Trial of Ga-doping on ZnO Nanoparticles by Thermal Treatment with Ga₂O₃ Nanoparticles

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Direct Ga-doping into ZnO nanoparticles (NPs) were tried by thermal treatment mixed with Ga₂O₃ particles. Residual Ga₂O₃ particles were completely removed by appropriate centrifugation process. To confirm the Ga-doping, variations of sheet resistances for sprayed NP-layers on glass substrates were investigated, showing successful and dramatic reduction from GΩ sq⁻¹-order to sub-kΩ sq⁻¹. The minimum sheet resistance reached to 225 Ω sq⁻¹. From X-ray diffraction and X-ray photoelectron spectroscopy analyses, it can be concluded that Ga atoms diffused from Ga₂O₃ into ZnO-NPs in the thermal treatment process, and some of them substituted for Zn atoms and were activated as donors. These results can contribute to continuous advance of ZnO-NP-based thin-film-transistor fabrication technique.

Keywords Zinc oxide; Nanoparticles; Ga-doping; Thermal diffusion; X-ray photoelectron spectroscopy

I. INTRODUCTION

Using semiconductor nanoparticle (NP) layers is one of the noticed methods to obtain channel layer of thin film transistors (TFTs) [1–5], because of its high selectivity of substrate materials and surface morphology, and its compatibility of the printing electronics, atmospheric processing, the low costing and the large area processing. Oxide semiconductors such as ZnO do not form an insulating layers at the NP surfaces when dispersed in water and/or handled in the air, which make it easy to TFT fabrication process. Therefore, many efforts have been made to form and demonstrate TFTs with the n-type ZnO-NP channels on various substrates [1, 6–12] including demonstration of the logic operations [13].

Recently, by using the ZnO-NPs synthesized in our laboratory [14, 15], not only n-channel but also p-channel back-gate TFTs on Si/SiO₂ substrates were successfully demonstrated by using the simple and easy spraying method [16], providing high expectation to realize complementary logic circuits using ZnO-based NP-layers. However, the performances of obtained TFTs were insufficient. Most

weak point is the extremely high resistivity of horizontal carrier transportation in the sprayed ZnO-NP layers (order of GΩ sq⁻¹). Such large parasitic resistances cause the significant degradation of the gain and switching speed in analog and digital operations, respectively. By simple estimation with assuming the logic gate capacitances of several pF, even 100 Hz logic operation will be impossible using these TFTs. It is essential to reduce the sheet resistances of obtained ZnO-NP layers for TFT channel applications. Additionally, achieving direct doping into NPs is preferable rather than doping onto the NP-layers, because such doping processes after NP-layer formation should disturb the simplicity of the particle-base process and the selectivity of substrate materials.

In this study, direct Ga-doping was tried to the ZnO-NPs synthesized in our laboratory by thermal treatment with Ga₂O₃-NPs, and the resistivity reduction of sprayed n-ZnO NP-layers were verified.

II. EXPERIMENTAL

ZnO-NPs were synthesized by arc-discharge-mediated

gas evaporation method. The backpressure of main chamber was less than 0.3 Torr. Dry air was introduced with the rate of 5 L min^{-1} , and the chamber pressure was regulated at 610 Torr by the regulating valve and the rotary pump through the synthesizing period. A metal Zn bulk (99.99%) and a carbon rod were used as arc-discharging electrodes. Arc current was 20 A. From our previous study, it is known that the chamber pressure and the arc current are key conditions to control the introducing amount of nitrogen atoms in the obtained ZnO nanoparticles. Details are described in Refs. 14 and 16, in which n-type conductive particle was recommended. Thus, the conditions to obtain ZnO particles with less nitrogen doping were used.

Thermal treatments were applied to some of obtained ZnO nanoparticles with Ga_2O_3 particles (Sigma-Aldrich). Particles of ZnO (0.2 g) and Ga_2O_3 (0.06 g) were mixed in the crucible and heated in the electric furnace with the temperature of 600–900°C for 60 min. In this study, two types of ambient gas were applied; one was the atmospheric air which was similar to the gas in NP-synthesizing, and the other was pure nitrogen which would expectedly generate the oxygen vacancies acting as native donors. In thermal treatment with the atmospheric air, the valve of the furnace was opened to the atmosphere and the fresh air (with humidity of about 60%) was supplied by thermal convection. In case with pure nitrogen, the nitrogen gas with the dew point of less than -60°C and the purity of 99.995% was supplied with the rate of 0.5 L min^{-1} . In both case, the temperature was increased from RT to each setting values within 10 min, and after 60 min thermal treatment, the samples were cooled down to less than 40°C in 2 h.

