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Inducing Thermoelectricity in C-axis Aligned Crystalline InGaZnO Thin Film via Hydrogen Annealing

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Abstract

C-axis aligned crystalline InGaZnO was thermoelectrically enhanced by hydrogen incorporation during annealing. A maximum PF of 0.087 mW/mK^2 was obtained for 4% H_2-annealed sample at 388 K. It was proposed that the almost simultaneous formation of oxygen vacancies and hydrogen substitution onto the oxygen vacancy sites led to high electrical conductivities up to 314 S/cm, which was mainly responsible for the superior thermoelectric properties. The thermoelectric enhancement performed during the annealing step likewise presents an improvement in stability owing to hydrogen passivation of oxygen vacancies.

1. Introduction

C-axis aligned crystalline InGaZnO (c-IGZO) is a specially engineered thin film which displays high crystallinity along the c-axis, but shows no grain boundaries along the a-b plane [1]. It has been known to solve reliability issues in amorphous IGZO in thin film transistor (TFT) applications. It would be interesting, though, to develop a thermoelectric device based on c-IGZO, as its structure makes a perfect thermoelectric material. The combination of an amorphous-like structure along the a-b plane makes the oxygen vacancies easily controllable, while the highly crystalline, superlattice c-axis plane enables good transport properties and can potentially decrease the thermal conductivity. However, as this material has been optimized for TFTs, it possesses extremely high resistivity, due to its specifically low amount of oxygen vacancies (Vo). Therefore, in this study, c-IGZO thin films were transformed into a highly efficient and reliable thermoelectric device by simply incorporating hydrogen into the annealing atmosphere. The effect of the amount of H_2 in the annealing atmosphere on the thermoelectric properties was also studied.

2. Experimental Procedure

C-IGZO thin films of 200 nm thicknesses were used. Metal electrodes (Mo/Au) were then deposited onto the samples via electron beam evaporation using a metal mask. Annealing was then performed at 400ºC for 2h under varying atmospheres – pure N_2, 1 H_2 : 50 N_2 (2% H_2) and 1 H_2 : 25 N_2 (4% H_2). Thermoelectric properties were measured in vacuum from 100 to 400 K using a physical properties measurement system (Quantum Design EverCool II).

3. Results and Discussion

Fig. 1 shows the cross-sectional TEM image of the c-IGZO. It reveals a highly periodic stacking, suggesting a natural superlattice structure, which is desirable for achieveing high Seebeck coefficients due to increased interface phonon scattering. However, as opposed to a typical superlattice wherein single crystallinity is observed along the a-b plane, the image reveals several individual crystals latched one after another. This unique structure was described by Yamazaki, et. al in their work to be existing as neither nanocrystalline nor single crystalline [2]. In any case, the crystallinity seems to be preserved along the a-b plane, as supported by the XRD pattern in Fig. 2.

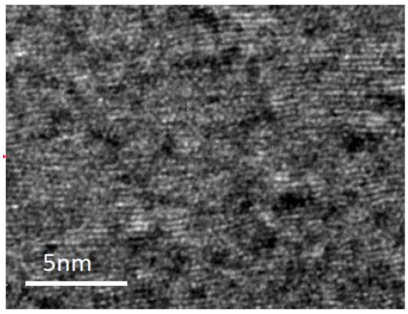

Fig. 1. Cross-sectional TEM image of as-deposited c-IGZO.

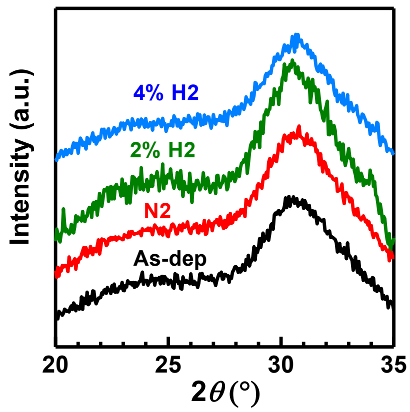

Fig. 2. XRD patterns of the as-deposited, N_2-annealed, 2% H_2-annealed and 4% H_2-annealed c-IGZO samples.

