Excimer laser processing of inkjet printed and sputter deposited transparent conducting SnO_2:Sb for flexible electronics

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Abstract

The feasibility of low temperature fabrication of transparent electrode elements from thin films of Antimony doped Tin Oxide (SnO2:Sb, ATO) has been investigated via inkjet printing, rf magnetron sputtering and post deposition excimer laser processing. Laser processing of thin films on both glass and plastic substrates was performed using a Lambda Physik 305i excimer laser, with fluences in the range 20mJcm^{-2} – 100mJcm^{-2} reducing sheet resistance from as-deposited values by up to 3 orders of magnitude. This is consistent with TEM analysis of the films that shows a densification of the upper 200 nm of laser processed regions.

Keywords

Transparent conducting oxide, inkjet printing, thin film, laser processing, excimer laser, displays, flexible substrates, conductivity.

1. Introduction

In the field of plastic electronics and displays, there is a need to develop materials and processes that are compatible with large scale, low cost, production techniques. For plastic electronics, and particularly flexible displays, one of the major challenges that this presents is the need to produce optimised transparent electrodes and light emitting layers on low temperature substrates. In terms of available transparent electrode materials, indium doped tin oxide (ITO) remains the material of choice for most display and lighting applications, due to its excellent optical transparency and conductivity. However, while the deposition of ITO by sputtering is a well developed process, it is one that poses several problems in the current and future requirements for this sector. A critical issue with commercial ITO deposition is the materials waste generated by conventional sputtering - where up to 65% of a target is unused. With indium demand outstripping supply, the need for a viable alternative material is consequently highlighted, and ideally one that can address the materials wastage issues associated with conventional deposition and subtractive patterning techniques.

The work presented here is the result of a collaborative investigation into the use of an alternative to indium tin oxide for a study of inkjet printing and laser processing. Antimony doped tin oxide, ATO (SnO_2:Sb) has been selected for the study, due to the feasibility of fabricating nanoparticulate source material suitable for both suspension in an aqueous solution for inkjet printing, and pressing into solid sputtering targets suitable for use in sputter deposition. The investigation has been specifically concerned with the study of low temperature deposition and patterning techniques for the production of transparent conducting layers of ATO. The processes investigated are inkjet printing and low temperature rf magnetron sputter deposition followed by excimer laser processing to enhance conductivity using processes that are compatible with flexible substrates.

2. Experimental Details

The ATO source material was supplied by Keeling & Walker Ltd as a nano-particulate aqueous dispersion with an agglomerate size of less than 100nm, which is sufficient to impart transparency. The aqueous solution was formulated for inkjet printing by Patterning Technologies Ltd. The formulation has been designed to provide stable jetting with good wetting characteristics on a variety of substrates and with minimal Marangoni effect. In all cases, unless otherwise stated, the ATO film was created with two wet passes in the inkjet printer, creating a single 90mm x 70mm layer.

For comparison with sputter deposition, the ATO powder was pressed into a 5mm thick 70mm diameter circular target, using a hydraulic target press operating at room temperature. Sputter deposition was performed in a custom built rf-magnetron sputtering system described previously [1] with the substrate facing down, and with no substrate heating. During the deposition process, the maximum temperature attained by the substrate is 80ºC. A range of printed and sputtered layers were deposited for the investigation onto substrates consisting of borosilicate glass and polyester flexible substrates (Cronar).

The effect of thermal and excimer laser annealing of the deposited films was investigated using atmospheric thermal annealing in a furnace, and excimer laser via krF 248nm irradiation. The resultant films were analysed for thickness, sheet resistance, transparency, crystallinity and microstructure. Sheet resistance (Rs) measurements were carried out using a linear four-point probe. The transmission spectrum of the sample from 400 – 1000nm was measured using a Filmetrics F20 thin film analyser and thickness measurements were taken using a Veeco optical profilometer (NT1100). Laser processing was carried out with a LPX305i KrF Excimer laser at fluences < 100mJcm-2.

The laser processing system used for both ablation and post print processing is shown in Figure 1. This is a configuration also used for laser processing work on thin film phosphors for displays [2, 3] and has been demonstrated to facilitate large area processing of display substrates via a sample step and repeat process [4]. Lower fluences (appropriate for this work) are obtained by attenuation of the raw beam prior to homogenation using the Fresnel reflections from fused silica plates (Hoya Plates) as shown in Fig 1. Beam energy during irradiation is monitored with an in-situ energy meter, as shown in Fig. 1.

