K. Hwang, S.-J. Lee, J.S. Kim, Effects of the annealing temperature on the properties of sulfur-graded $\text{Cu}_2\text{ZnSn}(\text{S, Se})_4$ thin films grown by a modified two-step process. *J. Ind. Eng. Chem.* **82**, 406–412 (2020)
17. D.B. Mitzi, O. Gunawan, T.K. Todorov, K. Wang, S. Guha, The path towards a high-performance solution-processed kesterite solar cell. *Sol. Energy Mater. Sol. Cells.* **95**(6), 1421–1436 (2011)
18. K.I. Nakazawa, Electrical and optical properties of stan-nite-type quaternary semiconductor thin films. *Jpn. J. Appl. Phys.* **27**, 2094 (1988)
19. W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. *Adv. Energy Mater.* **4**(7), 1301465 (2014)
20. S. Thiruvankadam, D. Jovina, A. Leo Rajesh, The influence of deposition temperature in the photovoltaic properties of spray deposited CZTS thin films. *Sol. Energy.* **106**, 166–170 (2014)
21. Y.H. Khattak, F. Baig, S. Ullah, B. Marí, S. Beg, H. Ullah, Enhancement of the conversion efficiency of thin film kesterite solar cell. *J. Renew. Sustain. Energy.* **10**, 033501 (2018)
22. M.A. Majeed Khan, S. Kumar, M. Alhoshan, Spray pyrolysed $\text{Cu}_2\text{ZnSnS}_4$ absorbing layer: a potential candidate for photovoltaic applications. *Opt. Laser Technol.* **49**, 196–201 (2013)
23. Z. Zakaria, P. Chelvanathan, M.J. Rashid, M. Akhtaruz-zaman, M.M. Alam, Z.A. AlOthman, A. Alamoud, K. Sopian, Effects of sulfurization temperature on $\text{Cu}_2\text{ZnSnS}_4$ thin film deposited by single source thermal evaporation method. *Jpn. J. Appl. Phys.* **54**, 08KC18 (2015)
24. Ö. Bayraklı, M. Terlemozoglu, H.H. Güllü, M. Parlak, Investigation of precursor sequence and post-annealing effects on the properties of $\text{Cu}_2\text{ZnSnSe}_4$ thin films

- deposited by the elemental thermal evaporation. *Mater. Res. Express.* **4**(8), 086411 (2017)
25. B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ absorber. *Prog. Photovolt. Res. Appl.* **21**(1), 72–76 (2013)
 26. O. Volobujeva, S. Bereznev, J. Raudoja, K. Otto, M. Pilvet, E. Mellikov, Synthesis and characterisation of $\text{Cu}_2\text{ZnSnSe}_4$ thin films prepared via a vacuum evaporation-based route. *Thin Solid Films.* **535**, 48–51 (2013)
 27. K. Jimbo, R. Kimura, T. Kamimura, S. Yamada, W.S. Maw, H. Araki, K. Oishi, H. Katagiri, $\text{Cu}_2\text{ZnSnS}_4$ -type thin film solar cells using abundant materials. *Thin Solid Films.* **515**(15), 5997–5999 (2007)
 28. S.W. Shin, S.M. Pawar, C.Y. Park, J.H. Yun, J.-H. Moon, J.H. Kim, J.Y. Lee, Studies on $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorber layer using different stacking orders in precursor thin films. *Sol. Energy Mater. Sol. Cells.* **95**(12), 3202–3206 (2011)
 29. T. Taskesen, J. Neerken, J. Schoneberg, D. Pareek, V. Steininger, J. Parisi, L. Gütaý, Device characteristics of an 11.4% CZTSe solar cell fabricated from sputtered precursors. *Adv. Energy Mater.* **8**(16), 1703295 (2018)
 30. Y. Miyamoto, K. Tanaka, M. Oonuki, N. Moritake, H. Uchiki, Optical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films prepared by sol–gel and sulfurization method. *Jpn. J. Appl. Phys.* **47**(1S), 596 (2008)
 31. Z. Su, K. Sun, Z. Han, H. Cui, F. Liu, Y. Lai, J. Li, X. Hao, Y. Liu, M.A. Green, Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ solar cells with 5.1% efficiency via thermal decomposition and reaction using a non-toxic sol–gel route. *J. Mater. Chem. A* **2**(2), 500–509 (2014)
