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Excimer laser sintering of indium tin oxide nanoparticles for fabricating thin films of variable thickness on flexible substrates

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ABSTRACT

Technology to fabricate electrically-conducting, transparent thin-film patterns on flexible substrates has possible applications in flexible electronics. In this work, a pulsed-laser sintering process applicable to indium tin oxide (ITO) thin-film fabrication on a substrate without thermal damage to the substrate was developed. A nanosecond pulsed laser was used to minimize thermal penetration into the substrate and to control the thickness of the sintered layer. ITO nanoparticles (NPs) of ~20 nm diameter were used to lower the process temperature by exploiting their low melting point. ITO thin film patterns were fabricated by first spin coating the NPs onto a surface, then sintering them using a KrF excimer laser. The sintered films were characterized using field emission scanning electron microscopy. The electrical resistivity and transparency of the film were measured by varying the process parameters. A single laser pulse could generate the polycrystalline structure (average grain size ~200 nm), reducing the electrical resistivity of the film by a factor of ~1000. The sintering process led to a minimum resistivity of $1.1 \times 10^{-4}\ \Omega \cdot m$ without losing the transparency of the film. The thickness of the sintered layer could be varied up to 150 nm by adjusting the laser fluence. Because the estimated thermal penetration depth in the ITO film was less than 200 nm, no thermal damage was observed in the substrate. This work suggests that the proposed process, combined with various particle deposition methods, can be an effective tool to form thin-film ITO patterns on flexible substrates.

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1. Introduction

Electrically-conducting transparent materials are used in various applications including flexible electronics, photovoltaics and nano-electronic devices, so effective methods to fabricate their thin-film patterns and coatings are important goals in technical and industrial applications. Recent research has developed low-temperature thin-film fabrication processes to form transparent conducting films on flexible substrates [1–4]. Indium tin oxide (ITO) is one of the most widely used materials [5–7]. There are several different methods to synthesize ITO thin films [8,9], among which sputtering is most popular. Recently, other processes that are more cost-effective and flexible than sputtering were proposed to form ITO thin films. One of the alternative processes is based on ink-jet printing [10–12]. The ink-jet printing method uses well-suspended ITO nanoparticles (NPs) in a colloidal solution; the process is relatively flexible, cost-effective and does not entail high-temperatures. However, in many practical applications, the ITO patterns formed by the various deposition methods do not satisfy the minimum required of electrical resistivity, so the patterns require post-treatment. The post-treatment, often termed as "annealing" in a broader meaning, is classified into two processes: (1) annealing (in a narrow sense) to convert the amorphous structure in a solid film into a polycrystalline structure [13,14] and (2) sintering to form solid thin films from powders [15]. Thermal annealing with a furnace or a hot plate is needed to enhance the electrical conductivity by recrystallizing the film [16,17]. Thermal sintering is most widely used in fabrication of bulk ITO objects [18–20]. During thermal sintering, necking occurs among particles and fused particles form crystallized grains. As high temperature is required to induce crystallization during thermal annealing or sintering, these processes cannot be applied to flexible substrates because they cannot withstand the thermal-treatment temperature. The maximum allowable temperature lies in the range of 60–190 °C for typical polymer substrates [21–23].

Laser treatment is considered as a promising alternative to thermal treatment, owing to advantages including capability of selective treatment, localized thermal effect, and fine spatial resolution. Laser annealing was first introduced in 1970s for applications in semiconductor thin films [24–26] and metal alloys [27]. Both continuous-wave lasers and pulsed lasers have been used to increase the conductivity and other properties of thin films by increasing crystallinity. Since the 1980s, laser sintering has been applied to manufacturing processes using various materials, including metals, polymers, and oxides [28]. Bieri et al. [29] introduced a laser sintering using 2–5 nm gold particles to fabricate thin-film Au patterns of width 20 μm. Recently, laser annealing/sintering processes have been developed and analyzed for

