

Reverse offset printing of metal acetylacetonate inks and its applications to a solution-processed IGZO-TFT

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Abstract

A single-micrometer resolution printing of various metal acetylacetonates was developed aiming at the fabrication of functional oxide layers. In the paper, the ink formulation scheme of precursor solutions for reverse offset printing is presented. Particularly, a printed molybdenum oxoacetylacetonate layer showed the resistivity of down to $2 \times 10^{-2} \Omega \text{ cm}$ after a hydrogen plasma reduction. With the hydrogen-plasma resistant and the plasma-reducible printed layers of $\text{Zr}(\text{acac})_4$ and $\text{MoO}_2(\text{acac})_2$, respectively, the operation of solution-processed IGZO TFTs is demonstrated.

1. Introduction

Printed electronics gathers much attention because of the facile fabrication of functional layers. Particularly, reverse offset printing is known to be a high-resolution patterning method with a good thickness uniformity and a low line-width variation [1]. Therefore, attempts have been made on the fabrication of electronic devices such as transparent metal mesh touch panels and organic TFTs by reverse offset printing. However, because functional inks of reverse offset printing dedicated to metal oxide formations are lacking, its applications have been limited so far. In this study, we present an ink formulation scheme of various metal acetylacetonate (acac) solution. With the aid of hydrogen plasma reduction process, we further demonstrate a solution-processed IGZO TFT with printed MoO_x source/drain electrodes.

2. Reverse offset printing of metal complex inks

Various metal acetylacetonates/oxoacetylacetonates of V (IV), Cr, Mn, Fe, Co (II), Co (III), Ni, Cu, Zn, Ga, Zr, Mo (VI) and In elements were tested for reverse offset printing. First, each metal complex was dissolved in a binary mixture of toluene and methanol with the weight ratio of 2:0.16. The amount of the metal complex was adjusted depending on its solubility. Then, iso-pentanol was added to the solution to control the drying on a polydimethylsiloxane (PDMS) surface. In the patterning test, (i) the precursor inks were first coated on a PDMS surface fixed on a printing roll by a slit coater. After waiting for semi-drying, (ii) the ink layer became contact with an etched cliché to remove unnecessary part of the ink film. Finally, (iii) the remnant ink pattern was transferred to a silicon wafer to complete the patterning (Figure 1a). The experiments were conducted at 23 °C and $30 \pm 5 \text{ RH}\%$. The

PDMS surface was slightly modified by exposing an excimer light (172 nm) for 10 sec. Figure 1b shows the transfer capability of molybdenum oxoacetylacetonate inks with varied fractions of iso-pentanol (reflecting the semi-drying situation, the solid fraction f_{sd} of the molybdenum complex against iso-pentanol is shown). As can be seen, in the absence of iso-pentanol, the transfer failed. As increasing the fraction of iso-pentanol, the perfect transfer of the applied ink layer was achieved. However, the appropriate margin of iso-pentanol fraction was limited to 50 to 70 wt% as further increase in iso-pentanol resulted in dewetting of inks on the PDMS. This result suggested that iso-pentanol remained in the ink layer after coating, thereby contributing to establish the semi-drying state of metal acetylacetonate solution. This is reasonably explained because iso-pentanol is considered to be slowly lost from the layer compared with toluene and methanol as it has higher boiling point and a polar functional group.

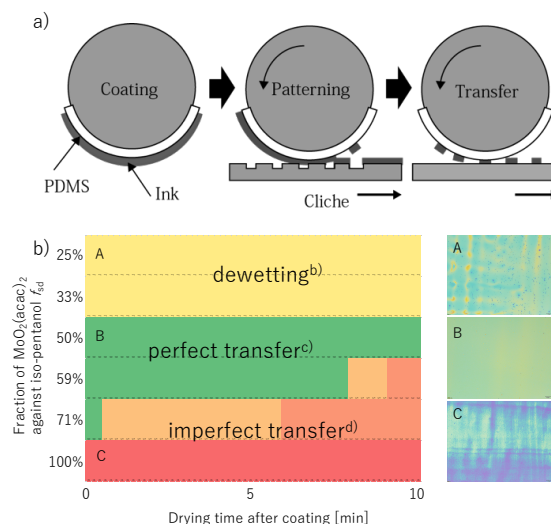


Fig. 1 (a) A schematic of reverse offset printing. (b) Temporal printing margins of $\text{MoO}_2(\text{acac})_2$ inks with varied fractions of iso-pentanol. Typical images of transferred ink layers are shown in A-C.

The patterning examples of Fe, V, In, Mn, Zr, Co (II), Ni, Mo and Zn (acac) layers are shown in Figure 2 ($L/S = 5/1.2 \mu\text{m}$). As can be clearly seen, the present strategy for the ink formulation was valid in various metal precursors. We note that Ga, Cr, Co (III) and Cu acetylacetonate inks had poor film-forming ability as they exhibited a prompt formation of microcrystals inside the films after coating on the PDMS.

