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Electrochromic Ni–Fe oxide thin films synthesized by an atmospheric pressure plasma jet for flexible electrochromic application

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ABSTRACT

Flexible-electrochromic organo-nickel-iron oxide ($NiFe_xO_yC_z$) films deposited onto flexible polyethylene terephthalate (PET)/indium tin oxide (ITO) substrates using atmospheric-pressure plasma-enhanced chemical vapor deposition with an atmospheric pressure plasma jet under various flow rates of oxygen gases are investigated. Precursors [nickelocence, $Ni(C_5H_5)_2$] and [ferrocence, $Fe(C_5H_5)_2$] vapors are carried by argon gas, mixed by oxygen gas and injected into air plasma torch for a rapid synthesis of $NiFe_xO_yC_z$ films by a short duration of the substrate, 32 s, in the plasmas. Uniform light modulation on PET/ITO/$NiFe_xO_yC_z$ is produced while the moving PET/ITO substrate is exposed to plasma torch at room temperature (~23 °C) and atmospheric pressure. Light modulation with up to a 43.2% transmittance variation at a wavelength of 708 nm even after 200 cycles of Li^+ intercalation and de-intercalation in a 1 M $LiClO_4$-propylene carbonate electrolyte is accomplished.

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1. Introduction

Low-temperature (cold) non-equilibrium plasmas have an obvious advantage in processing of easy-to-melt materials such as flexible polymer substrates. While low-pressure (vacuum) plasma systems require expensive vacuum systems and pumps, there has been a growing interest, mostly over the last two decades, to replace these systems with non-equilibrium cold atmospheric plasmas for surface processing and film deposition on (i) surface pretreatments for cleaning, and activation or passivation; (ii) deposition of films; and (iii) post-treatment on coated surfaces for adjusting the chemical composition or crystallinity of the coating [1]. Recently, the atmospheric pressure-plasma enhanced chemical vapor deposition (AP-PECVD) using cold atmospheric plasmas is intensively studied due to the economical (low cost, high processing speed and simple system which does not use vacuum equipment) and ecological advantages [2]. Atmospheric-pressure non-equilibrium discharges incorporate corona, spark, dielectric barrier and atmospheric-pressure glow discharge. Compared with other non-equilibrium atmospheric pressure plasmas, the geometries of an atmospheric-pressure glow discharge, namely, an atmospheric pressure plasma jet (APPJ), offer the advantage that the treated surfaces are not confined between electrodes. The samples are located in the downstream of the plasma jet, i.e., the quasi-field free region of the jet [3]. AP-PECVD has been used to deposit thin films such as SiO_x, SiN_x, TiO_x, SnO_x, InO_x, CeO_x, fluorocarbons, hydrocarbons [4], AlO_x [5] and ZnO:Ga [6] by an APPJ. In this study, AP-PECVD is investigated to deposit the $NiFe_xO_yC_z$ films onto the flexible polyethylene terephthalate (PET)/indium tin oxide (ITO) substrates using an APPJ.

Transition oxide films have been used in several electrochromic (EC)-associated devices: EC-smart windows, EC-sunroofs, EC-mirrors and EC-gas sensors [7]. Nickel oxide (NiO_x) is the most studied anodic EC material by changing from a transparent state to a neutral colored one upon extraction of protons (or Li^+ ions) or insertion of OH^- ions [8]. The EC performance of NiO_x films is typically investigated in an aqueous electrolyte (commonly KOH) in spite of water absorption caused by the degradation on EC properties of NiO_x films [9]. Upon extraction and insertion of Li^+ ions, the durability of Li^+ EC performance for NiO_x films has been demonstrated to undergo a reversible Li^+ intercalation–deintercalation process (Eq. (1)):

$$\mathrm{Li}_{\alpha_0}\mathrm{NiO}_x(\text{colored}) + \alpha_i\mathrm{Li}^+ + \alpha_i e^- \underset{\text{coloring}}{\overset{\text{bleaching}}{\rightleftharpoons}} \mathrm{Li}_{(\alpha_0+\alpha_i)}\left[\mathrm{Ni}^{3+}_{1-\alpha_i}\mathrm{Ni}^{2+}_{\alpha_i}\right]\mathrm{O}_x(\text{bleached}). \quad (1)$$

However, the optical properties between Li^+ intercalated into and deintercalated out from NiO_x films is not modulated to a large extent [10]. The iron oxide (FeO_x) thin films have the advantage of a high charge capacity [11]. In this study, the iron is rapidly co-synthesized into nickel oxides to provide the promising Li^+ EC performance for the $NiFe_xO_yC_z$ films. The EC $NiFe_xO_yC_z$ films are deposited onto flexible PET/ITO substrates at a short exposed duration (32 s) using an AP-PECVD method with an APPJ at various O_2 gas flow rates. This study inspects how the process parameter, namely, the flow rate of O_2 gases F_{O_2} (sccm) induces the film properties and the electrochromic performance

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of APPJ-synthesized $NiFe_xO_yC_z$ films. The nature of $NiFe_xO_yC_z$ films is analyzed by field emission scanning electron microscopy (FESEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental details

