Development of a simple method for fabrication of transparent conductive films with high mechanical strength

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Abstract
We have developed a simple method of fabricating transparent conductive films with a high mechanical strength on glass and indium tin oxide substrates. It does not require a large excess of organic solvents and polymerization catalysts and can yield smooth films by spin-coating of a mixture of a commercially available aqueous dispersion of poly(3,4-ethylenedioxythiophene)-poly(4-styrene sulfonate) and a neat liquid of tetraethyl orthosilicate. Preparation conditions such as feed ratio, kinds of additives, and annealing temperature and time were optimized to give highly conductive, transparent and mechanically strong films.

Keywords: poly(3,4-ethylenedioxythiophene) (PEDOT), sol–gel method, transparent conductive films, mechanical strength

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1. Introduction

Since Shirakawa et al. [1, 2] succeeded in the preparation of thin and smooth polyacetylene films and found a metal-like conductivity for the bright polyacetylene films doped with iodine, a large number of studies on conducting polymers have been carried out by many researchers and many types of applications such as batteries, electroluminescent displays, and solar cells have been investigated [3]. The application of conducting polymers to the transparent conducting films has been attracting attention from the viewpoint of possible alternatives to indium tin oxide (ITO), which is a common electrode material for flat panel displays and touch panels [4, 5]. Poly(3,4-ethylenedioxythiophene)-poly(4-styrene sulfonate) (PEDOT-PSS, figure 1) is a commercially available conducting polymer, and transparent conducting films can be prepared by spin-coating or ink-jet printing of an aqueous dispersion of PEDOT-PSS [6]. However, the resulting films are mechanically weak and are likely to shorten the device lifetime when used in electronic devices.

In our previous studies, to improve a mechanical strength of transparent and conducting films we have developed a new family of polysilsesquioxanes containing oligothiophenes with well-defined structures [7–10]. These polymers were synthesized by the sol–gel method with the corresponding bis(triethoxysilyl)-substituted monomers and could be covalently anchored on the metal oxide substrates such as ITO and glass. They showed a mechanical strength superior to PEDOT-PSS, although their conductivities were much lower than that of PEDOT-PSS. Furthermore, the synthetic pathway to obtain the monomers included many steps and was unfavorable for the practical applications.

In this study, we demonstrate the use of composite films having an interpenetrating network structure of PEDOT-PSS and silicon dioxide (SiO₂). SiO₂ can be viewed as an inorganic polymer composed of a three-dimensional siloxane network that can be easily synthesized by the sol–gel method with
Scheme 1. Schematic of the formation of a composite film of PEDOT-PSS and SiO$_2$ by the sol–gel reaction of TEOS in an aqueous dispersion of PEDOT-PSS.

Figure 1. Chemical structure of PEDOT-PSS.

Table 1. Feed ratio of TEOS and PEDOT-PSS dispersion and estimated molar ratio of SiO$_2$/EDOT in the film.

| Films | Feed ratio of TEOS/PEDOT-PSS (by volume) | Molar ratio of SiO$_2$/EDOT |
|-------|----------------------------------------|----------------------------|
| SE10  | 50/950                                  | 9/1                        |
| SE15  | 75/925                                  | 14/1                       |
| SE20  | 100/900                                 | 19/1                       |
| SE25  | 125/875                                 | 24/1                       |
| SE30  | 150/850                                 | 30/1                       |
| SE35  | 175/825                                 | 36/1                       |
| SE40  | 200/800                                 | 42/1                       |

2. Experimental details

2.1. Materials and instrumentation

TEOS and an aqueous dispersion of PEDOT-PSS were purchased from Aldrich and Heraeus (Clevios PH500), respectively, and were used without further purification. Dimethyl sulfoxide (DMSO), ethylene glycol (EG) and poly(ethylene glycol) (PEG, $M_n = 600$) were purchased from Nacalai Tesque, Wako Pure Chemical and Junsei Chemical, respectively. Mechanical strengths of the films were tested according to the ASTM Standard D 3363–92 [19], using a TQC Wolff-Wilborn tester (COTEC) with pencils varying in hardness from 6B to 6H. Electrical conductivities were measured by the four-probe method using a low-resistivity meter (Mitsubishi Chemical, Loresta-GP, MCP-T610). Transparencies were measured by a spectrophotometer (Shimadzu, UV-3150). Film thicknesses and morphologies were evaluated by laser microscopy (Keyence, VK-9700) and an atomic force microscopy (AFM) (Agilent Technologies, 5500 Scanning Probe Microscope). Ionization energies were estimated by a photoemission spectrometer (Bunko Keiki, BIP-KV201).