The short pulse width of the laser beam (20ns) coupled with the high absorption coefficient of ATO at 248nm (1.5 x 10^5cm^{-1}) is expected to confine the energy dissipation due to the incident beam to the upper 150-200nm of the film [5],with minimal effect on the substrate.

3. Results and Discussion

Initial results from a study of the effect of laser processing on inkjet printed films of ATO on glass were presented previously [6]. A variety of laser irradiation parameters were investigated to study the effect of varying fluence and number of pulses incident on the samples. Irradiation was at a repetition rate of 4Hz to avoid cumulative thermal effects [7]. The samples were processed in air at atmospheric pressure.

In all cases, laser processing of these printed ATO films resulted in reductions in sheet resistance from the as deposited figure of 4-5MOhm/sq, with optimum values obtained at 100 pulses of 40 – 70mJcm-2 . For example, values of Rs = 300kOhm/sq were obtained with 100pulses at 70mJcm-2 . The corresponding optical transmission of these samples decreased from 94% to 90% at 550nm following laser processing. Higher fluences, or a higher number of pulses resulted in an increase in Rs and an decrease in optical transmission, concomitant with the observation of ablation and roughening of the film.

In order to provide reference samples for comparison with the low temperature laser processing, thermal annealing of printed ATO on glass substrates was carried out in a Carbolite CWF 12/5 furnace ramping the sample from room temperature to 440ºC over 30mins and then slowly cooling back to room temperature over 90 minutes, resulting in a decrease in sheet resistance to typical values of 1-3kOhm/sq. Optical transparency of the printed films was very good with 94% transmission at 550nm, dropping to 92% after thermal annealing, which is in agreement with results reported for sol gel films [8,9].

For the new work presented here, further batches of samples were prepared to investigate the effect of combining thermal and laser processing, and to examine the feasibility of fabricating transparent conductive films on low temperature substrates. Laser processing was then undertaken on films that had previously been thermally annealed to 400ºC for 1 hour. The results, presented in Fig 2, show further reduction in Rs from the post thermal anneal value of 3.6kOhm/sq to a final figure of 1kOhm/sq. These films were more mechanically stable than films that had not been thermally annealed prior to laser processing – indicating an enhanced bonding with the substrate. This combined process also produced the most conductive films to-date from the inkjet printed films. A single sample was irradiated across the full sample area and Rs was measured before and after processing at 25 locations across the printed area. Uniformity of Rs was very good both before and after laser processing with average Rs = 831 Ohm/sq, σ (standard deviation) = 183 Ohm/Sq, after thermal annealing, and average Rs = 489 Ohm/sq, σ = 42Ohm/Sq after subsequent laser processing with 100 pulses at 70mJcm-2.

Samples that were thermally annealed following laser processing did not exhibit such an overall improvement, but attained values comparable to the results produced by thermal annealing alone, following initial reductions due to laser processing consistent with the results of the initial study reported in reference 5.

From XRD and scanning electron microscopy studies of these films, it is evident that there is no significant increases in crystallinity, or grain size, observed for either the thermally annealed or the majority of the laser processed films, There is, however, some limited evidence that higher fluence and/or pulse number of laser irradiations leads to enhanced crystalline ordering as indicated by a slight increase in XRD peak height, but this is inconclusive and will be the subject of a separate study using glancing XRD analysis.

Surface roughness measurements give a more direct indication of a sintering, or densification effect that correlates to improved conductivity. Ra values determined by optical profilometry and stylus profilometry show the as-deposited surface roughness varying between 20-35nm across the samples, with typical post-processed Ra values (both thermal and laser processed) at between 3-10nm. This indicates that the increase in conductivity is probably linked to the reduction of energy barriers at grain boundaries, possibly in combination with the modification of charge carrier densities due to the formation of enhanced donor sites via thermal processes. The low surface roughness measurements are also of interest for device fabrication – particularly display devices. Indeed, ATO deposited by sol-gel processes has recently been used to improve the surface roughness of ITO films for use in display applications, since with ITO films, localised spikes are an issue [10].