2.1. Co-synthesis of $NiFe_xO_yC_z$ films using an APPJ

Fig. 1a shows the schematics of the APPJ set-up for co-deposition of $NiFe_xO_yC_z$ films onto PET/ITO substrates (40 Ω/square, 125 μm thick, 3 cm × 3 cm) in ambient air. The PET/ITO substrates are launched 1.5 cm below the nozzle (inner diameter of 2.15 mm) of the air plasma jet. Fig. 1b illustrates that the air plasma jet is generated by an atmospheric-pressure non-equilibrium glow discharge with a power supply at an audio frequency of 20 kHz and a power of 300 W. To create the electrical discharge at a current of up to 0.1 A, a voltage of up to 3000 V is applied between the central electrode and the outer potential free electrode. The airflow transfers the active species in the electrical arc from the discharge zone of the nozzle and sprays them out to emit air plasma jet. To deposit the $NiFe_xO_yC_z$ films, the film-formable reactive species in the plasma jet are sprayed onto the surface of the PET/ITO substrate at a substrate moving speed of 12 cm/s for an exposed duration of 32 s. The detailed settings are shown in Table 1. The precursors [nickelocence, $Ni(C_5H_5)_2$] and [ferrocence, $Fe(C_5H_5)_2$] powders are separately placed in a sublimator and heated at 160 °C. Then, 2 sccm of Ar gas (99.9% pure) is individually fed into the tanks to carry 3.8 sccm of $Ni(C_5H_5)_2$ vapor and 0.4 sccm of $Fe(C_5H_5)_2$ vapor (the gas line was heated at 160 °C). The $Ni(C_5H_5)_2$ and $Fe(C_5H_5)_2$ vapors are injected into the air plasma jet at an angle of 30° (with respect to the nozzle). The tests on the specimens are accomplished within 30 min under a

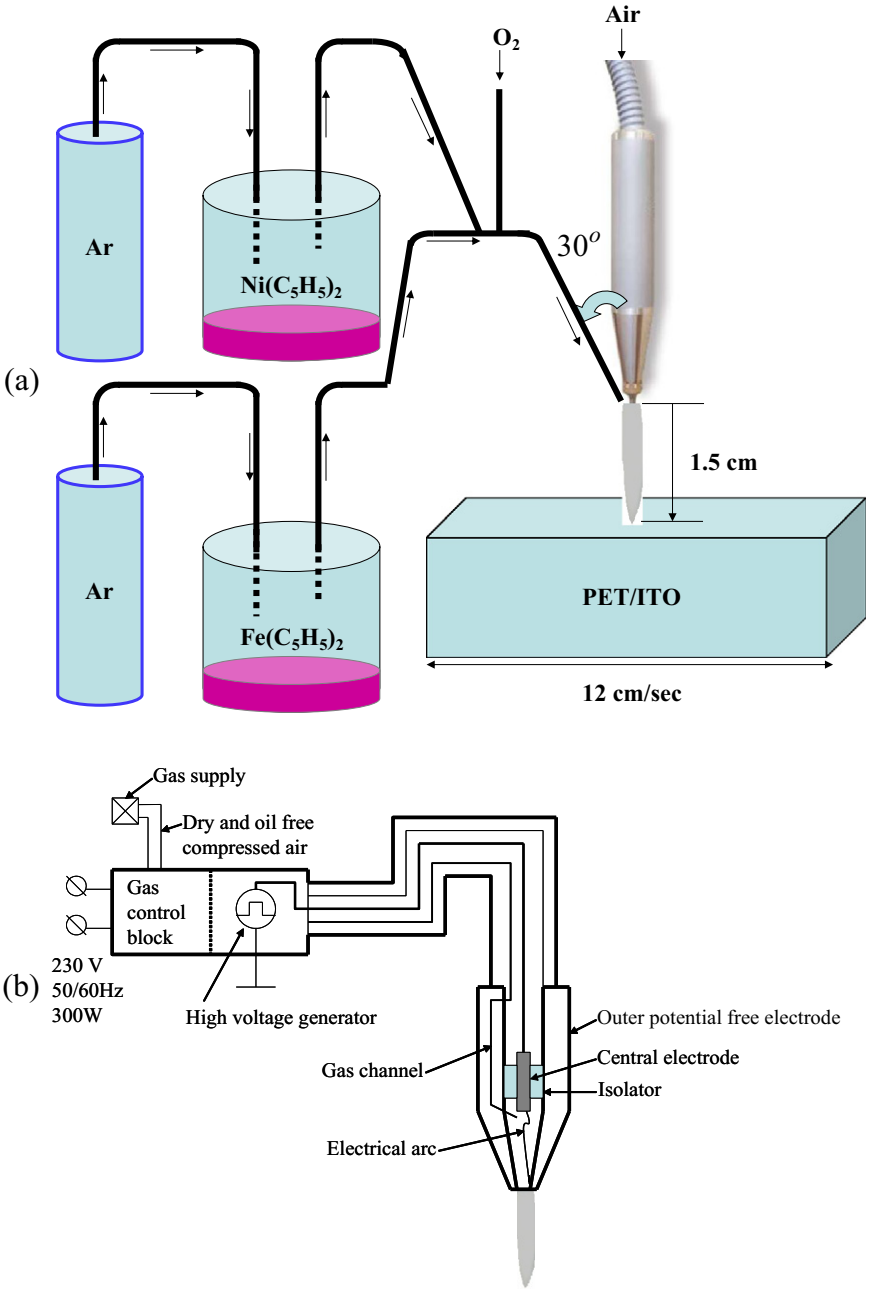

Fig. 1. Schematics of (a) the APPJ set-up and (b) the plasma unit for deposition of $NiFe_xO_yC_z$ films onto PET/ITO substrates.

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