Fabrication of Solution-Processed Oxide Thin Film Transistors

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Abstract

In recent years, the transparent amorphous oxide semiconductor (TAOS) has attracted attention as an active layer for next generation TFTs. With the aim of reducing manufacturing cost, the solution-processed TAOS has been also under review. In this paper, we report on film formation, material analysis and fabrication of $InGaZnO_4$ and In-Zn-O TFTs using the solution-based process.

1. Introduction

Oxide semiconductor material has attracted increased attention because of the two characteristics that it exhibits in the visible light region: optical transparency and electrical conductivity. In particular, in recent years, indium tin oxide (ITO) known for its good transparency and conductivity has been used widely as a transparent electrode material for solar cells and displays. The material is thus becoming more and more common in our daily lives. However, the attention has been limited to its transparency and conductivity and its potential as a functional material for semiconductor devices is yet to be considered.

Under such circumstances, Professor Hideo Hosono of the Tokyo Institute of Technology et al. released, in sequence, a monocrystal transparent oxide transistor using $InGaO_3(ZnO)_5$ in 2003 and a thin film transistor (TFT) deposited at room temperature with an amorphous $InGaZnO_4$ phase in 2004[1), 2)]. In spite of the films being deposited at room temperature, the latter, in particular, was discovered to exhibit high mobility, ten times that of amorphous silicon. Since then, oxide semiconductor materials, mainly those of the In-Ga-Zn-O system, have been attracting much attention as an active layer for next-generation display-use TFTs.

The achievements by Hosono et al. encouraged various research institutes and manufacturers to launch their own research and development of transparent amorphous oxide semiconductors (TAOS) including those of the In-Ga-Zn-O system, and they achieved technological breakthroughs. In particular, Japanese, Koreans and Taiwanese panel manufacturers have been playing leading roles in vigorous trial manufacture of large displays. After much discussion about reliability and stability, and with some advanced consideration of issues relating to mass production, the technology has nearly reached a practical level[3), 4)].

With the trend for larger displays, they have also actively engaged in the establishment of a strategy for next-generation flexible displays incorporating organic material substrates as well as research and development of lower cost manufacturing techniques involving solution-based TAOS-TFTs without using vacuum processes. Among such TFTs are ZnO (2003)[5)], Zn-Sn-O (2006)[6)] and In-Zn-O (2007)[7)] reported mainly by Oregon State University. Today, the number of those reported cases has been increasing dramatically. In addition, at SID 2009, Samsung Electronics introduced to the public a solution-processed 4-inch liquid crystal display driven by a TAOS-TFT[8)]. Expectations for the manufacture of solution-based TFTs have thus been increasing in the world. However, compared with vacuum deposition, the solution-based process requires a higher processing temperature and has difficulty in forming high-quality thin films. Those are the issues yet to be overcome for the future, and there has already been a fierce competition among research institutes from a technical perspective of *how to realize high-mobility and stable elements even in a low-temperature process.*

2. Approaches at Fujifilm

This section describes an outline of our research on oxide semiconductor materials, mainly those of the In-Ga-Zn-O system. Aiming to understand the genuine properties particular to oxide semiconductor materials and their potential, our group takes diverse approaches to the materials research encompassing amorphous to monocrystalline from a wide perspective. Furthermore, we have been carrying out various other researches including evaluation of the basic physical properties of materials and studies to increase the reliability and stability of TFT devices, looking to their practical application as well. The following are some of our concrete research achievements[9)].

I. With the ceramics solid-phase reaction method, we

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conducted an accurate evaluation of the basic physical properties of $In_{2-x}Ga_xZnO_{4-\delta}$ (δ: concentration of oxygen vacancy) in the region where semiconductive properties are exhibited. We elucidated the Ga solid solution region as a crystalline phase and the relevant electrical properties.

II. With reactive solid-phase epitaxy, we manufactured a single-crystal film of $InGaZnO_4$. While considering the possibility of process improvement, we evaluated the electrical properties of its single-crystal structure and, with the single-crystal film, elucidated the material-specific dependence on measurement environment.

III. We synthesized $InGaZnO_4$ and In-Zn-O ingredients that are compatible with the solution process. By applying spin coating and the inkjet method, we manufactured and evaluated devices and succeeded in the realization of oxide TFTs with good properties.

IV. To improve the reliability of the In-Ga-Zn-O TFT deposited by sputtering, we newly employed oxide gallium as its protective layer. With this, the reliability was increased in regard to the prevention of threshold shifting.

V. Aiming to improve the photostability of the In-Ga-Zn-O TFT in the visible light region, we modulated its synthesis, focusing on the In/Ga ratio of the film and thus improved the photostability by enlarging the optical band gap.