The ultimate aim of this work is to identify processes that could be used to fabricate transparent conductive layers by inkjet printing onto flexible substrates, rather than glass. This consequently requires a low temperature process that is compatible with the substrates used. Polyester substrates are of interest for use in flexible display and electronics manufacture, but require processing temperatures to be maintained at temperatures typically less than 150ºC - 200ºC. The potential for excimer laser processing of inkjet printed ATO on polyester is thus of interest for the feasibility of transparent conductive layers being patterned via an additive rather than subtractive process, and also for the benefit of low temperature processing. For this phase of the investigation, a range of ATO layers and patterns were printed onto polyester (Cronar) substrates at room temperature, with no post deposition thermal processing. Printing was undertaken using the same two pass process as performed previously on the glass substrates. Measured sheet resistance values across printed 3cm x 3cm samples give an average Rs of 2.7MOhm/sq with σ = 0.324MOhm/sq.

Laser processing of these films was performed at 20mJ/cm-2 and 100mJcm-2 for a range of total pulse number irradiations, with the results showing good reduction of Rs as a function of processing parameters, as shown in Fig 3, with optimum conditions resulting in printed films with an optical transparency of 89% at 550nm, and Rs = 200kOhm/sq.. In all cases, irradiation at 20mJcm-2 did not produce any visible damage to the substrates or film. At 100mJcm-2, some roughening of the film surface was observed, but there was no damage to the substrate. Hence, while further investigation and refinement is necessary to reduce Rs further, these results clearly demonstrate the feasibility of using excimer laser processing, or an equivalent flash annealing process, combined with inkjet printing for the fabrication of transparent conducting electrodes onto flexible substrates.

Fig 4 shows the result of high resolution transmission electron microscope analysis of inkjet printed ATO films on polyester substrates before and after laser processing. The nanoparticulate structure of the ATO film is clearly visible in the micrographs, confirming the primary particle size to be ~ 10nm. Following laser processing at 70mJcm-2 1000 pulses, Fig. 4b shows a clear region of densification at the surface of the film that is consistent with the expected penetration depth of the 248nm irradiation – to ~ 200nm. This physical transformation of the upper surface correlates to the improvement in conductivity observed, and indicates that there is a probable reduction in electron barrier height between grains as a result of defect and void removal via this densification. Similar results were observed by SEM analysis of samples on glass substrates –

indicating a densification at the film surface following laser processing, but the results shown in Fig 4 are more conclusive, due to the ease of preparing TEM samples from the films on polyester. Further analysis is underway, and there is evidently an opportunity to examine the use of longer wavelength irradiation in combination with the 248nm process, in an attempt to increase the conductivity by a more thorough in-depth densification of the ATO.

Finally, as a comparison to the inkjet printed thin films, a series of samples were deposited onto borosilicate glass substrates using a custom built rf-magnetron thin film deposition system [1]. Films were deposited using the following parameters: Ar:O2. 10% O2 sputtering gas maintained at 5mTorr pressure, with 100W rf power applied to the 70mm diameter pressed powder sputtering target, mounted onto a Kurt Lesker Torus electrode. The substrate was mounted onto a heated rotating substrate holder facing down, with the electrode head 15 cm from the substrate at an angle 30° to the normal. For this work, the heater was not used, but monitoring of the substrate temperature during deposition indicates that the maximum temperature attained due to the plasma heating effect is 80°C. Films were deposited to a thickness of 350 – 400nm. The resultant films were conductive with sheet resistances of the order of 3–10kOhm/sq, and optical transparency at 550nm of 88%. Hence, in comparison to the printed films, the as-deposited conductivity is enhanced, but transparency is reduced. SEM observation reveals the expected columnar polycrystalline structure of sputtered films.

Post deposition laser processing was performed as with the printed films. In all cases, the use of 248nm irradiation resulted in an improvement in conductivity, with the best improvements at fluences and pulse number similar to the optimum demonstrated for the printed films. A typical result is shown in Figure 5 where the initial sheet resistance of 10.7kOhm/sq ± 0.2kOhm/sq is reduced to 1.7kOhm/sq ± 0.02kOhm/sq following 100 pulses at 50mJcm-2. Unlike with the printed films, initial electron microscopy analysis does not indicate a dramatic change in the film density at the upper surface, but it is suspected that a similar process of defect removal is occurring to reduce energy barriers at grain boundaries, and this is currently being investigated further.

