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Fabrication of transparent p–n junction diode based on oxide semiconductors deposited by RF magnetron sputtering

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Abstract

Transparent p–n heterojunction diodes based on oxide semiconductors were fabricated by RF magnetron sputtering on alkali-free glass substrates below 500 °C. 3% Al-doped ZnO (~400 nm) was deposited as an n-type component, and $SrCu_2O_2$ (~290 nm) as a p-type component. Sn-doped In_2O_3 (~190 nm) and 7% V-doped Ni metals (~13 nm) were deposited as n- and p-type electrodes at room temperature, respectively. XRD pattern revealed the as-deposited n-/p-components were single phases. 3% Al-doped ZnO as an n-type component was deposited under 10% O_2 in Ar atmosphere at 400 °C, and showed a conductivity of 0.43 S/cm, carrier density of $10^{17}/cm^3$ order. $SrCu_2O_2$ as a p-type component were deposited under 1% H_2 in Ar atmosphere at 500 °C, and showed a conductivity of 0.078 S/cm, carrier density of $10^{17}/cm^3$ order. The as-deposited p–n heterojunction diode had a total thickness of 895 nm and showed very high optical transparency of about 69% at 550 nm. *I–V* measurement of the multilayered transparent p–n heterojunction diode exhibited rectifying characteristics, but the turn-on voltage was somewhat obvious depending on the sample preparation condition. A plausible explanation on the rectifying characteristics of the transparent p–n junction diodes will be suggested.

Keywords: A. Films; C. Electrical properties; C. Optical properties; $SrCu_2O_2$

1. Introduction

Transparent electronics including transparent diode, TFT, CMOS, functional window, etc. is an emerging advanced technology, and will be realized near future [1]. As a pre-requisition of realizing transparent electronics, technology for transparent conductive oxides (TCOs), which can control electrical conductivity, mobility, carrier concentration and so on should be developed.

TCOs exhibit simultaneously high electrical conductivity and optical transparency in the visible light range of 400–800 nm, and must have wide band gap over about 3 eV. TCOs such as Sn-doped In_2O_3 (ITO), F-doped SnO_2 (FTO) are widely used as transparent electrodes for LCD, touch panel, solar cells, and organic light emitting diodes (OLEDs) and so on [2–4]. But most TCOs exhibit n-type electrical conductivity, thus the applications of transparent devices based on the transparent p–n junctions are limited due to the lack of p-type TCOs.

Since first report on $CuAlO_2$ [5] by Hosono et al., various p-type TCOs, which have delafossite structure such as $CuGaO_2$ [6], $CuInO_2$ [7], $CuScO_2$ [8] and so on have been reported.

On the other hands, $SrCu_2O_2$ which is non-delafossite p-type TCOs can be deposited below 350 °C onto low-cost glass substrate and exhibits good electrical properties of 4.8×10^{-2} S/cm in conductivity, in 0.46 cm^2/V s in mobility and $6.1 \times 10^{17}/cm^3$ in carrier concentration, as was reported by Kudo et al. [9]

It is noteworthy that the low deposition temperature below 350 °C in $SrCu_2O_2$ (SCO) gives important advantages such as flexible choice of substrate materials and lowering process temperature.

Rectifying behavior in other oxide based p–n heterojunction diodes has also been reported, including near UV LED composed of p-$SrCu_2O_2$/n-ZnO [10], p-ZnO:N/n-ZnO [11], p-$CuYO_2$:Ca/n-ZnO [12], p-$CuInO_2$:Ca/n-$CuInO_2$:Sn [13], p-$CuAlO_2$:Ca/n-ZnO [14] and p-$ZnRh_2O_2$/n-ZnO [15]. However,

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Table 1
Summary of deposition parameters.

