Transferred Microelectrodes Fabricated with V$_2$O$_5$ Nanowires Embedded Polyelectrolyte Multilayers

Young Hun Kim$^1$, Sung Min Cho$^2$, Gui Young Han$^2$, Juhyun Park$^3$, and Pil J. Yoo$^{1,2, *}$

$^1$SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea
$^2$School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea
$^3$School of Chemical Engineering and Materials Science, Chung-Ang University, Seoul 156-756, Republic of Korea

Micropatterns of V$_2$O$_5$ nanowires embedded polyelectrolyte multilayers were straightforwardly fabricated with conventional layer-by-layer assembly and subsequent transfer printing onto a flexible substrate. Networked microelectrodes of complexed polyelectrolytes/nanowires were also successfully obtained via multiple transfer printings over a large-scale area. Atomic force microscopic observation confirmed the robustness of the proposed method. Electrically good conducting behavior and structurally stable binding onto the flexible substrate of the transferred microelectrodes can serve as a novel method for the development of flexible electronics.

Keywords: Transfer Printing, Vanadium Oxide Nanowires, Layer-by-Layer Assembly, Polyelectrolyte Multilayers, Transparent Electrodes.

1. INTRODUCTION

With a growing interest on thin film optoelectronic devices, such as flat-panel displays, light emitting diodes, and solar cells, a development of transparent and conductive thin film-electrodes has received much attention in many areas extensively.$^{1-3}$ Thus far, indium tin oxide (ITO) has mainly been employed for this purpose because of its high electrical conductivity and transmittance in the visible spectral region. However, the cost of sputtering metal oxide thin films is too high for a mass production of optoelectronic applications. Furthermore, with an advent of flexible organic devices, the use of ITO is challenged due to its brittleness leading to a failure of the device when it is bent or physically stressed.$^4$ Accordingly, there has been a need for alternative materials and processing methods to overcome these disadvantages.

Randomly networked mesh structures prepared by a solution-phase deposition of single wall carbon nanotubes (CNTs) has been recently proposed as the next-generation material for transparent electrodes.$^5-8$ Because of the highly conductive and acceptable elastic properties of CNT, it could successfully provide a low-resistance electrical contact and good flexibility for optoelectronic applications. In the same context, one dimensional nanowires can be another good candidate to meet this purpose.$^9-12$ Among a variety of materials libraries, a semiconducting vanadium pentoxide (V$_2$O$_5$) nanowire is of particular interest.$^{13}$ It is robustly synthesized in solution phase and the control over the length dimension can readily be achieved. Additionally, the intrinsically charged nature of V$_2$O$_5$ nanowires allows it to be facilitated for charge-involved applications such as Li-ion batteries or chemical sensors.

In order to utilize V$_2$O$_5$ nanowires for the fabrication of transparent flexible electrodes, it is required to relevantly disperse the nanowires over targeted substrates. However, efforts to date have primarily focused on the use of electrostatic interactions between charged V$_2$O$_5$ nanowires and an inorganic substrate,$^{14,15}$ such that the flexibility of the system could not be employed. It can be ascribed to the restricted availability for surface functionalization of flexible plastic substrates, which are mainly crosslinked and thus chemically inert. To address this challenge, instead of using the direct electrostatic interactions between nanowires and substrate, here we present a novel method of adopting the layer-by-layer assembled polyelectrolyte multilayers as an interlayer between nanowires and the substrate, providing a good adhesion property onto the plastic substrate as well as a uniform dispersion of charged V$_2$O$_5$ nanowires inside the matrix of polyelectrolyte multilayers.

