We synthesized ZnO nano-particulate films by a sol–gel method and evaluated their gas sensing properties. A ZnO colloidal solution of 5.6 nm sized nanocrystals was prepared from zinc acetate in n-propanol and dip-coated on silica glass substrates. The as-deposited ZnO film consisted of 30 nm grains. Annealing the films resulted in a growth of the particles, which was confirmed by scanning probe microscopy and UV-Vis spectrometry. The ZnO film annealed at 400°C worked well as a gas sensor device for volatile organic compounds (VOC) gases. The sensitivity was the best in the case of ethanol gas at 350°C. The sensing performances decreased by annealing at higher temperatures due to the coalescence of the ZnO particles.

Key-words : Zinc oxide, Nanocrystal, Solution process, Gas sensor

1. Introduction

Zinc oxide (ZnO) is n-type semiconductor with a direct wide bandgap (3.37 eV) and a large exciton binding energy (60 meV). It is widely used for electronic applications, such as varistors, phosphors, and gas sensors. Among many ZnO fabrication techniques, solution processes are expected to make complex nanostructures by simple methods at low temperatures. A wide variety of ZnO morphologies were reported and review papers on the synthesis of ZnO particles and thin films by solution-based processes were published.

These nanostructured ZnO materials have been expected for sensor applications due to their high surface-to-volume ratio. The performance of gas sensors strongly depends on the microstructures, and the control of the grain size and the surface morphology of the ZnO is important to improve gas sensing properties.

Previously, we have reported a sol–gel synthesis to produce ZnO nanocrystals with size around 5 nm. Transparent ZnO nano-crystalline thin films were produced from the nanocolloid for optical applications. In this study, we investigated the effect of the annealing temperatures of the ZnO films on their morphology and gas sensing property for volatile organic compounds (VOC) gases.

2. Experimental

In Fig. 1, the schematic diagram of the sample preparation route is shown. The ZnO nano colloid was prepared by suspending 0.02 moles of zinc acetate dihydrate (Wako) in 40 ml of n-propanol (Wako). The mixture was subsequently distilled on a rotary evaporator under ambient atmosphere during 10 min in a preheated silicon oil bath. 9 ml of a methanolic tetramethylammonium-hydroxide (Kanto Chem.) stock solution (2.37 M) were rapidly added under magnetic stirring to the hot mixture, yielding a turbid precipitate that transformed into a clear concentrated nanocolloid solution after a few minutes. The ZnO nanocrystals were purified by precipitation with heptane followed by centrifugation, and were finally redispersed in 20 ml of ethanol. The film deposition on pre-cleaned silica substrates was performed using a dip-coating apparatus. The films were first annealed in air at 400°C for 15 min to remove the organic residues. Then, some of the films were further annealed for another 15 min at either 600°C or 800°C.

The size of the ZnO nanocrystals in the colloidal suspension were determined by transmission electron microscopy (TEM, JEOL JEM-1400). The thickness of the ZnO films was determined by observations of their cross section using a scanning electron microscope (SEM, JEOL JSM-6500F). The surface morphology of the ZnO films was observed by using a scanning...
probe microscope (SPM, SPA400, SEIKO Instruments) with a dynamic force mode. UV–Vis absorption spectra of the ZnO thin films on the silica substrates were recorded using a spectrophotometer (SolidSpec-3700, Shimadzu) in the spectral range of 240–500 nm.

For sensor devices, gold interdigital electrode with 100 nm pitch was sputtered on the ZnO films. The electric resistance under gas flow (50-ppm ethanol, 50-ppm toluene and 1000-ppm H2 gases) was measured in air at 350°C as a function of time. Air and the target gases were alternately flowed into a measurement system at 70 sccm. A standard resistor was connected with the sensor, and the voltage across the standard resistor was measured under an applied DC voltage of 4 V to evaluate the electrical resistance of the device. Figure 2 shows the schematic diagram for the measurement. The change in the resistance between the two rectangular electrodes was measured by a Keithley 2000 multimeter connected to a computer. The gas sensitivity ($R_{\text{air}}/R_{\text{gas}}$) was defined as the ratio of the sensor resistance in air ($R_{\text{air}}$) to that in the object gas ($R_{\text{gas}}$).

