Solvent-free Printing of Organic Semiconductor, Insulator, Metal, and Conductor Particles on Flexible Substrates

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ABSTRACT

Multi-material and solvent-free printing for printed electronics is developed using toner-type patterning of organic semiconductor, insulator, metal and other conductor particles, and the subsequent thin-film formation by ultrasonic sintering. Although conventional toner technology was only for insulating complex materials charged by friction charging, in this work, we expanded this technology for metals and other conductive materials, for example, graphite, carbon nanotube, graphene, ZnO, ITO, Au, Ag, Cu and so on. In the electrostatic transfer patterning, approximately 9 - 30 micrometer resolution pattern printing, which depends on the material, was achieved in our laboratory. High throughput and large area page printing are also expected in this type of technologies. Furthermore, ultrasonic sintering was also applied on the wide range of materials. Ultrasonic sintering is a powerful tool to melt organic semiconductor and insulators, and to sinter the oxide semiconductor or metal particles within several seconds. Ultrasonic sintering generates local and instantaneous high temperature at the material interface, so we can sinter even oxides and metals on plastic film surface.

Keywords: printed electronics, flexible electronics, organic electronics, toner printing, ultrasonic sintering

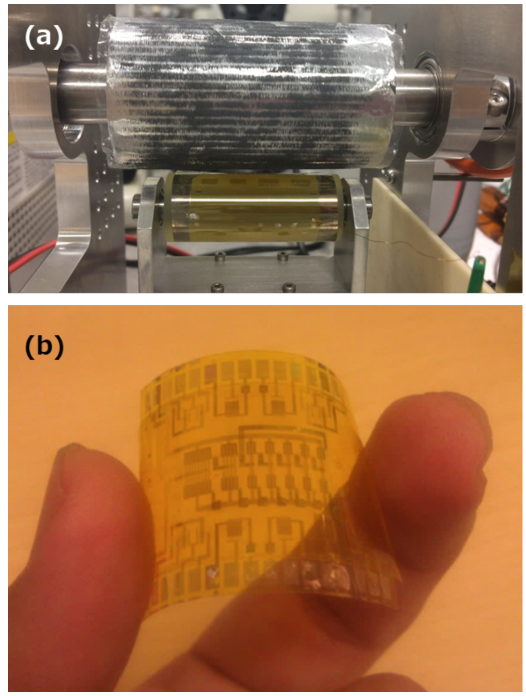

Figure 1: (a) Roller-type toner marking prototype. (b) Photograph of the flexible OFET device fabricated by toner printing of organic semiconductor.

1 INTRODUCTION

Recently, flexible and wearable devices begin to spread in our life. However, wearable devices must more lightweight and flexible to become more general electronics. Production of flexible electronics by printing methods are being developed all over the world. In conventional printing methods, special inks including electronics materials including organic semiconductors, oxide semiconductors, insulators and metals, and their solvents are inevitably used. It is necessary for these solvents to dissolve electronics materials in sufficient concentration, and to keep optimum viscosity necessary for each printing such as inkjet, photogravure printing and so on. So there are no sufficient choice of proper solvent in general. Moreover, as is often the case with many effective candidate solvents, these solvents have negative impacts such as inflammability, toxicity, and carcinogenic, etc. Emission not only the solvents itself but also their vapor should be strictly regulated not to be a new source of volatile organic compound (VOC) problem.

Our research group propose an alternative for printed electronics without inks. We have developed solvent-free printing method using toner-type printing for pattering[1, 2, 3, 4, 5], and ultrasonic melting and sintering for fix thin film[6].

2 TONER PRINTING

2.1 Toner Printing of Organic Semiconductor and Insulators

Toner printing process on organic semiconductor and insulator is nearly the same with that of conventional toner printing. Conventional toner printing is based on the friction charging of toner particles with carrier par-