The electrostatic layer-by-layer (LbL) assembly technique is an alternating deposition method between complementary charged species, which allows the creation of functionalized complex thin films and highly tunable surfaces.$^{16-18}$ Due to its versatility and simplicity,
LBL self-assembly has been widely employed for various applications. Negatively charged V$_2$O$_5$ nanowires can be incorporated into polyelectrolyte matrix through the control of electrostatic interactions between them. V$_2$O$_5$ nanowires can stably be dispersed within the polymeric matrix and can form a randomly networked structure, ensuring the structural flexibility as well as the electrical conductivity. Since LBL self-assembly allows the facile deposition on the surface of almost any type of materials, including silicon wafers, glasses, and plastics, it is expected that the LBL assembled thin film has a good adhesion property with flexible plastic substrates.

In order to demonstrate the feasibility of this technique for micro-optoelectronic applications, furthermore, we come up with a selective patterning of the polyelectrolytes/nanowires complex onto a plastic substrate using a transfer printing method. Toward this goal, we alternatively coated the polyelectrolytes and charged V$_2$O$_5$ nanowires over a patterned stamp made of polydimethylsiloxane (PDMS). Then, the patterns of LBL assembled complex were selectively transferred to the targeted plastic substrate through the manipulation of interfacial interactions between the stamp and the substrate. The current-voltage ($I$–$V$) characteristic of the transferred patterns was measured to verify the electrical conductivity. As a result, micropatterns of polyelectrolytes/V$_2$O$_5$ nanowire complexes can easily be generated with a large-scale area (2 cm $\times$ 2 cm) over a flexible PET film while maintaining good electrical conductivity, which indicates a potential attractiveness of this method for flexible optoelectronic applications.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Master Pattern and PDMS Mold

The master from which the PDMS stamp was made was prepared using a silicon wafer that had been thermally oxidized to a thickness of 1 $\mu$m. Micrometer-scaled line patterns (line width = 2.5 $\mu$m, spacing = 4.5 $\mu$m) were embossed onto the wafer surface by photolithography. The PDMS stamps were prepared by mixing a siloxane base oligomer and a curing agent (Sylgard 184, Dow Corning) at the ratio of 10 to 1 by weight, followed by curing at 80 °C for 12 hours.

2.2. Synthesis of Vanadium Pentoxide Nanowires

V$_2$O$_5$ sols were prepared from a solution of 0.2 g ammonium (meta)vanadate (Aldrich) and 2 g acidic ion exchange resin (DOWEX 50WX8-100, Aldrich) in 40 ml water. After a few hours of stirring at 75 °C, the formation of orange-colored sols was observed and the color was darkened with time. After 3 days of reaction, V$_2$O$_5$ fibers with a length of micrometer scales were obtained. Then, supernatant V$_2$O$_5$ sols were selectively separated from the solution and diluted with water before use.

2.3. Layer-by-Layer Assembly of Polyelectrolyte/V$_2$O$_5$ Nanowire Complexes

Cationic linear polyethylenimine (LPEI, 25,000 M$_w$, Polysciences) and anionic poly(acrylic acid) (PAA, 90,000 M$_w$, 25% aqueous solution, Polysciences) were used as-received and prepared as 30 mM and 20 mM solutions in deionized water, respectively, on a repeated cycle basis. The pHs of both solutions were carefully adjusted to 4.7 with diluted solutions of hydrochloric acid and sodium hydroxide. Patterned PDMS stamps were used as a substrate for LBL deposition. In order to provide some hydrophilicity for a successful adsorption of polyelectrolytes in aqueous condition, the PDMS stamps were slightly plasma-treated with a conventional plasma cleaner for 2 min (PDC-001, Harrick Scientific Corp.). The layer-by-layer deposition was performed by using a programmable slide stainer (HMS70, Microm) with a deposition condition of 8 minutes adsorption of polyelectrolytes, followed by three sequential washing steps in the baths of deionized water. For a construction of a complex film of polyelectrolyte/V$_2$O$_5$ nanowires, a mixture of negatively charged V$_2$O$_5$ sols (diluted solution of 3% v/v) and PAA was used and alternatively deposited with cationic LPEI by the LBL assembly method. After a film deposition, the PDMS stamp was removed from the solution and dried under ambient atmosphere.

