Journal of Alloys and Compounds 544 (2012) 111–114

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Bandgap tuning of MgZnO in flexible transparent n^+-ZnO:Al/n-MgZnO/p-$CuAlO_x$:Ca diodes on polyethylene terephthalate substrates

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ARTICLE INFO

Article history:
Received 18 May 2012
Received in revised form 30 July 2012
Accepted 2 August 2012
Available online 9 August 2012

Keywords:
MgZnO
$CuAlO_2$
Oxide materials
Heterojunctions
Transition metal alloys and compounds
Electronic properties

ABSTRACT

Transparent p–n heterojunctions composed of p-type $CuAlO_x$:Ca and n-type MgZnO thin films are fabricated on indium tin oxide (ITO) coated polyethylene terephthalate (PET) using RF magnetron sputtering at room temperature without additional heat-treatment. The rectifying characteristics of the diodes are observed through the current density–voltage (*J*–*V*) curves. The characteristics of the heterojunctions vary with the Mg content in MgZnO. The absolute values of the turn-on voltage and breakdown voltage increase with the Mg content. The diode properties can be designed by adjusting Mg content in the MgZnO layers. The UV responses of the diodes are evaluated by measuring the *J*–*V* characteristics under UV irradiation at a wavelength of 365 nm. The absorption decreases with an increase in the Mg content in the diodes. The results show that these transparent diodes can be used as UV detectors on plastics.

1. Introduction

Flexible electronics have attracted considerable research attention because of their versatile applications. For next generation electronics, it is of great interest to implement electronics on flexible plastics, which are light-weighted, compact and particularly suitable for mobile electronic devices [1–8]. Hydrogenated amorphous silicon is the current mainstream industry technology for large area electronics; however, its electron mobility is less than 1 $cm^2\,V^{-1}\,s^{-1}$ [3,9], which limits its application to devices that require high refresh rates, such as large-area displays and 3D displays. One potential candidate material of higher mobility for large-area electronics is oxide [2,7,10–12]. Furthermore, in an electronic system, one of the key components is the diode. As such, to realize large-area electronics on plastic, it is essential to develop well-functioning diodes having adjustable properties on plastics.

Among oxides for use in electronics, ZnO has been widely studied as a candidate n-type material. Owing to the lack of stable p-type ZnO-based materials, several delafossite p-type oxides have been used in conjunction with ZnO to fabricate transparent heterojunction p–n diodes [13–19]. In these studies, however, high temperature processes are required to fabricate the p–n diodes on rigid glass substrates. Few studies thus far have focused on fabricating transparent oxide p–n junction diodes on plastic substrates; one study regarding the electrochemical deposition of a p-type Cu_2O film on a flexible substrate has been reported [20]. In this paper, we investigate the performance of RF-sputtered flexible transparent n^+-ZnO:Al/n-MgZnO/p-$CuAlO_x$:Ca heterojunction diodes on clear polyethylene terephthalate (PET) substrates. The devices are fabricated at room temperature without any additional heat-treatment. $CuAlO_x$:Ca is selected as the p-type material because $CuAlO_2$ has a wider bandgap than Cu_2O and can potentially be used as a UV detector and a transparent electronics material. Dong et al. have studied $CuAlO_2$:Ca having a low Ca concentration (<1.5 at.%) [21]. The introduction of Ca into $CuAlO_2$ increases the electrical conductivity because of the increase in carrier concentration, which can be used to reduce the series resistance of the diode.

MgZnO is selected as the n-type material because of its bandgap tuning characteristics, which allows the adjustment of the diode properties. MgZnO has also been applied in various applications such as thin-film transistors [12,22–27], light-emitting diodes [28–30], UV detectors [31–33], and MgZnO/ZnO heterostructure high-speed electronics [11,34–40]. MgZnO is made by alloying MgO and ZnO. MgO has a cubic structure and ZnO, a hexagonal lattice. MgZnO undergoes phase separation or precipitation when the Mg concentration is above a certain limit that is dependent on the film deposition processes [41–43]. The bandgap of MgO is approximately 7.7 eV and that of ZnO, approximately 3.3 eV. Therefore,

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http://dx.doi.org/10.1016/j.jallcom.2012.08.004

MgO can be alloyed with ZnO to adjust the bandgap and intrinsic carrier density without much lattice distortion owing to the similar ionic radii of Mg^{2+} and Zn^{2+}. The existence of Mg in ZnO also helps reduce the oxygen vacancy density in the materials due to the higher ionic fraction nature of Mg–O bonds compared with Zn–O ones [11,12,22,27,41,44–50]. This bandgap engineering allows the properties of transparent n-MgZnO/p-CuAlO$_x$:Ca diodes to be designed.