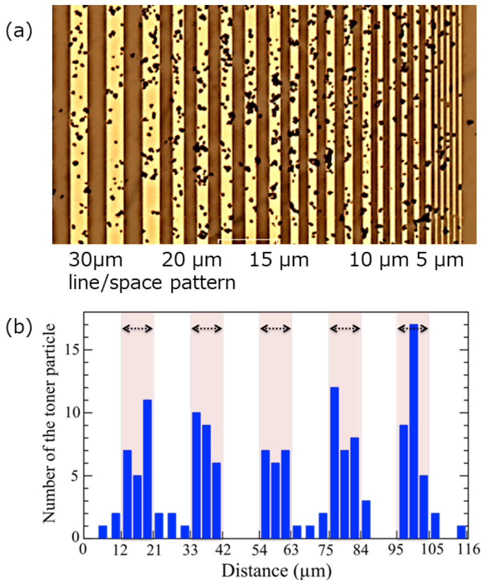

Figure 2: (a) Optical micrograph of the organic semiconductor toner particles patterned on the Au line/space pattern fabricated on the plastic film. (b) Histogram of the organic semiconductor toner particles dispersed on the periodic 9.1μm-width line/space pattern by the electrostatic force. 87% of the transferred organic semiconductor toner reached on the Au target electrode.

ticles. The agitation of mixture of the organic semiconductor toner and carrier particles generate charged toner particles[1], therefore, the charged toner particles can be transferred by an external electric field. Fig. 1 shows the photograph of our roller-type toner printing prototype. The mixture of the toner and carrier particles is seen as gray powder on the surface of upper roller. The upper roller is motorized and rotate during the toner transfer, only toner particles are transferred by the external electric force to the plastic film substrate surface on the lower roller. Fig. 1(b) is photograph of flexible device using toner printing of organic semiconductor. The printed organic semiconductor withstood 2 mm radius bending 10,000 times.

Fig. 2(a) is the optical micrograph of the organic semiconductor toner particles transferred and patterned on the Au line/space pattern fabricated on the plastic substrate film. Organic semiconductor toner particles (black particles in the photo) were electrostatically transferred from the toner source to the electrode pattern. To show this patterning clearly, we made a histogram of the organic semiconductor toner particles dispersed on 9.1μm line/space pattern as shown in 2(b). 87% of the transferred organic semiconductor toner precisely distributed on the Au target electrode. Approximately 9 μm of the printing resolution is superior to the industrial standard.

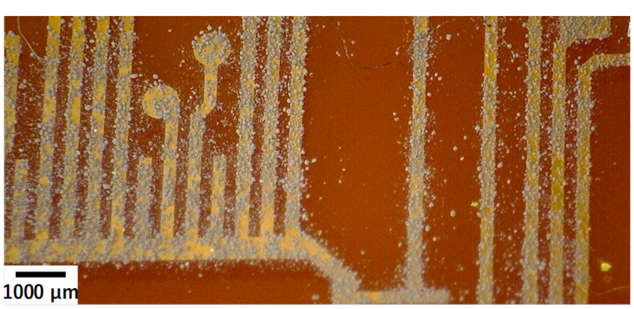

Figure 3: Close-up photograph of Ag toner particles dispersed on the plastic film surface.

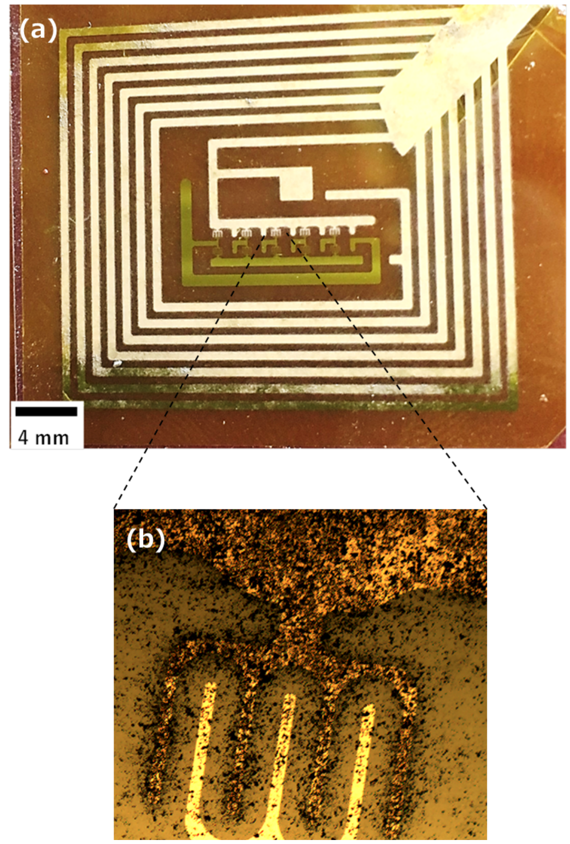

Figure 4: (a) Ag toner particles dispersed on the RFID antenna pattern including simple IC circuit in the center of the loop antenna. (b) Optical micrograph of interdigital electrode pattern in the IC circuit region.

