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Nano-crystalline p-ZnGa₂Te₄/n-Si as a new heterojunction diode

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ARTICLE INFO

Article history: Received 13 January 2012 Received in revised form 21 October 2012 Accepted 6 November 2012 Available online 15 November 2012

Keywords: A. Thin films B. Vapor deposition C. Atomic force microscopy D. Electrical properties

ABSTRACT

In this communication, $ZnGa_2Te_4$ thin film was prepared by thermal evaporation technique on n-Si substrate. P-ZnGa_2Te_4/n-Si heterojunction diode was fabricated. The structure of $ZnGa_2Te_4$ thin film was checked by XRD pattern and confirmed by AFM micrographs. The dark current–voltage characteristics of the heterojunction diode were investigated to determine the electrical parameters and conduction mechanism as a function of forward and reverse biasing conditions in the range (-10 V to 10 V) at temperature interval (303-423 K). The conduction mechanism was controlled by thermionic emission, space charge limited (SCLC) and trap-charge limited current (TCLC) mechanisms. The basic parameters such as the series resistance R_s , the shunt resistance R_{sh} , the ideality factor n and the barrier height ϕ_b of the diode, the total density of trap states N_0 and the exponential trapping distribution P_o were determined. The obtained results showed that $ZnGa_2Te_4$ is a good candidate for the applications of electronic devices.

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1. Introduction

ZnGa₂Te₄ is one of the defect chalcopyrite compounds, which has received considerable interest in recent years [1-3]. The ternary semiconducting compounds $A^{II}B_2^{III}C_4^{VI}$ (A = Cd, Zn and Hg; B = Al, Ga and In; C = Se, S and Te) are a promising material for semiconductor industry [4]. This family of semiconductors shows a great interest on technological applications as possible infraredtransmitting windows materials. Also, these compounds were used in various optoelectronic, nonlinear optical devices and as gyro-tropic media in narrow-band optical filters [5-8]. For instance, HgGa₂S₄ and Cd_{1_x}Hg_xGa₂S₄ are widely used as nonlinear optical materials, ZnGa₂Se₄ as photosensitive materials and CdGa₂S₄ as narrow-band optical filters [9]. Also, some compounds like CdGa₂Se₄ and CdAl₂S₄ have already found practical applications as tunable filters and ultra-violet photodetectors [10]. Important features of these compounds are their low sensitivity to impurities and high resistance to ionizing radiation [4]. This feature arisen a technological importance of these compounds and led them to play an important role in the optimization of solar cells [11]. Most of these compounds have ordered defect-chalcopyrite (space group $= S_4^2$) or defect stannite (space group $= D_{2d}^{11}$) structure [9,12].

The electronic and optoelectronic devices require new functional materials with special optical and electrical properties [13]. Defect chalcopyrite ordered vacancy compounds are a special class of ternary semiconducting compounds with high technological interest [14]. They usually have wide regions of transparency, high optical strength, high photosensitivity, used for phase change memories (PCMs) and intense luminescence, thus are promising semiconductor materials for optoelectronic applications [15]. ZnGa₂Te₄ is one of the defect chalcopyrite compounds which have many fundamental properties are not sufficiently evaluated or are even unknown. The previous work on ZnGa₂Te₄ supporting the novel optical properties for this material as an absorption layer for solar cell devices [16].

In electronic devices, such as metal-semiconductor (MS) Schottky diodes, metal-insulator-semiconductor (MIS) structures, solar cells and p-n junctions, different current-transport mechanisms may dominate the others at a certain temperature and at voltage regions, such as thermionic emission (TE), thermionic field emission (TFE), field emission (FE), space charge limited-conduction (SCLC), generation-recombination (GR), minority carrier injection, multistep tunneling and leakage current. The electronic properties of semiconductor materials are strongly affected by the

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^{0025-5408/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.materresbull.2012.11.013

presence of carrier trapping centers in forbidden band gap. The space charge limited current technique is used to explain the electrical properties of semiconductors and insulator materials, in this model current shows a power-law dependence on applied voltage $I \propto V^m$ [17]. The current-transport conduction mechanisms are dependent on the process of surface preparation, formation of barrier height (BH) (between the metal and semiconductor and its homogeneity), impurity concentration of semiconductor, density of interface states/traps or dislocations, series resistance (R_s) of a device, shunt resistance (R_{sh}) of a device, sample temperature and applied biasing voltage. The current–voltage–temperature (I-V-T) and capacitance–voltage–temperature (C-V-T) characteristics of these Schottky devices have been extensively studied and reported in the literature for more than four decades because of simplicity in the fabrication [18–22].

