

環境調和熱電ハーベスタ実現のための 高分子ナノ粒子導入された酸化物薄膜の開発

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Development of Oxide Thin Films Embedded with Polymer Nanoparticles for Realization of Environmentally Friendly Thermoelectric Harvesters

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SnO₂ ナノ粒子を添加した Al ドープ ZnO の薄膜を有機金属堆積法(MOD)により作製した。室温での最高の熱電性能は 600°C の Ar+1%H₂ 流下で 6 時間のポストアニールを行ったところ、室温で最高のゼーベック係数 $S = 73 \mu\text{V/K}$ 、力率 $PF = 7.10 \mu\text{W/mK}^2$ であった。

We fabricated by metal-organic deposition technique (MOD) thin films of Al-doped ZnO added with SnO₂ nanoparticles. The best thermoelectric performance at room temperature is: Seebeck coefficient $S = 73 \mu\text{V/K}$ and power factor $PF = 7.10 \mu\text{W/mK}^2$, after a post-annealing of 6h in flowing Ar+1%H₂ at 600 °C.

1. Introduction

A huge amount (66%) of the total energy obtained from natural fossil resources is lost every year as exhaust heat ^[1]. A highly promising method for energy recovery from such heat sources is the utilization of thermoelectric (TE) materials that can convert various types of waste heat flows directly into electricity without moving parts.

The major obstacle to the wide diffusion of TE materials is the conversion efficiency, measured with the scale of figure of merit $ZT = (\sigma S^2) \times T / (\kappa_{\text{el}} + \kappa_{\text{ph}})$ (eq.1), where σ is the electrical conductivity, S is the Seebeck coefficient ($S = \Delta V / \Delta T$, being V the electrical voltage), κ is the total thermal conductivity ($\kappa = \kappa_{\text{el}} + \kappa_{\text{ph}}$, where κ_{el} and κ_{ph} are the electronic and phononic contribution, respectively) and T is the operation temperature. To commercialize a module based on thermoelectric materials, $ZT \geq 1$ (efficiency $\geq 10\%$) is required. The parameters σ , S , κ are not independently tunable: it is not possible to increase σ and reduce κ at the same time since $\kappa_{\text{el}} = LT\sigma$ (eq. 2) with $L = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^2$ (Lorentz number). On the other hand, $\kappa_{\text{ph}} = 1/3 C v \Lambda$ (eq. 3) with C = heat capacity, v = speed of phonons, Λ = phonons mean free path.

Purpose of this research is to improve the conversion efficiency of thermoelectric materials by enhancement of ZT through depression of κ . To this purpose, we aim to reduce Λ inserting artificial nanoparticles as phonon scatterers inside thermoelectric materials. According to equations (1), (2) and (3), to reach the goals of $\kappa = 1 \sim 3 \text{ W m}^{-1} \text{ K}^{-1}$ and $ZT > 1$ at $T > 600 \text{ K}$, it is needed to insert in the film nanodefects which size is 20 nm or less and

density $10^{24} \sim 10^{25} \text{ m}^{-3}$.

To realize this goal, we used at first stable, earth-abundant, inexpensive, and environmentally friendly oxide thin films of n-type Al-doped ZnO (AZO) added with SnO_2 nanosized inclusions. The introduction of artificial nanodefects (nanoparticles, nanopores, nanolayers) in thermoelectric oxide thin films has been tried using several vacuum deposition techniques (atomic layer deposition: ALD^[2], pulsed laser deposition: PLD^[31]), but not using room pressure chemical route like metal-organic deposition (MOD).

In this work, we focused on the systematic addition of SnO_2 nanoparticles to AZO films via MOD and we preliminary characterized the obtained thin films at room temperature.

2. Experimental details

The fabrication of n-type AZO thin films was carried on by means of metal-organic deposition (MOD) system consisting on a spin coater (Kyowariken K-35951) and a firing furnace (AS-ONE TMF-700N) equipped with Mass flow controller (Horiba SEC-E40MK3).

The AZO solution for MOD was prepared via chemical reaction between stoichiometric amounts of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Cica 18008-00) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Cica 01155-00) using as solvent a mixture of 1:3 = EtOH : 2-propanol (Cica 14032-79 and 20322-09, respectively) with $\text{HOCH}_2\text{CH}_2\text{NH}_2$ (MEA, Aldrich E9508) as chelating agent. The reaction was conducted at 60°C in a beaker under continuous stirring for 1 h.