4. Conclusions

A study of potential low temperature techniques for use in the fabrication of transparent conducting oxides on flexible substrates has been undertaken. Inkjet printing of ATO films has been demonstrated as a viable technique for the additive patterning of transparent conducting layers onto glass and polyester substrates. Thermal annealing of these films at 400ºC results in useful conductivities in the range of ≤ 1KOhm/Sq, which is applicable to device work on glass substrates, and which indeed has been used as a basis for the fabrication of inorganic electroluminescent display demonstrators [11]. The use of thermal annealing, however, precludes use of low temperature substrates, but laser processing with 248nm KrF irradiation has been demonstrated to be a viable method for reducing the as-printed sheet resistance by an order of magnitude. This improvement is consistent with an observed densification of the upper 200nm of the ATO films following the irradiation treatment. The reduced Rs values are due to a low resistance upper layer in parallel with the higher resistance lower section of the film. It is thus expected that this effect can be exploited by the use of variable wavelength irradiation in an attempt to process the full depth of the film for higher conductivities. In addition, the fluence levels that have been demonstrated to be optimum for this work are < 100mJcm-2, which implies that alternative UV based pulsed annealing techniques could be suitable for this application. Finally, the use of Excimer laser processing to realise conductive transparent films deposited by low temperature rf-magnetron sputter deposition has been demonstrated, based on sputter deposition of the ATO nanoparticulate powder that has been used for the inkjet printing trials. Optimum laser processing parameters are similar to those appropriate for the printed films.

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Figure Captions

Fig.1. Schematic diagram to show the optical system used for excimer laser processing of ATO thin films.

Fig. 2. Sheet resistance, Rs, as a function of laser processing irradiation pulse number, for printed ATO thin films on glass substrates that have been laser processed at 60mJcm^{-2} following a thermal anneal to 400ºC for 1 hour. The data point at 0 pulses represents the film following thermal annealing.

Fig 3. Sheet resistance, Rs, as a function of laser processing irradiation pulse number, for printed ATO thin films on polyester substrates following laser processing at 20mJcm^{-2}. The data point at 0 pulses represents the as-deposited film.

Fig 4. Transmission electron micrographs showing cross sectional images of 1 μm thick ATO thin films inkjet printed onto polyester sunstrates: (a) as-deposited film illustrating primary nanoparticulate structure of the film, (b) identical sample following laser processing at 70mJcm^{-2}, 1000 pulses, indicating enhanced densification of upper 200nm.

Fig 5. Sheet resistance, Rs, as a function of laser processing irradiation pulse number, for rf-sputtered ATO thin films on glass substrates, following laser processing at 80mJcm^{-2}. The data point at 0 pulses represents the as-deposited film.

