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Work Function controlled Zn:Cu electrode for all-printed polymer diode

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Introduction

In recent years, flexible wiring is the key technology to downsize information appliances and mobile devices. In the wiring technology, the most important issue is process-cost, through-put, quality of products (electrical properties, among others), for fabricating the devices on flexible plastic substrates. In particular, in order to fabricate flexible antennas for wireless communications (e.g. Radio Frequency Identification (RFID)), many issues, which are improvement of electrical properties and efficiency of their production processes, have still remained.[1,2,3] Further, in the global electronics market, lead-free process has become indispensable. With a shift to the lead-free process, we have to look for proper materials and to re-design circuits for adjusting to these materials. The most promising method to solve these issues is the printing process.

Employing the printing process will save wasteful production energies and will produce a large amount of electrical circuits effectively. Conventional photolithography process and chemical etching process are a subtractive process while the printing process is an additive process. Therefore, only minimum materials are required in order to produce electrical circuits by using the printing process, in other words, this process is quite resource-saving.[4] However, high-temperature annealing is necessary to decrease resistance of printed conductive patterns by using conductive inks, because metal contacts have to be formed among metal fillers in printed patterns. It is difficult to apply the high-temperature annealing process to the conductive pattern formation on plastic substrates. These facts are the cause to disturb the spread of circuit pattern formations by using the print process.

Electrical properties of the printed electronic devices tend to be inferior to those of conventional electronic devices.[5] This is because of difficulty of supplying high quality inks to print conductors, semiconductors, and dielectrics. In order to print high-definition patterns, the functional inks are composed of the multi-components, that is, functional fillers, binder resins, surfactants, solvents, among others. The components except the functional fillers affect the electrical properties of the printed patterns. For example, binder resins disturb the charge carrier transport among the conductive or semiconductive fillers.[6] Therefore, in order to improve the electrical properties of printed patterns, calcination of binder resins is indispensable. However, high-temperature annealing for calcination of binder resins is not applicable to plastic substrates, because the plastic substrates tend to be distorted or to be melted at high temperature.[7] Annealing temperatures of the conductive inks including metal nano-particles are relatively low (100-250°C) and these provide relatively low resistivity conductive patterns [2], but their high costs have been an obstruction of the spread of the nano-metal inks to the electronics market.

A printing technique of an electrode on a plastic substrate is one of the most important techniques for developing a printed large area device, as previously mentioned. In particular, 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 [8,9], 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[10], because these are necessary to fabricate printable EL devices, printable CMOS devices, among others. Low-work function metals are also 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. [11]

Until now we have developed a mechanical sintering technique in which mechanical forces is applied on a printed metal pattern. By using this technique, 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 using this technique, printed electrode with various work functions from 3.8eV to 5eV could be prepared on a plastic substrate. These printed alloys were effective to improve the performance of printed diode and transistors.

EXPERIMENT

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). Ag paste was purchased from Henkel AG & Co. (AchesonTM ED PM-406) The drying process was carried out by using a far-infrared heating unit. The press-annealing process was carried out by using our developed press machine. This process is completed almost within 30 seconds (depended on pattern size).
Electrical properties of printed diodes were measured by using semiconductor parameter analyzer (Keithley 4200) with the low temperature prober system (Nagase Electronic Equipments service, co.). Electrical resistance values were measured by using electrical test unit (PC-500, Sanwa Electric Instrument CO., LTD.). Component of contact resistance was completely removed.

DISCUSSION

As shown in Fig.3, metal particles were deformed and metal contacts were formed between adjacent particles. sure-annealed Zn:Cu electrodes.

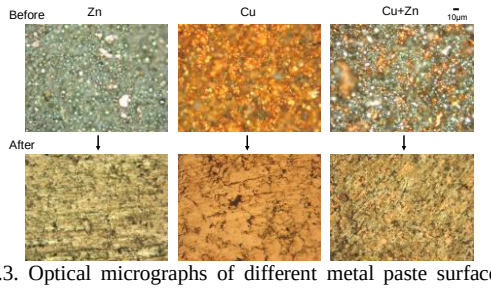

Fig.3. Optical micrographs of different metal paste surfaces before and after the pressure annealing process

In spite of such a high applied pressure, pattern deformation was hardly observed after the pressure annealing process. As shown in Fig.4 and Fig.5, considering these XRD results, Zn atoms were solid-solved into Cu lattice and Cu:Zn solid solution was formed in the pressure annealed Cu:Zn metal paste patterns. Then workfunction values of Cu:Zn metal paste depends on the content ratio of Cu and Zn(Fig.6). As shown in Fig.7 rectification properties of all-printed diode can be controlled by using the work function controlled pres

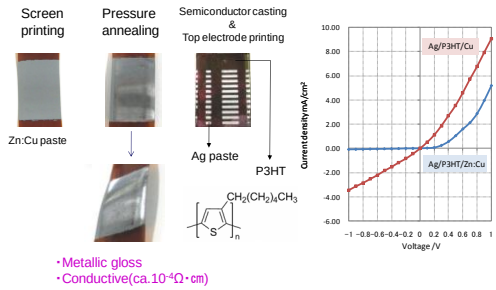

Fig.7 Fabrication process and IV properties of all-printed diode using Zn:Cu electrode.

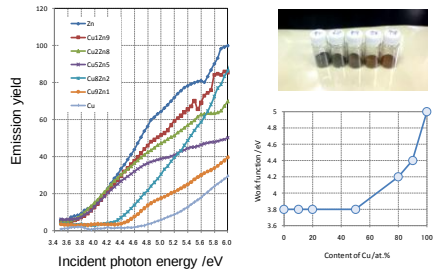

Fig.6 Workfunction changes for Zn:Cu paste with different content ratio.

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