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Oxygen-deficient indium tin oxide thin films annealed by atmospheric pressure plasma jets with/without air-quenching

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ABSTRACT

This paper reports the experimental results of oxygen-deficient ITO thin films annealed by atmospheric pressure plasma jets (APPJs) with and without air-quenching. The as-deposited oxygen-deficient ITO thin films are dark in color and gradually become transparent after N_2 APPJ treatment. Quartz tubes with and without side holes are installed downstream of the APPJ to control the introduction of air into the plasma jets. Air-quenching reduces the plasma jet temperature from 580 to 385 °C but enhances the reactivity and renders faster conversion of dark ITO to transparent ITO despite the lower plasma jet temperature. With air-quenching, the transmittance ($\lambda = 550$ nm) of a 100-nm-thick ITO thin film on glass substrate reaches 87% after 90 s of APPJ treatment, compared to 7.2% in the case of the as-deposited ITO thin film. The resistivity decreases dramatically from 1.81×10^{-2} to 8.58×10^{-4} Ω cm after 15 s of APPJ treatment with air-quenching owing to crystallization and oxidation processes that reduce the defect density in the material. Subsequently, the resistivity increases slightly to 1.71×10^{-3} Ω cm after 90 s of APPJ treatment with air-quenching because of the reaction of oxygen and ITO that reduces the oxygen vacancies. Our results demonstrate that APPJ treatment can be used as a rapid thermal annealing process for ITO thin films.

1. Introduction

Indium tin oxide (ITO) is an n-type semiconductor that has been widely used as a transparent conducting electrode in opto-electronics devices such as touch panels [1], solar cells [2,3] and organic light emitting devices [4,5]. Its wide bandgap (≈3.5–4.3 eV) offers high transparency (>80%) in the visible wavelength region, whereas oxygen vacancies and substitutional tin dopants provides low resistivity ($<10^{-3}$ Ω cm) [6–10]. Numerous techniques have been developed for depositing high-quality ITO thin films, including magnetron sputtering [11–13], electron beam evaporation [14,15], pulsed laser deposition (PLD) [16,17], sol–gel deposition [18,19], spray pyrolysis [20,21], and chemical vapor deposition [22]. In all of these techniques, the oxygen content in the ITO films must be properly controlled to achieve high transparency and low resistivity. Low-oxygen-content ITO appears dark in color with low visible light transparency, whereas ITO becomes more resistive with low oxygen vacancy density. The oxygen content of the ITO film is usually adjusted via oxygen partial pressure control during the vacuum deposition process or during post-annealing [7,9,12,16,18,19,23].

Low-pressure plasmas have been extensively used in semiconductor manufacturing. However, they require vacuum systems that are expensive and require maintenance. Furthermore, the substrate size is limited by the dimensions of vacuum chamber. Atmospheric pressure plasma jets (APPJs) overcome these disadvantages of vacuum operations. Recent jet designs have successfully prevented arcing and improved uniformity, leading to the rapid development of APPJ technology in various applications [24]. APPJs have been applied in many fields such as biomaterial sterilization and treatment [25,26], inactivation of bacteria [27,28], surface modification [29–31], thin-film deposition [32–35], rapid annealing of

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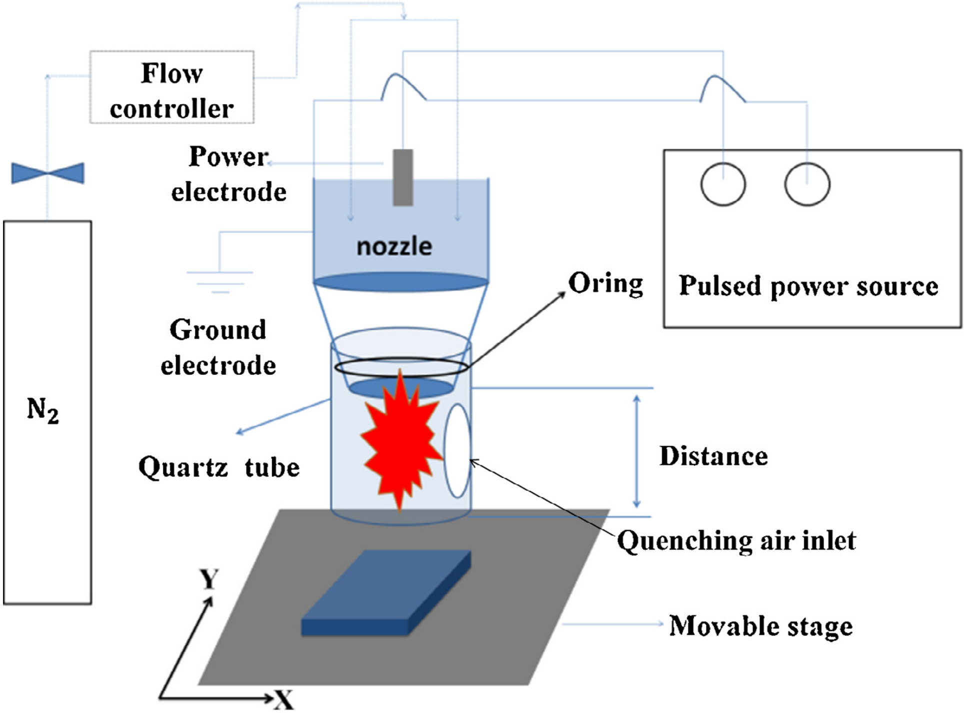

Fig. 1. Schematic diagram of APPJ apparatus.

