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Carbon monoxide gas sensing properties of Ga-doped ZnO film grown by ion plating with DC arc discharge

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Abstract. The carbon monoxide (CO) gas sensing properties of low-resistance heavily Ga-doped ZnO thin films were evaluated. The ZnO films with a thickness of 50 nm were deposited at 200 °C by ion plating. The electrical properties of the ZnO films were controlled by varying the oxygen assist gas flow rate during deposition. The CO gas sensitivity of ZnO films with Au electrodes was investigated in nitrogen gas at a temperature of 230 to 330 °C. CO gas concentration was varied in the range of 0.6–2.4 % in nitrogen gas. Upon exposure to CO gas, the current flowing through the film was found to decrease. This response occurred even at the lowest temperature of 230 °C, and is thought to be the result of a mechanism different than the previously reported chemical reaction.

1 Introduction

ZnO is a substance for which various applications such as gas sensors and ultraviolet light sensors are anticipated. In recent years, the properties and applications of ZnO nanostructured films have been also studied (Zhao et al., 2010; Lao et al., 2003).

Carbon monoxide (CO) gas, being both colorless and odorless, is a dangerous gas for which it is hoped that high-sensitivity sensors may be developed. The lethal concentration by CO gas is 1500 ppm. There have been a number of attempts to evaluate the sensitivity of ZnO to CO gas. There have also been reports of carbon nanorods and nanowires reacting with high sensitivity to CO gas (Hassan et al., 2013; Kim et al., 2009). Experiments using catalysts such as Pd have also been reported (Trung et al., 2014). In these cases, the response mechanism is understood to have involved chemical reactions between gas molecules and the ZnO surface. All of these films had a high electrical resistance, and the presence of the gas was indicated by a change in resistance. Several investigations have been conducted on CO gas sensing properties of Ga-doped ZnO nanostructured films (Han et al., 2011; Pearce et al., 2009; Phan and Chung, 2013). Phan and Chung (2013) have reported the effects of Ga-doping on CO sensing properties of Ga-doped ZnO nanorods. Their p–n junctions-based nanorods sensors have a fast response.

We have previously reported transparent low-resistance Ga-doped ZnO (GZO) films produced using ion plating (Shirakata et al., 2003; Yamada et al., 2007a, b, 2010). In the present study, we carried out an evaluation of the sensitivity of these polycrystalline ZnO thin films to CO gas.

2 Experimental

The polycrystalline ZnO films were grown using DC arc discharge ion plating (Yamamoto et al., 2012). The growth temperature was 200 °C and a ZnO tablet incorporating 3 wt % Ga was used as the source material. During growth, flowing oxygen was used as an assist gas, with the flow rate being varied between 5–25 cm^3 in order to control the structure and properties of the films. The film thickness, controlled by means of the growth time, was 50 nm. In the previous report, Ga 3 wt %-doped ZnO film was good polycrystalline with a hexagonal structure (Yamada et al., 2006).

The crystallinity of the films was characterized by high-resolution X-ray diffraction (XRD; ATX-G, RIGAKU). Their electrical properties were evaluated by Hall-effect measurements (HL5500PC, Nonometrics) in the van der Pauw configuration at room temperature.

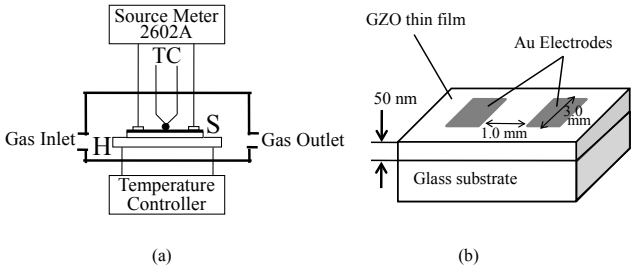

Figure 1. Schematic diagrams of **(a)** measurement setup and **(b)** sample dimension. TC: thermocouple; H: heater; S: Ga-doped ZnO film on glass substrate.

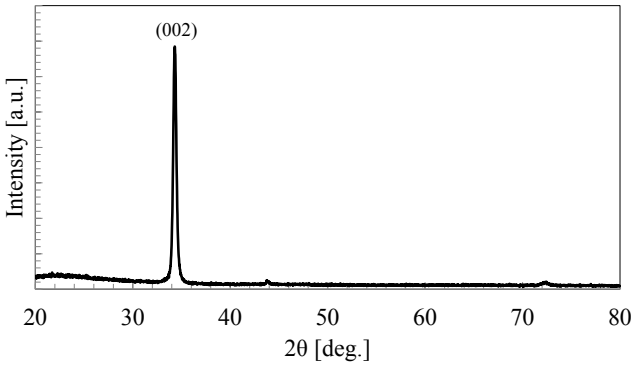

Figure 2. High-resolution XRD pattern result of the ZnO film with 50 nm thickness.

