Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp976-977

# Printed Electrode for All-Printed Polymer Diode

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## 1. Introduction

Today, a print technique of an electrode on a plastic substrate is one of the most important techniques for developing a printed large area device. Especially, preparation of a metal electrode with low work function by printing is very important to develop printed active devices such as diode and transistors. Work function values of electrodes strongly affect device properties (1,2), because the work function difference between a semiconductor and an electrode is related to charge injection from the electrode to the semiconductor. Recently, many solution-processable n-type semiconductors have been developed (3), because these are required to fabricate printable EL devices, printable CMOS devices, and so on. Low-work function metals are necessary to inject electrons to n-type semiconductor. In spite of this fact, very few printable low-work function metal inks have been developed, because low-work function metals are easily oxidized during print process owing to high temperature annealing treatment and their conductivities are lost.

In this study, we have examined to develop a new annealing technique on a printed electrode to reduce the process temperature during metal printing. We have newly developed a mechanical sintering technique in which mechanical forces is applied on a printed metal pattern. Control of the direction balance of applied mechanical force was effective to reduce resistivity of the printed metal without any destruction of plastic substrate. Furthermore, distribution control of metal particle in the metal ink was also effective to reduce resistivity. By using this technique, we have succeeded in the preparation of an aluminum, zinc, copper and tin electrode on a plastic substrate. On the other hand, we have tried to prepare a metal alloy ink to control the work function of printed electrode. Metal alloy ink was composed of two kinds of metal particles. Work function of the electrode was controlled by changing composition of these metal contents in an alloy ink. By applying our developed mechanical sintering technique on the printed alloy pattern, printed electrode with various work functions from 3.5eV to 5eV could be prepared on a plastic substrate. These printed alloys were effective to improve the performance of printed diode and transistors.

## 2. Experimental

As shown in Fig.1, at first, metal patterns were printed by using the screen-printing machine (Micro-tech co., Ltd. MT-320TV) and the screen mask (Tokyo process service co., Ltd.). The best pattern resolution is less than 20 micron by using this machine. Metal paste was prepared by mixing a metal powder and a binder polymer. The metal powders were commercial available (Alfa-Aesar®). The binder polymer was purchased from TOYOBO co., Ltd. (VYLOMAX®). Mixing process was carried out by using the mixer (THINKY corp. ARE-10). The drying process was carried out by using a far-infrared heating unit. The press-annealing process was carried out by using the conventional roll-press machine (Nitto-han-nouki co., Ltd.) or our developed press machine. Our developed press machine can apply pressure to the surface of metal patterns in the horizontal and vertical directions. Ratio of horizontal pressure to vertical pressure can be changed freely. The particle size distribution of the purchased powders was estimated by using the laser diffraction particle analyzer (HORIBA, Ltd. LA-950V2 ) The particle distribution for the commercial aluminum powder (particle size<325 mesh) was measured. From this result, average particle sizes was 18.0μm. The lattice distortion and residual stress in metal crystallite were estimated by using XRD spectra (Rigaku corp. Ultima IV protectus).

The lattice distortion is corresponding to the XRD peak

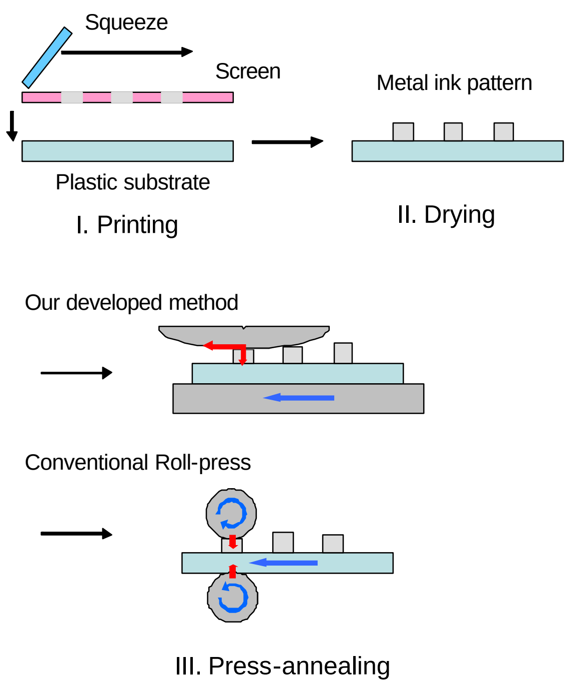


Fig.1 Schematic diagram of fabrication process for the printed metal pattern

shift. The residual stress in the crystallite can be estimated by using the lattice distortion after the press-annealing process.