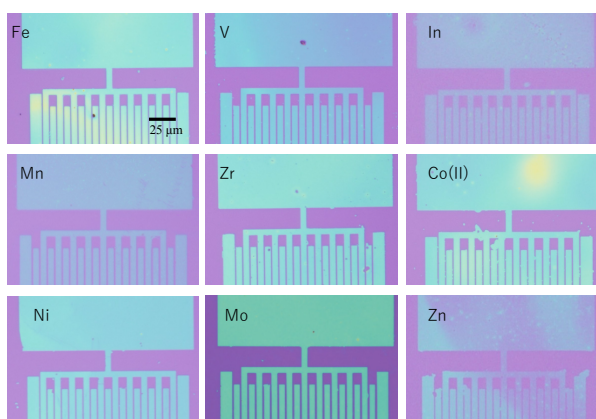


Fig. 2 Interdigitated patterns of various metal acetylacetonates (oxo-acetylacetonates for Mo and V) inks by reverse offset printing.

3. Hydrogen plasma reduction of printed metal complex layers.

Among the precursor inks tested here, vanadium, molybdenum and cobalt (II) inks were found to be reducible by hydrogen plasma treatments. Figure 3 shows the dependence of resulted resistivity on processing conditions. As expected, higher processing temperature of the chamber stage or longer plasma exposure time showed lower resistivity of molybdenum inks; however, the effect of reduction was limited in the cases of V and Co elements. Those metal complex inks had rather small equilibrium constants of oxygen in the corresponding solid-state oxides as the partial oxygen pressure $\log[p(\text{O}_2)]$ of MoO_3 , CoO and VO_2 required for reduction are -26.8, -44.3 and -54.1 at 200 °C. On the other hand, Zr and Mn inks where $\log[p(\text{O}_2)]$ of ZrO_2 and MnO are -111 and -77 were found to be insulating and resistant after the hydrogen plasma treatment up to 300 °C for 300 s.

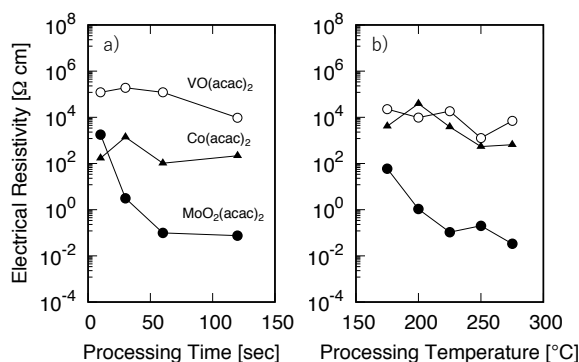


Fig. 3 Dependence of resistivity of H_2 plasma-treated Mo (VI), Co (II) and V (IV) ink layers on (a) the plasma processing time at 250 °C and (b) the stage temperature for the processing time of 120 s.

4. IGZO-TFT fabrication.

With the above inks, a solution-processed IGZO-TFT was fabricated in the following process. First, a 0.1M nitrate solution of In, Ga and Zn with the molar ratio of 67:3:30 was spin-coated on a heavily-doped silicon wafer with a 300-nm-thick

oxidized SiO_2 . The film was pre-annealed for 5 min at 130 °C, treated with a deep UV light for 30 min at 130 °C and then post-annealed for 60 min at 300 °C under air to complete the conversion into an IGZO layer [2]. On the top of the IGZO layer, $\text{Zr}(\text{acac})_4$ and $\text{MoO}_2(\text{acac})_2$ layers were printed to form a barrier and S/D electrodes, respectively (Figure 4a). Each layer was pre-annealed for 5 min at 130 °C and then treated by the hydrogen plasma at the condition of 1.5 kW, 200 °C for 60 sec. The resulted thicknesses of IGZO, ZrO_x , and MoO_x layers were 20, 35 and 28 nm, respectively. Figure 4b shows a 6-inch-scale pattern with the bottom-gate top-contact TFT. We note that ZrO_x layer was placed on the top of TFT channel to protect the IGZO layer from H_2 plasma exposure as the IGZO was easily converted into conductive state by a reduction process and damaged due to the ion bombardment.

Figure 4c shows the fabricated TFT and its representative transfer curve. The fabricated TFT exhibited the mobility of $0.24 \text{ cm}^2/\text{Vs}$, on/off ratio of 7×10^6 , subthreshold swing (SS) value of 0.72 V/dec, and V_{th} of -4.45 V under the drain voltage of 40 V. This performance was rather inferior to that of vapor-deposited aluminum S/D electrodes where the mobility is about $2 \text{ cm}^2/\text{Vs}$; however, we consider that the present result opened the possibility of printed electronics for oxide materials with high resolution patterns.

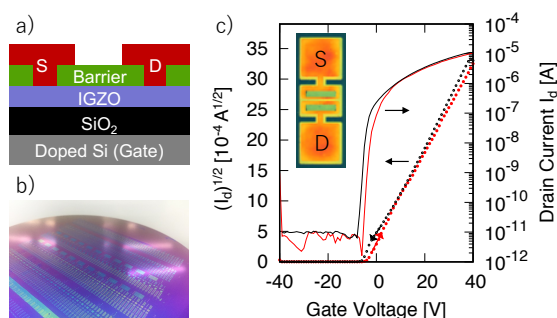


Fig. 4 (a) Schematic illustration of the fabricated TFT structure with spin-coated IGZO, and printed MoO_x S/D and ZrO_x barrier layers. (b) An example of a 6-inch scale printed TFT pattern. (c) A typical transfer curve of the IGZO TFT under the drain voltage of 40 V.

5. Conclusions

The present study demonstrated a novel approach for a facile, rapid and high-resolution printing of metal complex inks aiming at the metal oxide patterning. We expect to apply the present framework to other electronic devices such as capacitors and resistive memory as various metal complexes could be patterned.

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References

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