2. Experimental details

Transparent n$^+$-ZnO:Al/n-MgZnO/p-CuAlO$_x$:Ca heterojunction diodes are fabricated on flexible indium tin oxide (ITO) coated PET (sheet resistance: 113 Ω, average transmittance between 400 and 700 nm: 83%) by RF magnetic sputtering at room temperature. The Ca doping level in CuAlO$_x$ is fixed at 10 at.%. Three weight percentage Al doped ZnO (AZO) films are used as the n$^+$-layer contact electrode. The Mg content of the MgZnO layer is varied as 0 (ZnO), 5, 10, and 30 at.%.

Two hundred nanometer thick CuAlO$_x$:Ca (with 10 at.% Ca) thin films are deposited on ITO-coated PET by RF magnetic sputtering. ITO is chosen as the lower transparent electrode owing to its ohmic contact nature with $CuAlO_2$. The deposition conditions are listed as follows: RF power, 100 W; working pressure, 2 mTorr; sputtering gas, argon–oxygen mixture with Ar:O_2 ratio of 3:2. Next, 40 nm thick $Mg_xZn_{1-x}O$ (x = 0, 0.05, 0.1, and 0.3) thin films are deposited on p-CuAlO$_x$:Ca as the n-layer. The deposition conditions for $Mg_xZn_{1-x}O$ are as follows: RF power of 120 W; working pressure, 2 mTorr; sputtering gas, pure Ar. 100 nm thick higher conductivity n$^+$-AZO is deposited as the top transparent electrode to reduce the contact resistance. The deposition conditions for n$^+$-AZO are as follows: RF power, 120 W; working pressure, 2 mTorr; sputtering gas, pure Ar. All films are deposited at room temperature without additional heat-treatment.

The transmittances of the MgZnO films are measured by UV–Vis spectrophotometers (Jasco V-670). The J–V characteristics of the diodes are measured using an electrometer (Keitheley 2636A) in the dark and/or under illumination from a UV lamp (UVP, Blak-Ray B-100). The illumination UV power density is calibrated using a UV meter (Lutron Electronic, UV-340).

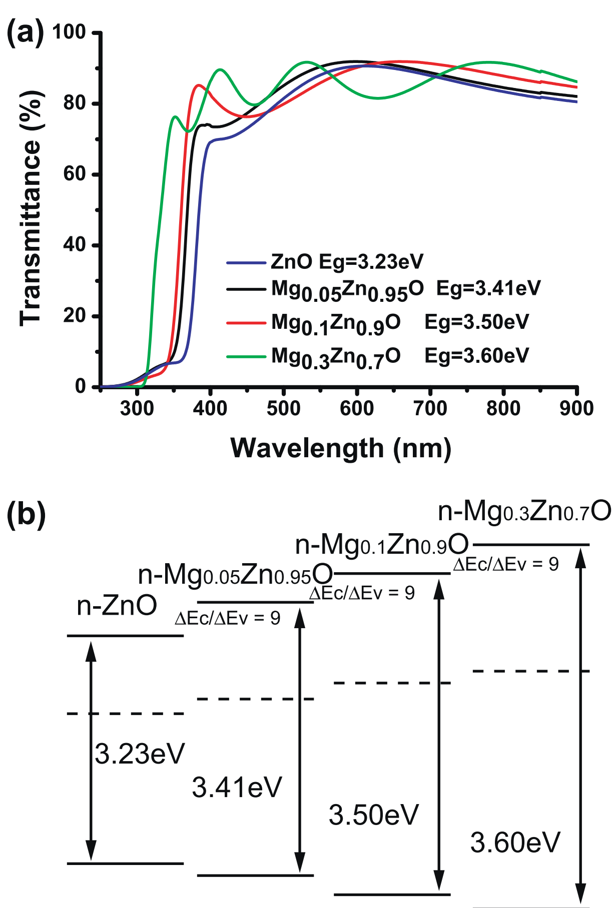

Fig. 1. (a) Transmittance of $Mg_xZn_{1-x}O$ (x = 0, 0.05, 0.1, and 0.3) thin films. (b) Bandgaps and band offsets for $Mg_xZn_{1-x}O$ materials.