Fig. 2 shows XRD peak shifts after the pressure annealing process and Table 1 shows parameters calculated by using the XRD results and the sheet resistance of the printed and pressure-annealed metal patterns having 1cm$^2$ area. Apparent peak shifts are observed comparing XRD peak of the as-dried metal pattern and that of the metal pattern pressure-annealed by using our developed method. On the other hand, only very little XRD peak shift is observed for the metal pattern pressure-annealed by using the conventional roll press. Further, observing sheet resistance results in Table 1, only the metal patterns pressure-annealed by using our developed method are conductive. Observing the residual stress results, the metal patterns can be effectively pressed by using our developed method and then, the surface metal oxide layer, i.e. insulator, can be destructed and form the conductive path between adjacent metal particles. As previously mentioned, our developed press machine can apply pressure to the sample surface in horizontal and vertical directions, therefore binder polymer and insulator layer are effectively removed and metal particle shape is deformed.

Our developed method can provide printed metal alloy patterns. Metal contents of the printed metal alloy patterns can be freely changed. As shown in Fig.6, change of Ag and Al contents in metal paste results in the change of work function. In other word, the work function of the metal alloy can be freely changed in the range from 3.5 eV to 5.0 eV.

Using the printed metal alloy electrode, the printed diode having various rectification properties as shown in Fig.4

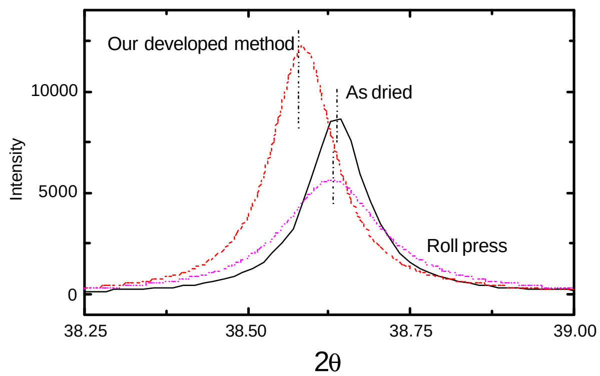


Fig.2 Shift of XRD peak of Al (111)

Table 1. Each parameter calculated from XRD peak shift and Sheet resistance of press-annealed metal patterns

| Al-powder | 2θ max (°) | FWHM (°) | Crystallite size (nm) | Lattice constant (nm) | Distortion ε (%) | Stress σ (MPa) | Sheet resistance (Ω/□) |
|---|---|---|---|---|---|---|---|
| As-dried | 38.64 | 0.107 | 78.7 | 0.2329 | | | Over range |
| Our developed method | 38.59 | 0.114 | 73.8 | 0.2331 | 0.125 | **86.0** | 1.0 |
| Roll press | 38.63 | 0.179 | 47.0 | 0.2329 | 0.025 | **17.2** | Over range |

(right) This property results from the control of the Schottky barrier height formed at the interface between P3HT and the metal electrodes having various work functions as shown in Fig.4 (left).

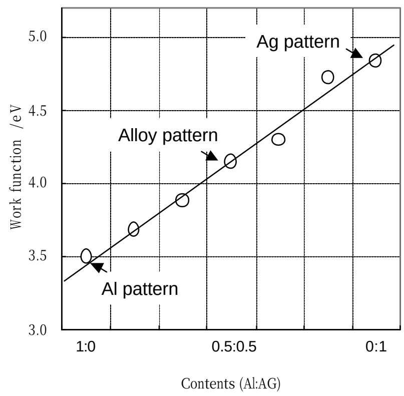


Fig.3 Relation between metal contents and work functions

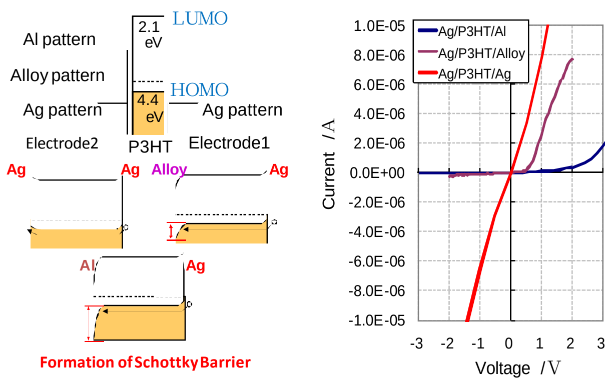


Fig.4 Energy levels of each electrode and P3HT as a semiconductor (left). IV properties for P3HT diodes having printed metal electrode (right).


## Acknowledgements

This work is supported by Industrial Technology Research Grant Program in 2008 from New Energy and Industrial Technology Development Organization (NEDO) of Japan..


## References


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