Target	Ni/V	SCO	Zn (3% Al)	ITO
RF power [W/cm^2]	0.65	3	2/2.5	3
Sputtering gas	100% Ar	1% H_2/Ar	10% O_2/Ar	5% O_2/Ar
Deposition pressure [Pa]	6.6	2.6	2.6	2.6
Deposition temp./time	RT/30 min	500 °C/35 min	400 °C/90 min	RT/20 min
Annealing	–	–	–	400 °C/60 min
Film thickness [nm]	13	300	230/400	185

the adopted deposition methods for p-TCOs were limited in PLD [16] or E-beam [17].

In this work, in order to realize commercially available transparent diodes, p–n heterojunction composed of n-AZO (3% Al-doped ZnO) and p-$SrCu_2O_2$ have been fabricated by RF magnetron sputtering on alkali-free glass substrates below 500 °C, and electrical properties of each component layer, *I–V* characteristics have been evaluated.

2. Experimental

2.1. Deposition of diode layers

p–n hetero-junction diode films were deposited on 20 mm × 20 mm-sized alkali-free glass (eagle 2000, Corning, USA) by RF magnetron sputter (LSS-01, J&L Tech, Korea). Substrates were washed with acetone, methanol and rinsed in D.I. water. The base pressure of the chamber prior to deposition was better than 9×10^{-4} Pa and all targets were pre-sputtered for 10 min.

The ITO films were deposited on the glass substrate as an Ohmic electrode for n-AZO. After deposition of ITO, n-AZO films were deposited by reactive sputtering using a Zn–3% Al metal alloy target (purity 99.95%) under the atmosphere of 10% O_2 in Ar. The sputtering power was adjusted in the range of 2–2.5 W/cm^2. p-$SrCu_2O_2$ thin films were grown on the as-sputtered AZO film using a single crystalline $SrCu_2O_2$ target synthesized by solid-state reaction of stoichiometric mixture of CuO and $SrCO_3$. Ni–7% V metal alloy as a p-electrode was deposited on the as-prepared $SrCu_2O_2$ film. Specific conditions of the deposited each layers were listed in Table 1.

2.2. Evaluation of p–n heterojunction properties

Crystalline phases of the films were confirmed using X-ray diffraction (D MAX2200, RIGAKU, Japan, Cu Kα, 40 kV/30 mA). Thickness of ITO, AZO, SCO, Ni/V film was measured with a surface profiler (Alpha step 500, TENCOR, USA), and confirmed as 190 nm, 230 nm/400 nm, 290 nm, 13 nm, respectively. Optical transmittance spectra of the films were measured in the wavelength range from 200 to 1100 nm with a UV–VIS spectrophotometer (V-570, JASCO, Japan).

Electrical properties of each layer were measured by Hall measurement system (HMS-3000, ECOPIA, Korea) using a van der Pauw method. The current–voltage (*V–I*) characteristics of the p–n heterojunction specimen were evaluated using a source measurement unit (Model 2400, KEITHLY, USA) with supply voltage range of −5 V to +5 V.

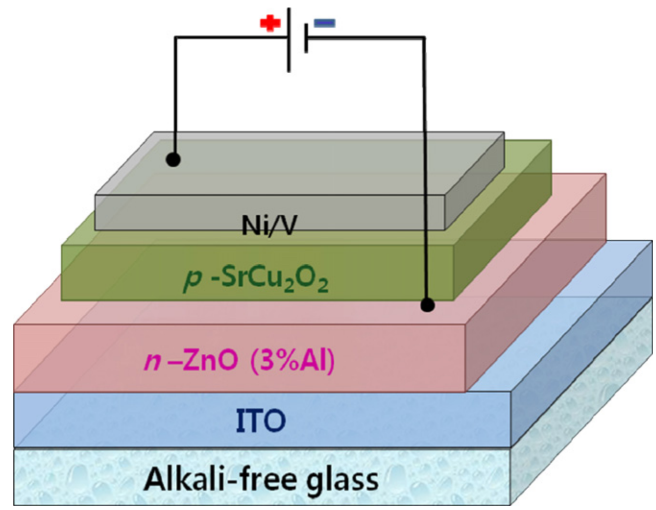

Fig. 1. Structure of the heterojunction diode.

