



Local work function control of indium tin oxide by micro-contact printing for electroluminescent devices

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ABSTRACT

We demonstrate here that light emission of an electroluminescent (EL) device was enhanced on chemically modified ITO areas over a patterned ITO anode with a self-assembled monolayer (SAM) of 4-chlorophenylphosphoryl dichloride ($\text{ClC}_6\text{H}_4\text{OPOCl}_2$: CPPDC) prepared by micro-contact printing (μ -CP). The EL device was fabricated by vapor-depositing a hole transport layer, a light emitting and electron transport layer, and a $\text{C}_6\text{H}_5\text{COOLi}/\text{Al}$ bilayer cathode on the patterned ITO anode. The enhanced light emission under lower drive voltages on the modified areas can be interpreted by the increase in the work function of the ITO covered with the SAM measured with a Kelvin probe force microscope (KPFM) and thus the decrease in the hole injection barrier height. In addition, we could demonstrate the much smaller pattern images than the previously reported ones [F. Nüesch, Y. Li, L.J. Rothberg, Appl. Phys. Lett. 75 (1999) 1799] by the use of ink-pads.

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1. Introduction

Chemical modification of conducting transparent oxide (CTO) electrodes has been studied extensively to provide the electrodes with various functions [1–3]. Among various functions pursued so far, controlling the work function [4–9] has become one of the most interesting issues in application of CTO electrodes to optical devices such as electroluminescent (EL) [4–8] and photovoltaic (PV) devices [9]. In our earlier studies, characteristics of EL devices were improved drastically using ITO chemically modified with organic acid chlorides [8]. By the use of reactive $-\text{OPOCl}_2$ anchoring groups, ITO surfaces were easily modified (Fig. 1). The work function of the modified ITO was changed depending upon permanent dipole moments introduced in the para-position of phenyl group of such acid chloride derivatives [8–11].

Micro-contact printing (μ -CP) using an elastomeric stamp made of polydimethylsiloxane (PDMS) is a promising method to fabricate small structures [12,13]. This technique was first applied to protect gold surfaces from etching by printing self-assembled monolayers (SAMs) of alkanethiols [14] on the gold surfaces. Nüesch et al. [15] used tetrabutyl-ammonium hydroxide as a ink for blocking hole injection from an ITO anode to a hole transport layer. They first prepared a patterned ITO surface by μ -CP, then vapor-deposited a hole transport, a light emitting and electron transport layer, and a LiF/Al bilayer cathode successively to

fabricate an EL device, and finally succeeded in observing a patterned EL image.

In the present work, we attempted to prepare an EL device, which exhibits strong EL light emission in printed areas by enhancing the hole injection rather than by blocking to reduce operating voltages of the resulting patterned EL device. In addition, we pursued to improve the EL image resolution by changing the inking method from the wet-inking to the ink-pad method [13,16].

2. Experimental

PDMS pre-polymer (Dow Corning Toray SILPOT 184 and CATALYST SILPOT 184) was poured on a master plate, which has $20\ \mu\text{m}$ line and space structure, to form a PDMS stamp [16,17]. After being heated in an oven at $60\ ^\circ\text{C}$ for over 2 h, it was peeled off from the master plate. PDMS sheets with flat surfaces heat-treated on a flat substrate were immersed in a 100 mM or a 1 M 4-chlorophenylphosphoryl dichloride (CPPDC) (Tokyo Kasei Kogyo) dichloromethane (DM) (Kanto Chemical) solution for overnight and taken out to form two kinds of ink-pads (Fig. 2(a)) [16] with two different ink concentrations. The stamps were inked by placing the stamp on one ink-pad (formed in the 100 mM CPPDC DM solution) for 30 s (Fig. 2(b)), while on the other ink-pad (formed in the 1 M CPPDC DM solution) for 10 s. To make the pattern by μ -CP, the inked stamp was then placed onto a cleaned ITO surface (Figs. 2(c)–(e)). The cleaned ITO surface was prepared first by pre-cleaning as-received ITO (Sanyo Vacuum Industries

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Co., $14\ \Omega/\text{square}$) with detergents and Milli-Q water, then by cleaning the pre-cleaned ITO with acetone and isopropanol (Kanto Chemical), and finally by boiling further in isopropanol [9]. Printing time was 30 s for the stamp inked on the 100 mM ink-pad, while 10 s for that inked on the 1 M ink-pad.

The distribution of contact potential differences (CPDs) between an ITO surface and a gold-coated AFM tip (a Seiko Instruments micro cantilever Type SI-DF3-A) covered with a decanethiol SAM was imaged over three kinds of ITO surfaces, i.e. a cleaned, a chemically modified with CPPDC, and a patterned ITO surface, with a Kelvin probe force microscope (KPFM) (a SEIKO Instruments SPA400 AFM unit with an SPI3800N AFM controller) [8,18].