2.2 Toner Printing of Metals and Conductors

Toner printing of metallic and other conductive materials such as graphite, graphene, nanotube, ITO, ZnO is not entirely same with that of organic semiconductor, but these materials also can be printed by toner-type printing. Fig. 3 is photograph of Ag particles patterned on the plastic film surface. Yellow circuit pattern seen below the gray particles is the target electrode pattern and gray Ag particles are dispersed along the circuit

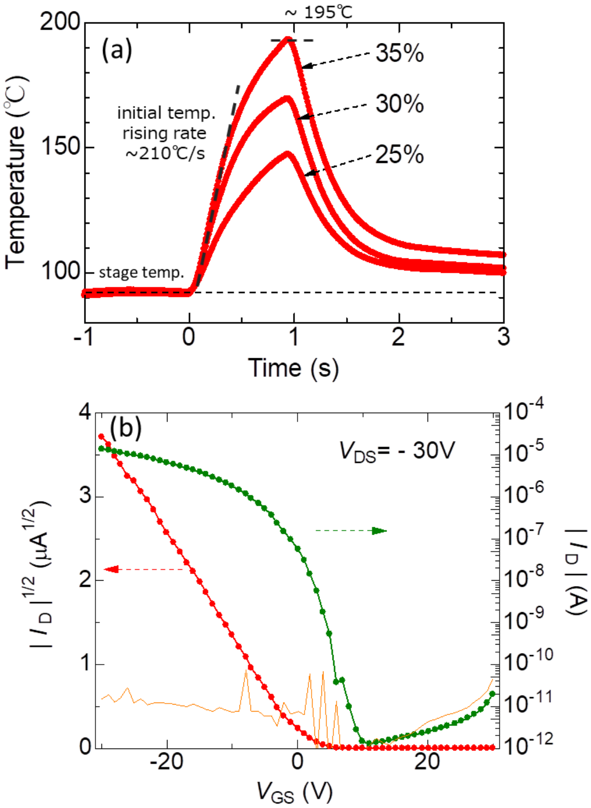

Figure 5: (a) Time variation of temperature between two plastic film and induced by application of ultrasonic vibration. Instantaneous heat was locally generated only in the vicinity of the plastic film interfaces. (b) Transfer characteristics of organic semiconductor thin film transistor fabricated by ultrasonic melting.

pattern. Ag particles make fine circuit pattern which is equivalent to the 250μm line/space pattern resolution.

Figure 4(a) shows Ag toner particles dispersed on the RFID antenna pattern including simple IC circuit pattern in the center of the loop antenna. Ag particles exist on the brightly glittered region which is certainly forming loop antenna pattern. On the other hand, both lower half of the IC circuit pattern in the center of this picture and lower edge of the loop antenna are still dark because we did not apply bias voltage in lower half of IC circuit, and we intentionally let the lower edge of the loop antenna be lack of toner particle. Figure4(b) is optical micrograph of interdigital electrode pattern in the IC circuit region. In this micrograph, many Ag particles are seen on the upper interdigital electrode side. On the other hand, Ag particle does not dispersed on the lower interdigital electrode because no external voltage to transfer Ag particles was applied, so that we can clearly see the effect of the external electric field.