3. Results and discussion

Fig. 1 shows the structure of the hetero-junction diode. ITO as n-electrode, was deposited under 5% O_2 in Ar atmosphere at room temperature. 3% Al-doped ZnO (AZO) as an n-type component were deposited under 10% O_2 in Ar atmosphere at 400 °C, and $SrCu_2O_2$ as a p-type component were deposited on the as-deposited AZO under 1% H_2 in Ar atmosphere at 500 °C. Ni–V alloy as p-electrode was deposited on the as-deposited $SrCu_2O_2$ in Ar atmosphere at room temperature. Table 1 presents a summary of deposition parameters.

Table 2 shows electrical properties of each component layer of p–n hetero-junction diode. Conductivities of 3% Al-doped ZnO (AZO) as an n-type component and $SrCu_2O_2$ as a p-type component were 0.43 S/cm and 0.078 S/cm, respectively. Carrier densities of each layer were 10^{17}/cm^3 order. 13 nm-thick Ni/V alloy film in order to maintain high transmittance resulted in somewhat low conductivity. XRD pattern revealed the as-deposited n-/p-component were single phases.

Fig. 2 presents cumulative optical transmittance spectra of NiV/p-$SrCu_2O_2$/n-AZO/ITO multilayer on alkali-free glass. The cumulative optical transmittance after depositing each multilayer shows 80.2% for ITO, 81.6% for AZO on ITO layer, 71.6% for SCO on AZO, and the final cumulative transmittance reveals 69.4% at 550 nm, respectively. The higher transmittance of AZO/ITO multilayer than that of ITO single layer is

Table 2
Electrical properties of p–n heterojunction layers.

Target	Ni/V	SCO	ZnO (3% Al)		ITO
			230 nm	400 nm	
Electrical conductivity [S/cm]	176	0.078	0.12	0.43	469.8
Mobility [cm^2/V s]	3.21	3.34	5.72	6	1.97
Carrier concentration [/cm^3]	3.43×10^{20}	1.45×10^{17}	1.35×10^{17}	4.49×10^{17}	1.49×10^{21}
Hall-coefficient	−0.018	+42.92	−46.26	−13.91	−0.004

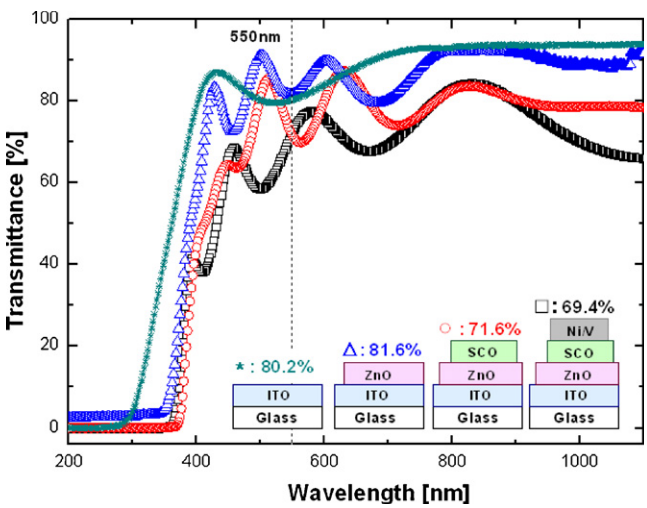

Fig. 2. Cumulative optical transmittance spectra of NiV/p-$SrCu_2O_2$/n-AZO/ITO heterojunction diode on alkali-free glass.

thought to be originated from reduction of surface reflectance of light owing to lower refractive index of AZO layer than ITO. Because of the initial transmittance of ITO film was somewhat low, it is expected that high transmittance more than 70% can be easily obtained by increasing the transmittance of ITO layer. From $(\alpha h\nu)^2$ vs. $h\nu$ plots, the optical band gap of 3% Al-doped ZnO and $SrCu_2O_2$ thin films were estimated to be <3.16 eV and 3.24 eV at room temperature, respectively. This value was the similar results reported value of 3.3 eV for $SrCu_2O_2$ by Kudo et al. [9].