MOD method consisted of 3 steps: (i) dropping of few mL of oxide organic solution on a silica glass substrate (preliminary cleaned to assure good adhesion of solution) then spun at high rate: this high-speed stirring determines the formation of amorphous thin layer; (ii) firing the sample (substrate + layer) in a tube furnace at proper temperature in air; (iii) annealing the sample under controlled gas flow, leading to the crystallization of a pure thin film layer. The three steps were repeated several times to obtain a multilayered thin film of the proper thickness.

All the parameters to prepare pure AZO films were varied to find the optimal conditions as follows: concentration of AZO solution = 0.15 M; Al content = 3%; amount of MEA = 5 drops; No. of layers = 5; spinning rate = 3000 RPM; spinning time = 30 s; pre-annealing $T = 350^\circ\text{C}$; annealing $T = 600^\circ\text{C}$; annealing atmosphere: Ar+ 1% H_2 ; gas flow: 200 sccm. The search for proper annealing time (considering 1, 3, 6, 9h) is described in the results section.

The effect of SnO_2 nanoparticles was evaluated after addition of increasing number of drops (1, 3, 6 and 10) of SnO_2 solution (Aldrich 901079-10ML) to the AZO solution before performing the spinning, firing, and annealing steps. According to the vendor's specifications, the SnO_2 concentration is 2.5 wt% in butanol and the nanoparticles' size is in the order of 7~10 nm.

The crystallinity of the pure and SnO_2 -added films was evaluated by X-ray diffractometer Smart Lab 3 (Rigaku). Surface of the films was observed by SEM-EDS (JEOL/JSM-7100F). The thickness of a typical AZO film was evaluated by profilometer Filmetrics Profilm 3D (KLA). The room-temperature Seebeck coefficient of AZO films was evaluated by the probe PTM-3 (Joule Yacht) and the room-temperature resistance was evaluated by a tester.

3. Experimental results

3.1 Pure AZO films

The effect of annealing time on AZO films prepared with the optimal conditions described in experimental section was studied.

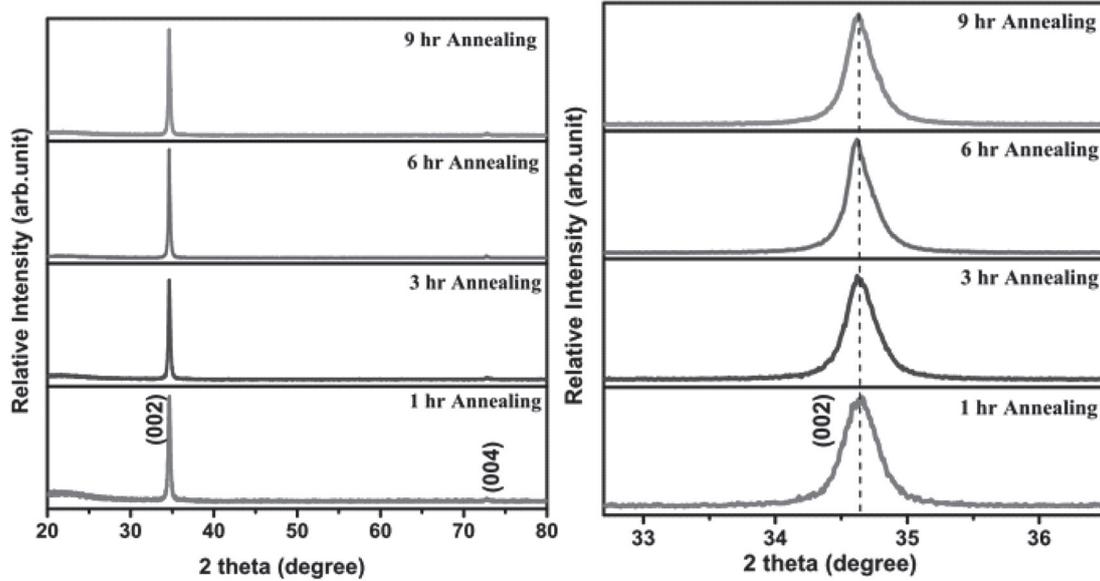


Fig. 1 (left) XRD patterns for AZO films annealed at 600 °C at different times under Ar+H₂ gas flow; (right) magnification of the (002) peak

Figure 1 shows the XRD pattern of AZO films by MOD technique with different annealing time. The observed plane is consistent with ZnO structure matching with PDF card no: 01-082-9744. The hexagonal phase structure is attained for the prepared AZO thin films with different annealing time. Crystallite size D was calculated using the conventional relation $D = 0.9\lambda/\beta\cos\theta$ and lattice strain by the relation $\varepsilon = \beta \cot\theta/4$, where β , θ and λ represent the FWHM, Bragg's angle and X-ray CuK α wavelength (1.5406 Å), respectively.