EL devices on the patterned ITO anode were fabricated by vapor-depositing a triphenyl diamine (*N,N'*-bis-3-methylphenyl)-*N,N'*-1,1'-biphenyl-4,4'-diamine, TPD) (Aldrich) hole transport layer, a tris (8-hydroxyquinoline) aluminum (Alq_3) (Dojindo Laboratories) light emitting and electron transport layer, and a $\text{C}_6\text{H}_5\text{COOLi}$ (WAKO)/Al bilayer cathode [19] (or an Al cathode without $\text{C}_6\text{H}_5\text{COOLi}$), successively. TPD and Alq_3 were used

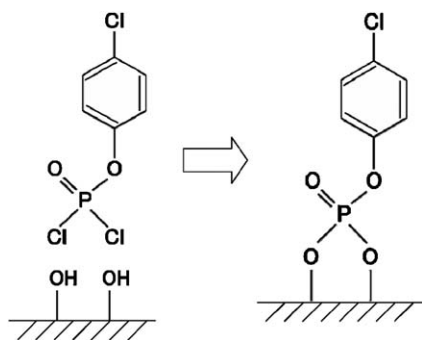


Fig. 1. Reaction of 4-chlorophenylphosphoryl dichloride (CPPDC) with an ITO surface. Cl groups of dichlorophosphate are considered to react with HO groups on an ITO surface to form a self-assembled monolayer by the removal of HCl.

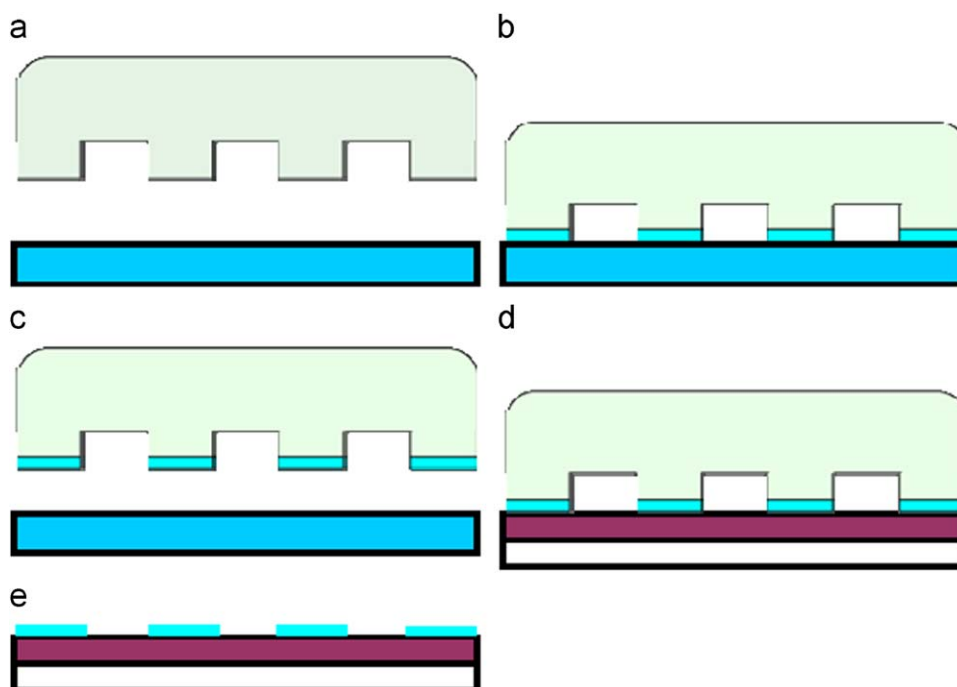


Fig. 2. Schematic illustration of μ -CP using an elastomeric stamp and an ink-pad: (a) a PDMS stamp and a PDMS ink-pad before inking, (b) inking the stamp by placing it on the ink-pad, (c) peeling off the stamp from the ink-pad, (d) placing the inked stamp on a bare surface of a cleaned ITO, and (e) peeling off the stamp from a patterned ITO surface.

without further purification. The EL device operation was the same as that reported previously [8,19]. Luminescence contrast was imaged from the ITO side with an optical microscope (a Nikon DIAPHOT TMD 300) together with a Keyence fluorescence digital microscope camera modelVB-7010.

3. Results and discussion

3.1. CPD images

In Fig. 3 are shown the distribution of CPDs for (a) a $30 \times 30\ \mu\text{m}^2$ cleaned ITO, (b) a $30 \times 30\ \mu\text{m}^2$ chemically modified ITO with CPPDC, and (c) a $150 \times 150\ \mu\text{m}^2$ patterned ITO surface imaged with KPFM. The modified ITO surface was prepared by immersing the cleaned ITO surface in a 1 mM CPPDC DM solution for 5 min. The averaged CPDs measured on the cleaned and the modified surface were -233 ± 6 and -598 ± 4 mV, respectively. The CPDs for the cleaned ITO was slightly lower than the previous one, while that of the modified ITO with CPPDC was slightly higher than the previous one. The chemical modification of ITO surfaces after cleaning with boiled isopropanol was most likely for these deviations from the previous ones because the higher water contact angle on the boiled ITO surface than that on a cleaned ITO surface using isopropanol at room temperature [20]. In other words, an isopropanol monolayer formed on the cleaned ITO surface protected the ITO surface from the chemical modification with CPPDC. The results revealed that the work function of the modified ITO was about 400 mV higher than that of the cleaned ITO in the present work.

Fig. 3(c) clearly shows contrast in CPD between the printed and the unprinted ITO surface areas. The areas that correspond to convex parts of the PDMS stamp are the areas where the ink was transferred (Fig. 2). These areas are called the printed areas, while the rest of the surface the unprinted areas. It can be safely concluded from the measured difference in CPD between the cleaned and the modified ITO in Figs. 2(a) and (b) that the areas

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