Title	直接インプリント法によるIn203系酸化物薄膜の形成と薄膜トランジスタへの応用に関する研究
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Investigation of In_2O_3-based Oxide Films by Direct Imprinting for TFT Application

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1. Research content

1.1 Introduction

Indium oxide (In_2O_3) and indium tin oxide (ITO) are very mature metal-oxides, which have been in research from many years due to the advantages that they show n-type semiconducting behaviour with high transparency in visible light. Due to these properties, ITO is used as a transparent electrode in thin-film-transistor liquid-crystal display (TFT-LCD), organic solar-cells, electrochromic devices, window coatings, gas sensors, and touch screens.

To fabricate In_2O_3 and ITO films, various methods have been used such as sputtering, pulsed laser deposition (PLD), spray pyrolysis, vacuum evaporation, and solution process, etc. Among them, the solution process has advantages over other techniques, such as low-cost (as it does not require costly vacuum system), less time requirement (as no need for vacuum formation). Also, solution process is compatible with printing techniques, ease to coat on substrates with different geometries, simple processing, feasibility of direct patterning, with good source consumption efficiency.

Printed electronics have recently gained attention due to their low environmental impact, fewer fabrication steps, large area fabrication, ease of patterning on organic and inorganic substrates and low cost. Among various printed electronics techniques, inkjet printing is a popular method, but is not appropriate for the miniaturization of advanced electronic devices as the required resolution is sub-micrometers or less, which cannot be realized by inkjet printing. Furthermore, it is hard to achieve precise shape control of the film via inkjet printing. A novel printing technique known as nano-rheology printing (n-RP), based on direct imprinting of precursor gel films, can fabricate patterns as small as 100 nm with good shape control. n-RP is a resist-free, direct printing method which utilizes the rheological properties of a metal-oxide precursor gel to form patterns in the precursor gel.1)

In this work, at first electrical and patterning properties of In_2O_3 and ITO were studied by n-RP process. Also, the electrical properties of imprinted In_2O_3 and ITO films were also studied and compared with that of non-imprinted films. Finally, bottom gate thin film transistor (TFT) using n-RP, has been fabricated with solution process derived In_2O_3 as a channel and source/drain; while solution process derived HfO_2 as a gate insulator. Platinum (Pt) is used as gate electrode.

2. Research Purpose

The objective of this research is to study the electrical properties of In_2O_3 and ITO film prepared by the n-RP process and to fabricate TFT using n-RP process with chemical solution processed In_2O_3 as channel and solution processed HfO_2 as a high-*k* gate insulator.

2.1 Results and Discussion

At first In_2O_3 thin films were prepared by solution process using indium acetyacetonate ($In(acac)_3$) as a precursor in propionic acid (PrA). The electrical properties of In_2O_3 were studied by varying annealing time and annealing temperature. An optimum condition was obtained at which high mobility and carrier concentration were obtained. It is found that high mobility of around 42.7 cm^2 /Vs with a carrier concentration of 9.47 x 10^{18} cm^{-3} is obtained when In_2O_3 precursor gel film was annealed in O_2 at 600 °C annealing for 1h. Then ITO thin films were prepared using two different precursors of tin (Sn), keeping $In(acac)_3$ in PrA, same. One precursor was tin acetylacetonate ($Sn(acac)_2$) and another was tin chloride ($SnCl_2$). ITO films were also annealed in O_2 for 1 h at 600 °C. ITO concentration was varied from 1 to 10 wt.%. It is found that as the Sn concentration increases, mobility decreases due to the reason that Sn acts as impurity in In_2O_3 cubic bixbyite structure. Therefore, more the Sn content, more impurity scattering, hence less mobility. The resistivity as low as 2.6 x 10^{-3} Ωcm for our ITO films was obtained for 1 wt.% ITO via $Sn(acac)_2$ with a mobility of 24 cm^2/Vs and carrier concentration of 1.0 x 10^{20} cm^{-3}, when ITO film was annealed in O_2 for 1 h at 600 °C. Figure 1 shows resistivity of ITO films prepared by $SnCl_2$ and $Sn(acac)_2$. Resistivity of In_2O_3 films is also shown in Fig. 1, for reference.

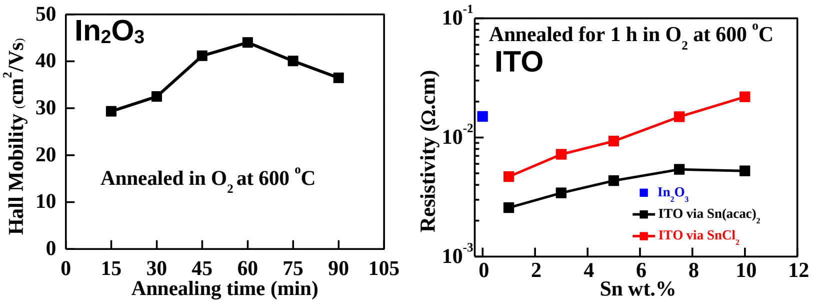


Fig. 1: (a) Hall mobility of In_2O_3 and (b) resistivity of ITO with respect to Sn wt.%.

