Effect of Microwave Annealing on Oxide-Semiconductor-Precursor Ink

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1. Introduction

Printed electronics offer a simple and inexpensive way of fabricating electronic and photoelectronic devices by printing, and this technique further offers high resolution, high speed, and large-area capability. The viscosity of the ink is an important parameter, and the ability to vary the viscosity can improve the process margin of printing technology [1]. For example, low-viscosity ink can be used for inkjet and spin coating, and high-viscosity ink can be used for screen, gravure, and offset printing.

As a step toward printed electronics, we recently reported the fabrication of amorphous indium gallium zinc oxide (a-IGZO) thin film transistors (TFTs) from low-viscosity (under 0.01 Pa·s) IGZO precursors using microwave annealing [2]. IGZO semiconductors have been extensively studied for obtaining high-performance TFTs with high mobility and reasonable on/off ratios in the field of flexible electronics [3].

In this work, we synthesized high-viscosity (92 Pa·s) precursors consisting of metal salts, diethanolamine (DEA), and urea. We first discuss the characteristics of the precursor and the sintering processes, and then we electrically evaluate the TFTs fabricated using the precursor.

2. Experimental

The IGZO precursor was prepared as follows. In (NO₃)₃·3H₂O, Ga(NO₃)₃·8H₂O, and Zn (NO₃)₂·6H₂O were dissolved in Milli-Q water and stirred in a beaker at room temperature in air. Urea was added and stirred in the aqueous metal nitrate solution. After the urea had dissolved completely, DEA was added [1]. The solution was heated at 150 °C at 1 h during stirring and cooled to room temperature. Finally the viscous IGZO precursor was obtained.

We fabricated a bottom contact onto a SiO₂ (300 nm)/p-type Si substrate for fabrication of a TFT structure using Cr (2 nm) and Au (60 nm). The channel width (W) and length (L) of the resulting TFT were 1000 µm and 20 µm, respectively.

The IGZO precursor was deposited onto an electrode on the substrate by spin-coating at 3000 rpm for 30 s. The precursor film was annealed using a Fuji Electrical Industrial microwave generator (FSU201VP-02) at 400 °C with a frequency of 2.45 GHz. The temperature was measured using a radiation thermometer (FTK9, Japan Sensor). The precursor film was also annealed in a conventional oven at 400 °C for comparison with the microwave-annealed film. Figure 1 shows a schematic of the cross-section of the IGZO TFT. After fabrication of the TFTs, the performance of the devices was measured under a
nitrogen atmosphere using a Keithley 4200 system. Thermogravimetric and differential thermal analyses (TG-DTA, SII Exstar TG/DTA 6200) were performed in an air atmosphere. X-ray diffraction (XRD) measurements were performed using a Rigaku Ultima IV-Photectus diffractometer with Cu Kα radiation for phase identification. We analyzed the XRD peaks using the International Centre for Diffraction Data (ICDD) pdf2 database.

3. Results and discussion

Fig. 2 (a) shows the TG-DTA curves of the IGZO precursor. The DTA curve has an endothermic peak around 210 °C that arises from evaporation of DEA [1]. Also, a large mass decrease can be observed. The exothermic peaks observed at 250 and 300 °C are interpreted as the alloying of metal hydroxides to the multicomponent oxides. The large exothermic peaks in the DTA curves with a mass decrease around at 450 and 500 °C are due to combustion of the organic residue. Fig. 2 (b) shows the time-dependent TG-DTA at 400 °C. The solvent starts to evaporate in about 10 min. The weight loss due to the evaporation and the subsequent decomposition of the organic residue can be observed. After about 200 min, the weight loss is about 90 %. The loss is consistent with that heated at 500 °C as shown in Fig. 2 (a). On the basis of these data, we decided that the annealing time in a conventional oven for fabrication of the TFT.

Fig. 3 (upper line) shows the XRD pattern of the sample annealed in a conventional oven at 400 °C for 240 min, which has a broad peak located around 30° indicative of an amorphous phase. In this case, the film consists of the amorphous metal oxides and the organic residue as shown in Fig. 2. In contrast, the IGZO precursor film microwave-annealed for 5 min exhibits an indium oxide crystal peak (lower line). Possible reasons for these results are as follows. During microwave annealing, the IGZO films were not only directly heated by energy conducted from the gate electrode, but also indirectly heated by absorbing microwaves [2]. Furthermore, because the temperature gauge only...
detected the surface temperature of the film, the temperature inside the film would be higher than 400 °C during microwave heating. Moreover, these XRD results affected the TFT characteristics (Fig. 4). Fig. 4 shows the transfer characteristics of TFTs consisting of IGZO films formed by annealing with the conventional oven and with microwaves. The gate voltages $V_G$ was applied from -40 V to +40 V with a voltage step of 2 V. The drain voltage $V_{DS}$ was +40 V. The transfer characteristics were measured at room temperature in air and in the dark. For the film microwave-annealed at 400 °C for 5 min, the $I_{on}/I_{off}$ ratio and field effect mobility were $10^6$ and $10^{-2}$ cm$^2$·V$^{-1}$·s$^{-1}$, respectively. On the other hand, the film annealed with a conventional oven at 400 °C for 240 min showed poor TFT performance: an $I_{on}/I_{off}$ ratio of $10^2$ and a field effect mobility of $10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$ were obtained. In the case of the oven annealing the high $I_{off}$ is due to the increase in the density of oxygen vacancy. The low $I_{on}$ is considered to be caused by the organic molecules remaining in the semiconductor layer, which act as electron traps [4]. In Fig. 2, decomposition of the organic residue was observed even above 450 °C.

On the other hand, since microwaves were effectively absorbed by the organic residue, which was then was rapidly removed [2], the $I_{on}$ was increased by decreasing trap sites. Finally, as shown in Fig. 3 indium oxide was crystalized during microwave annealing. It is also advantageous for fast electron transport. In summary, we have demonstrated a high-efficiency microwave annealing technology that can enhance the electrical characteristics of TFTs prepared using high-viscosity IGZO precursors. The process is advantageous for short-time annealing high-viscosity precursor-film.

References
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