VI. We evaluated the effect of post annealing at around 200°C on the conductivity of the amorphous In-Ga-Zn-O film deposited by sputtering. By scrutinizing it via *in-situ* measurement, we revealed that moisture contained in the film greatly affects the conductivity after post annealing.

In the next section, we report the details of the manufacture of the solution-processed oxide TFTs described in III above.

3. Manufacture and evaluation of solution-processed $InGaZnO_4$ and In-Zn-O TFTs

3.1 Synthesis and evaluation of precursor materials

There are several possible ingredients that can be used to manufacture solution-processed oxide materials, such as metal alkoxide, metal organic acid salt, nitrate and chlorides. We employed, as a starting ingredient, metal alkoxide, which is an organometallic compound, and manufactured a precursor solution for oxide semiconductors. The ingredient consists of metal atoms bonding with alcohol groups and is naturally free of unnecessary elements such as chlorine, which is convenient for the manufacture of electronic devices[10].

Fig. 1 shows the synthesis sequence of $InGaZnO_4$ precursor solution. For In, Ga and Zn ingredients, In-(O-C_3H_7)$_3$ (Kojundo Chemical Laboratory, 3N), Ga-(O-C_3H_7)$_3$ (Soekawa Chemical, 3N) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (Kojundo Chemical Laboratory, 3N) were used respectively. The dosages of those ingredients were measured precisely to achieve the required composition of $InGaZnO_4$ film. The solvent used to improve solubility and temporal stability was $(C_2H_5)_2NC_2H_5OH$, i.e., diethylethanolamine (Wako Pure Chemical Industries). We calculated the composition ratio of the manufactured precursor solution with an ICP measurement method and gained the result of In:Ga:Zn = 1:1:0.95.

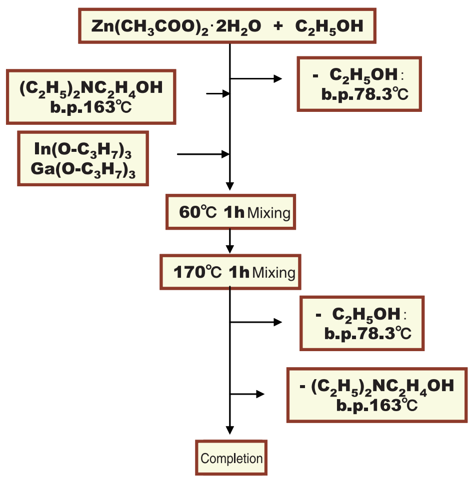

Fig. 1 Synthesis flow of $InGaZnO_4$ precursor solution.

We then measured the pyrolysis characteristic of the $InGaZnO_4$ precursor solution via thermogravimetry-differential thermal analysis (TG-DTA) (Fig 2).

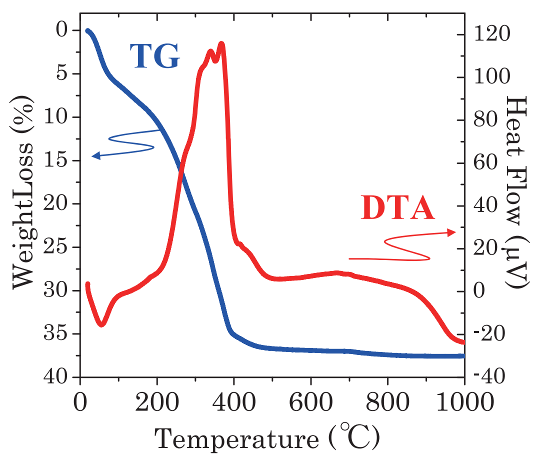

Fig. 2 TG-DTA characteristics of $InGaZnO_4$ precursor solution.

Weight loss by burning of organic matter had stopped when the temperature reached about 400°C, and it was confirmed that dehydration polycondensation progressed with the increase of annealing temperature. Fig. 3 indicates the dependence of the X-ray diffraction (XRD) patterns on annealing temperature with the $InGaZnO_4$ solution-applied film (spin coat film). As shown, they kept a stable amorphous phase up to 600°C annealing and were crystallized in a single phase at 700°C or above. This is the same level of tendency as reported with vacuum-processed films. It was thus recognized that the precursor solution, as the starting ingredient, can form single-phase $InGaZnO_4$.