In the present study, it is believed that $ZnGa_2Te_4$ thin film is useful in electronic technology as a diode. With this aim, the p- $ZnGa_2Te_4/n$ -Si heterojunction diode was fabricated for the first time. The dark current–voltage characteristics of the heterojunction diode at different temperatures were investigated. The electronic conduction mechanisms and the electronic parameters were extracted for this diode. Comparison study between p- $ZnGa_2Te_4/n$ -Si and p- $ZnGa_2Se_4/n$ -Si was taken in our account.

2. Experiment technique

Bulk defect chalcopyrite of ZnGa₂Te₄ was prepared by the melt and slowly cooled technique as reported before [16]. The elementary constituents Zn. Ga and Te of high purity (5 N), were weighed according to their stoichiometric ratio. Then, the elementary constituents put in an evacuated silica ampoule (10^{-5} Torr) with length 15 cm and internal diameter 1.5 cm. The ampoule was placed in an especially designed calibrated oscillatory furnace whose temperature was raised gradually up to 1450 K at rate 50 K/h and was kept at this value for 24 h. Then, the sample was gradually cooled down steeply until reached to the temperatures 1073, 873 and 573 K. The sample was kept constant for 1 h at each temperature stage [23]. The long duration of synthesis and the mechanical shaking of the mixture in the oscillatory furnace were used to ensure the high homogeneity of the investigated compound. Finally, the sample was slowly cooled by the same rate of rising to reach the room temperature. Previous experience indicates that, this procedure providing a high quality polycrystalline structure [23].

The synthesized ingot of the proposed system was crushed into small grains. These grains were put into a cleaned and dry molybdenum boat which placed inside a helical tungsten wire as an evaporation source. The n-Si single crystal substrate was placed flat on a suitable holder (rotated horizontally). For the purpose of obtaining a parallel sided film on a plane substrate, it was sufficient to ensure that the pressure of the residual gas in the vacuum chamber was low enough and the distance between the source of material and the substrate holder was about 21 cm. The vacuum chamber was pumped down to ${\sim}2\times10^{-5}\,\text{Torr.}$ Thin film of ZnGa₂Te₄ was obtained from bulk sample by thermal evaporation technique, using high vacuum plant (Edward's 306 A) onto a highly polished and cleaned n-Si single crystal substrate. The temperature of the defect chalcopyrite grains of investigated compound was then raised until the whole material evaporated with a deposition rate 10 nm/s. The substrate temperature was held at room temperature during deposition. The film thickness was measured during deposition using a thickness monitor (Edwards, FTM4) and confirmed after deposition by Tolansky's interferometric method [24]. The investigated film thickness was found to be 601 nm.

To assess surfactant film morphology for this sample, the film on glass was checked out using X-ray diffractometer (PANalytical



Fig. 1. Schematic diagram of the current-voltage measurement system at different temperatures.

philips X'Pert PRO DIFFRACTOMETER), by utilizing monochromatic $CuK\alpha$ radiation operated at 40 kV and 30 mA. The diffraction patterns were recorded automatically with a scanning speed 2°/ min. The AFM micrographs were investigated by Park System XE-100E atomic force microscopy (AFM) with high performance processing unit of 600 MHz and 4800 MIPS speed. It is indispensible to isolate the instrument from ambient light and acoustic noise. The acoustic enclosures were designed by Park Systems provide environmentally sealed measurement conditions for optimal AFM operation.

The current–voltage (I-V) measurements were held by using n-Si wafer substrate with [100] orientation and resistivity (5-10 Ω cm). For this purpose, the substrate was chemically cleaned using the RCA cleaning procedure (i.e. a 10 min boil in $NH_4 + H_2O_2 + 6H_2O_3$ followed by a 10 min boil in $HCl + H_2O_2 + 6H_2O$). Then, a low-resistivity ohmic back contact to n-Si wafer was made by evaporating of high purity Al using a high vacuum system (Edward's E 306 A) and annealed at 400 °C for 10 min under N₂ flow. The native oxide on the front surface of Si wafer was removed in HF/H₂O (1:10) solution and finally was rinsed in de-ionized water for 30 s before re-enter again to the vacuum chamber.

The current–voltage (*I–V*) characteristics of the investigated heterojunction diode were measured by using a computer controlled Keithley 4200-SCS semiconductor characterization system as shown in Fig. 1. The standard configuration includes two medium power source measure units (SMUs) and a ground unit. Two terminal cables of this device SMU 1 and SMU 2 were connected to the specially designed point contact holder made



Fig. 2. X-ray diffraction pattern of the ZnGa₂Te₄ in powder form, as-deposited thin film and annealed film at 673 K.

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