Figure 2 shows the patterns of In_2O_3 and ITO formed by using n-RP, while Fig. 3 shows the electrical properties of imprinted and non-imprinted In_2O_3 and ITO films. Figure 2 shows that with the addition of tin (Sn) to In_2O_3 (i.e. ITO) degrades the n-RP properties because the tan δ value of ITO is smaller than that of In_2O_3 (tan δ is a measure of viscoelasticity of a material. It is 1 for viscoelastic material, less than1 for solids and greater than 1 for liquids). From Fig. 3, it is seen that, the electrical properties of imprinted ITO films are not altered as much as compared to non-imprinted ITO films, but are greatly affected in the case of imprinted In_2O_3 compared to the non-imprinted In_2O_3 films. The Hall mobility of imprinted In_2O_3 decreases due to the trapped carbon, as confirmed by SIMS measurements, which showed that even after annealing at 600 °C for 1 hour, there was more carbon in the imprinted In_2O_3 than non-imprinted In_2O_3. An increase in the carrier concentration in imprinted films is due to the increase in oxygen vacancies in In_2O_3 after imprinting, as confirmed by XPS studies.

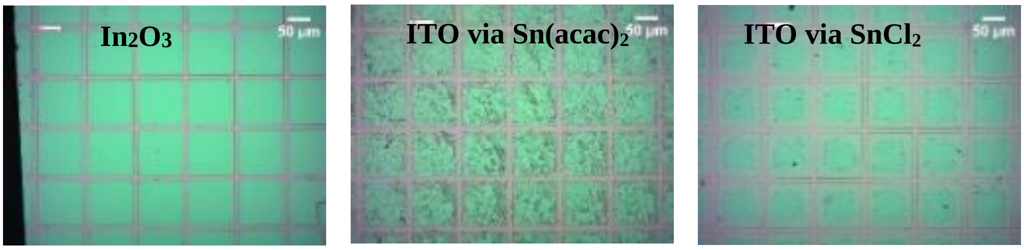


Fig. 2: Patterns of In_2O_3 and ITO.

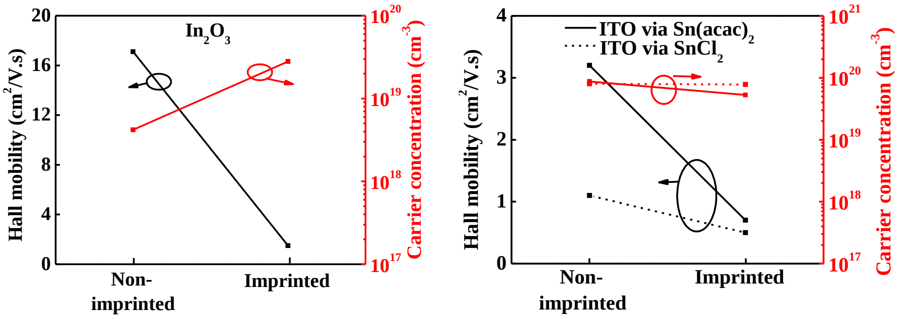


Fig. 3: Electrical properties of imprinted and non-imprinted In_2O_3 and ITO.

Since the high-*k* gate insulator is required to fabricate TFTs using In_2O_3 with relatively high carrier concentration, HfO_2 films were fabricated by the solution process. Polarization-electric field (P-E) and capacitance-voltage (C-V) of the solution processed HfO_2, fabricated using hafnium acetylacetonate ($Hf(acac)_4$) in PrA and annealed in O_2 at 700 °C for 15 min is shown in Fig 4. It is seen from Fig. 4 that pure HfO_2, is linear in nature and shows paraelectricity. The extracted relative dielectric constant (ε_r) from the P-E slope and C-V is 17, while the leakage current density at 1 MV/cm is 1.0×10^{-6} A/cm^2 with breakdown field of 5.8 MV/cm.