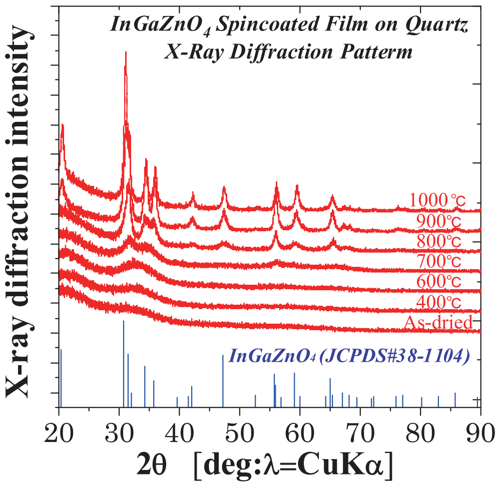

Fig. 3 Annealing temperature dependence of the XRD patterns of $InGaZnO_4$ film.

3.2 Manufacture and evaluation of TFTs

We manufactured Top-Gate TFTs from the above $InGaZnO_4$ solution, respectively with spin coating and inkjetting, and evaluated their electrical properties. For patterning deposition with the latter method, it is necessary to select optimal solution parameters, such as viscosity, surface tension and wettability, considering suitability to each inkjet equipment in use. We used the DMP2831 inkjet system manufactured by FUJIFILM Dimatix and adjusted parameters focusing on the viscosity of the solution. Specifically, by adding alcohol-soluble, high-viscosity cyclohexanol to that $InGaZnO_4$ solution (viscosity: 4.5 cps), we prepared an inkjet-compatible $InGaZnO_4$ solution (printable ink) with a viscosity of 9.89 cps.

Fig. 4 shows the TFT manufacturing sequence. We deposited

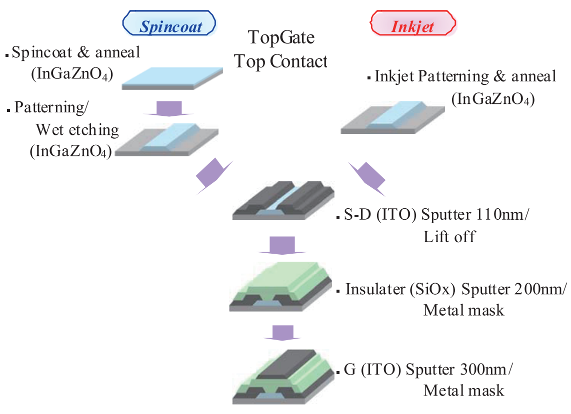

Fig. 4 Process flow of TFT fabrication.

$InGaZnO_4$ thin films on a quartz substrate. In the case of the spin-coated film, photolithography was applied for patterning. The source/drain electrode manufacturing process and the subsequent stages were the same, regardless of the deposition method of the films. Fig. 5 shows the characteristics of the TFTs manufactured with the spin-coated and inkjetted films both of which underwent 900°C annealing. Both TFTs were confirmed to have good characteristics. However, compared with the spin-coated TFT, those of the inkjetted TFT were slightly inferior. We presume that it was caused by the disorder of patterns and non-homogeneity of films derived from the drying speed during the deposition process. That is the issue in the future.

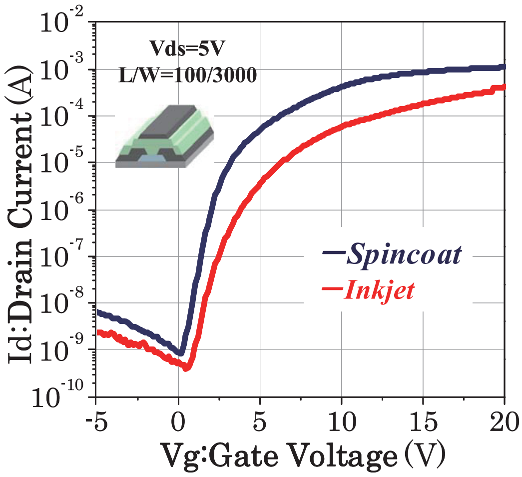

Fig. 5 Vg-Id characteristics of spin-coated and inkjetted $InGaZnO_4$ TFTs (At an annealing temperature of 900°C).

3.3 Lowering of the processing temperature

The above TFTs exhibited fine characteristics. However, the processing required a high temperature of 900°C. That will greatly limit the choice of substrate material in practical applications. Moreover, high-temperature annealing made $InGaZnO_4$ films polycrystalline; therefore, there are concerns about the impact of grain boundaries on the element properties, in particular, about non-homogeneity. When in the amorphous state, the manufactured $InGaZnO_4$ films did not exhibit satisfactory characteristics, causing the on-state current to significantly drop. Therefore, we improved the starting ingredients so that the film can achieve good TFT characteristics while keeping the oxide semiconductor layer of the active layer in the amorphous state, putting emphasis on lowering the processing temperature. To do so, there are several approaches to the composition, morphology (such as nanoparticles), solution design, process control, etc. In this section, focusing on Ga that is considered to control the density of the carriers of the In-Ga-Zn-O system, we tried to increase the on-state current while lowering the processing temperature by decreasing the Ga concentration and increasing the carrier density. In the meantime, the

In-Zn-O system without Ga (i.e., IZO, in the case of this paper, the composition is In:Zn=1:1) achieved a characteristic result. We will describe it below.