The crystallite size has been increased with increasing annealing time as demonstrated by the decrease of FWHM value. Consequently, the calculated strain values were decreased gradually. Here, there is no peak shift occurs with respect to the annealing temperature. Moreover, the peak intensity is consistently increased as a function of annealing temperature. On the other side, the lattice constant and cell volume has been increased and the higher values were obtained for 6 h annealing time. All the crystalline parameters and related results are summarized in Table 1.

The morphology of films is reported in figure 2. The film annealed 1h shows a meandering structure, which disappears by increasing the annealing time. The films are porous, and hexagonal grains which size is about 100 nm start appearing with 6 h of annealing time

The values of room temperature ρ , S and power factor $PF = S^2/\rho$ are shown in Table 2 using as thickness the value of 200 nm for all films. The ρ value has been decreased from 0.176 to 0.074 Ω cm from the sample annealed 1 h to the sample annealed 6h in Ar+H₂.

Table 1 – Crystalline parameters of pure AZO films annealed at 600 °C in Ar+H₂

Annealing time (h)	FWHM (°)	Crystallite size D (nm)	Strain ε	Lattice constants a=b (Å)	Lattice constant c (Å)	Cell volume (Å) ³
1	0.306	27.19	0.00428	3.2199	5.1907	46.6086
3	0.275	30.26	0.00385	3.2268	5.1925	46.8239
6	0.2383	34.92	0.00333	3.2331	5.1903	46.9878
9	0.2505	33.21	0.00350	3.2290	5.1918	46.8810

This is due to the improvement in film's crystallinity. The magnitude of the S values considerably decreases with respect to increase of doping concentration. The magnitude of the S values slightly reduced as a function of annealing time. The calculated PF has been increased from 3.83 to 7.10 $\mu\text{W}/\text{m.K}^2$ from the sample annealed 1 h to the sample annealed 6 h in Ar+H₂. The best annealing time has been found as 6 h.

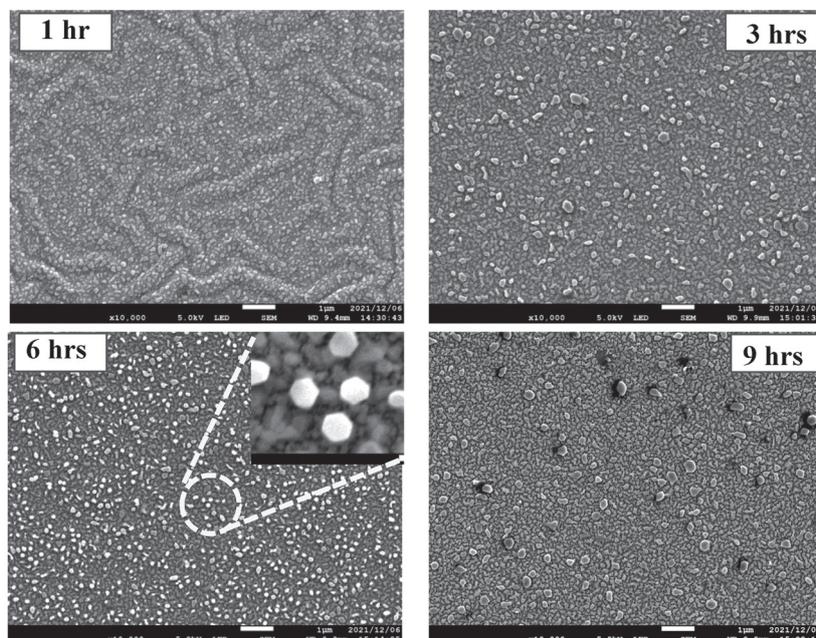


Fig. 2 Morphology of AZO films annealed at 600 °C at different times under Ar+H₂ gas flow

Table 2 – Room temperature transport and thermoelectric properties of pure AZO films annealed at 600 °C in Ar+H₂

Annealing time in Ar+H ₂ (h)	Resistivity (Ωcm)	Seebeck coefficient (μV/K)	Power Factor (μW/mK ²)
1	0.176	-82	3.83
3	0.132	-91	6.26
6	0.074	-73	7.10
9	0.184	-87	4.14