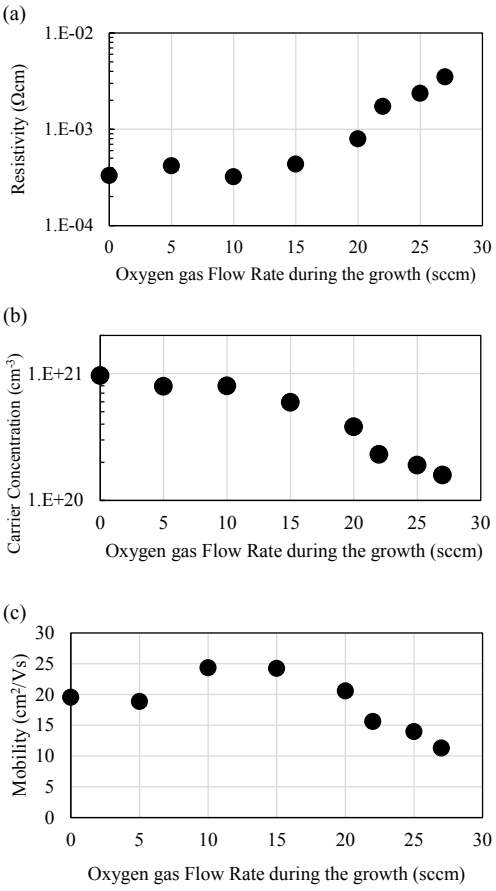

Figure 3. Resistivity as a function of oxygen gas flow rate for GZO films **(a)**. Carrier concentration as a function of oxygen flow rate for GZO films **(b)**. Hall mobility as a function of oxygen flow rate for GZO films **(c)**.

Evaluation of the gas sensitivity was performed using the following method. Figure 1 shows the layout of the sample and electrodes along with the sample chamber. First, Au electrodes (separated by 1 mm) were formed with a thickness of at least 150 nm, and the sample was cut into 5 mm × 5 mm chips, which were placed in a compact chamber for evaluation. The electrodes of the ZnO film were connected to a DC power supply (System SourceMeter 2602A, Keithley), which applied 5 V, and this current was measured for the films. The temperature of the sample films was controlled at between 230 and 330 °C using a ceramic heater set beneath the sample. These temperatures are slightly higher than the desorption temperatures of oxygen from metal oxide (Iwamoto et al., 1978). The sample chamber was flowed continuously with nitrogen gas at a flow rate of 400 sccm. In order to evaluate the intrinsic reaction to CO gas, CO gas sensing properties were investigated in nitrogen gas. Under these conditions, the amount of CO gas necessary to produce the specified concentration was mixed with the nitrogen gas and allowed to flow for 10 s, and the change in the sample current was measured. In order to maintain the reaction satisfactorily, the evaluation was conducted at an extremely high CO gas concentration of 2.5 (0.6 %) to 10 (2.4 %) sccm. The gas was evacuated and released at atmospheric pressure. The gas inlet was placed in such a way that the gas entering the sample chamber did not directly impinge on the sample. The volume of the cylindrical sample chamber was approximately 200 cm^3.

3 Results and discussions

Figure 2 shows the XRD results for the deposited ZnO films. It can be seen that the main diffraction peak is associated with (002) planes, so that the film is *c* axis oriented. Under the same growth condition, these Ga-doped ZnO films were polycrystalline with a wurtzite-type hexagonal structure from a cross-section transmission electron microscopy (TEM) and in-plane XRD measurements (Yamada et al., 2007b).

