Fabrication of ZnO-Based Thermoelectric Micro-Devices by Electrodeposition

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In order to fabricate micro-thermoelectric devices, ZnO films were prepared via electrodeposition, and the effect of deposition condition on the films was investigated. It was found that morphology and crystallinity of ZnO films were strongly affected by applied potential, bath composition and bath temperature, and using the optimized condition, ZnO-based micro-thermoelectric devices were fabricated and device performance was evaluated. For electrodeposition, acetate ion was added into the bath to prevent several drawbacks such as formation of pits and cracks. From the solution containing zinc nitrate and sodium acetate as a source of acetate ion, ZnO films were electrodeposited. The films with smooth morphology and sufficient adhesion strength were obtained at about 0.9 V vs. Ag/AgCl with the addition of 10 mmolL−1 sodium acetate. The films with higher crystallinity and thermoelectric properties were obtained from the bath with higher temperature of 80°C. The micro-thermoelectric device, which consisted of four arrays and each array had 55 pairs of thermoelectric elements, was fabricated and it generated 0.73 mW as maximum power. The power density was approximately 40 times larger than that of the ZnO thin films, which demonstrated that electrodeposited ZnO could be applied to thermoelectric micro-devices.

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Thermoelectric generators can convert thermal energy into electrical energy using Seebeck effect without actuators, which allows self-generation by even small amount of various waste heat which are derived from automobiles, IoT devices, and so on. Miniaturized thermoelectric devices have promising features because high voltage and high output can be achieved by integration of small thermoelectric elements. Moreover, the miniaturized devices are applicable to various fields in combination with micro-electro-mechanical system (MEMS), e.g., electronics, sensors and communication devices.

Up to date, numbers of micro-thermoelectric devices have been proposed, and in most cases, their forms are π-structures which consist of p and n-type thermoelectric elements combined electrically in series with the bridging metals. π-structured micro-devices based on Bi-Te materials were fabricated through electrodeposition in our previous work. Bi-Te based materials such as Bi-Sb-Te for p-type semiconductors show high performance at low temperature, ~250°C and have been studied widely. On the other hand, metal oxides compensate some drawbacks of metal materials and are advantageous from the view of environmental-friendly nature, cost and thermal stability.

As alternative candidate for the thermoelectric material, metal oxides have been proposed such as layered cobalt oxides, e.g. Na2Co3O5 or [Co2CoO3]xCoO2, Titanium oxides, e.g. SrTiO3 and ZnO. Among them ZnO is a promising candidate at high temperature because ZnO demonstrates non-toxicity, abundance in nature and good stability within a wide temperature range. Numbers of studies relating to preparation of ZnO have been reported including hydrothermal synthesis, chemical vapor deposition, sol-gel processes, etc. Electrochemical deposition has numbers of advantages among these methods such as low reaction temperature and process simplicity. Moreover, electrodeposition is suitable to form micro-structures using combination of lithography techniques due to its selective deposition.

In the electrochemical growth of ZnO, fundamental reaction is reduction of oxygen precursors producing OH−, followed by reaction with Zn2+ according to Eq. 1. Then Zn(OH)2 is dehydrated instantaneously and transforms into ZnO over 60°C according to Eq. 2.

$$\begin{align*} \text{Zn}^{2+} + 2\text{OH}^- &\rightarrow \text{Zn(OH)}_2 \\
\text{Zn(OH)}_2 &\rightarrow \text{ZnO} + \text{H}_2\text{O} \end{align*}$$

Different precursors of oxygen are proposed such as dissolved oxygen, hydrogen peroxide and nitrate ion. Especially, deposition using nitrate ion as a precursor has been studied widely by Izaki and other researchers. Compared to other species, nitrate ion has higher solubility to water and Zn2+ plays a role of catalyst in nitrate reduction, which promotes ZnO growth. The deposition using nitrate ion as a precursor has been extensively studied by Izaki et al. as well as other researchers. The reduction reaction of nitrate is as follows.

$$\begin{align*} \text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{NO}_2^- + \text{OH}^- \end{align*}$$