3. Results and discussion

The TEM image in Fig. 3(a) shows that the ZnO nanocrystals have an average size of 5.6 nm. The SEM photograph [Fig. 3(b)] shows that the thickness of the ZnO film after annealing at 400°C was about 50 nm. Figure 4 shows the SPM images of the ZnO films before and after annealing at 400°C, 600°C or 800°C. The as-deposited ZnO film before annealing consisted of 30 nm grains [Fig. 4(a)], which originate from the agglomeration of the ZnO nanocrystals upon drying on the substrate. The ZnO thin films annealed at 400, 600 and 800°C [Figs. 4(b)–4(d)] were made of grains about 30, 50 and 100 nm, respectively. The grain size almost did not change by annealing at 400°C, whereas it became larger with further annealing at higher temperatures.

In Fig. 5, the UV–Vis absorption spectra of the ZnO films on the silica substrates annealed at 400–800°C are shown. The absorption edge wavelengths were estimated from the intersection of the dashed lines shown in Fig. 5, and the values were 364, 360 and 369 nm for the ZnO films annealed at 400, 600 and 800°C, respectively. The absorption edge shifted to longer wavelengths compared with the as-deposited film (353 nm). Although the difference in the grain size [Figs. 4(a), 4(b)] between the samples non-annealed and annealed at 400°C was small, the shift of the absorption edge implies that a growth of the crystallites inside the agglomerates of 30 nm by annealing at 400°C. The absorption edge wavelengths for the samples annealed at 600 and 800°C were the same, which implies that the quantum size effect of the nanoparticles vanished over 600°C through the coalescence of particles.

![Fig. 2. Schematic diagram for the measurement of sensing properties.](image)

![Fig. 3. (a) TEM image of the ZnO nanocrystals. (b) SEM image of the ZnO film annealed at 400°C for 15 min.](image)

![Fig. 4. SPM images of the ZnO films (a) no-annealed and annealed at (b) 400, (c) 600 and (d) 800°C.](image)
In order to consider the sensing mechanism for the reducing gases, the dynamic response of the ZnO film annealed at 400°C was first measured by using a mixed gas of H₂ in air (1000 ppm) at 350°C. The measured typical dynamic response of ZnO to 1000 ppm H₂ measured is shown in Fig. 6. After the H₂ gas was introduced, the resistance of the ZnO film decreased by half in 15 s and about one order of magnitude in 160 s. The resistance recovered completely in 550 s after the reverse exchange from H₂-air to air. The gas sensing mechanism can be explained as follows: in air atmosphere and at high operating temperatures, oxygen molecules are adsorbed onto the surface of the ZnO sensor to form O⁺ or O₂⁻ ions by attracting electrons from the conduction band of the ZnO. When the ZnO gas sensor is exposed to reducing gases, the gas reacts with oxygen ion molecule on the surface and gives back electrons into the conduction band, thereby lowering the resistance of ZnO sensors.11),12)

Next, we studied the sensing properties of the ZnO films to the reducing gases such as H₂, ethanol and toluene. The results are shown in Fig. 7, where the sensitivity is defined as the ratio \( R_{\text{air}} / R_{\text{gas}} \). The ZnO film annealed at 400°C [Fig. 7(a)] showed higher sensing properties for all gas than the film annealed at 600°C [Fig. 7(b)]. This can be explained by a decrease in the surface area with the particle growth occurring when annealing at high temperatures. For the ZnO film annealed at 400°C, the highest sensitivity was found for 50 ppm ethanol with a \( R_{\text{air}} / R_{\text{gas}} \) value of about 30. The values for 1000 ppm H₂ and 50 ppm toluene were about 80 and 50% of the one obtained for 50 ppm ethanol, respectively. For the ZnO film annealed at 600°C, the highest sensitivity was found for 1000 ppm H₂ with a \( R_{\text{air}} / R_{\text{gas}} \) value of 5.5. The values for 50 ppm ethanol and 50 ppm toluene were almost same and about 60% of the one obtained for 1000 ppm H₂. Thus, the nano particulate film worked well as a gas sensor device for VOC gases, thanks to the high surface area of these nanostructured materials.

### 4. Summary

We synthesized ZnO nano-particulate films by a sol–gel method and evaluated their gas sensing properties. A ZnO colloidal solution of 5.6 nm sized nanocrystals was prepared from zinc acetate in n-propanol and dip-coated on silica glass substrates. While the 5.6 nm sized ZnO nanocrystals were deposited on substrates, they agglomerated to form grains of 30 nm. The grain growth by annealing was confirmed by SPM and UV–Vis absorption spectroscopy. The ZnO film annealed at 400°C worked well as a gas sensor device for VOC gases. The sensitivity was the best for ethanol at 350°C. The sensing performances decreased by annealing at higher temperature due to coalescence, which is highlighting the interest of nanostructured materials with high surface area.
Acknowledgement The authors gratefully acknowledge the supports of the Collège Doctoral Franco-Japonais and the Région Bretagne.

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