Thermoelectric performances in transparent ZnO films including nanowires as phonon scatterers

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Abstract. We report the fabrication technique and electrical properties of embedded-ZnO nanowires (NWs) structure for high-performance transparent thermoelectric materials. In fabrication technique, we revealed that the length of NW is less than 2 μm for embedding NWs. Our embedded-ZnO NWs structures showed a little smaller electrical conductivities than ZnO films (without ZnO NWs) at the carrier concentration of ~ 10¹⁸ cm⁻³. However, at high carrier concentration, our embedded-ZnO NWs structures are expected to show high thermoelectric performances due to the drastic reduction of υ and smaller σ degradation, because there is the difference of MFP between electron and phonon. Our work showed the design guide to enhance the performance of transparent thermoelectric materials.

1. Introduction
Thermoelectric applications require materials with high value of $ZT = S^2 \sigma T / \kappa$ ($S$: seebeck coefficient, $\sigma$: electrical conductivity, $T$: absolute temperature, and $\kappa$: thermal conductivity). However, these parameters are correlated with each other and it has been difficult to control them independently. Nanostructuring has recently been found to be an effective way to decrease $\kappa$ [1] or to increase $S^2 \sigma$ [2]. ZnO is a semiconductor composed of ubiquitous elements with wide energy band gap (3.3 eV). Therefore, ZnO-based materials are expected as transparent thermoelectric materials due to high $S^2 \sigma$, which harvests the wasted heat from transparent products such as hot glass windows in the buildings [3]. However, their $ZT$ is quite low at room temperature compared with the value for practical application ($ZT \sim 1$), because the $\kappa$ is high (~ 45 Wm⁻¹K⁻¹ at room temperature) [4]. Here, we propose an embedded-ZnO nanowires (NWs) structure for high $ZT$ thermoelectric ZnO material [5]. The design concept is that crystal interfaces of NWs scatter phonons to reduce $\kappa$, and power factor can also be increased due to one-dimensional carrier conduction [6] or energy filtering effect at the interfaces [2] (Figure 1). In this paper, we develop formation of embedded-ZnO NWs structure that enhances thermoelectric properties due to scattering of phonon and low energy electron.

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2. Sample preparation and measurements
ZnO films were formed on quartz glass substrates as a seed template at 400ºC under an oxygen pressure of 1 Pa for 1 h by pulsed laser deposition (PLD) (Figure 2(a)). The targets were put 3 cm away from Si substrates and irradiated with 10 Hz pulsed laser (ArF excimer laser with 193 nm wavelength). Highly-oriented ZnO NWs were grown on the seed films under an Ar carrier gas of 20 sccm by physical vapor transport (Figure 2(b)). The temperature at the position of source material was increased to 780ºC in 1 h and was maintained for 1 h. Finally, ZnO was deposited again by PLD over ZnO NWs to form embedded-ZnO NWs structure (Figure 2(c)).

The surface and cross-sectional morphologies of the samples were observed by scanning electron microscopy (SEM) with a 10 keV electron beam. Electrical properties of the samples were measured by van der Pauw method.

3. Nanostructure formation and thermoelectric properties
Figures 3(a) and (b) show the cross-plane and plane-view scanning electron microscope images of highly-oriented ZnO NWs, respectively. We confirmed that NWs were formed with areal density of \(4.4 \times 10^9 \text{ cm}^{-2}\) and the length of \(\sim 300 \text{ nm}\) from these results. In the case of NWs with the length of \(> 2 \mu \text{m}\), NWs were not embedded fully, because filling ZnO was trapped at the front edge of NWs. Therefore, it is important that NWs have the length less than \(2 \mu \text{m}\) for forming embedded-ZnO NWs structure. After depositing ZnO for embedding, the structures of NWs were maintained as shown in Figure 3(c).

Table 4 shows that \(\sigma\) of embedded-ZnO NWs structures were smaller than ZnO films (without ZnO NWs) at the carrier concentration of \(~ 10^{18} \text{ cm}^{-3}\). The interfaces between NWs and films may scatter electrons, leading to reduction of \(\sigma\). In general, thermoelectric materials show the best characteristics at high carrier concentration (~10^20 cm^{-3}). At high carrier concentration, the NW interface scattering of electron is considered to be smaller due to shorter length of the mean free path (MFP) based on ionized impurity scattering process. Therefore, in the present case (low carrier concentration of \(~ 10^{18} \text{ cm}^{-3}\)), the NW interface scattering of electron may degrade \(\sigma\), but its contribution become smaller at high carrier
concentration, which indicates the difference of $\sigma$ between embedded-ZnO NWs structures and ZnO films can become smaller.

On the other hands, the MFP of phonon is much longer than electron. Our previous work demonstrated ~200 times reduction of by introducing the nanoscale interfaces in Si films (Connected Si nanocrystals: CSN) [1]. Considering the present embedded-ZnO NWs structures, the NW structures can reduce $\kappa$, resulting in high thermoelectric performances.

![Figure 3 Scanning electron microscope images before ((a) cross-plane (b) plane-view) and after forming filling ZnO.((c) plane-view).](image)

**Table 1.** Electrical conductivities of embedded-ZnO NWs structures (ZnO NWs) and ZnO films at the carrier concentration of ~$10^{18}$ cm$^{-3}$

|          | ZnO NWs | ZnO films |
|----------|---------|-----------|
| $\sigma$ ($\Omega^{-1}$ cm$^{-1}$) | 3.1     | 18.8      |

**4. Conclusions**

We developed embedded-ZnO NWs structures for high performance transparent thermoelectric materials. In fabrication technique, we revealed that the length of NW is less than 2 $\mu$m for embedding NWs. Our embedded-ZnO NWs structures showed a little smaller $\sigma$ than ZnO films (without ZnO NWs) at the carrier concentration of ~$10^{18}$ cm$^{-3}$. However, at high carrier concentration, our embedded-ZnO NWs structures can show high thermoelectric performances due to the drastic reduction of $\kappa$ compared with the small reduction of $\sigma$, because there is the difference of MFP between electron and phonon.

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