



Chemical mechanical polishing of transparent conductive layers using spherical cationic polymer microbeads



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ARTICLE INFO

Article history:

Received 7 May 2014

Received in revised form 15 December 2014

Accepted 15 December 2014

Available online 23 December 2014

Keywords:

Chemical mechanical polishing

Transparent conductive oxide

Cationic polymer

Spherical microbeads

Surface morphology

Organic light emitting diodes

ABSTRACT

Spherical cationic polymer microbeads were used to chemically mechanically polish transparent conductive oxide (TCO) layers without the need for inorganic abrasives. Poly(methyl acrylate) (PMA) was used as the polymer matrix. Surface cationization of the spherical PMA microbeads was achieved by aminolysis using 1,2-diaminoethane. The amino group content of the microbeads was controlled using the aminolysis reaction time. The surface roughness of the TCO polished using the cationic polymer microbeads was similar to that of TCO polished with an inorganic abrasive. The microbead-polished TCO layer was slightly thinner than the unpolished TCO layer. The sheet resistance of the TCO layer polished using the microbeads was lower than that polished using the inorganic abrasive. The TCO polishing ability of the microbeads was dependent on their cationic properties and softness.

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1. Introduction

Transparent conductive oxides (TCOs) are widely used as electrolytes in organic electronic devices, including liquid crystal devices, solar cells, and organic light emitting diodes (OLEDs). TCOs, including indium tin oxide (ITO), zinc oxide, aluminate zinc oxide, and F-doped tin oxide are generally formed on substrates by DC magnetron sputtering, vacuum deposition using resonance heating, or spray pyrolysis [1–6]. Crystalline conductive oxides grow vertically on substrate surfaces, and tall projections and spiked structures several tens of nanometers high can form on targets sputtered with TCOs [7]. ITO is a widely used TCO because of its high conductivity and transparency. Amaral et al. reported that the surface roughness of ITO increased with deposition thickness [7].

The influence of thermal annealing on the microstructure and surface morphology of ITO has been investigated by Raoufi et al., who found that a higher film annealing temperature increased the surface roughness [8]. Leakage current flows toward spiked structures on ITO

layer surfaces, causing short circuiting between the anode and cathode. This causes dark spots in OLED displays owing to the resulting absence of light emission [9,10]. Because rough ITO surfaces promote the generation of defects, a smooth ITO surface morphology allows the preparation of OLEDs with long lifetimes [11–13]. Jung et al. investigated the effects of the mechanical polishing and annealing of ITO surfaces on OLED performance, and found that the current density and luminance of a device containing highly planar ITO were nearly 10 times greater than those of that containing as-received ITO [14]. However, a comprehensive study on the abrasiveness and surface resistance of ITO layers remains lacking. ITO layers sputtered during thermal treatment in oxygen plasma contain no surface projections, allowing flat ITO thin layers to be fabricated [9,10]. However, such treatments tend to increase the sheet resistance [10], and high ITO sheet resistances are unfavorable in liquid crystal devices, solar cells, and OLEDs. Because ITO thin films of low sheet resistance and flatness cannot readily be formed by sputtering, newly formed ITO thin layers are typically polished when fabricating devices.

In the current study, the polishing of ITO using cationic polymer microbeads was carried out as an alternative to inorganic abrasive polishing. The conductive properties of the TCO layer were retained without damage to the ITO surface. The structure of the abrasive material is shown schematically in Fig. 1. The planarization of the ITO surface

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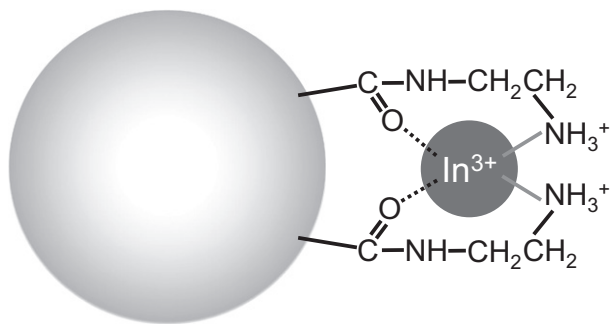


Fig. 1. Structure of the abrasive material. Planarization of the ITO surface was promoted by the chelating effect of the cationic PMA microbeads toward In^{3+} .

was promoted by the chelating effect of the cationic PMA microbeads toward In^{3+} , and was the driving force for the polishing process.