The dispersions were prepared by dispersing 0.2 g of above mixed and thermally treated particles with 10 g of ultrapure water using ultrasonic homogenizer with the power of 150 W for 3 min and by following centrifuging with 3000 G for 1 min.

To form particle layers [16], 30 mL of dispersion fluid were sprayed to heated quartz substrates using standard airbrush, as shown in Figure 1, with 5-s intervals for 15 min. The setting value of the hot plate temperature was 500°C (the actual surface temperature was about 370°C determined using thermographic measurement). The estimated thickness

Figure 1: Schematic illustration of the spraying method.

of particle layers were about 10 μm . Additional Al/Au electrodes with the width and length of 0.3 mm were formed for I - V measurements.

I - V measurements to determine the variation of sheet resistances were performed using a shielding prover system and E5270B Precision measurement mainframe with E5287A Atto-level High Resolution SMU module (Keysight Technologies). Powder X-ray diffraction (XRD) (SmartLab, Rigaku Corporation, $\lambda = 1.54 \text{ \AA}$) was used for 2θ -scan with scanning speed of $0.001^\circ/\text{step}$. Elemental analyses were performed by X-ray photoelectron spectroscopy (XPS) with monochromatic Al $K\alpha$ radiation. The measurements were carried out on the surface of as-sprayed NP-layers without additional cleaning process. Binding energies were calibrated by shifting the C 1s peak position to 285.0 eV [17, 18].

III. RESULTS AND DISCUSSION

ZnO and Ga_2O_3 particle size distributions are shown in Figure 2(a), which were prepared by dispersing each particles in ultrapure water by ultrasonic homogenizer without centrifugal separation procedure. The ZnO particles that were synthesized in our laboratory have a main peak at around 150 nm and a tail distribution over 1000 nm. On the other hand, the Ga_2O_3 particles have sharp distribution with median size of 667 nm. In Figure 2(b), the dispersions that contain ZnO/ Ga_2O_3 mixed and thermally treated particles

Figure 2: Particle size distributions for (a) separately measured ZnO and Ga_2O_3 nanoparticles without centrifugal separation and (b) mixed and thermally treated ZnO and Ga_2O_3 particles after centrifugal separation.

Figure 3: SEM image of the surface of quartz substrate after spraying procedure. Particles labeled “Only ZnO” in Figure 4 were used.

with centrifugal separation procedure show only a sharp distribution with a median size of 153 nm. This result indicates that large ZnO particles and all Ga₂O₃ particles were removed by centrifuging, and only small sizes of ZnO particles remained in the dispersion fluid. By the spraying method, NP-layers were formed onto the quartz substrates. The scanning electron microscopy (SEM) image of the sprayed ZnO-NP layer is shown in Figure 3, confirming the quartz surface was covered with NPs with less aggregation.

The sheet resistance variations among various kinds of particle layers used in this study are summarized in Figure 4, which were measured by two probe I - V measurements with the voltage range from -10 V to $+10$ V. The current flow area has a $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ square shape, so the sheet resistance can be directly obtained from the slope of I - V curves, and each point indicates the average value obtained from 6 to 10 measurements. The sprayed particle layers formed using as-prepared ZnO particles and only mixed with Ga₂O₃ particles (without thermal treatment) show very high sheet resistance in the order of $\text{G}\Omega\text{ sq}^{-1}$. These data are labeled “Only ZnO” and “ZnO/Ga₂O₃ only mixed”, respectively, and are shown with filled triangles ($\blacktriangle$) in Figure 4.

Figure 4: Sheet resistance variation of various kinds of particle layers used in this study measured by two-probe I - V measurements.

Circular marks indicate the sheet resistance values for the samples using thermally treated particles; filled circles ($\bullet$) indicate that the thermal treatments were carried out in atmospheric air and open circles ($\circ$) in pure nitrogen. From these results, the temperature of thermal treatment less than 700°C had no effect to reduce the sheet resistance, meaning no reaction between mixed ZnO and Ga₂O₃ particles. On the other hand, thermal treatment with the temperature of 800°C and 900°C showed significant reduction of 4 to 7 orders of magnitude. Especially, the conditions of 800°C in atmos-

Figure 5: XRD results for (a) ZnO nanoparticles (particulates) and (b and c) NP-layers on quartz substrates sprayed with ZnO/Ga₂O₃ mixed and thermally treated (800°C) particles in air and N₂, respectively. For (b and c), dispersion was prepared with centrifugal separation process. The inset in (b) shows the XRD spectra for Ga₂O₃ particles (particulates).

pheric air are the most effective, and the minimum value reached $225 \Omega \text{ sq}^{-1}$. As a reference, the sheet resistances obtained using thermally treated “Only-ZnO” particles (at 800°C) are also indicated in Figure 4, resulting no effect to reduce the sheet resistance. Thus, it is confirmed that the property of the ZnO particles had been influenced by mixing with the Ga_2O_3 particles and thermally treating with a temperature over 800°C .

