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Effect of dispersant agents on morphology and optical–electrical properties of nano indium tin oxide ink-jet ink

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Abstract

In this study, the effect of dispersant agents on rheology, surface tension, dynamic light scattering and morphology of two nano-ITO inks were investigated. The inks were formulated using two different dispersant agents and the rest of constituents remained unchanged. The inks were printed onto a glass substrate using an ink-jet printer. The printing task was set to one, three and five runs, in order to evaluate variations in optical and electrical properties, by changing the thickness of the printed film. Following initial drying of the printed pattern on to the substrate, the samples were subsequently heat-treated at different temperatures (350 °C, 450 °C, 550 °C) to assess the effect, if any, of heat-treatment temperature on morphology, optical and electrical properties of the treated ITO films. It was concluded that the type of dispersant, heat-treatment parameters and number of printing runs had a substantial effect on the electrical and optical properties of the ITO films.

Keywords: Ink-jet printing; Conductive; Nano-ITO; Dispersion

1. Introduction

The use of transparent conducting oxides (TCOs) in opto-electronic devices has grown significantly over the last decade. Indium tin oxide (ITO) is the most widely used raw material due to its marvelous combination of environmental stability, relatively low electrical resistivity and high transparency to visible light.[1,2] ITO can be found in a wide variety of applications, including flat-panel displays, electro-chromic windows, functional glass, solar cells, and light emitting diodes.[2–5] There are several common processes for preparation of the nano-ITO-particles such as co-precipitation,[6,7] vapor–liquid–solid (VLS),[8–10] sol–gel,[10–12] hydrothermal synthesis,[13,14] micro-emulsion technique[15] and high-temperature aminolysis.[16] In this study, nano-ITO-particles were synthesized through a sol–gel method to improve chemical homogeneity of indium nitrate and tin chloride combination. Thus far various methods have been proposed for the transfer of nano-ITO-particles on to chosen substrates to produce ITO films, including chemical vapor deposition[17] or sputtering.[18–20] Much time and effort has been devoted to producing an ITO film using a solution-based process like spray pyrolysis, sol–gel, dip-coating, spin coating, silk-screen printing, and hydrothermal methods.[14,21–26] However, these processes are still limited in terms of selective deposition of the ITO films on the desired surface. Therefore, development of potential alternative technology, with low cost via a simple process, would be considered an important topic of research not only for replacing conventional ITO procedures but also providing further possibilities in its nanotechnology related applications.

The ink-jet printing method has a great potential in manufacturing TCOs without patterning or etching.[27–30] Ink-jet printing is known as a non-contact process that deposits a desired amount of a functional material directly from a computer designed image onto a selected area of a substrate with no contamination. Despite all the advantages of the ink-jet printing technology, nozzle clogging has always been a major problem. This is because, inks used for ink-jet printing contain insoluble micro or nanoparticles that can be agglomerated and precipitated during the printing

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process. Therefore, preparing the ink-jet inks is often a challenging issue for researchers. According to the Derjiaguin, Landau, Verwey and Overbeek (DLVO) theory, the potential energies of attraction and repulsion are summed to provide a total interaction potential energy between the colloidal particles.[31] Therefore, a stable colloidal dispersion of the ITO particles should be possible by employing an electrostatic or steric stabilization method. It can be assumed that this causes a repulsive layer to form, which suppresses coagulation of the nano-ITO-particles stabilizing them.

In this study, two nano-ITO inks with differing types of dispersant agents, cetyltrimethylammonium bromide (CTAB) and poly(acrylic acid-co-itaconic acid) or poly(AA-co-IA), were compared. CTAB is a cationic small molecule dispersant agent and poly(AA-co-IA) is an anionic polymer dispersant agent. However, the presence of a dispersant, which covers the particle surface, is a negative factor when considering the electric conductivity of the printed film. The heat-treatment temperature of the film largely depends on the decomposition temperature of the dispersant agent used.

2. Experimental

2.1. Materials

The materials used in this experiment were; tin (IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) with 97.5% purity; indium (III) nitrate hydrate ($In(NO_3)_3{\cdot}XH_2O$) with 99.99% purity, which were procured from BDH Chemical Company and Alfa Aesar Company, respectively. CTAB as a cationic dispersant agent was provided by Aldrich; poly(AA-co-IA) as a polyelectrolyte dispersant agent was synthesized by acrylic/itaconic acid copolymerization (2:1) in accordance with the procedure described in reference.[32] All other chemicals employed throughout this work were laboratory grade chemicals as provided by Merck Company, UK.

