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Atmospheric-pressure plasma-enhanced chemical vapor deposition of electrochromic organonickel oxide thin films with an atmospheric pressure plasma jet

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ABSTRACT

Deposition of electrochromic organonickel oxide (NiO_xC_y) films onto glass/indium tin oxide (ITO) substrates using atmospheric-pressure plasma-enhanced chemical vapor deposition with an atmospheric pressure plasma jet under various precursor injection angles is investigated. A precursor [nickelocene, $Ni(C_5H_5)_2$] vapor, carried by argon gas and mixed with oxygen gas, is injected into an air plasma torch for the deposition of NiO_xC_y films by a short exposure of the substrate, 20 s, in the plasma. Uniform light modulation on glass/ITO/NiO_xC_y is produced while the moving glass/ITO substrate is exposed to the plasma torch at room temperature (~23 °C) and under atmospheric pressure. Light modulation with up to a 40.9% transmittance variation at a wavelength of 513.9 nm under Li^+ intercalation and de-intercalation in a 1 M $LiClO_4$–propylene carbonate electrolyte is achieved.

1. Introduction

Non-equilibrium cold atmospheric plasmas have been studied over the last two decades mostly in order to replace low-pressure plasma systems with low cost, high processing speed simple systems that do not use vacuum equipment and possess economical and ecological advantages [1]. Atmospheric pressure-plasma enhanced chemical vapor deposition (AP-PECVD) has been utilized to deposit thin films such as SiO_x, TiO_x, ZnO_x, SnO_x, InO_x, diamond-like coating, fluorocarbons, and hydrocarbons [2]. Cold atmospheric plasmas can be created by atmospheric-pressure non-equilibrium plasma sources that include corona discharge, dielectric barrier discharge (DBD), and an atmospheric-pressure plasma jet (APPJ). The corona discharge is limited in its applications due to the restricted area for film deposition and the inherent non-uniformity as no grounded surface can be near the field emission points. To ensure stable plasma operation in DBD, the material processing is confined in the gap between the electrodes, i.e., typically a few millimeters. In contrast to the corona discharge and DBD sources, the APPJ source not only produces a stable, homogeneous, and uniform discharge, but also offers downstream processing to increase the chemical selectivity and reduce the surface damage [3]. In this study, the electrochromic NiO_xC_y films were deposited onto glass/indium tin oxide (ITO) substrates by AP-PECVD with an APPJ.

Electrochromic nickel oxides (NiO_x) thin films are the most commonly used anodic oxide-based electrochromic materials to complement cathodic-electrochromic tungsten oxides (WO_x) thin films in applications of electrochromic devices that are included in automotive (glazing of sunroofs and mirrors), architectural (energy efficient glazing-smart, switchable windows, privacy glass, partitions, and skylights), and informational display industries [4]. The electrochromic performance of Ni oxide thin films has been frequently demonstrated in aqueous electrolytes (normally KOH) in spite of the poor stability of these materials in aqueous basic media [5]. A reversible lithium intercalation–deintercalation process with a net electrochromic effect using an electrochemical process in a lithium containing electrolyte with the following Eq. (1) has been investigated by Passerini et al. [6].

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

If electrochromic NiO_x film is produced via a vapor deposition method through fast deposition, then the concerns regarding scale-up and irreversible water trapped in the films can be taken care of. The advantages of PECVD over sputtering include its higher deposition rates which result in a cost that is one-third that of sputtering, as has been emphasized by Garg et al. [7]. This study endeavors to develop the fast deposition of electrochromic NiO_xC_y film onto glass/ITO substrates via low temperature AP-PECVD using an APPJ with a short exposed duration of 20 s in an air plasma jet. The injection of a precursor [nickelocene, $Ni(C_5H_5)_2$] vapor carried by argon gas and mixed with oxygen into air plasma jet to synthesize electrochromic NiO_xC_y films onto moving glass/ITO substrates is investigated. This study examines how the process parameter,

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namely, the precursor injection angles, affects the film properties and electrochromic performance of APPJ-synthesized NiO_xC_y films.