However, some drawbacks have still remained in the films deposited from the conventional nitrate bath, to form rough morphology and low adhesion strength mainly due to gas evolution caused by nitrogen derived from nitrate ion. In addition, elongated rod-like structures of ZnO are easily formed in the case of the nitrate bath form porous conditions. Such a morphology could cause residue of photoreist through the device fabrication process. Switzer et al. also reported the formation of hexagonal nanopillars at the surface. These drawbacks prevent evaluating thermoelectric properties and applying to thermoelectric micro-devices. In order to solve this problem, we focus on the bath containing acetate ion because hydrogen generation can be inhibited by higher pH value than that of a nitrate bath. Moreover, acetate ion also has an effect of adsorption on (0001) face of growing ZnO similar to chloride ion, which promotes lateral growth of ZnO and leads to compact, fully covered films. Although the electrodeposition from the bath containing only zinc acetate was carried out, the bath was unstable and only metallic Zn was deposited preferentially instead of ZnO because of the small amount of OH− generated by dissolved oxygen. Therefore, the bath mixing the nitrate and acetate ion was proposed. Previously, we succeeded to obtain ZnO films with smooth surface and enough adhesion strength from the bath containing zinc nitrate and sodium acetate by changing the applied potential and bath temperature.
Au substrates have low resistivity about conductive F-doped tin oxide (FTO) substrate (20 × 20 mm). Samples for measuring the Seebeck coefficient were deposited on the FTO substrate (20 × 20 mm) covered with 100 nm Au/10 nm Cr was used. Samples for measuring the Seebeck coefficient were deposited on the FTO substrate (20 × 20 mm), because Au substrates have low resistivity about ~10^{-6} Ωcm and Seebeck coefficient of ZnO on Au shows almost the same value of Au substrates. For this reason, ZnO was deposited on FTO substrates with relatively low resistivity about ~10^{-4} Ωcm. Before the electrodeposition, the substrate surface was cleaned through plasma ashing process, followed by rinse with HCl and pure water. Temperature of the bath was maintained at 65 °C or 80 °C and the applied potential was modified from −0.8 V to −1.0 V. The reduction reaction of nitrate ions occurs from −0.8 V. All deposition was performed using paddle agitation which speed was 120 rpm and the duration time was 60 min.

For fabrication of the micro-thermoelectric devices, photolithography and electrodeposition were combined. The simplified scheme of fabrication procedure is shown in Figure 1. At first, Au bottom electrodes were deposited into the patterns with 200 μm diameter and 10 μm thick fabricated using photolithography, followed by the electrodeposition of n or p type thermoelectric materials into the patterns. Then, a thin resist selectively covered onto the patterns for p-type materials keeping the patterns for n-type open. After the patterned deposition of n type ZnO, the thin resist covered onto ZnO and the resist on patterns for p-type materials were removed. Then p-type materials were deposited into patterns. Following these process, upper electrodes of Ni were formed through electrodeposition after removing the resist on n-type patterns. Finally, 10 μm thick photoresist was removed using acetone followed by plasma ashing, resulting in accomplishment of a thermoelectric micro-device. Details of the fabricating process including the SEM images of π-structured thermoelectric elements were described in our previous report. Thermodiode devices consist of n and p-type materials connecting in series, but in this study ZnO for n-type materials was focused. Patterned deposition of ZnO was conducted using the same condition as film deposition for 40 min, and Cu was deposited instead of the p-type materials from the aqueous solution containing CuSO4 · 5H2O at room temperature. During the Cu deposition, current density was controlled at 40 mAcm^{-1} with paddle agitation of 120 rpm.

Morphology of the samples was characterized using a scanning electron microscope (SEM, SU-8240, Hitachi High-Technologies or VE-7800, KEYENCE). The RMS roughness of the samples was measured by a laser microscope (VK-9510, KEYENCE). The film structure and crystallinity were analyzed by a Raman spectrometer (Nanofinder 30, Tokyo Instruments, excitation wavelength of 633 nm) source. Seebeck coefficient was measured with a home-made device by generating thermal gradient of 1 Kcm⁻¹ at both ends of a thin film using a small resistive heater. The voltage-current characteristics were also measured by thermal gradient at one edge of a film or upper electrodes of a device using focused light from a halogen lamp as a heat source. During measurement, the temperature on the surface was set to 200 °C using Pt resistance thermometers.