2.2. Equipment and instrumentation

The prepared ink formulations were filtered through a 0.45 μm and 0.2 μm Sartorius Minisart filter (Göttingen, Germany). The microscope glass slides were ink-jet printed, using an Epson Stylus Photo P50 printer. The printed microscope glass slides were dried and heat-treated in an Azar 1250 furnace. The values of pH, surface tension and viscosity of the prepared inks were ascertained using an 827 pH Metrohm meter; Tensiometer K100MK2 and Rheometer MCR 300, respectively. The surface morphology and cross sectional view of the printed nano-ITO on the microscope glass slides were observed by means of a Scanning Electron Microscope (SEM). Additionally, morphology and size of the nano-crystalline ITO inks were observed under a transmission electron microscopy (TEM) (JEM-100CXII). The phase composition and characterization of the nano-ITO-particles were determined by X-ray diffraction (SIMENS D500X) using CuK radiation to evaluate the mineral composition. Optical transmittance of the ink-jet printed nano-ITO films were measured, within the wavelength range of 300–800 nm, by means of a UV/visible spectrometer (Agilent 8453). Sheet resistance of the ink-jet printed nano-ITO films was measured by a WS-1 type four-probe apparatus. Particle size was determined by dynamic light scattering (DLS) equipment (Malvern Instrument, UK; model ZEN 3600), which measured the random changes in the intensity of light scattered from an ink.

2.3. Experimental procedures

2.3.1. Preparation of ITO nanoparticles

The nano-ITO-particles were prepared using the sol–gel method. In this method, indium (III) nitrate [$In(NO_3)_3{\cdot}4H_2O$] (5 g, 0.016 mol) and tin (IV) chloride [$SnCl_4{\cdot}5H_2O$] (0.647 g, 0.0018 mol), were used as the sources of indium and tin, respectively. Indium (III) nitrate and tin (IV) chloride, in the molar concentration ratio of In:Sn 9:1, were dissolved into 50 ml of de-ionized water. The resulting solution was stirred for 2 h at 65 °C and then, PVP (0.3% wt) was added to the solution. The mixture obtained was stirred for 35 min, after which 25 ml of ammonium solution (25%) was added dropwise to increase the pH to 7.5–8 at room temperature. Then, the resulting white solution was stirred at room temperature for a further 5 h. By this time, the indium tin precursor had precipitated to form Sn-doped In hydroxide, and the ammonia had reacted with the chlorine atoms of the precursor to produce ammonium chloride. The PVP interacts with In^{2+} and Sn^{3+} at N or C=O sites with their lone electron pairs. In addition, after formation of the nanoparticles, the steric effect of PVP inhibits further growth of the nanoparticles and prevents agglomeration by the same mechanism. The precipitated indium tin hydroxide was then centrifuged at 3000 rpm for 5 min. The heavier precipitate, which settled was collected from the solution and washed five times with de-ionized water to remove impurities including ammonia, chloride and nitrate ions; it was then dried at 100 °C for 2 h to remove any moisture. After being air dried in an oven at 300 °C for 3 h, the white particles of indium tin hydroxide were thermally oxidized to indium tin oxide.

2.3.2. Nano-ITO based inks

In order to produce a stable and homogeneous nano-ITO inks, the synthesized nano-ITO-particles were dispersed using 2 wt% of the dispersing agent in de-ionized water, diethylene glycol (DEG) and ethanol over 72 h using the ball-milling process. The concentration of the nano-ITO-particles in the ink was set to 8 wt%.

In formulation of the nano-ITO inks, CTAB (Ink1) and poly(AA-co-IA) (Ink2) were used as the dispersing agents. The pH value of the inks was later adjusted to 7–7.5 by a buffer solution to prevent any damage to print-head and cartridge. The prepared nano-ITO inks (Ink1 and Ink2) were filtered through a 0.45 μm and 0.2 μm Sartorius Minisart filter in order to remove the ITO particles, which had agglomerated during the ink formulation process.

2.3.3. Ink-jet printing of nano-ITO inks

Ink-jet printing was carried out with Epson Stylus Photo P50 printer at 1200 dpi using the prepared inks (Ink1 and Ink2) onto