MgZnO/ZnO heterostructure [36], ITO glass cleaning [8,37], and rapid sintering of nanoporous TiO_2 [38]. With regard to applications of atmospheric pressure plasmas to ITO thin film processes, Chiang et al. investigated the effects of oxygen addition and treatment distance on surface cleaning of ITO glass using APPJs [37]. Both metastable N_2 and ozone photo-induced dissociation were important in cleaning ITO glass [37]. Homola et al. used atmospheric pressure diffuse plasma for ITO cleaning [8]. Treatment for as less as 1 s was shown to significantly reduce the water contact angle. Detailed X-ray photoelectron spectroscopy analysis was performed on the plasma-cleaned ITO surface [8]. In our previous studies, we have demonstrated that APPJs can be used for rapid annealing (30 s) on ZnO for MgZnO/ZnO heterostructures [36] and for rapid sintering (60 s) of nanoporous TiO_2 photoanodes for dye-sensitized solar cells [38]; the device performances were comparable to those of devices fabricated by conventional thermal processes that required around 15–30 min. This ultrafast process capability of N_2 APPJs was attributed to the synergistic effect of the temperature and plasma reactivity. N_2 APPJ were highly active owing to the presence of excited nitrogen molecules that possessed energies >6 eV above the ground state for each molecule. The molecules underwent transitions of 1st positive $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ and 2nd positive $C^3\Pi_u \rightarrow B^3\Pi_g$ to release energy upon the plasma jetting process [37,39]. These energetic N_2 molecules in the plasma jets provided extra energy that assisted the processes of ZnO annealing and nanoporous TiO_2 sintering [36,38].

In this study, we further demonstrate that APPJs can also be used for rapid annealing on oxygen-deficient ITO thin films. The transmittance (at a wavelength of 550 nm) of 100-nm-thick ITO thin film on glass substrate increases to 87% from 7.2% for an as-deposited film after merely 90 s of APPJ treatment. We further study the influence of ambient-air-quenching on APPJ-annealed oxygen-deficient ITO thin films. Because the ITO annealing process is highly sensitive to O_2, the introduction of ambient air to the plasma jet significantly influences the ITO conversion process. With air-quenching, the temperature of the N_2 plasma jet reduces from 580 to 385 °C; however, the reaction rate increases despite the lower processing temperature. The results indicate that APPJs can be used for rapid thermal annealing on ITO thin films. This air-quenching APPJ technique can also be applied to processes in which oxygen is required in the reaction or lower reaction temperature is necessary.

2. Experimental details

100-nm-thick ITO (99.99%, In_2O_3:SnO_2 = 90:10 wt%) thin films were deposited on glass substrates (Corning Eagle 2000) by e-beam evaporation without any intentional heating. Prior to deposition, the substrates were cleaned by Piranha solution (H_2SO_4:H_2O_2 = 3:1) for 15 min, following which they were rinsed with DI water. The ITO film was then annealed by N_2 APPJ for 15, 30, 45, 60, and 90 s. To control the isolation of ambient air, a 2-cm-long quartz tube with/without side holes was installed downstream of the APPJ, as shown in Fig. 1. The APPJ system is described in detail in a previous study [33]. The APPJ system was operated with

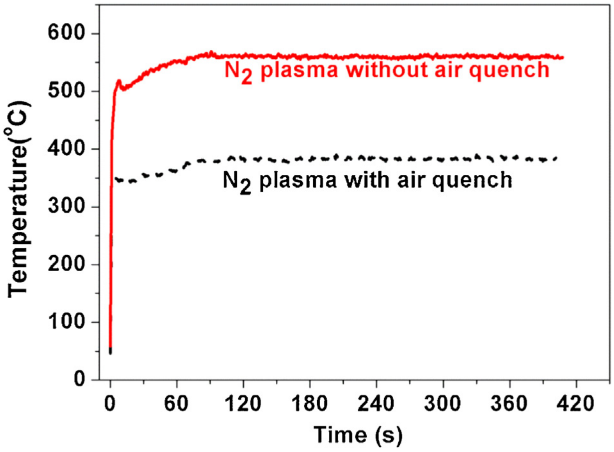

Fig. 2. Evolution of substrate surface temperature during APPJ treatment process.