 32. R. Adhi Wibowo, E. Soo Lee, B. Munir, K. Ho, Kim, Pulsed laser deposition of quaternary $\text{Cu}_2\text{ZnSnSe}_4$ thin films. *Phys. Status Solidi (a)* **204**(10), 3373–3379 (2007)
 33. G.M. Ilari, C.M. Fella, C. Ziegler, A.R. Uhl, Y.E. Romanyuk, A.N. Tiwari, $\text{Cu}_2\text{ZnSnSe}_4$ solar cell absorbers spin-coated from amine-containing ether solutions. *Sol. Energy Mater. Sol. Cells.* **104**, 125–130 (2012)
 34. A. Shavel, J. Arbiol, A. Cabot, Synthesis of quaternary chalcogenide nanocrystals: stannite $\text{Cu}_2\text{Zn}_x\text{Sn}_y\text{Se}_{1+x+2y}$. *J. Am. Chem. Soc.* **132**, 4514 (2010)
 35. J.-J. Wang, J.-S. Hu, Y.-G. Guo, L.-J. Wan, Wurtzite $\text{Cu}_2\text{ZnSnSe}_4$ nanocrystals for high-performance organic–inorganic hybrid photodetectors. *NPG Asia Mater.* **4**, E2 (2012)
 36. F.J. Fan, L. Wu, M. Gong, S.Y. Chen, G.Y. Liu, H.B. Yao, H.W. Liang, Y.X. Wang, S.H. Yu, Linearly arranged polycrystalline CZTSSe nanocrystals. *Nat. Sci. Rep.* **2**, 952 (2012)
 37. H.H. Radamson, A. Hallén, I. Sychugov, A. Azarov, *Analytical methods and instruments for micro-and nanomaterials*, 1st edn. (Springer, Dordrecht, 2023)
 38. Ş. Altındal, H. Kanbur, D.E. Yıldız, M. Parlak, Current conduction mechanism in Al/p-Si Schottky barrier diodes with native insulator layer at low temperatures. *Appl. Surf. Sci.* **253**(11), 5056–5061 (2007)
 39. M. Terlemezoglu, Ö. Bayraklı, H.H. Güllü, T. Çolakoğlu, D.E. Yıldız, M. Parlak, Analysis of current conduction mechanism in CZTSSe/n-Si structure. *J. Mater. Sci. Mater. Electron.* **29**, 5264–5274 (2018)
 40. E.H. Rhoderick, R.H. Williams, *Metal-semiconductor contacts*, 2nd edn. (Clarendon, Oxford, 1978)
 41. H.R. Liu, S. Chen, Y.T. Zhai, H.J. Xiang, X.G. Gong, S.H. Wei, First-principles study on the effective masses of zinc-blend-derived IV–VI₄ (IV = sn, Ge, Si and VI = S, Se. *J. Appl. Phys.* **112**, 093717 (2012)
 42. C.D. Balbasi, M. Terlemezoglu, H.H. Gullu, D.E. Yildiz, M. Parlak, Electrical characterization of CdZnTe/Si diode structure. *Appl. Phys. A* **126**(614), 1–7 (2020)
 43. H.H. Gullu, D.E. Yildiz, Ö.B. Sürücü, M. Terlemezoglu, M. Parlak, Temperature dependence of electrical properties in In/ $\text{Cu}_2\text{ZnSnTe}_4$ /Si/Ag diodes. *Bull. Mater. Sci.* **42**(45), 1–8 (2019)
 44. A. Ashery, M.M. Mohamed, I.M. Elnasharty, M. El Radaf, Fabrication and electrical characterization of the Al/n-Si/CZTSe₄/Ag heterojunction. *Phys. B Condens. Matter* **609**, 412707 (2021)
 45. A. Ashery, I.M. El Radaf, M.M. Mohamed, Elnasharty, Electrical and dielectric characterizations of $\text{Cu}_2\text{ZnSnSe}_4$ /n-Si heterojunction. *Silicon* **11**, 2567–2574 (2019)
 46. K. Moraki, S. Bengi, S. Zeyrek, M.M. Bülbül, Ş. Altındal, Temperature dependence of characteristic parameters of the Au/ $\text{C}_{20}\text{H}_{12}$ /n-Si Schottky barrier diodes (SBDs) in the wide temperature range. *J. Mater. Sci. Mater. Electron.* **28**, 3987–3996 (2017)
 47. A.A. Ojo, W.M. Cranton, I.M. Dharmadasa, *Next generation multilayer graded bandgap solar cells* (Springer, Cham, 2019)
 48. F. Yigiterol, H.H. Gullu, O. Bayrakli, D.E. Yildiz, Temperature-dependent electrical characteristics of Au/Si₃N₄/4H n-SiC MIS Diode. *J. Electron. Mater.* **47**, 2979–2987 (2018)
 49. H.C. Card, E.H. Rhoderick, Studies of tunnel MOS diodes I. Interface effects in silicon Schottky diodes. *J. Phys. D Appl. Phys.* **4**, 1589 (1971)
