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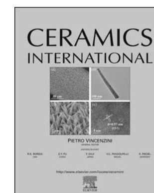

Studies of thermoelectric transport properties of atomic layer deposited gallium-doped ZnO

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ABSTRACT

The thermoelectric transport properties of atomic layer deposited (ALD) gallium doped zinc oxide (GZO) thin films were investigated to identify their potential as a thermoelectric material. The overall thermoelectric properties, such as the Seebeck coefficient and electrical conductivity, were probed as a function of Ga concentration in ZnO. The doping concentration was tuned by varying the ALD cycle ratio of zinc oxide and gallium oxide. The GZO was deposited at 250 °C and the doping concentration was modified from 1% to 10%. Sufficient thermoelectric properties appeared at a doping concentration of 1%. The crystallinity and electronic state, such as the effective mass, were investigated to determine the enhancement of the thermoelectric properties. The efficient Ga doping of GZO showed a Seebeck coefficient of 60 μV/K and an electrical conductivity of 1808.32 S/cm, with a maximum power factor of 0.66 mW/mK^2.

1. Introduction

Thermoelectric materials, which are conductors or semiconductors that can convert heat energy directly into electrical power, have attracted interest because of the exhaustion of fossil fuels and concerns over greenhouse gas emissions [1].

Thermoelectric materials generate electricity from a temperature gradient in the materials, called the Seebeck effect. The efficiency of thermoelectric materials is defined by the figure of merit, ZT [2], which is calculated by Eq. (1):

$$ZT = \alpha^2 \sigma T / K \tag{1}$$

where, α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and K is the thermal conductivity [2,3].

However, previous research on thermoelectric materials has focused on intermetallic compound materials [4–7], which are toxic and expensive and require an additional process to prevent vaporization and chemical reaction [8]. Because of these disadvantages, oxide-based thermoelectric materials have been investigated. Oxide-based materials are eco-friendly, inexpensive, and stable even at high temperature [9]. Materials based on SnO_2 [10,11], In_2O_3 [11], and ZnO [11–13] have high potential as good thermoelectric materials due to their high electrical conductivity, and some have a high Seebeck coefficient [13,14]. A Additionally, some groups have reported that the thermal conductivity of the oxide-based materials is also relatively low [15,16]. The low thermal conductivity, high electrical conductivity, and high Seebeck coefficient are important parameters for efficient thermoelectric materials.

Among these ZnO-based oxides, Al-doped ZnO (AZO), In-doped ZnO (IZO) and Ga-doped ZnO (GZO) are good candidates as thermoelectric materials [13–19], based on investigations of GZO thermoelectric materials deposited by atomic layer deposition (ALD) [20,21].

Therefore, we investigated the thermoelectric properties of GZO via the Seebeck coefficient, electrical conductivity deposited by ALD, and power factor as calculated by Eq. (2):

$$\text{Power factor} = \alpha^2 \sigma \tag{2}$$

The ALD method has many advantages. First, thin film deposited by ALD has fewer impurities due to the surface reaction. Second, regulation of the thickness in the angstrom scale can be realized by a self-limited reaction. Lastly, the film can be deposited conformally and with high quality by the self-limited reaction on the surface. Therefore, the GZO film deposited by ALD is expected to exhibit good thermoelectric properties.

2. Experimental details

GZO thin films were produced by modulating the sequence of each ALD cycle of ZnO and Ga_2O_3. Diethylzinc (DEZ) and H_2O (water) were used to deposit the ZnO layer, and trimethylgalluim (TMG) and ozone

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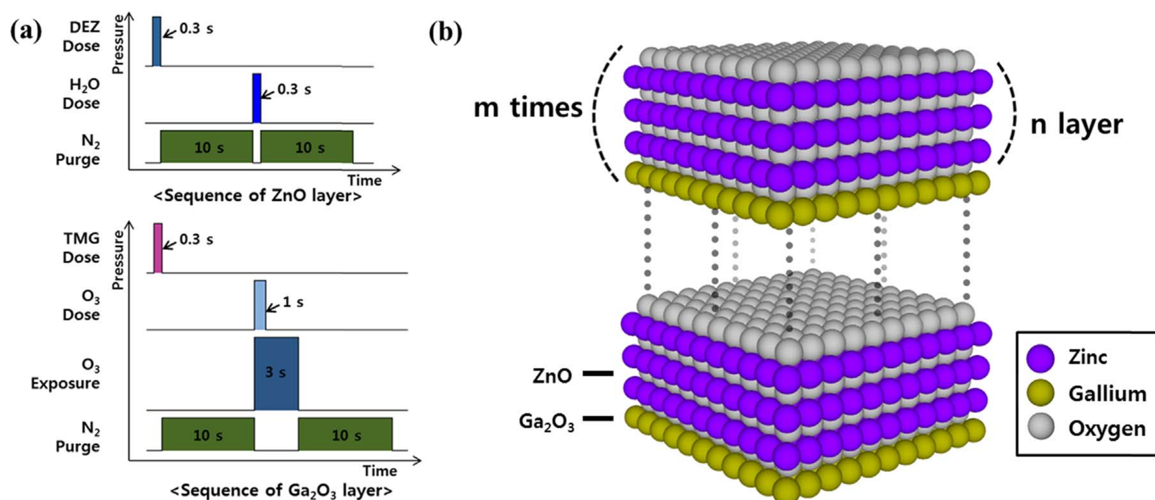

Fig. 1. (a) Atomic layer deposition sequence of the ZnO and Ga_2O_3 layers. (b) Structure of the Ga-doped ZnO thin film modulated by the atomic layer deposition sequence.