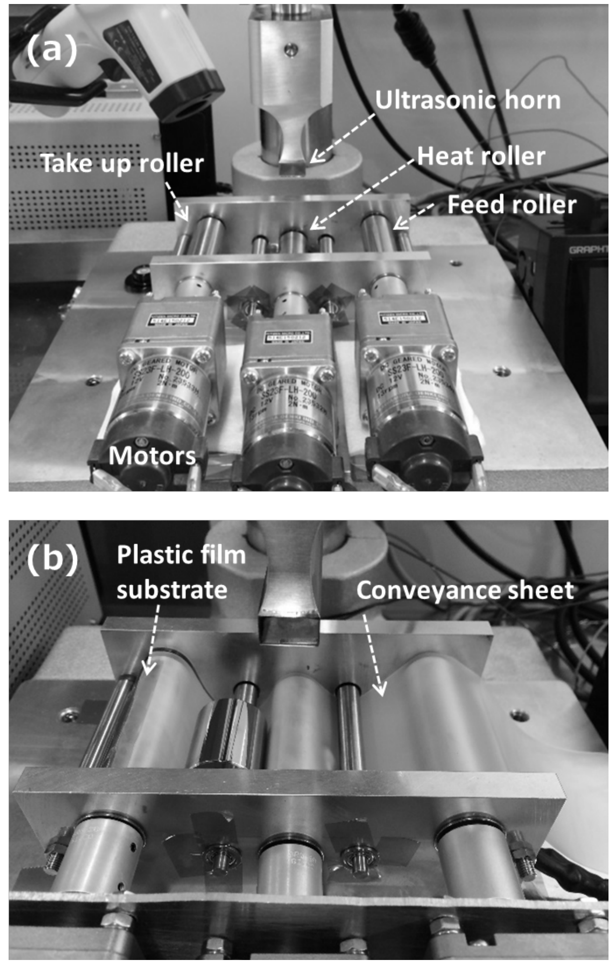

Figure 6: Photograph of continuous ultrasonic melting prototype.

3 ULTRASONIC MELTING AND SINTERING

The advantage of the ultrasonic melting is instantaneous and local heat generation at the plastic film surface without damaging the substrate[6]. Time variation of temperature between two plastic film and induced by application of ultrasonic vibration, which is picked up by very fine thermocouple placed between two plastic films. Instantaneous heat was locally generated only in the vicinity of the film interface, therefore, two plastic films or parts can be thermally jointed without melting whole plastic film itself. If one increase ultrasonic output from 25 to 35 %, maximum temperature increase to 195 °C in this condition. Figure 5(b) shows the transfer characteristics of organic semiconductor thin film transistor fabricated by ultrasonic melting. Field effect effective hole mobility of 0.19 cm^2/Vs was observed in this sample. Organic semiconductor layer was formed on the plastic film substrate without harming plastic film and gate insulator layer. Melting point of the organic semi-

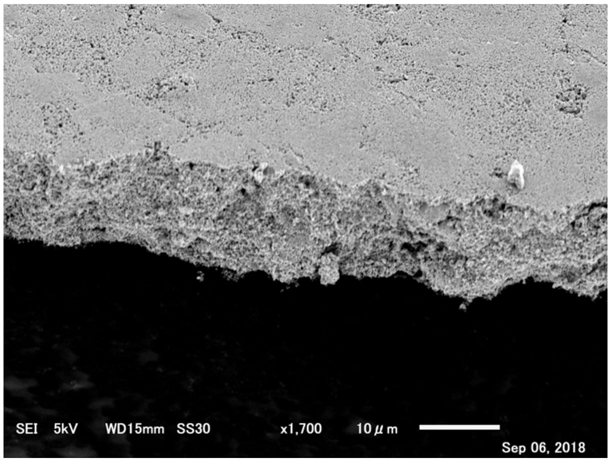

Figure 7: Scanning electron micrograph of the Ag film sintered by the ultrasonic sintering.

conductor (C_8-BTBT) was 126.5°C.

Ultrasonic melting can be also applied to the continuous roll to roll production flow. Figure 6 shows a photograph of continuous ultrasonic melting prototype. Organic semiconductor toner between two plastic film substrate which was settled on the conveyance sheet was conveyed from feed roller side to the take up roller side by motors. Ultrasonic horn mechanically descend on the heat roller and apply ultrasonic vibration to the sample during passing through between heat roller and the horn.

3.1 Ultrasonic Sintering of Metals and Conductors

Scanning electron micrograph of the Ag film sintered by the ultrasonic sintering is seen in the Fig.7. Ag particles connect each surface and make low electrical resistance Ag film on the plastic film surface without harming the substrate.

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