2. Experimental details

2.1. Deposition of NiO_xC_y films using APPJ

The schematic diagrams of the APPJ set-up and the plasma unit for the synthesis of NiO_xC_y films onto the glass/ITO substrates (15 Ω/square, 1.1 mm thick, 3 cm × 4 cm) in air are shown in Fig. 1a–b. An atmospheric-pressure, non-equilibrium glow discharge with a power supply at an audio frequency of 20 kHz and a power of 300 W is used to create an air plasma torch with a diameter of 0.33 cm when the air flow rate is 33.3 l/min. The NiO precursor powders are placed in a sublimator and heated at 140 °C. Next, 4.1 sccm of Ar gas (99.9% pure) is fed into the tank to carry 9.4 sccm of the NiO precursor vapor, then mixed with 7.9 sccm of oxygen gas (99.9% pure; the gas line is heated at 140 °C) and injected into the air plasma torch at the angles of 15°, 30°, 45°, and 60° with respect to the nozzle. The glass/ITO substrates are located 1.1 cm below the nozzle of the air plasma torch. A substrate moving speed of 8 cm/s is set for the film-formable reactive species to react on the surfaces of the glass/ITO substrates. The diameter of the air plasma torch for glass/ITO substrate exposure is typical, at 0.33 cm, which is an exposed duration of about 0.041 s for one pass under a substrate moving speed of 8 cm/s. To keep the thickness variation less than 7%, the glass/ITO substrates are exposed directly to the air plasma torch for 480 passes at a substrate moving speed of 8 cm/s; i.e., the cumulated exposure duration for the reactive species sprayed onto the substrate is about 20 s (calculated based on 0.041 s/pass × 480 passes). The glass/ITO/NiO_xC_y is then analyzed for further characterization. In this study, experiments are repeated five times. The variation in experiments between the prepared samples is controlled at less than 10%.

2.2. Sample characterization

Field emission scanning electron microscopy (FESEM) images of the top surfaces and cross sections of the specimen are used to evaluate the surface morphology and thickness of the NiO_xC_y films, respectively. The grain boundary fraction (%) on the surface of each sample is determined by dividing the area of grain boundary by the total area of coatings on the FESEM images, analyzed using the Image-Pro Plus-Version 4.5.0.29 software (purchased from Media Cybermetics, Inc.). The grain sizes of the NiO_xC_y films are analyzed by the frequencies of nano-grains on the FESEM images. Deposition rates of the APPJ-synthesized NiO_xC_y

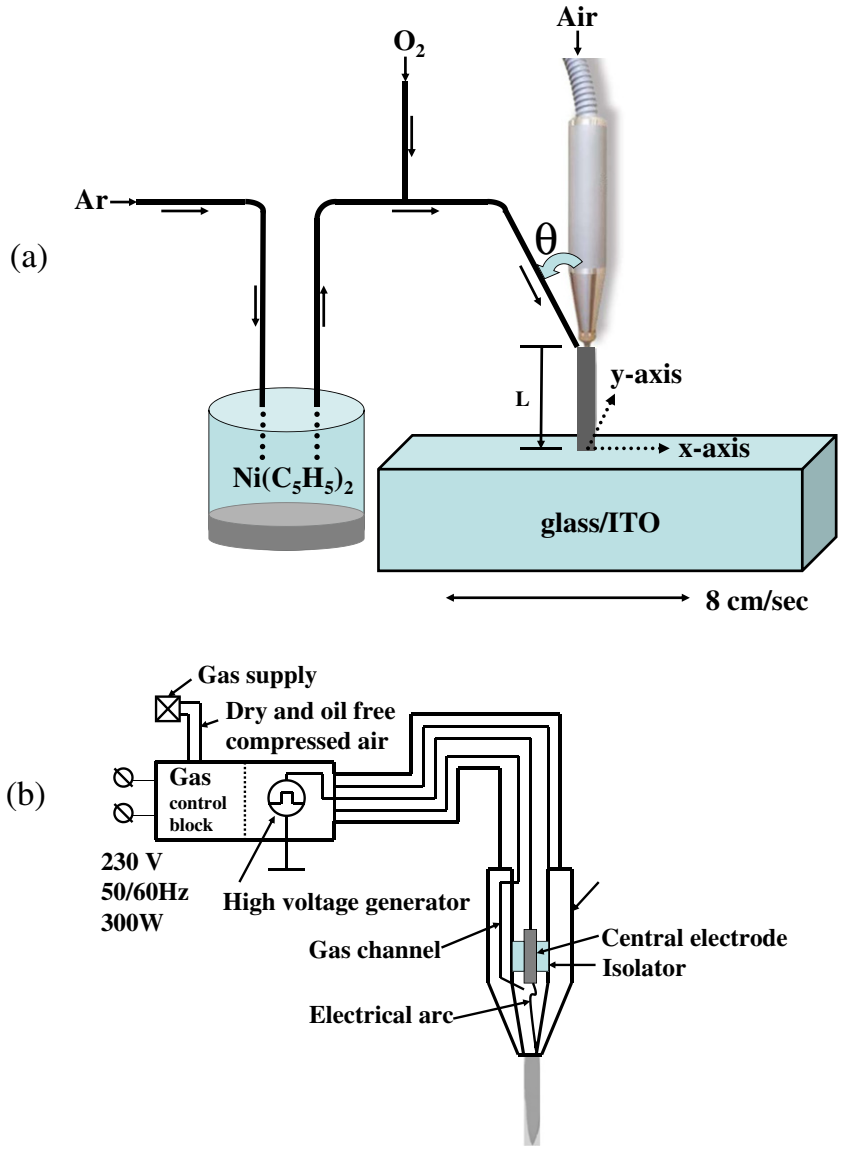

Fig. 1. Schematics of (a) the APPJ set-up and (b) the plasma unit for deposition of NiO_xC_y films onto glass/ITO substrates.