(O_3) were used to deposit the Ga_2O_3 layer on Si, SiO_2 and glass substrates. N_2 gas (99.9999%) was used as the carrier gas and its flow rate was 50 sccm to sustain a working pressure for 300 mtorr. DEZ and TMG were contained in a canister composed of stainless steel. DEZ and water were maintained at room temperature and TMG was cooled to 10 °C. The amount of the TMG dose in the reactor decreased when a gasket type orifice of 500 µm was used [21].

Fig. 1(a) illustrates the sequences of the ZnO and Ga_2O_3 ALD cycle as follows: ZnO; DEZ dose (0.3 s) – N_2 purge (10 s) – H_2O dose – N_2 purge (10 s) and Ga_2O_3; TMG dose (0.3 s) – N_2 purge (10 s) – O_3 dose (1 s) – O_3 exposure (3 s) – N_2 purge (10 s). The exposure time of the ozone was sufficient for a reaction with the methyl group on the surface, and during exposure, the reactor was isolated with a rotary vane pump. The growth temperature was 250 °C and then the growth rate of ZnO and Ga_2O_3 was 1.36 Å/cycle and 0.67 Å/cycle, respectively. Because the growth rate of Ga_2O_3 varied with the growth temperature, the growth temperature was fixed at 250 °C [21]. The concentration of the Ga dopant was controlled by changing the ratio between the ZnO and Ga_2O_3 cycles. The GZO samples were prepared with five different Ga concentrations, 0%, 1%, 2%, 5%, 10%, and the cycle ratios between ZnO and Ga_2O_3 were n:0, 49:1, 24:1, 10:1, 5:1, respectively. The total film thickness was 140 nm, and this structure is illustrated in Fig. 1(b).

The film thickness was measured by a spectroscopic ellipsometer (SE, Ellipso Technology, UV-FM8). Hall measurements (Ecopia) were conducted at various temperatures to verify the electrical properties (carrier type, carrier concentration, conductivity and Hall mobility). Seebeck coefficient measurement equipment (Homemade) was used to measure the Seebeck coefficient. The crystal structure was examined by X-ray diffraction (XRD, Rigaku D/Max-2200V) using a theta −2 theta scanning method with a Cu K_α X-ray source.

3. Result and discussion

The crystal structures of ZnO and GZO are shown in Fig. 2. The XRD patterns of the 0%, 1%, 2%, 5% and 10% GZO samples indicate that all of the samples have a poly-crystalline phase based on the wurtzite structure in various directions [22–24], which is attributed to the relatively high growth temperature during the ALD process [25,26]. The (100), (002), and (110) diffraction peaks appeared for a Ga concentration between 0% and 10%. There were no other peaks, and therefore, the phases of ZnO and GZO were based on the wurtzite structure. The change of the crystal orientation was observed according to the Ga doping concentration. The intensity of the (002) peak decreased as more Ga was introduced. As shown in a previous report from the Gordon group [24], the relative peak intensity of (002) and

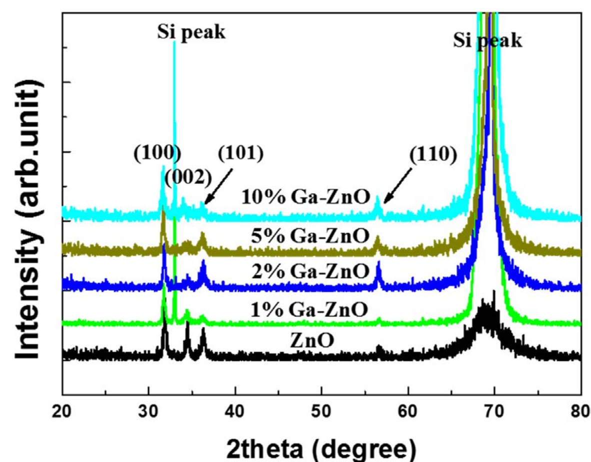

Fig. 2. X-ray diffraction of Ga-doped ZnO thin film grown by atomic layer deposition.

(101) changed depending on the crystal orientation along the c-axis. As shown in Fig. 2, the (002) and (101) peak intensity decreased, which means the preferred orientation along the c-axis was suppressed as the Ga doping concentration increased. A small amount of Ga dopant can suppress the orientation of films along the c-axis and stimulate the growth of other orientations, such as (110). However, by adding only 1% Ga to ZnO, the intensity of the (101) and (110) peaks decreased. Therefore, when 1% Ga is doped in ZnO, the (100) orientation is dominant. As the Ga doping concentration increased, the other peaks increased again because a dopant greater than the maximum solubility (1%) does not trigger the c-axis orientation. Unlike the crystal behaviors of Al doped ZnO (AZO) ALD films [27], GZO films did not show any significant enhancement of the preferred crystal orientation because of the discrepancy of Ga and Al ionic sizes in ZnO matrix, which are Al^{3+}(0.054 nm), Ga^{3+}(0.062 nm), and Zn^{2+} ions (0.074 nm) [28]. If Ga in ZnO exceeds the maximum solubility, neutral atoms could be located at grain boundaries. At 10% Ga, the most neutral atom that induces a potential barrier was generated in this experiment. These results help to understand the following experimental results.

The electrical properties (carrier concentration, conductivity, and Hall mobility) according to the Ga composition at room temperature are shown in Fig. 3. The carrier concentration increased sharply as more Ga dopants were added. As more Ga atoms were doped, the carrier concentration increased from 1.04×10^{20} cm^{-3} to 9.31×10^{20} cm^{-3}. The Ga-ZnO film has an n-type property because the Ga atom replaces the Zn atom with increasing free electron carriers [29,30]. The Ga atom has one more outermost electron related to the

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