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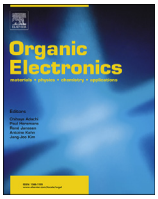

Significant effect of the molecular formula in silver nanoparticle ink to the characteristics of fully gravure-printed carbon nanotube thin-film transistors on flexible polymer substrate

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ABSTRACT

Single-walled carbon nanotubes (SWNTs) are a valuable material for use in not only nanoelectronics but also printed electronics because of their stability, tunable operation speed, and scalability. However, the device characteristics of fully printed, SWNT-based thin film transistors (SWNT-TFTs) often have large variations, and the fundamental cause of these inconsistencies are not yet well understood. Therefore, fully printed SWNT-TFT-based electronic devices have not been practically realized in the market. In this study, the significant variation in the electrical parameters of printed SWNT-TFTs that is caused by minor molecular variations in the formulation of silver nanoparticle-based ink is reported. Strikingly, a very small difference in the chemical structure between ethylene glycol and diethylene glycol in the silver nanoparticle-based ink, which is used to print drain-source electrodes in the SWNT-TFTs, with everything else identical, induced a difference of approximately 70 meV in the barrier height between the drain-source electrodes and the SWNT layer at 300 K. The modification of the absorbed polymer binder in the silver nanoparticle ink due to the additive is the major cause of the observed barrier height difference. These results allow for a better understanding of the relationship between the ink rheology at the molecular level and the printed device properties, and enable a more precise design and control of device properties which will have profound impacts on printed electronic devices.

1. Introduction

Fully printed thin-film transistor (*f*TFT)-based disposable and large area electronic devices will be practically realized at low cost when *f*TFTs with a constant threshold voltage (V_{th}) can be manufactured using a high-throughput printing method such as gravure, offset or flexo, because *f*TFT-based devices with unlimited size and human interactive functional variations can be printed at extremely low manufacturing costs compared with the current Si-based technology [1]. To demonstrate a novel concept for printed electronics, partially printed TFT (*p*TFT)-based flexible devices with a narrow range of the V_{th} variation were fabricated using vacuum deposited drain-source electrodes and ultra-thin dielectric layers [2–5]. These vacuum-deposited dielectric layers and drain-source electrodes are indispensable for maintaining the narrow range of the V_{th} variation in the *p*TFTs and are considered fully printable. However, high-quality dielectric layers with sub-micrometer thickness and well-controlled work functions for drain-source electrodes cannot be simply replicated using a scalable printing method. A major reason for the difficulty in replicating the vacuum deposited layers using a printing method is the lack of understanding of the device physics that, underlie the unexpected electrical behavior of the printed layers in relation to the rheological variation of inks. Because angstrom-scale surface roughness in the dielectric layers with a high capacitance and well-controlled work function of the drain-source electrodes such that it matches the electron affinity level of the semiconducting layers cannot be achieved using a scalable printing method, the number of integrated *p*TFTs in novel demo devices cannot be replicated using a full printing method. Therefore, understanding the mechanisms of how the inadequate electrical properties are generated due to the printed drain-source electrodes and the dielectric layers in the

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*f*TFTs is important for developing electrical properties that are comparable to those of the vacuum-deposited layers in *p*TFTs.

Because the number of integrated TFTs used for the construction of electronic devices is determined by the variation range of V_{th} [6], the ability to replicate vacuum-deposited layers using a fully printed method is key for fabricating *f*TFT-based demo devices. However, the variation range of V_{th} in *f*TFTs is significantly wider than that in *p*TFTs because the trapped charges and the parasitic capacitances in the *f*TFTs have not been fully investigated regarding the roles of the inks and the printing system. The variation range of V_{th} directly depends on the trapped charge density (N_{tr}) and the capacitance (C_o), as given by the equation $\Delta V_{th}(t) = eN_{tr}(t)/C_o$ [7]. Because the inconsistency in N_{tr} and C_o generally originates from the non-uniform structures of printed layers and the heterogeneous interfaces of the semiconductor to the dielectric layers and the drain-source electrodes [8], the vacuum-deposition method is much more effective for providing a narrow variation range of V_{th} than the printing method. Although the non-uniform structure of the printed layers can be controlled to some degree, the fixed and mobile trap ions caused by the inks are difficult to control in the inks because the inks often need additives to modify their rheological characteristics depending on the printing conditions, such as surface roughness, wetting, humidity, shear rate, and printing speed. Therefore, the role of additives in the electronic inks must be systematically understood in relation to the variation of V_{th} in *f*TFTs to practically print novel flexible devices.

Among a few commercially available electronic inks for fully printing TFTs, a silver-nanoparticle-based conducting ink (N_{Ag}-Ink) has been well developed and is commercially available for use in a wide range of printers that are used to print wires, antennas, and electrodes. In addition, it is advantageous regarding its cost, printability, air stability, and electrical conductivity [9–12] compared with conducting polymers, carbon nanotubes and graphene. Especially for fully printing novel active devices via a scalable printing method, N_{Ag}-Ink is more convenient to print the drain-source electrodes of the *f*TFTs with a uniform physical dimension from batch to batch, and to formulate conducting inks with a diverse spectrum of viscosity. To fully print TFTs, N_{Ag}-Inks have generally been used to print gate electrodes to provide a wide range of carrier motilities (30–0.01 $cm^2/V\cdot s$) for organic [13–15], inorganic [16,17] or SWNT based *f*TFTs [18–21]. However, there is no report yet on the role of additives in formulating N_{Ag}-Ink to meet the rheological properties for printing drain-source electrodes on printed active layers with printed dielectric layers.