**Results and Discussion**

In order to form the ZnO films with sufficient smoothness and adhesion strength, electrodeposition was performed from the bath containing zinc nitrate and sodium acetate. Morphologies of the films with different concentration of sodium acetate are shown in Figure 2. In the case of 5 mmolL⁻¹ 10 mmolL⁻¹ of sodium acetate, hexagonal structures are observed (Figures 2a and 2b). Compared with ZnO

**Figure 1.** Fabrication procedure for π-structured micro-devices.
deposited from only nitrate bath, ZnO are growing compactly and there is no minute space among ZnO, indicating acetate ion promotes lateral growth. However, as was pointed out by the case using the conventional nitrate bath, some drawbacks such as crack formation and low adhesion strength were also observed in Figure 2d using 5 mmolL⁻¹ of sodium acetate due to gas generation such as nitrogen. On the other hand, the film deposited from the bath containing 50 mmolL⁻¹ of sodium acetate has platelet-like structures vertically aligned to the substrate (Figure 2c). It is inferred these structures are Zn-containing precursors, Znₙ(CH₃COO)ₓ(OH)ᵧ·nH₂O, for similar structures were also observed from the bath containing zinc nitrate and high concentration of potassium acetate. From these results, the following electrodeposition was carried out using 10 mmolL⁻¹ of sodium acetate.

Figure 3 shows the morphologies of deposited films with various applied potential. The films basically have smooth morphologies, while grain size becomes larger with an increase in the potential from −0.8 V to −0.9 V. It is considered that reduction of nitrate ion followed by OH⁻ generation is promoted, which enhanced the growth of ZnO. In contrast, deposited films at −1.0 V have a number of cracks because of gas generation by applying more negative potential.

Raman spectra of deposited films at different potential corresponding to the films depicted in Figure 3 are shown in Figure 4. In this figure several peaks are observed, and among them two peaks at 119 cm⁻¹ and 460 cm⁻¹ are attributed to E2(low) and E2(high) vibration mode of ZnO. It confirms that the obtained films consist of ZnO. The peaks around 600 cm⁻¹ are attributed to oxygen defects, while no peaks at 600 cm⁻¹ are observed in Figure 4, suggesting that the deposited ZnO films have a few oxygen defects. Moreover, the film applying at −0.9 V shows sharpest peaks, which indicates high crystallinity.

For electrodeposition of ZnO, bath temperature is also a significant factor to affect the dehydration reaction. Therefore, in order to investigate the effect of dehydration, ZnO was deposited under higher bath temperature conditions such as at 65°C and 80°C. For both cases, the films with homogeneous and hexagonal morphology are obtained as is shown in Figure 5. RMS roughness and grain size estimated from laser microscope and SEM for the films deposited at 65°C and 80°C were 0.50 μm, 2.40 μm and 0.25 μm, 1.23 μm, respectively. These results indicate that increase in bath temperature results in the decrease in the roughness and grain size, which could be caused by faster generation rate of OH⁻ promoted by higher temperature. According to the previous study, the rates of OH⁻ generation and Zn²⁺ diffusion affect the growth orientation of ZnO. In the case of slower diffusion rate of Zn²⁺ than OH⁻ generation, ZnO tends to grow along the longitudinal axis that is c-axis. On the other hand, when the diffusion rate of Zn²⁺ and generation rate of OH⁻ are the same, ZnO grows along both vertical and horizontal axis, resulted in the formation of larger grain size. In this case, it is considered that OH⁻ generation rate is faster than Zn²⁺ diffusion rate at 80°C due to increasing temperature. XRD spectra in Figure 6 indicate the film deposited at 80°C has larger intensity ratio of (111) orientation of Au substrate to (002) orientation of ZnO compared with at 65°C, which shows ZnO deposited at 80°C with higher crystallinity. This is because the promotion of dehydration reaction as described in introduction section. In the electrolyte at 80°C, dehydration reaction corresponding to Eq. 2 is more promoted than at 65°C, resulting in higher crystallinity. OH⁻ generation rate also affects for the (002) orientation. Previous report suggested that faster
generation rate of OH$^-$ than Zn$^{2+}$ diffusion caused preferential growth of ZnO mainly along longitudinal axis. At 80°C the generation of OH$^-$ is further promoted, enhancing the (002) preferential orientation. In addition, the deposits turned to non-transparent to transparent by increasing the bath temperature, suggesting the dehydration of ZnO accelerates at higher bath temperature. Thus, it is confirmed that acetate ion, applied potential and bath temperature intensely affects the morphology and crystallinity of deposited films.