2.4. Pattern Transfer of Polyelectrolyte/V$_2$O$_5$ Nanowire Complex Films

Prior to the pattern transfer, target substrates (slide glasses or flexible PET films) were cleaned by ultrasonification with methanol and deionized water and finally treated under plasma. A patterned PDMS stamp coated with the complex of polyelectrolyte/V$_2$O$_5$ nanowires was placed onto the target surface in humid environment (relative humidity > 90%). A slight pressure around a few bars was applied to promote a conformal contact between the stamp and the substrate. Then, after 30 minutes of contact, the PDMS stamp was detached from the substrate and micropatterns of the complexed thin film were selectively transferred to the substrate.

2.5. Characterization of Transferred Films

The surface topology of micropatterns of polyelectrolyte/V$_2$O$_5$ nanowire complex thin films was observed with an optical microscope and an atomic force microscope (AFM, Dimension 3100 and Innova, Veeco) in dry condition. In order to minimize any possible misreading during data acquisition and to enhance the image resolution, we used a slow scanning tapping mode (0.7~1.0 Hz of a scan speed). The current-voltage ($I$–$V$) characteristics of the complex micropatterns were measured using a probe station (MST-8000C, MSTech).
3. RESULTS AND DISCUSSION

Vanadium pentoxide nanowires were robustly synthesized and incorporated with polyelectrolytes as shown in Figure 1. To obtain dimensional information on nanowires, the synthesized sols with a dark orange color (Fig. 1(a)) was highly diluted and drop-cast onto a silicon wafer. The atomic force microscopic image presented in Figure 1(b) reveals that the average length of V$_2$O$_5$ nanowires is around 7~8 μm, which verifies the accelerated growth of nanowires at elevated temperature (75 °C). $^{24,25}$ One interesting observation in Figure 1(b) is that the nanowires are folded in places and generate knots along the axial direction of nanowires. It can be attributed to the fact that a V$_2$O$_5$ nanowire is intrinsically a nanoribbon with a uniform geometric cross section of 1.5 nm × 10 nm, $^{13}$ which is prone to be deformed as compared to the nanowires with a symmetric cross section. Negatively charged characteristic of V$_2$O$_5$ nanowires facilitates their incorporation into polyelectrolytes using LbL assembly technique, which leads to the realization of randomly interconnected networks of V$_2$O$_5$ nanowires within the polymeric matrix. As seen from Figure 1(c), V$_2$O$_5$ nanowires are uniformly dispersed and embedded in polyelectrolyte multilayers, confirming that the LbL assembly of the polyelectrolyte/nanowires is highly beneficial for controlling the spatial distribution of nanowires and maintaining the structural stability of the complex film.

Figure 2 illustrates the transfer printing of microelectrodes of polyelectrolytes/V$_2$O$_5$ nanowires onto the target substrate. To prepare complex films on a patterned PDMS stamp, three bilayers of both LPEI and PAA were alternately deposited onto the plasma-treated stamp as the base layers to enhance the subsequent adsorption of V$_2$O$_5$ nanowires. Then, the negatively charged V$_2$O$_5$ nanowires were mixed with the polyanionic building block of PAA and alternatively deposited with the counter-charged LPEI. After additional deposition of three bilayers of LPEI and PAA/V$_2$O$_5$ nanowires, the outermost surface is treated with

Fig. 1. (a) Synthesized sol of vanadium pentoxide nanowires. (b) Three-dimensional AFM image of V$_2$O$_5$ nanowires deposited on a silicon substrate (scan size = 4 μm × 4 μm). (c) AFM image of V$_2$O$_5$ nanowires embedded polyelectrolyte multilayer film (scan size = 5 μm × 5 μm).