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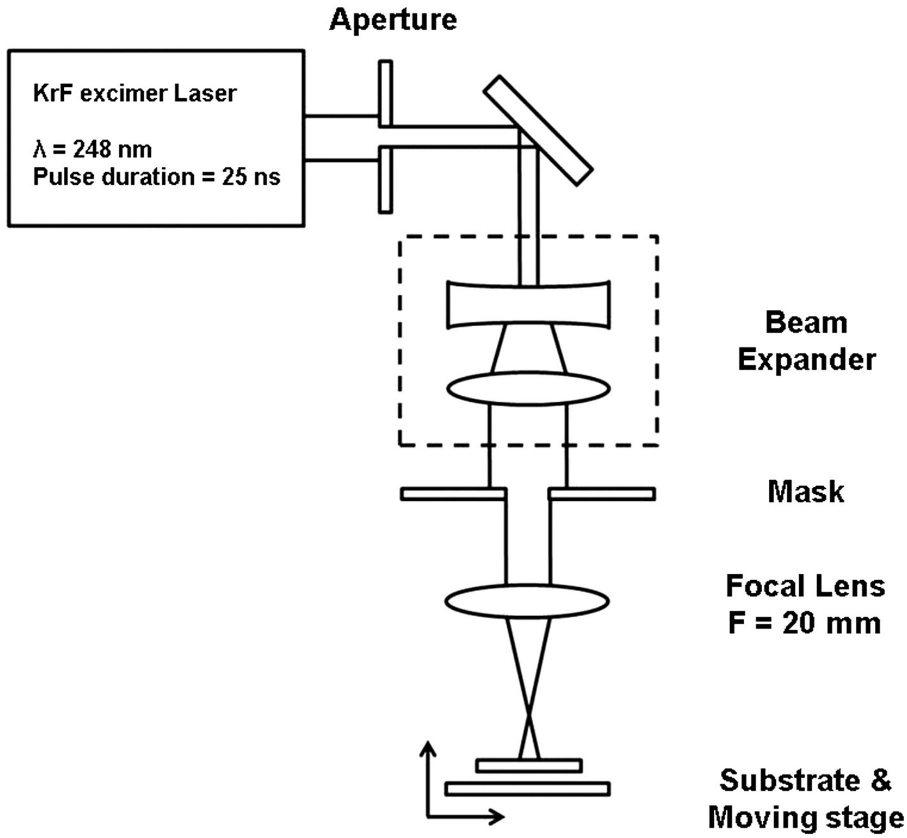

Fig. 1. Schematic diagram of experimental setup.

ITO, zinc oxide, and copper indium gallium selenide thin films [30–33]. In those processes, excimer lasers are employed most frequently because they produce ultraviolet wavelengths that are strongly absorbed by transparent films.

As an alternative to the conventional thin-film fabrication process such as sputtering and chemical vapor deposition, laser sintering processes that use a wet coating of NPs have been proposed [15,34]. In these processes, NPs are first deposited by various methods; subsequent laser sintering generates polycrystalline thin films. A doctor blade method has been combined with a CO_2 laser to form ITO films of 3-μm thickness and surface resistance of 400 Ω/□ on a flexible substrate [34]; the process includes a thermal-annealing step at 200 °C to increase the crystallinity. Pulsed (0.2–20 ms) Nd:YAG laser irradiation has been used to increase the crystallinity of ITO thin films, deposited by spin coating [15]; by combining thermal annealing process at 350 °C and the Nd:YAG laser treatment the methods produced films that were 800 nm-thick with a surface resistance of 640 Ω/□ and an average grain size of 25–45 nm.

The main objective of this work is to develop a nanosecond pulsed laser sintering process combined with a spin coating process to form ITO thin films of high conductivity on flexible substrates without elevating the substrate temperature. ITO NPs were deposited by spin coating a suspension and a KrF excimer laser was employed to sinter the particles. Nanosecond laser pulses were used to avoid thermal damage to the substrate by reducing the thermal-penetration depth. Also, to exploit the size effect, i.e., reduced melting temperature [35,36], ITO NPs of diameter ~20 nm were used in the process. The crystal and electrical properties of the sintered film were analyzed by varying the process conditions. The thermodynamic behavior of the ITO particles was analyzed by differential scanning calorimetry (DSC) before the main experiment. The surface topography and the grain structure in the ITO thin film were characterized using field emission-scanning electron microscopy (FE-SEM). By analyzing cross sectional images using SEM, the thickness of the sintered layer was measured for different laser fluences *F*. The electrical conductivity and transparency of the ITO film were measured and compared with the results of structural analysis to obtain an optimal process condition to maximize the film conductivity while maintaining its transparency.

2. Experiment

ITO NPs (nominal diameter <50 nm, nominal purity 99.9%) were purchased from Aldrich and mixed with ethanol to prepare a NP suspension (ink) that consisted of 10% ITO by weight. The mean diameter of the NPs measured from the SEM images before laser

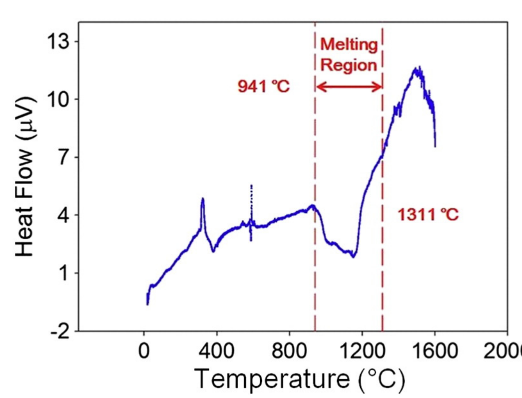

Fig. 2. DSC results of the ITO nanoparticles. The dashed lines indicate beginning and end of the melting process.

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