Next, to investigate the electric properties, thermoelectric properties of ZnO films were evaluated. Power curves of the films prepared at 65°C and 80°C were measured by generating thermal gradient between both ends of films using Au substrates. The obtained power curves are shown in Figure 7. Thermoelectric properties containing electric resistivity, open-circuit voltage and maximum power are calculated from Figure 7, and these values are summarized in Table I. Electric resistivity is estimated by using the resistance corresponding to the slope of the straight line, cross sectional area and measuring length. Open circuit voltage, that is the intercept of left axis, is defined as the thermoelectromotive force derived from Seebeck effect. Measured voltage multiplied by the current is power and the maximum value of the curve is defined as a maximum power. Figure 7 and Table I show the film deposited at 80°C shows higher open circuit voltage and maximum power. This is because dehydration from Zn(OH)$_2$ to ZnO is promoted at higher bath temperature, 80°C. Through dehydration the crystallinity of ZnO increases as described in Figure 5, indicating the decrease of the native defects which are oxygen vacancies responsible for donor level. Carrier generation is based on the native defects, resulting on the decrease of carrier concentration at higher temperature. Furthermore, the films deposited at 80°C show smaller grain size than the film at 60°C, which could be the origin of the increase in Seebeck coefficient and decrease in electrical conductivity. While, open circuit voltage is dependent on Seebeck coefficient which is a function of carrier concentration, and in general, Seebeck coefficient increases with a decrease in the carrier concentration. In other words, the decrease in native defects and increase in carrier scattering caused by dehydration leads to obtain higher open circuit voltage and maximum power under higher temperature. Crystallinity and grain size are also crucial factors to control the thermoelectric properties. In addition, surface roughness of the films is an important factor to obtain sufficient adhesion strength and electrical conductivity. However, both films have open circuit voltages which are products of Seebeck effect and demonstrate the possibility of application to thermoelectric devices.

In order to fabricate thermoelectric micro-devices, the electrodeposition into patterns with 200 μm diameter and 10 μm thick was carried out using both bath temperature, 65°C and 80°C. Figure 8 shows SEM images of ZnO into patterns at each temperature. In Figure 8, ZnO was successfully deposited keeping smooth morphology in both conditions. RMS roughness of each pattern was 1.58 μm. Decrease of grain size at 80°C show smaller grain size than the film at 60°C, which could be the origin of the increase in Seebeck coefficient and decrease in electrical conductivity. Moreover in the case of 80°C, the photoresist used to the patterning was locally denatured by thermal damage. The deformation of patterns caused disconnection of ZnO, which disturbed following steps of device fabrication. Therefore, ZnO was deposited at 65°C through the following device fabrication process.

![Figure 5. SEM images of ZnO films deposited at different bath temperature with (a) 65°C and (b) 80°C. The applied potential was −0.9 V and the bath contain 10 mmolL$^{-1}$ of sodium acetate.](image1)

![Figure 6. XRD Spectra of ZnO deposited from the bath at (a) 65°C and (b) 80°C. The applied potential was −0.9 V and the bath contain 10 mmolL$^{-1}$ of sodium acetate.](image2)

![Figure 7. Power curves of ZnO films at (a) 65°C and (b) 80°C. The applied potential was −0.9 V and the bath contain 10 mmolL$^{-1}$ of sodium acetate.](image3)

![Figure 8. SEM images of ZnO into the patterns at (a) 65°C and (b) 80°C. The applied potential was −0.9 V and the bath contain 10 mmolL$^{-1}$ of sodium acetate.](image4)