Figure 5 shows XRD results for ZnO nanoparticles (particulates) and NP-layers sprayed with ZnO/ Ga_2O_3 mixed and thermally treated (800°C) particles in the air and N_2 . From Figure 5(a), generally known peaks of the ZnO particles with single crystalline state [19–21] were obtained. All these peaks were observed after the thermal treatment and spraying procedures as shown in Figure 5(b), however, the intensity ratio changed. The signals from the (100) and (200) planes are dominant, i.e., hexagonal column structured particles laid with the column face up (m-plane) by the spraying procedure. In Figure 5(a, b), full-width at half-maximum (FWHM) values were changed from 0.20° to 0.08° for the (100) peaks by thermal treatment in the air. Using Scherrer's equation and the crystallite-effect-less FWHM value of 0.08° in this XRD system, the size of crystallite changed from 45 nm to more than 100 nm by the thermal treatment in the air, while it was changed only to 55 nm [the FWHM of 0.17° from Figure 5(c)] by the thermal treatment in N_2 . On the other hand, the Ga_2O_3 particles used in this study provided XRD peaks as shown in the inset of Figure 5(b). These peaks are consistent with previous results of the $\beta\text{-Ga}_2\text{O}_3$ particles [22]. But there were no Ga_2O_3 -related peaks in Figure 5(b, c). It is confirmed, again, that almost of the Ga_2O_3 particles were removed by the centrifugal separation process.

To discuss about the sheet resistance reductions, XPS spectra were analyzed. Figure 6(a) shows Ga 3d spectra for sprayed particle layers made of ZnO/ Ga_2O_3 mixed with and without centrifugal separation process (no thermal treatment), ZnO/ Ga_2O_3 mixed and thermally treated at 800°C in the air and N_2 with centrifugal separation and, as a reference, only ZnO. Overlapping O 2s spectra are also shown. The peak intensities were normalized with those of the Zn 3d spectra, as shown in the inset of Figure 6(a). Also, the peak positions were shifted to adjust Zn 3d at 10.0 eV. So, the horizontal axis indicates the energy difference from the Zn 3d peak. Here, the shifts of energy positions were within ± 0.1 eV. The Ga 3d spectrum obtained from ZnO/ Ga_2O_3 mixed without centrifugal separation shows the largest intensity because all Ga_2O_3 particles remained, but after centrifugal separation, only the slight Ga 3d component was observed. This again indicates the residual Ga_2O_3 particles can be removed by the suitable centrifugal separation process throughout this study. On the other hand, a relatively large Ga 3d peak was observed from ZnO/ Ga_2O_3 mixed and thermally treated (800°C) both in the air and N_2 , in spite of processed with centrifugal separation. This strongly suggests that Ga atoms diffused from Ga_2O_3 into the ZnO particles in the thermal treatment process at 800°C . Another analysis on

O 1s spectra was carried out as shown in Figure 6(b). In this figure, (A) ZnO/ Ga_2O_3 and (B) only ZnO particles with thermal treatment (800°C , air) and centrifugal separation were compared. The intensities are normalized, and the difference “(A)–(B)” is shown. The main peak at 530.5 eV is assigned to wurtzite ZnO, and the tail part at the higher binding energy is usually explained by V_O and/or OH group with a chemical shift of over 1.5 eV [23–25]. Here, the difference “(A)–(B)” shows an energy difference of about 0.8 eV. In both samples, the condition difference is only the ex-

Figure 6: (a) XPS Ga 3d spectra for various samples. The peak position and intensity were normalized with the Zn 3d peak. The inset shows the overall spectra of Zn and Ga 3d. (b) Comparison of XPS O 1s spectra between particle layers using thermally treated only-ZnO and ZnO/ Ga_2O_3 -mixed particles. As a reference, Ga_2O_3 O 1s spectrum is also shown. (C.S. : centrifugal separation)

istence of Ga_2O_3 particles in the thermal treatment process, and they were removed by following centrifugal separation. Considering the fact that the difference between the O 1s spectra of O-Zn and O-Ga is 0.8 eV which can be determined using the O 1s spectrum of Ga_2O_3 shown in Figure 6(b) as a reference, the difference “(A)–(B)” indicates the new component caused by the Ga incorporation into ZnO-NPs.