3.2 SnO₂-added AZO films

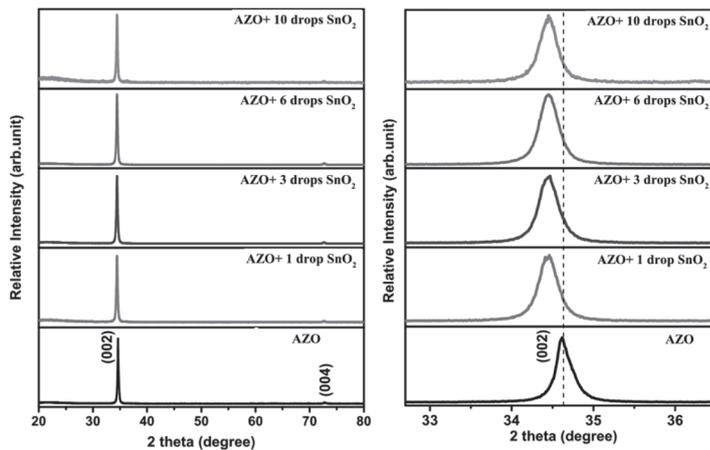


Fig. 3 (left) XRD patterns for SnO₂- added AZO films annealed at 600 °C for 6 h under Ar+H₂ gas flow; (right) magnification of the (002) peak

Figure 3 (right) shows the enlarged XRD pattern of the predominant peak (002) for all the prepared films. The figure indicates that there is an identified peak shift occurs with respect to SnO₂ addition. This may be attributed to atomic substitution of Sn in AZO lattice but should be confirmed by further analyses.

Table 3 shows that the full width at half maxima (FWHM) value initially increased and then decrease when increasing SnO₂ solution amount into AZO solution. The variation of crystallite size (D) follows an inverse trend. The calculated strain values were also changed consistently with FWHM. The lattice constants (a and c) and cell volume values for all the prepared films are also reported.

Figure 3 (left) illustrates the XRD patterns for pure AZO and SnO₂ added AZO thin films prepared by MOD technique. The observed planes are consistent with hexagonal phase structure of ZnO matching with PDF card no: 01 - 071 - 3830 . The hexagonal phase structure is attained for all the prepared films. Moreover, there is no observed impurity or secondary peaks like SnO₂ or other Sn-related compounds.

Table 3 – Crystalline parameters of SnO₂- added AZO films annealed at 600 °C for 6h in Ar+H₂

SnO ₂ solution (drops)	FWHM	Crystallite size D (nm)	Strain ϵ	Lattice constants $a=b$ (Å)	Lattice constant c (Å)	Cell volume (Å) ³
0	0.2383	34.92	0.00334	3.2331	5.1903	46.9878
1	0.284	29.28	0.004	3.2546	5.2038	47.7380
3	0.2925	28.43	0.00412	3.2539	5.2069	47.7459
6	0.2799	29.71	0.00394	3.2544	5.2045	47.7397
10	0.259	32.11	0.00364	3.2511	5.2020	47.6198

The SEM images (not reported here) does not show any significant change of morphology respect to the undoped AZO film deposited in same conditions.

Table 4 – Room temperature transport and thermoelectric properties of SnO₂- added AZO films annealed at 600 °C for 6h in Ar+H₂

SnO ₂ solution (drops)	Resistivity (Ωcm)	Seebeck coefficient (μV/K)	Power Factor (μW/m.K ²)
0	0.074	-73	7.10
1	0.182	-104	5.90
3	0.144	-94	6.13
6	0.136	-98	7.06
10	0.360	-106	3.12

The values of room temperature ρ , S and power factor PF are shown in Table 4 using as thickness the value of 200 nm for all films. The ρ slightly decreases and S increases with amount of SnO₂ solution up to 6 drops. 10 drops appear to be an excessive amount of dopant. The Seebeck coefficient values shows a negative sign as confirming the n-type conductivity of all samples. The obtained PF value is enhanced with the addition of SnO₂ but has been

slightly decreased respect to the case of pure AZO film, being the best performance $7.06 \mu\text{W}/\text{m}\cdot\text{K}^2$ when 6 drops SnO_2 were added.

4. Conclusion and perspective

Pure and SnO_2 -added AZO films were prepared by MOD. The addition of SnO_2 nanoparticles affected the crystal structure of the films, but was not dramatically changing their thermoelectric properties, at least at room temperature.

Further experiments are required in two directions: long X-rays acquisitions followed by Rietveld analysis, and cross-sectional TEM are needed to understand if the nanoparticles of SnO_2 have been incorporated into the films or if Sn has substituted Zn in the AZO cell; measurement of transport and thermoelectric properties at increasing temperature are due to understand if the role of SnO_2 becomes beneficial at higher temperatures.

5. Remark

Respect to the original plan, polymer nanoparticles were not used systematically because in a preliminary experiment their solution segregated. In substitution, the SnO_2 nanoparticles solution was mixed properly, so it was used as replacement.

6. Bibliography

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