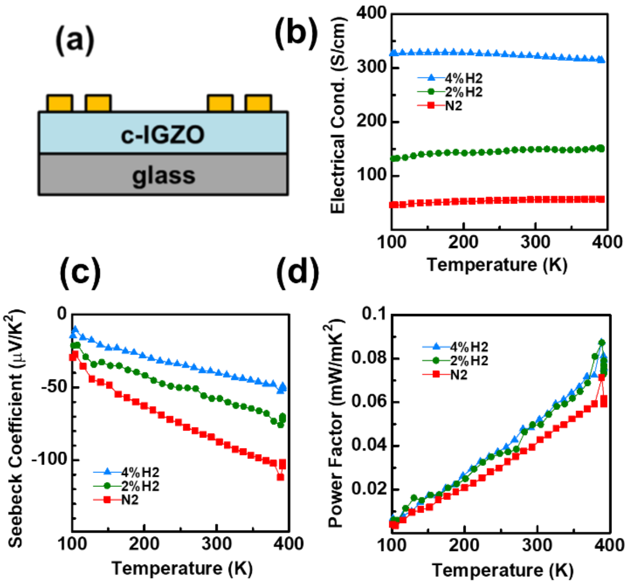

Fig. 2. (a) thermoelectric device configuration, (b) electrical conductivity, (c) Seebeck coefficient and (d) power factor of the c-IGZO as an effect of amount of H_2 in annealing environment.

Shown in Fig. 3 are the thermoelectric properties of the c-IGZO samples at from 100 to 400 K. Prior to any annealing treatment, the thermoelectric properties were well below the measurable range due to the high sample resistance of about the GΩ range. However, upon annealing with pure N_2, the electrical conductivity (σ) rose to a maximum of 56.6 S/cm at a measurement temperature of 390 K. When 2% H_2 was added to the annealing environment, the conductivity tripled throughout the temperature range up to 149 S/cm at 390 K. On the other hand, a six-fold improvement of up to 314 S/cm was observed when the H_2 content was increased to 4%. This can probably be explained by the simultaneous formation of Vo under an oxygen-poor environment and substitution of H atoms in the Vo. The Vo formation is well-known to increase the electrical conductivity, while H substitution most likely introduces additional free carriers to further boost the electrical conductivity. Lastly, no significant temperature-dependence of the σ was observed.

Seebeck coefficients (S), on the other hand, decreased significantly at 400 K from -103.6 μV/K under pure N_2 to -69.9 μV/K and -50.9 μV/K with 2% and 4% hydrogen contents, respectively. This is expected with the dramatic increase in electrical conductivity, as S is inversely proportional with carrier concentration while the σ is directly related. However, the decrease in S is not so severe such that the extreme rise in electrical conductivity compensated for it, leading to an increase in power factor, as shown in Fig. 1d. This can probably be due to an improvement in crystallinity with hydrogen incorporation, as seen in the XRD patterns in Fig. 3. A maximum power factor (PF) of 87.4 μW/mK^2 at 390 K was achieved. This value is highly comparable to previous reports on c-axis aligned crystalline InGaZnO as shown in Table 1. The study by Nguyen et. al reached a PF of about <100 μW/mK^2 which was also said to be Vo-derived [3]. However, an oxygen-poor atmosphere was used for their deposition conditions, which is a more difficult way to control the amount of oxygen vacancies. On the other hand, the Vo formation in this study was done simultaneously with H incorporation during the annealing stage. In this manner, the H incorporation step instantaneously generates free carriers, as well as passivates the oxygen-related defects. This potentially leads to efficient thermoelectricity as well as high stability.

In order to confirm good device reliability, stability against air and moisture was also proven for the c-IGZO samples. Even after exposure under 95% RH at 80ºC for up to 16h, the PF remains almost the same. Likewise, storage in air for up to three months led to negligible change in thermoelectric properties.

Table 1. Power factor value of c-IGZO in comparison to previously reported studies at around 400 K.

	PF (μW/mK^2)	Annealing Conditions
[3]	<100	773 K, in air
[4]	88.6	none
This work	87.4	673 K, N_2/H_2

4. Conclusions

C-axis aligned crystalline InGaZnO which was optimized for thin film transistor applications was transformed into an efficient thermoelectric material via hydrogen incorporation during annealing. A high electrical conductivity of up to 314 S/cm at 390 K was achieved with 4% H_2 in N_2 annealing at 673 K, which led to a maximum power factor of about 87.4 μW/mK^2. This induced thermoelectricity in c-axis aligned crystalline InGaZnO can potentially present an alternative electrical source in future IGZO-based transparent systems-on-panel applications.

Acknowledgements

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