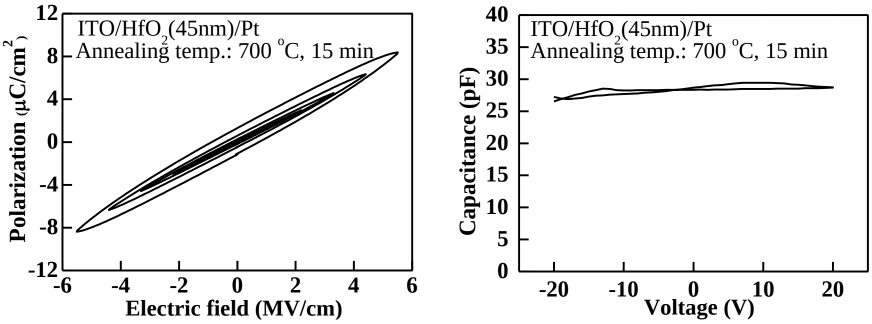
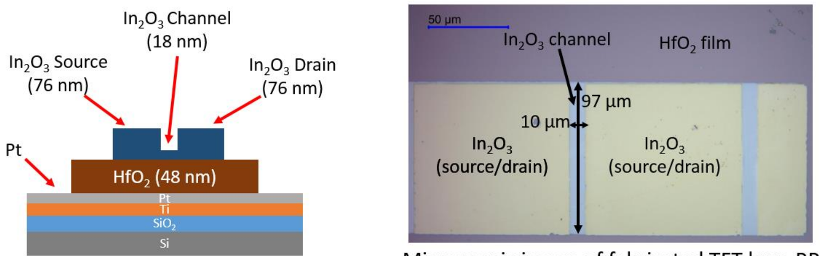


Fig. 4: Electrical properties of HfO_2 thin films annealed at 700 °C for 15 min in O_2.

Figure 5 shows the schematic structure of TFT fabricated by n-RP process. It can be seen that using n-RP, the fabricated TFT has source/drain and channel, all are fabricated by the same material in just one press, simultaneously.



Schematic of fabricated TFT by n-RP
(side view)

Microscopic image of fabricated TFT by n-RP
(top view)

Fig. 5: Schematic of TFT fabricated by n-RP process.

Normal n-channel transistor operation was observed. The calculated TFT parameters are, on/off ratio is in the order of ~10^5, SS: 2.3 V/dec, mobility: 0.13 cm^2/Vs, and threshold voltage: 1.9 V.

References:

1. T. Kaneda *et al.*, *J. Mater. Chem. C* **2** 40 (2014).

Research Accomplishments

Journal Publications

1. "Electrical Properties of In_2O_3 and ITO Thin Films Formed by Solution Process using In(acac)$_3$ Precursors", **Puneet Jain**, Yuji Nakabayashi, Ken-ichi Haga, and Eisuke Tokumitsu (submitted in Japanese Journal of Applied Physics).
2. "Electrical and Patterning Properties of Indium Oxide (In_2O_3) and Indium Tin Oxide (ITO) by Direct Nanoimprinting Technique", **Puneet Jain**, Chang Su, Ken-ichi Haga and Eisuke Tokumitsu, *Jpn. J. Appl. Phys.*, **58** SDDJ051-SDDJ058 (2019).

International conferences

1. "Hall Mobility and Carrier Concentration of In(acac)$_3$ Precursor Derived Solution Processed In_2O_3 and ITO Thin Films", **Puneet Jain**, Ken-ichi Haga, and Eisuke Tokumitsu, The 7th International Symposium on Organic and Inorganic Electronic Materials and Related Nanotechnologies (EM-Nano' 19), June 19-22, 2019, Shinshu University, Nagano, Japan (poster).
2. "Electrical Properties of In_2O_3 and In-Sn-O Films Prepared by Direct Nanoimprinting", **Puneet Jain**, Ken-ichi Haga, and Eisuke Tokumitsu, The 31st International Microprocessor and Nanotechnology Conference (MNC' 18), November 13-16, 2018, Sapporo Park Hotel, Sapporo, Japan (poster).

Domestic conferences

1. "Electrical Properties of In_2O_3 and ITO Thin Films Prepared by Solution Process using In(acac)$_3$ Precursor", **Puneet Jain**, Ken-ichi Haga, and Eisuke Tokumitsu, Japan Society of Applied Physics (JSAP 66th Spring Meeting' 19), March 9-12, 2019, Tokyo, Japan (poster).
2. "Direct Imprinting and Electrical Properties of ITO Precursor gel", **Puneet Jain**, Ken-ichi Haga, and Eisuke Tokumitsu, Japan Society of Applied Physics (JSAP 65th Spring Meeting' 18), March 17-20, 2018, Tokyo, Japan (oral).
3. "Study of Electrical and Imprinting Properties of ITO Precursor Gel using Direct Imprinting", **Puneet Jain**, Chang Su, Ken-ichi Haga, and Eisuke Tokumitsu, Japan Advanced Institute of Science and Technology (JAIST) Japan-India Symposium, March 5-6, 2018, JAIST, Japan (poster).

Keywords: solution process, imprinting, oxide-semiconductors, high-*k* dielectric, thin film transistors