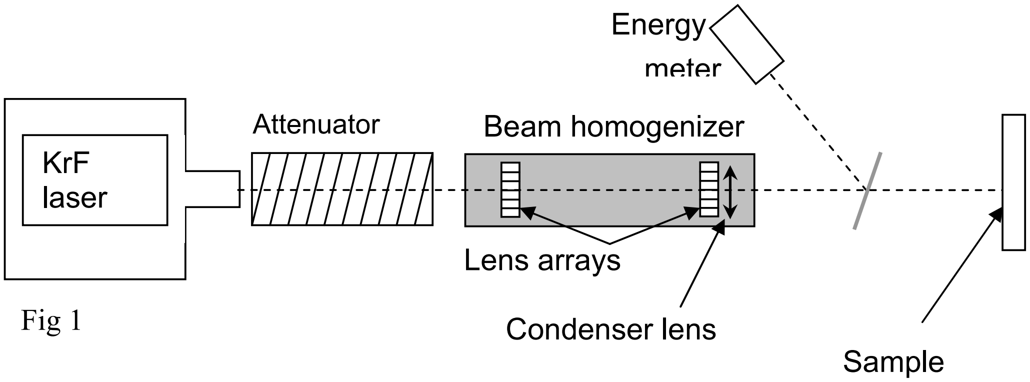

Fig 1

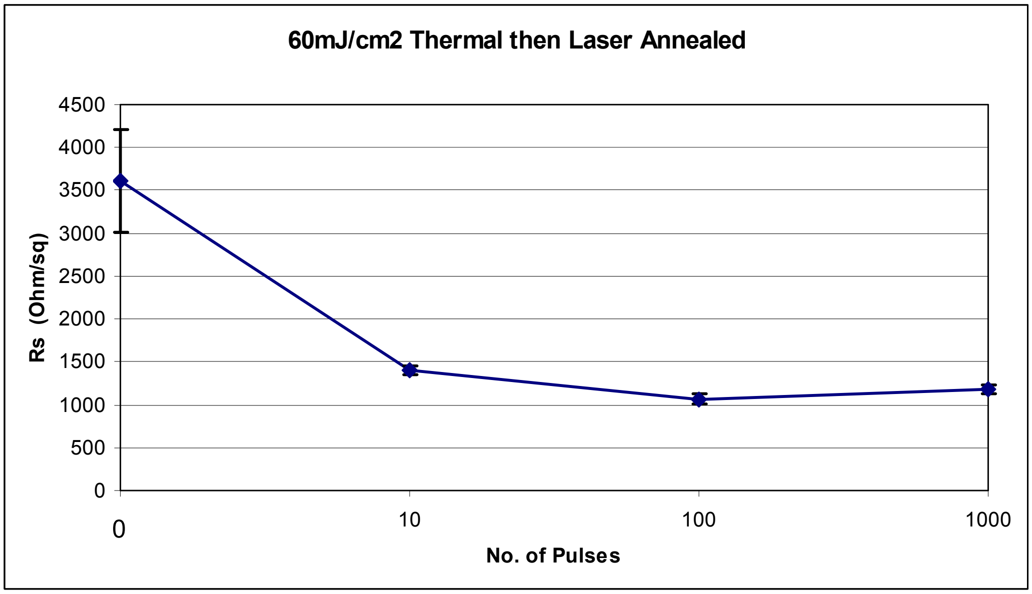

Fig 2

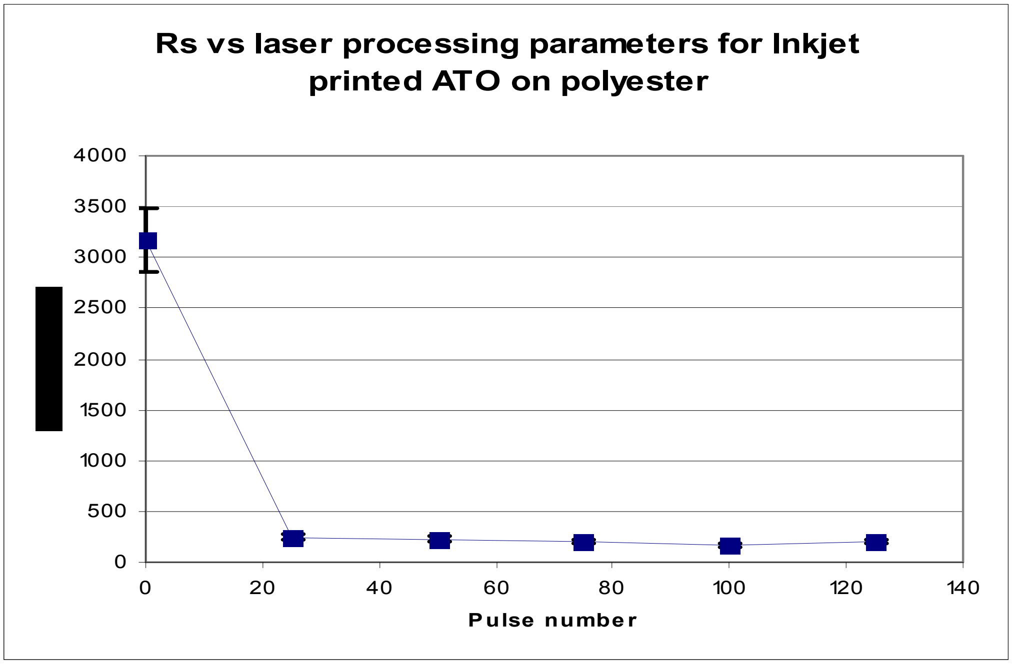

Fig 3

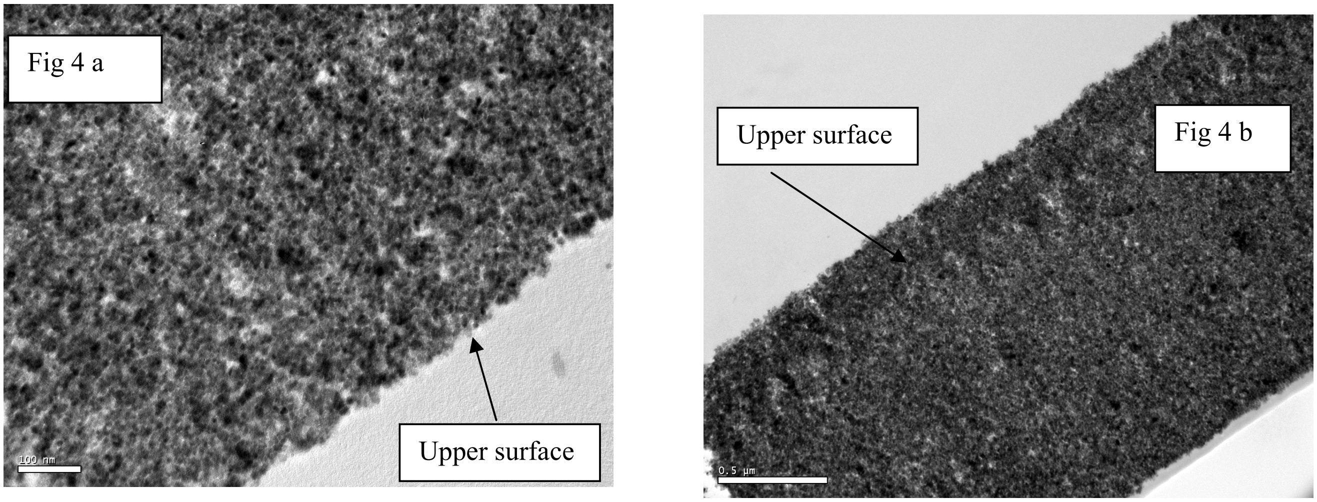
Fig 4 a
Upper surface