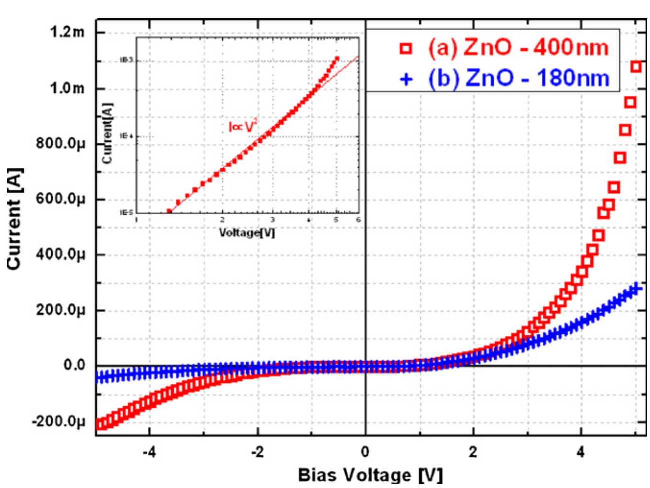

Fig. 3. *I–V* characteristics of p-$SrCu_2O_2$/n-AZO heterojunction diode.

I–V characteristics of p-$SrCu_2O_2$/n-AZO heterojunction diode are shown in Fig. 3. The *I–V* characteristics reveal non-linear rectifying behavior with turn-on voltage of 0.7–1.2 V, and the ratio of forward to reverse current was 5.5–7.4 in the range of −5 to 5 V. Nakamura et al. sputtered $SrCu_2O_2$ on single-crystalline ZnO, and reported rectifying behavior with the turn-on voltage 0.7–2.2 V according to crystallographic axis of ZnO [18]; 0.7 V for Zn-terminated polar plane, 0.9 V for non-polar plane, and 2.2 eV for O-terminated plane. The value of 0.7–1.2 V obtained in this work is reasonable considering the non-orientation characteristics of the AZO layer. In this work, *I–V* curve showed $I \propto V^2$ relationship, which is characteristics of space charge limited current associated with insulating layer [19]. And Jayaraj et al. reported this space charge limited current mechanism in p-$CuYO_2$/n-AZO heterojunction diode [20]. It is thought that this space charge limited current mechanism arises from change in the interfacial resistivity of $SrCu_2O_2$ and AZO layer during deposition of $SrCu_2O_2$ in reducing atmosphere. Further work including *C–V* characterization is needed.

4. Conclusions

Highly transparent p-$SrCu_2O_2$/n-AZO (3% Al-doped ZnO) heterojunction diodes were fabricated by RF magnetron sputtering on alkali-free glass substrates below 500 °C.

The as-deposited p–n heterojunction diode showed very high transparency of about 69% at 550 nm. Hall measurement revealed conductivity, mobility and carrier concentration of n-AZO as an n-type semiconducting layer were 0.43 S/cm, 6 cm^2/V s, 10^{17}/cm^3 order, respectively. Those of $SrCu_2O_2$ as a p-type semiconducting layer were 0.078 S/cm, 3.3 cm^2/V s, and 10^{17}/cm^3 order, respectively.

I–V characteristics showed non-linear rectifying behavior with turn-on voltage of 0.7–1.2 V, and the ratio of forward to reverse current was 5.5–7.4 in the range of −5 to 5 V. The *I–V* curve showed $I \propto V^2$ relationship, which is characteristics of space charge limited current associated with insulating layer. It is thought that a reduction atmosphere during deposition of $SrCu_2O_2$ is the reason for the change in the surface properties of AZO layer. Further work including *C–V* characterization is needed.

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