Fig. 2. Schematic illustration of the experimental procedure.
cations of the polyelectrolyte/V2O5 nanowire complex. The success of pattern transfer was achieved over a large area of 2 cm × 2 cm with little defects (Fig. 3(a)). The three-dimensional AFM image in Figure 3(b) suggests that the transferred micropatterns have smooth edges without tattered residues, which indirectly confirm the strong adhesion between the complex film and the substrate. Cross-sectional analysis also verifies the robustness of this transfer printing process. The measured height of the transferred pattern (50~55 nm) is nearly close to the value obtained by ellipsometry. One notable observation in Figure 3(b) is that there is no exposure of embedded V2O5 nanowires out of the surface of transferred patterns. Since the V2O5 nanowires are perfectly encapsulated with polyelectrolyte multilayers in this case, it would be beneficial for further stacking or integrating the microstructures.

In order to verify the feasibility of multiple transfers and the stability of transferred patterns, we have tested two-step sequential transfer printings onto the flexible PET film. As shown in Figure 4(a), the second layer of the transferred patterns is perpendicular to the pre-deposited first layer, forming a meshed network. As compared to aforementioned simple line patterns in Figure 3, presented networked structure can provide the interconnection between transferred micropatterns and result in good electrical conductivity. Additionally, the multiple transfer process is potentially applicable for an ultimate construction and integration of three-dimensional structures. The cross-sectional analysis shows that multiple levels of the transferred patterns are observed in accordance with the number of transfer printing process. Notably, the transferred film atop the flexible PET film is mechanically stable against bending as shown in Figure 4(b).

Finally, the electrical conductivity of the transferred micropatterns was investigated. For a quantified analysis and comparison of measured values, two types of samples were prepared. One is transferred microelectrodes of polyelectrolyte/V2O5 nanowire complex and the other is randomly interconnected V2O5 nanowires prepared by a drop-casting method. To measure the I–V characteristics, a key indicator of the electrical behavior of conducting materials, we sputtered gold electrodes as a current collector onto the surface with a gap distance of 0.5 mm. As shown in Figure 5, remarkably, an ohmic contact behavior was observed in both cases. However, the relatively suppressed conductivity was observed for micropatterns possibly due to the increased resistance. Although the semiconducting behavior of V2O5 nanowire has generally been known, the observed result is attributed to the existence of structural defects in synthesized V2O5.
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Fig. 4. (a) AFM image of networked microelectrodes prepared via multiple transfer printings (scan size = 50 µm × 50 µm). (b) Large area demonstration of transfer printing the complexes of polyelectrolytes/V$_2$O$_5$ nanowires on a flexible PET film.

Fig. 5. Current–voltage (I–V) characteristics of the transferred microelectrodes of polyelectrolytes/V$_2$O$_5$ nanowires. For a comparison, drop-casted random network of V$_2$O$_5$ nanowires was measured.

that the known n-type semiconducting behavior of V$_2$O$_5$ nanowires is primarily dominant at low temperature condition (<200 K). For higher temperature, the conductance increases and the ohmic behavior governs the system. Therefore, it is anticipated that this conducting behavior of the transferred patterns fabricated with this method is potentially useful for the development of flexible and transparent electronics.

4. CONCLUSIONS

In summary, the micropatterns of V$_2$O$_5$ nanowires embedded polyelectrolyte multilayers were readily fabricated with the conventional layer-by-layer assembly and subsequent transfer printing onto a flexible substrate. The transferred microelectrodes were observed with AFM, confirming the robustness and large-area applicability of this method. The current–voltage characteristics of transferred microelectrodes was also investigated and yielded a good conducting behavior. There are two important advantages associated with the polyelectrolytes utilized in this method for the fabrication of transparent electrodes. First, as compared to previously reported studies where a direct binding of nanowires onto the substrate has been employed, a polyelectrolyte matrix used in this study serves as an interlayer between nanowires and substrate, and offers a good adhesion ability with an underlying substrate, rendering a structural stability of the micropatterns against bending or physical stress. Second, polyelectrolytes matrix enables a uniform dispersion of charged nanowires inside the film structure, which can provide the uniform transparency allowing for a good electrical conductivity. If further tailored and controlled, it is anticipated that an economically viable and facile processing technique for the fabrication of flexible transparent electrodes can be presented.

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References and Notes

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