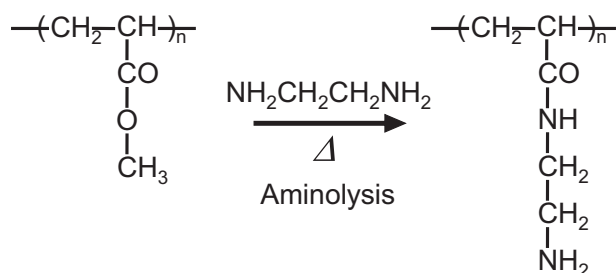
2. Experimental

2.1. Preparation of soft chemical mechanical polishing materials

Various spherical surface-cationized polymer microbead samples were prepared by the aminolysis of spherical poly(methyl acrylate) (PMA) microbeads (15 μm , Sekisui Plastics Co. Ltd., Osaka, Japan) using 1,2-diaminoethane [15], as shown in Scheme 1. The sample names of the aminated polymer microbeads are shown in Table 1. PMA spherical microbeads (10 g) were aminated by stirring in 150 mL of 1,2-diaminoethane at 90 °C for 24, 48, 96, or 192 h. The obtained microbeads were collected by filtration, washed with water and methanol, and dried under vacuum. The amino group content of the microbeads was determined by stirring in aqueous 0.05 M HCl for 1 h. The microbeads were removed by filtration, and the filtrate was titrated against aqueous 0.05 M NaOH [16]. Fourier transform-infrared (FT-IR) spectra were collected using a Jasco FT/IR-700 spectrometer (Jasco Co. Ltd., Tokyo, Japan). The microbeads were observed using field-emission scanning electron microscopy (FE-SEM; SU-8000; Hitachi High Technologies, Co. Ltd., Tokyo, Japan). The TCO surface was observed using atomic force microscopy (AFM; di Innova; Veeco Instruments Inc., New York, USA). The transparency of the TCO substrate was evaluated using ultraviolet–visible (UV–vis) absorption spectroscopy (UV-VIS650; Jasco Co. Ltd., Tokyo, Japan). Quantitative analysis of the adsorption of In^{3+} by the aminated microbeads was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 6300; Thermo Fisher Scientific K. K., Yokohama, Japan).

2.2. Polishing experiments

ITO (thickness: 329 nm; sheet resistance: 4.65 $\Omega/\text{sq.}$; Geomatec Co. Ltd., Yokohama, Japan) was used as the TCO layer. Planarization of the ITO layer was carried out using a polishing machine with rotating plates (60 rpm, Lapolish; Tokyo Seimitsu Co. Ltd., Tokyo, Japan). Various



Scheme 1. Aminolysis of PMA microbeads using 1,2-diaminoethane.

Table 1
Aminated polymer microbead sample names and amino group contents.

Microbeads	Reaction time (h)	Amount of amino group (meq/g)	Swelling degree (wet-ml/dry-g)
PMA	0	0	Aggregate in water
PMA24	24	1.63	2.33
PMA48	48	3.84	5.53
PMA96	96	4.58	7.68
PMA192	192	5.89	16.5

abrasive materials and polishing urethane hard pads (Lam Plan Industries Ltd., Sevenoaks, UK) were used. The ITO layer was stressed at 8.62 kPa, as shown in Fig. 2. Commercial colloidal silica abrasives Si-20 (20 nm particle size) and Si-80 (80 nm particle size) (JGC Catalysts and Chemicals Ltd., Kawasaki, Japan) were also tested for comparison. Polishing was also carried out using 2-aminoethanol instead of an abrasive, as a control. The ITO layer thickness was measured using spectral ellipsometry (FE5000; Otsuka Electronics Co. Ltd., Osaka, Japan).

3. Results and discussion

3.1. Preparation of spherical surface-cationized polymer microbeads

The aminolysis of the spherical PMA microbeads was confirmed by the decreased absorption at 1730 cm^{-1} [$\nu_{\text{C}=\text{O}}(\text{ester})$] as the aminolysis reaction proceeded, as shown in the FT-IR spectra in Fig. 3. Absorptions at 1650 cm^{-1} [$\nu_{\text{C}=\text{O}}(\text{amide})$] and 3400 cm^{-1} ($\nu_{\text{N-H}}$) also increased with reaction time. The amino group contents of the polymer microbead samples were estimated to be 1.63 (PMA24), 3.84 (PMA48), 4.58 (PMA96), and 5.89 (PMA192) meq $^{-1}$, as shown in Table 1. The microbeads were typically spherical, as shown in Fig. 4(b)–(e). The amino group content and swelling degree of the microbeads were plotted against the aminolysis reaction time in Fig. 5(a) and (b), respectively. Both amino group content and swelling degree increased with aminolysis reaction time. The swelling degree of PMA192 was 16.5 wet-ml/dry-g. PMA192 had the typical morphology of a highly swollen gel with a spherical shape, as shown in Fig. 4(e). The uneven surface of PMA 192 was caused by severe swelling and shrinking.

The adsorption properties of the aminated PMA microbeads toward In^{3+} were investigated. 100 mg of aminated PMA48 microbeads were added to 50 ml of aqueous 1.0 mM InCl_3 , and the resulting solution was stirred for 1 h. The microbeads were removed by filtration, and the In^{3+} content of the filtrate was analyzed using ICP-OES. The In^{3+} concentration of the filtrate after adsorption by PMA48 was 0.48 mM. Thus, the adsorption capacity of PMA48 for In^{3+} was 0.26 meq/g. The adsorption capacities of the unmodified PMA microbeads and colloidal

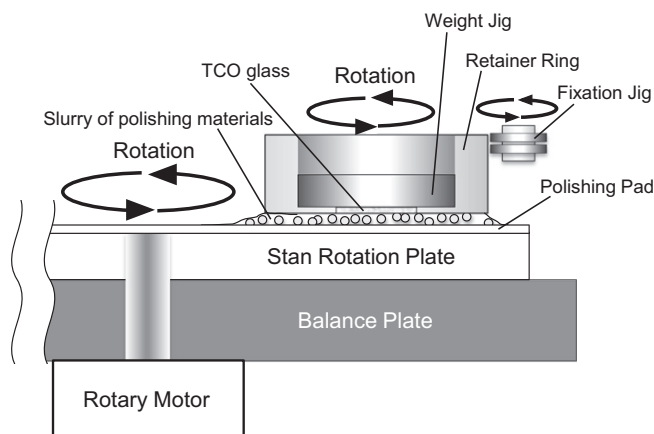


Fig. 2. Apparatus used to polish the ITO thin layers.

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