3. Results and discussion

Fig. 1(a) shows the optical transmittance of the $Mg_xZn_{1-x}O$ (x = 0, 0.05, 0.1, and 0.3) thin films. The absorption edges of the $Mg_xZn_{1-x}O$ thin films shift toward a short wavelength, indicating bandgap tuning by the Mg content of the $Mg_xZn_{1-x}O$ layer. The optical band gap is determined by the Tauc equation [51]:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where A is a constant; $h\nu$, the photon energy; E_g, the optical band gap; α the absorption coefficient, and $n = 2$ for the direct band gap. The Tauc bandgaps of $Mg_xZn_{1-x}O$ are fitted as 3.23, 3.41, 3.50, and 3.60 eV, for x = 0, 0.05, 0.1, and 0.3, respectively. MgZnO

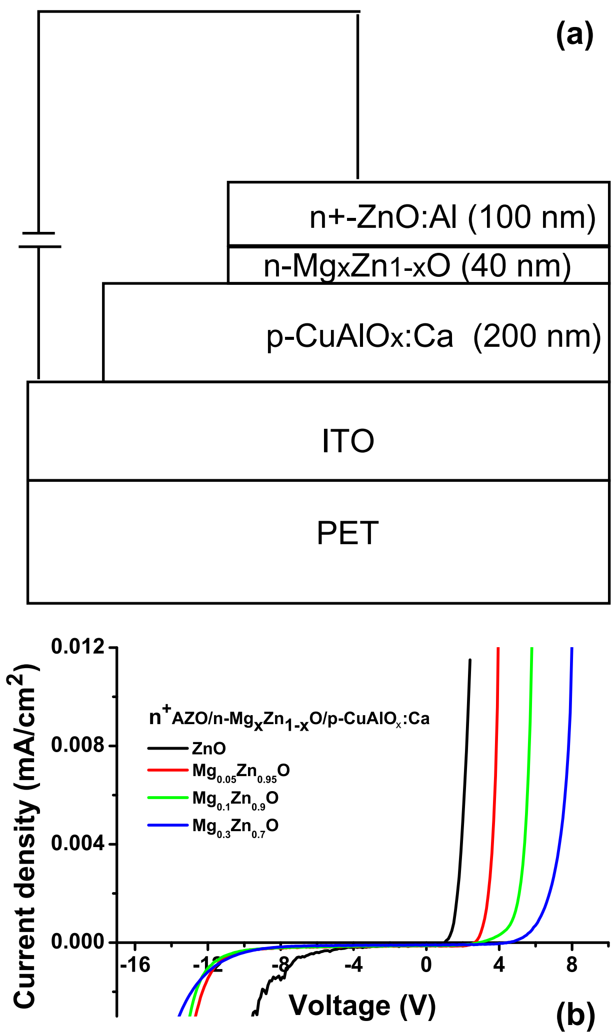

Fig. 2. (a) Schematic diagram of n$^+$-ZnO:Al/n-$Mg_xZn_{1-x}O$/p-CuAlO$_x$:Ca diode. (b) J–V characteristics of the diodes.

Table 1
Turn-on voltages and breakdown voltages for n-$Mg_xZn_{1-x}O$/p-CuAlO$_x$:Ca heterojunctions with different Mg contents.

$Mg_xZn_{1-x}O$	x = 0	x = 0.05	x = 0.1	x = 0.3
V_{on} (V)	2.0	2.8	4.7	5.7
V_{BR} (V)	−7.5	−11.5	−12.3	−13.1
Leakage current (at −4 V) (nA)	2.36	1.63	1.49	1.16
Series resistance (Ω)	4.22×10^6	2.74×10^7	4.33×10^7	4.89×10^7