 50. P. Cova, A. Singh, R.A. Masut, A self-consistent technique for the analysis of the temperature dependence of current–voltage and capacitance–voltage characteristics of a tunnel

- metal-insulator-semiconductor structure. *J. Appl. Phys.* **82**, 5217–5226 (1997)
51. S. Altındal, S. Karadeniz, N. Tuğluoğlu, A. Tataroğlu, The role of interface states and series resistance on the I–V and C–V characteristics in Al/SnO₂/p-Si Schottky diodes. *Solid State Electron.* **47**(10), 1847–1854 (2003)
 52. N. Tuğluoğlu, S. Karadeniz, Ş. Altındal, Effect of series resistance on the performance of silicon Schottky diode in the presence of tin oxide layer. *Appl. Surf. Sci.* **239**, 481–489 (2005)
 53. J.H. Werner, Güttler. Barrier inhomogeneities at Schottky contacts. *J. Appl. Phys.* **69**(3), 1522–1533 (1991)
 54. P.G. McCafferty, A. SellaI, P. Dawson, H. Elabd, Barrier characteristics of PtSi/p-Si Schottky diodes as determined from IVT measurements. *Solid State Electron.* **39**, 583–592 (1996)
 55. A. Gümüş, A. Türüt, N. Yalçın, Temperature dependent barrier characteristics of CrNiCo alloy Schottky contacts on n-type molecular-beam epitaxy GaAs. *J. Appl. Phys.* **91**, 245–250 (2002)
 56. S. Chand, J. Kumar, On the intersecting behavior of current–voltage characteristics of inhomogeneous Schottky diodes at low temperatures. *Semicond. Sci. Technol.* **19**, 82 (2004)
 57. V.W.L. Chin, M.A. Green, J.W.V. Storey, Current transport mechanisms studied by IVT and IR photoemission measurements on a P-doped PtSiSchottky diode. *Solid State Electron.* **36**, 1107–1116 (1993)
 58. H. Altuntaş, Ş. Altındal, H. Shtrikman, S. Özçelik, A detailed study of current–voltage characteristics in Au/SiO₂/n-GaAs in wide temperature range. *Microelectron. Reliab.* **49**, 904–911 (2009)
 59. R.F. Schmitsdorf, T.U. Kampen, W. Mönch, Explanation of the linear correlation between barrier heights and ideality factors of real metal-semiconductor contacts by laterally nonuniform Schottky barriers. *J. Vac. Sci. Technol. B* **15**, 1221–1226 (1997)
 60. Ş. Aydoğan, M. Sağlam, A. Türüt, On the barrier inhomogeneities of polyaniline/p-Si/Al structure at low temperature. *Appl. Surf. Sci.* **250**, 43–49 (2005)
 61. R.T. Tung, Electron transport of inhomogeneous Schottky barriers. *Appl. Phys. Lett.* **58**(2), 2821–2823 (1991)
 62. S.K. Cheung, N.W. Cheung, Extraction of Schottky diode parameters from forward current-voltage characteristics. *Appl. Phys. Lett.* **49**, 85–87 (1986)
 63. S. Chand, J. Kumar, Current transport in Pd₂Si/n-Si(100) Schottky barrier diodes at low temperatures. *Appl. Phys. A* **63**, 171–178 (1996)
 64. M. Özer, D.E. Yıldız, Ş. Altındal, M.M. Bülbül, Temperature dependence of characteristic parameters of the Au/SnO₂/n-Si (MIS) Schottky diodes. *Solid State Electron.* **51**, 941–949 (2007)
 65. M. Nasr, I.M. El Radaf, A.M. Mansour, Current transport and capacitance-voltage characteristics of an n-PbTe/p-GaP heterojunction prepared using the electron beam deposition technique. *J. Phys. Chem. Solids.* **115**, 283–288 (2018)
 66. G. Bhattacharya, A. Venimadhav, Temperature dependent electron transport and interface state studies on Ni/n-Si/Al/Ag lateral Schottky junction. *Microelectron. Reliab.* **153**, 115302 (2024)
 67. B. Akkal, Z. Benemara, A. Boudissa, N.B. Bouiadjra, M. Amrani, L. Bideux, B. Gruzza, Modelization and characterization of Au/InSb/InPSchottky systems as a function of temperature. *Mater. Sci. Eng. B* **55**, 162–168 (1998)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.