2.2. General preparation method of composite films

A neat liquid of TEOS was added to an aqueous dispersion of PEDOT-PSS. The mixture was phase-separated, but became homogeneous after being stirred at room temperature for 12 h. The resulting solution was spin-coated on a glass substrate at 3000 rpm for 30 s after being filtered by a syringe filter. Composite films containing additives were prepared by the sol–gel reaction of TEOS in the presence of acidic or basic catalyst [11]. When the composite films are prepared from tetraethyl orthosilicate (TEOS) and an aqueous dispersion of PEDOT-PSS, a sulfonic acid group in PSS can act as an acidic catalyst for the sol–gel reaction; thus one can expect that the composite film can be obtained by just mixing PEDOT-PSS and TEOS (scheme 1). To the best of our knowledge, there have been no reports on this simple method of preparing the composite film of PEDOT-PSS and SiO$_2$ applicable to transparent conductive films, except for several patents reporting the preparation of the PEDOT-PSS/SiO$_2$ composite films in a large excess of water–alcohol solvents, using nitric acid, hydrochloric acid or NH$_3$ as polymerization catalysts [12–18]. Preparation conditions such as feed ratio, kind of additives, and annealing temperature and time are examined to optimize conductivity, transparency and mechanical strength of the composite films on glass substrates.
also prepared in a similar manner. The film was cured at a temperature $T_a$ for a period $t_a$. The feed ratio of TEOS and PEDOT-PSS was changed as shown in table 1. The density and concentration of the PEDOT-PSS dispersion and the weight ratio of PEDOT/PSS were $1 \text{ g ml}^{-1}$, 1.3 wt%, and 1/2.5, respectively. From these data, the molar ratio of SiO$_2$/ethylenedioxythiophene (EDOT) unit was estimated (table 1). The films were named SE$n$, where $n$ denotes a rounded value of the SiO$_2$/EDOT ratio.
3. Results and discussion

When the composite films were prepared by mixing TEOS and an aqueous dispersion of PEDOT-PSS, their conductivities were very low and decreased drastically with increasing ratio of TEOS (which forms an insulating SiO$_2$). However, the mechanical strength of the film was improved greatly by using TEOS, as expected (vide infra). The conductivity of the SE10 film, for example, was as 10$^{-4}$ S cm$^{-1}$, much lower than 0.1 S cm$^{-1}$ for the neat PEDOT-PSS film (figure 2). Recent studies have shown that the conductivities of PEDOT-PSS films can be improved by adding a small amount of organic compounds with high boiling points owing to the morphological changes of PEDOT-PSS (relaxation of the polymer chains) induced by the addition of the solvent [20–27]. The conductivities of PEDOT-PSS films containing 5 wt% of additives (DMSO, EG or PEG) were about thousand times higher than that of a PEDOT-PSS film without additives (figure 2). Surprisingly, the conductivities of SE10 films were increased by 4 × 10$^4$, 2 × 10$^5$ and 1.5 × 10$^5$ times by the addition of 5 wt% of DMSO, EG and PEG, respectively.

Figure 3 shows conductivities of the composite films containing 5wt% additives measured as a function of the molar ratio of SiO$_2$/EDOT. The conductivities decrease gradually with increasing SiO$_2$/EDOT ratio irrespective of the kind of additives, and conductivities beyond 1 S cm$^{-1}$ are realized when the SiO$_2$/EDOT ratio is smaller than 20. DMSO and EG were the most effective additives at high and low molar ratios, respectively, and we used EG in the subsequent experiments. It is expected that the conductivity of the composite films can be increased at least 10 times when using other PEDOT-PSS dispersions having higher conductivities (for example, Clevios P1000, $\sigma = 850$ S cm$^{-1}$).

Mechanical strengths of the composite films were examined by the pencil hardness test according to the ASTM Standard D 3363–92 (figure 4) [19]. The PEDOT-PSS film itself showed a cohesive fracture even when the film was scratched by a 5B pencil. The hardness of the composite films increased with the fraction of TEOS, so that no damage by a 5H pencil was observed in films prepared with SiO$_2$/EDOT ratios above 20. We have already reported that the SiO$_2$/EDOT ratio of 20 yields composites with conductivities larger than 1 S cm$^{-1}$.

Figure 5 shows the effects of annealing time and temperature on the mechanical strength of the SE10 films doped with EG (5 wt%). When the composite film was not annealed ($t_a = 0$) or kept at room temperature ($T_a = 25^\circ$C), it was very vulnerable to scratching. The film exhibited the maximum hardness when the annealing time and temperature were longer than 30 min and higher than 100 °C, respectively, although the conductivities were almost the same (see Supplementary data, figure 1S (available online at stacks.iop.org/STAM/13/045005/mmedia)). It is known that the higher the temperature of the sol–gel reaction, the more rapidly the reaction proceeds. Thus, the improvement of the mechanical strength of the composite films annealed at high temperatures is likely to be caused by the well-expanded structure of the SiO$_2$ network. The strengthening of the films by increasing the annealing time may be explained on the same basis.

Transmission spectrum of the SE10 film on glass was measured in the visible region and compared with those of PEDOT-PSS film and the glass substrate (figure 6). Transmittance of the SE10 film was slightly lower than that of the substrate, but it was similar to that of the PEDOT-PSS film.
over the wavelength range of 400–800 nm. The effect of the SiO$_2$/EDOT ratio and the kind of additives on the transparency was also investigated and we found no significant variation of transmittance in the films prepared using different feed ratios and additives.