### Table I. Thermoelectric properties at different bath temperature.

|               | Electric resistivity/Ωcm | Open circuit voltage/mV | Maximum power/nW |
|---------------|--------------------------|-------------------------|------------------|
| (a) 65°C      | 0.455                    | 0.205                   | 0.112            |
| (b) 80°C      | 5.31                     | 1.31                    | 0.424            |

Table I. Thermoelectric properties at different bath temperature.
Table II. Results of power measurements.

| Total resistance/Ω | Open circuit voltage/mV | Maximum power/nW |
|--------------------|------------------------|------------------|
| 1 array            | 11.1                   | 0.0642           | 0.0923 |
| 2 arrays           | 24.8                   | 0.267            | 0.734  |
| 3 arrays           | 15.0                   | 0.185            | 0.570  |
| 4 arrays           | 45.1                   | 0.234            | 0.301  |

For thermoelectric materials, Seebeck coefficient is the most significant factor since the figure of merit, ZT is a function of the square of Seebeck coefficient. Thus Seebeck coefficient of ZnO films deposited at 65°C was measured using FTO substrates for three times and their average value was estimated. It turned to be $-36.6 \mu V K^{-1}$ and confirmed n-type semiconductor properties.

Finally, ZnO based π-structured micro-device was fabricated using the process applied to our previous work. ZnO was deposited into patterns under the same condition as the patterned electrodeposition above, at $-0.9 \text{ V}$ and 65°C. Figure 9 shows a whole image of the fabricated device with 220 pairs of thermoelectric elements, and SEM images of each π-structured element corresponding to ZnO and Cu are shown in Figure 10.

Figure 11 shows power curves obtained by the fabricated device. As described in Figure 9, the fabricated device consists of four arrays of thermoelectric elements and each array has 55 pairs of n and p-type thermoelectric materials. Power curves could be obtained by connecting from one array with 55 pairs of thermoelectric elements to all the arrays containing 220 pairs of those. Table II shows the total resistance, open circuit voltage and maximum power obtained from power curves of the device with the different number of arrays. From Figure 11, maximum power of 0.73 nW is obtained by connecting two arrays. In comparison with the power density between the device and films, the density was 2.6 nW/cm² using the device and 0.060 nW/cm² using the films respectively, which confirms the power density increases by fabricating devices. On the other hand, in the case of connecting more than three arrays, the power decreases from 0.73 nW to 0.57 or 0.30 nW. On connecting three arrays, lower open circuit voltage was measured in Figure 11, which indicates third array has lower thermoelectric properties and shows metal-like behavior. While on connecting four arrays, the resistance at connecting parts between upper electrodes and thermoelectric materials becomes higher, resulting in the decrease of device power. In Figure 10, it is found that Ni for upper electrodes does not deposit on some parts of ZnO elements. This causes the increase of resistance, which leads to low output. To improve the power of this thermoelectric device, decrease of resistance and development of p-type oxide materials are required in future study.

Summary

In order to fabricate π-structured micro-thermoelectric devices using ZnO, deposition condition for ZnO films was investigated in detail, and then using the optimized condition ZnO-based micro-thermoelectric device was fabricated. As a result, concentration of acetate ion, applied potential and bath temperature have large influence on morphology, crystallinity and thermoelectric property of ZnO films. Then in order to fabricate devices, the electrodeposition into patterns was carried out using the condition found out through film deposition. ZnO was deposited into patterns keeping smooth morphology at 65°C. Seebeck coefficient of ZnO films was $-36.6 \mu V K^{-1}$, indicating the prepared ZnO was a n-type semiconductor. Finally, using the optimized condition, a thermoelectric micro-device was fabricated. From power curves, maximum power of 0.73 nW was obtained when two arrays of thermoelectric materials were connected, and power density increased dramatically compared with ZnO films. In future study, it is necessary to develop p-type metal oxide materials such as Cu$_2$O or metal-doped ZnO instead of Cu.
because the device performance will be enhanced by connecting n and p-type semiconductors in series.

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