Among the many types of *f*TFTs, a network structure of SWNT-based *f*TFTs (*nw*SWNT-*f*TFTs) on flexible substrates has been fully printed and has been demonstrated to be extremely low cost and suitable for disposable electronics such as wireless cyclic voltammetry tags [22], full adders [23], D-flip-flops [24], and active matrix arrays [25]. Although a few fully-printed simple devices based on *nw*SWNT-*f*TFTs have been reported, to maximize the advantages of printed electronics in low-cost and high-throughput manufacturing, a scalable printing method such as gravure printing should be further studied for understanding the relationship between the variation of V_{th} and the printed drain-source electrodes using N_{Ag}-Ink in *nw*SWNT-*f*TFTs, whereas the dielectric layers are also printed with a constant capacitance. In other words, the role of additives in controlling the rheological properties of N_{Ag}-Ink should be understood in relation to not only the structural variation of printed patterns, but also considering the variation of V_{th}. The role of additives in N_{Ag}-Ink should be thoroughly studied in order to make it more feasible to fabricate stable and reliable fully-printed *nw*SWNT-*f*TFTs with a narrow range of V_{th} variation. For example, although the edge waviness and surface roughness of printed patterns can be kept constant even with the use of different solvent molecules in inks [26,27], this simple variation in solvents often causes quite different electrical properties of printed *nw*SWNT-*f*TFTs.

In this study, we report for the first time the role of additives in N_{Ag}-Ink in relation to the electrical properties of *nw*SWNT-*f*TFTs on plastic substrates, where uniform structures of source-drain electrodes were printed using N_{Ag}-Ink with different additives. Specifically, we studied the variations in device characteristics including mobility, V_{th}, and transconductance. Then, we analyzed the statistical data from two groups of *nw*SWNT-*f*TFTs using N_{Ag}-Ink that was, formulated based on two different molecular formulas, with either, ethylene glycol (EG) or diethylene glycol (DEG) as an additive, while keeping the other ingredients in the inks and the printing conditions constant. The major cause of the variations in the device characteristics was investigated using transmission line measurements [28] between the two groups of *nw*SWNT-*f*TFTs with channel lengths of 50, 70, 130, and 180 μm. Furthermore, temperature-dependent current measurement as a function of the gate voltage (V_{gs}) [29], and the displacement current measurement (DCM) [30] for a selected channel length were also assessed to verify the results from the transmission line measurements. The results obtained from these measurements were attributed to the cause of the observed electrical variations in the *nw*SWNT-*f*TFTs using N_{Ag}-Ink with the different additives (but with very similar molecular structures), but the physical quality of the printed patterns was maintained constant.

2. Experimental section

Printing by R2P (Roll-to-Plate) gravureN_{Ag}-Ink (PG-007) containing 60 wt% Ag with an ethylene glycol vehicle was purchased from Paru Co., Korea. The surface tension and the viscosity of the PG-007 are 52 mN/m and 900 cP (0.9 Pa s), respectively. A $BaTiO_3$ nanoparticle-based dielectric ink (PD-100) with a viscosity of 300 cP (0.3 Pa s) and a SWNT-based semiconductor ink (PR-040) with a viscosity of 24 cP (0.024 Pa s) were also obtained from Paru Co. and used for the roll-to-plate (R2P) gravure printing (Fig. 1a) without any further formulation. The surface tensions of PD-100 and PR-040 were 32 and 27 mN/m, respectively. The fully R2P gravure-printing process (Fig. 1b) was performed in a class 1000 clean room under controlled temperature (24 ± 1 °C) and humidity (30 ± 2%). We designed and printed 32 *nw*SWNT-TFTs in the circuit: 6 TFTs with a channel length of 50 μm, 10 TFTs with a channel length of 70 μm, 6 TFTs with a channel length of 130 μm, and 10 TFTs with a channel length of 180 μm were printed as shown in Fig. 1e.

The surface tension and viscosity of the inks were measured using respectively a DCAT21 (Dataphysics Co., Germany) and an SV-10 Vibro viscometer (AND Co., Japan), respectively. A semiconductor characterization system (Keithley 4200, USA) was used to characterize the printed *nw*SWNT-TFTs on the plastic film. The morphology of the printed gate electrodes and the dielectric layers was measured using surface a profiler (NV-220, Nanosystem, Korea). All measurements were performed under ambient conditions.

For the measurements of the temperature-dependent current, the drain current (I_D) was measured in a vacuum in a Laked Shore model HFTTP4 cryogenic probe station (10^{-5} Torr base pressure) using a semiconductor characterization system (Keithley 4200, USA) during the application of a constant drain voltage (V_{DS}: − 20 V) and constant gate voltages (V_{GS}: 0 V, − 10 V, − 20 V). The temperature was controlled using a variable temperature cryogenic probe system from 100 to 300 K.

For the displacement current measurement (DCM), ramp-wave gate voltages (Tektronix AFG 3102, USA) passed through an amplifier (Agilent 33502A, USA) with a frequency of 100 Hz and a