100 nm
Upper surface
Fig 4 b
0.5 µm

Fig 4

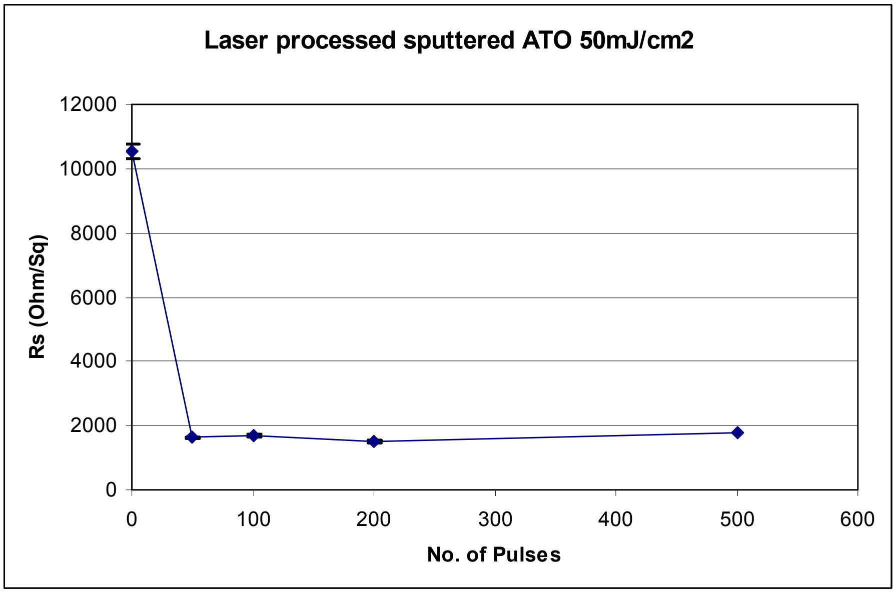
Laser processed sputtered ATO 50mJ/cm2
Rs (Ohm/Sq)
12000
10000
8000
6000
4000
2000
0
0
100
200
300
400
500
600
No. of Pulses

Fig 5.