To investigate the electronic properties of the composite films, SEn films were coated on glass substrates under the optimized conditions (5 wt% EG, $T_a = 100^\circ$C, $t_a = 30$ min), and their ionization energies were measured by the photoemission spectroscopy. The ionization energies of the SEn films ($n = 10 – 40$) were in the range of 4.79–4.95 eV and did not differ much from the value of 4.83 eV obtained for the PEDOT-PSS film.

The surface roughness of the transparent conductive coating is a key factor for the performance of a display device. Surface morphologies of the composite films were measured using the tapping-mode AFM (figure 7). Whereas the surface of a commercially available ITO was very rough ($S_2 = 5.1$ nm), the composite film coated on glass had a smoother surface ($S_2 = 1.3$ nm). Much smoother composite films may be obtained by optimizing the film preparation conditions (spin-coating or ink-jet printing, rotation speed and time in the spin-coating method).

4. Conclusions

Organic–inorganic composite films were prepared by the spin-coating method using a mixed solution of a commercially available aqueous dispersion of PEDOT-PSS and a neat liquid of TEOS. The composite films obtained under the optimized conditions (SiO$_2$/EDOT = 9, EG additive = 5 wt%, $T_a = 100^\circ$C, $t_a = 30$ min) exhibited high transparency, conductivity and mechanical strength. The proposed method provides a simple way of fabricating transparent conductive films with a high mechanical strength without using a large excess of solvents and polymerization catalysts.

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References

[1] Shirakawa H, Louis E J, MacDiarmid A G, Chiang C K and Heeger A J 1977 J. Chem. Soc. Chem. Commun. 578
[2] Chiang C K, Fincher C R jr., Park Y W, Heeger A J, Shirakawa H, Louis E J, Gau S C and MacDiarmid A G 1977 Phys. Rev. Lett. 39 1098
[3] Skotheim T A and Reynolds J R 2007 Handbook of Conducting Polymers 3rd edn (Boca Raton, FL: CRC Press)
[4] Hecht D S and Kaner R B 2011 MRS Bull. 36 749
[5] Hecht D S, Hu L and Irvin G 2011 Adv. Mater. 23 1482
[6] Elschner A, Kirchmeyer S, Lovenich W, Merker U and Reuter K 2011 PEDOT: Principles and Applications of an Intrinsically Conductive Polymer (Boca Raton, FL: CRC Press)
[7] Imae I, Takayama S, Tokita D, Ooyama Y, Komaguchi K, Ohshita J, Sugioka T, Kanehira K and Harima Y 2009 Polymer 50 6198
[8] Harima Y, Ohshita J, Imae I, Sugioka T and Kanehira K 2010 Japan Kokai Tokkyo Koho 2010-266727, 25 November 2010
[9] Imae I, Tokita D, Ooyama Y, Komaguchi K, Ohshita J and Harima Y 2011 Polym. Chem. 2 868
[10] Imae I, Tokita D, Ooyama Y, Komaguchi K, Ohshita J and Harima Y 2012 J. Mater. Chem. at press (DOI:10.1039/C2JM32259E)
[11] Wright JD and Sommerdijk N A J M 2001 Sol–Gel Materials (Amsterdam: Gordon and Breach)
[12] Jonas F and Dhein R 1994 German Patent 4229192 March 3
[13] Jonas F, Lerch K and Guntermann U 1998 German Patent 19633111 February 26
[14] Mager M, Jonas F, Elbing A and Guntermann U 1998 German Patent 19650147 June 10
[15] Tong H-S and Hu C-M 1998 US Patent 5773150 June 30
[16] Lee C H 2000 International Patent 200074103 December 7
[17] Lee Y-E, Han M-Y, Chang Y-R, Hong J-J and Jang S-H 2005 US Patent 20050239933 October 27
[18] Hosokawa T, Satake M and Ogasawara A Japan Kokai Tokkyo Koho 2006-119355 May 11
[19] The American Society for Testing and Materials (ASTM) D 3363-92 Test Method for Film Hardness by Pencil Test
[20] Kim J Y, Jung J H, Lee D E and Joo J 2002 Synth. Met. 26 311
[21] Louwet F, Groenendaal L, Dhaen J, Manca J, Van Luppen J, Verdonck E and Leenders L 2003 Synth. Met. 135–136 115
[22] Jönsson S K M, Birgerson J, Crispin X, Grenczynski G, Osikowicz W, Denier van der Gon A W, Salanec W R and Fahlman M 2003 Synth. Met. 139 21
[23] Lai S L, Chan M Y, Fung M K, Lee C S and Lee S T 2003 Mater. Sci. Eng. B 104 26
[24] Martin B D, Nikolov N, Pollack S K, Saprinin A, Shashidhar R, Zhang F and Heiney P A 2004 Synth. Met. 142 187
[25] Ouyang J, Xu Q, Chu C-W, Yang Y, Li G and Shinar J 2004 Polymer 45 8443
[26] Wang T, Qi Y, Xu J, Hu X and Chen P 2005 Appl. Surf. Sci. 250 188
[27] Ouyang J, Chu C-W, Chen F-C, Xu Q and Yang Y 2005 Adv. Mater. 15 203