Using the molecular weights of ZnO and Ga_2O_3 and the intensity ratios of the Ga 3d or O 1s spectrum, the estimated Ga amount in NP-layer of “*ZnO/Ga₂O₃ mixed and thermally treated (800°C, air)*” is about 5–7 at% with assuming a uniform Ga distribution. If this estimate is correct, the measured resistance in Figure 4 should be one or two orders of magnitude smaller. The reason why so much Ga was detected in Figure 6 can be considered that diffused Ga was mainly distributed near the surface of the ZnO particles, increasing the effective irradiated area by X-ray and emphasizing the apparent intensity of the Ga 3d and Ga-related O 1s signals. From Figure 6(a), a thermal treatment in N_2 caused a larger Ga signal, which can be explained using the smaller particulate size estimated by XRD. The smaller size gave the larger surface and/or grain-boundary-like sites to distribute the diffused Ga atoms. This can support the above assumption, however, further consideration is difficult at this stage. Anyway, it can be concluded that the Ga atoms diffused into the ZnO-NPs by the thermal treatment, and, because of following reasons, a part of them certainly substituted for the Zn atoms and were activated as donors.

One reason is the difference in the peak position of the Ga 3d spectra. In Figure 6(a), the obtained Ga 3d peak positions from $\beta\text{-Ga}_2\text{O}_3(100)$ single crystal substrate (20.5 eV, i.e., +10.5 eV from Zn 3d) and a sputtered Ga-doped ZnO (GZO) film (19.6 eV, i.e., +9.6 eV) are also shown. Generally, the Ga atoms in the GZO film are activated with substituting for the Zn atoms, which will cause the variation of a chemical bonding state and the difference of the peak position in the Ga-related spectra. In the case of “*ZnO/Ga₂O₃ mixed (without centrifugal separation)*”, all of the Ga 3d signal originated from the mixed Ga_2O_3 particles, naturally showing a similar peak position with that of the $\beta\text{-Ga}_2\text{O}_3$ single crystal. On the other hand, in the case of “*ZnO/Ga₂O₃ mixed & thermally treated (800°C, with centrifugal separation) in N_2 and in the air*”, the peak position shifted towards lower binding energies tending to that of the GZO film. However, the peak position is not the same as that of the GZO film, suggesting that some of the diffused Ga atoms substituted for the Zn atoms.

The other reason is a lattice constant variation. The estimated lattice constants using the Bragg’s law on the hexagonal system and the accurate peak positions of XRD (002) signals are 5.2057 Å ($2\theta = 34.415^\circ$) and 5.2044 Å ($2\theta = 34.424^\circ$) from Figures 5(a) and 5(b), respectively, i.e., about a 0.001-Å reduction was observed after the thermal treatment with the Ga_2O_3 particles. Generally, the lattice constant will be reduced by the substitution of Ga (0.47 Å) for Zn (0.60 Å) because of a smaller ion radius [26]. In our case,

the observed change was small but this can also explain that some of the diffused Ga atoms substituted for the Zn atoms.

From the XRD and XPS analyses, direct Ga-doping to ZnO-NPs by simple mixing and thermal treating with Ga_2O_3 particles was confirmed, which reduced the resistivity of the sprayed ZnO NP-layers dramatically.

Finally, as described in Sec. II, it was expected that the thermal treatment in pure N_2 tended to generate more defects comparing that in the open air, which would act as native donors improving the conductance. However, the obtained sheet resistances tended to show the opposite behavior. One possible reason is that the oxygen vacancies were generated mainly at the surfaces of NPs, which cannot contribute to generation of carriers different from the bulk. Another possible reason is that the defects were not generated as expected. Recent photoluminescence analyses (not shown here) support the latter case, i.e., the thermal treatment in the pure N_2 ambient lead less defects comparing with that in the open air. Controlling of the defects is important for the diffusion and the substitution behaviors, so it needs continuous investigation about the defect properties on ZnO-NPs to achieve more effective Ga-doping.

IV. CONCLUSIONS

From detail analyses in the XRD and XPS results, expected Ga-doping on ZnO-NPs was confirmed by mixing and thermally treating with Ga_2O_3 particles, resulting dramatic reduction of the sheet resistances of the sprayed n-ZnO NP-layers successfully. Dependence of the temperature and the ambient gas (air and N_2) in the thermal treatment upon the sheet resistance was also shown.

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