Figure 3 shows the results of Hall-effect measurements for the samples. Due to the Ga doping, the resistivity was extremely low. The carrier concentration was found to decrease with increasing oxygen flow rate during growth. In all cases, the carrier concentration was $\geq 1.0 \times 10^{20}$ cm^{-3} and, from the temperature dependence of the Hall-effect measurement for samples deposited under same conditions, it was found

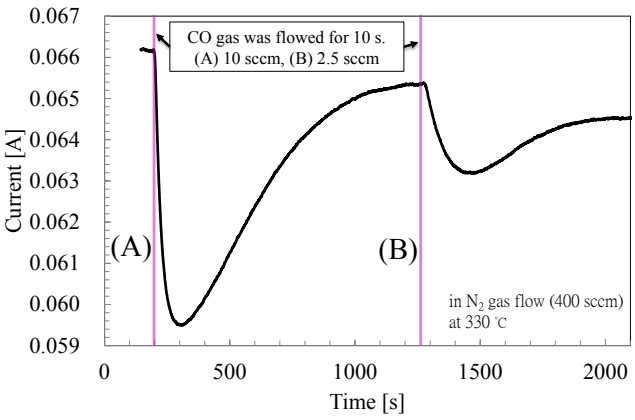

Figure 4. Changes in current in ZnO films at 330 °C due to CO gas. A constant nitrogen gas flow of 400 sccm was used and CO gas was allowed to flow for 10 s.

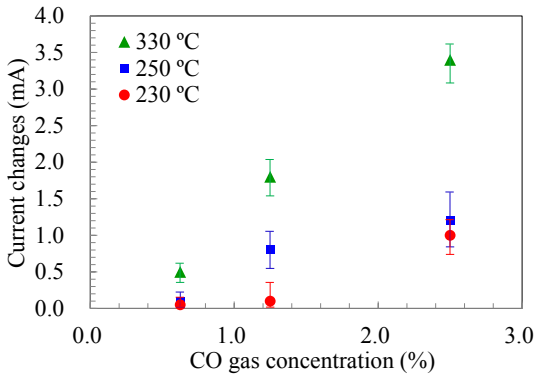

Figure 5. Dependence of current change in ZnO films on CO gas concentration. The carrier concentration was 1.8×10^{20} cm^{-3}. The sample temperatures were 230, 250 and 330 °C.

that the samples were degenerated. From studies of samples deposited under the same conditions (Yamamoto et al., 2012), both intra-grain scattering and grain boundary scattering are the mechanisms limiting carrier transport.

Figure 4 shows the change in the film current when a sample (oxygen gas flow rate during the growth was 25 sccm) was exposed to a flow of CO gas. In addition to the 400 sccm flow of nitrogen gas, 10 and then 2.5 sccm of CO were sequentially flowed for 10 s, and the change in sample current was measured. The current prior to exposure is determined by the original film resistance. The current shows a decrease upon exposure to the gas, with a minimum occurring at around 100 s following exposure, before showing a tendency to return to its original value. Previously, it was reported that exposure to CO caused a decrease in the resistance of ZnO film due to the chemical reaction (Tanaka et al., 1976) occurring on the surface given in

$$CO_{(g)} + O^{-}_{(ads)} \rightarrow CO_{2(g)} + e^{-}. \quad (1)$$

Since the results shown in Fig. 3 indicate the opposite behavior, the mechanism must be different than that previously reported. In other words, it does not involve a chemical reaction with CO molecules on the film surface. It may be that the absorption to the grain boundary of oxygen gas molecules plays the role of a physical barrier for carriers.

In fact, since even at 330 °C there is a large response of several milliamps, it is thought that the reaction involves the entire film rather than just the surface. Since it is difficult to imagine the reaction occurring within the grains in the polycrystalline film, it is possible that it is actually taking place at the grain boundaries. For samples with a relatively low carrier concentration and Hall mobility, the current showed a large decrease of about 5.0 mA at a temperature of 330 °C in response to CO gas. The large current response observed in the present study clearly indicates the practical potential of a ZnO-based CO detector.

Figure 5 shows the change in the current response as a function of CO gas concentration. The current change increased with increasing the CO gas concentration. Furthermore, even at a low temperature of 230 °C, a large decrease in current was found in response to CO gas. For the elucidation of the reaction mechanism, it requires further experiments.

4 Conclusions

The reaction characteristics of heavily Ga-doped low-resistance ZnO films in response to CO gas were investigated. The ZnO thin films were polycrystalline with a columnar structure and were highly oriented along the *c* axis. In response to an inflow of CO gas, the current flowing through the film was found to decrease, which is the opposite to the previously reported effect associated with a chemical reaction on the film surface.

In the present study, a CO gas concentration of 6.21 % was chosen in order to observe the reaction clearly, and a large reaction current of 2 mA was obtained. This may have been the result of the heavy Ga doping level.

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