We synthesized a precursor solution of the In-Zn-O system in the same way as $InGaZnO_4$, using alkoxide as the starting ingredient. In the XRD evaluation of the spin-coated film, it was confirmed that the film retained the amorphous state in annealing up to 600°C and, including the pyrolysis characteristic, had almost the same material characteristics as those of $InGaZnO_4$.

Next, we deposited an In-Zn-O film on a silicon substrate having a thermal oxide film by spin coating and manufactured a simplified evaluation-use TFT element via 600°C annealing. In normal atmospheric conditions, it exhibited electrical conductivity but, when measured in dry air where moisture was removed, it showed TFT behavior. Furthermore, under the same conditions, TFT behavior was also observed in an In-Zn-O film annealed at 400°C. It became apparent that the processing temperature can be lowered to a level that allows the use of common glass substrates (Fig. 6). It is highly likely that composition control by decreasing the Ga concentration (i.e., Ga removal) had a positive effect on lowering the processing temperature.

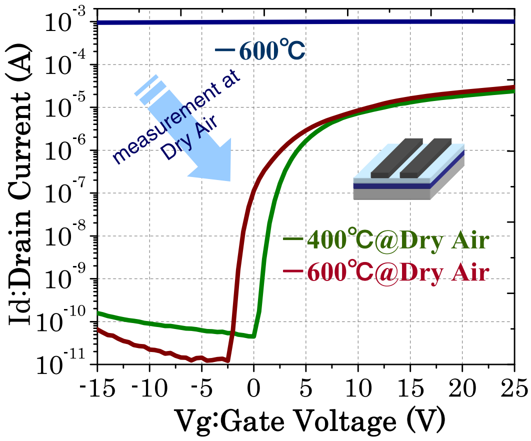

Fig. 6 Influence on measurement environment for spin-coated In-Zn-O TFTs, and annealing temperature dependence.

Structurally, as the active layer (In-Zn-O layer) of the simplified evaluation-use specimen was directly exposed to the external air, the electrical property was affected greatly by the atmosphere. A similar tendency has already been reported about vacuum-processed oxide TFTs. The film used in the current specimen was manufactured with the solution process. It is assumed that, compared with vacuum-processed specimens, such TFTs are more susceptible to the solvent ingredients of the solution, and residuals and defects in the film [11), 12)].

Finally, preparing an inkjet-compatible solution in the same way as $InGaZnO_4$, we manufactured an In-Zn-O Top-Gate TFT and evaluated its physical properties. As shown in Fig. 7, in the case of 600°C annealing, both spin-coated and inkjetted films achieved as good TFT characteristics as $InGaZnO_4$. Also, because the gate insulator of the TFT manufactured in this experiment functioned as a protective layer and isolated the active layer from the external air, TFT behavior was observed in a normal measurement atmosphere.

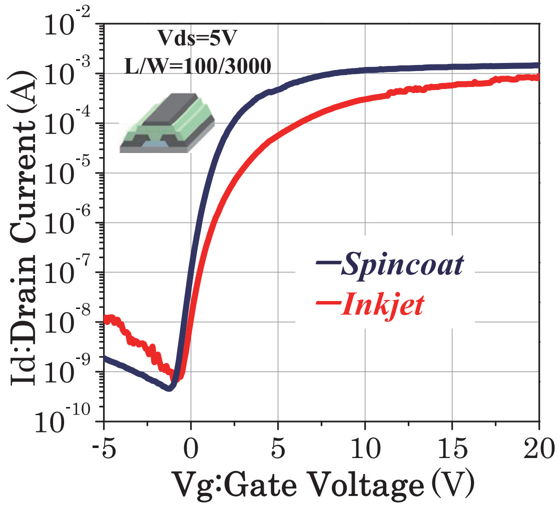

Fig. 7 Vg-Id characteristics of spin-coated and inkjetted In-Zn-O TFTs (At an annealing temperature of 600°C).

4. Conclusion

As described, based on the idea of building thin film transistors via the solution process instead of vacuum processing, solution-processed TFTs have been emerging. Under such circumstances, there is an increasing demand for diverse printing technologies and the corresponding material design. In this research, we synthesized precursor solutions for the deposition of an $InGaZnO_4$ film that allows the proper functioning of TFTs and an In-Zn-O film that is effective for the lowering of processing temperature. In addition, we succeeded in the manufacture of inkjet-compatible *printable ink*. In the future, based on these technologies, we will expand new application fields, aiming at further innovation.

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