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Rapid photonic curing of solution-processed In_2O_3 layers on flexible substrates

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Graphical Abstract

Highlights:

- In_2O_3 thin films have been fabricated using a sol-gel route.
- Polyimide and polyethylene naphthalene were used as flexible substrates.
- In_2O_3 thin films were cured using photonic processing.
- Photonic curing achieves excellent precursor conversion rates and very low roughness.
- Valence band measurements reflect high film quality.

Abstract (200 words)

In_2O_3 is one of the most important semiconducting metal oxides primarily because of its wide band gap, high electron mobility and processing versatility. To this end, high-quality thin films of In_2O_3 can be prepared using scalable and inexpensive solution-based deposition methods, hence making it attractive for application in a number of emerging electronic applications. However, traditional solution processing often requires high temperature and lengthy annealing steps, making it impossible to use in combination with temperature-sensitive plastic substrates, which would be desired for numerous emerging flexible device applications. Here, rapid photonic curing of In_2O_3 layers is explored as an alternative to thermal annealing. Oxide thin films are successfully prepared on a range of substrates, including glass, polyimide, and polyethylene naphthalate. The effect of substrate and post-processing treatment on the morphology, surface chemistry, and electronic properties is investigated by atomic force microscopy and X-ray photoelectron spectroscopy. Systematic trends are identified, particularly in the degree of conversion of the precursor and its influence on the electronic structure.

1. Introduction

Post-transition metal oxide thin films have found wide application in electronic and optical applications due to their excellent charge carrier mobility and optical transparency. In particular, In_2O_3 and its combinations with other post-transition metals, including Sn, Zn, Ga, and Tl, have received a great deal of attention.[1–5] Thin films of these materials have been prepared by a wide range of methods including sputtering, atomic-layer deposition, electrodeposition, combustion, and solution-based methods.[6–12] Metal oxides lend themselves to solution processing, as a range of relatively simple precursors can be prepared, exploiting the advantages of these deposition methods, including low cost and large scale coating.[13–15] However, the vast majority of solution methods rely on thermal annealing at temperatures typically above 200 °C and for durations of an hour and more to transform the metal precursors into the desired semiconductor thin films. This post-deposition annealing step is necessary to initiate the cleavage of ligands bound to the dissolved metal ions and the formation/reorganisation of an amorphous M–O–M network. The high temperature required to achieve good quality oxide thin films has prevented the implementation of this technique for polymer substrates, hence limiting its potential application in flexible electronic device fabrication.

Photonic curing has been investigated as an alternative to traditional thermal annealing for metal oxide thin film fabrication.[4,16–22] This technique utilises lasers or flash lamps, which generate high energy pulses of light, which are then absorbed by a thin metallisation layer deposited onto the substrate underneath the oxide layer. This metallic layer converts absorbed photons into lattice phonons, and hence thermal energy, causing a short burst of heat atop the substrate, initiating precursor conversion to the thermally stable metal oxide. The extremely short nature of these pulses and the process as-a-whole, significantly reduces the thermal load on the substrate, whilst also reducing overall fabrication time. Several publications have already shown promising results using this technology, with transistor performances on glass and silicon substrates reaching values comparable to devices annealed thermally.[21] There has however been little investigation into use of the technique on flexible plastic substrates, motivating further research in this area. There is strong motivation for flexible devices fabricated in this way, as it opens the way for alternative manufacturing possibilities such as roll-to-roll fabrication, challenging conventional wafer-based technologies with lower cost and high throughput. Furthermore, the bendability and foldability of these thin and light-weight materials allows to break away from form factor constraints which might pave the way for completely novel devices and applications in consumer electronics.

The photonic-induced conversion process exploited for photonic curing is indirect in nature. Incident photons from the short light burst are absorbed by the underlying metallisation layer, which subsequently rises in temperature, inducing conversion of the precursor layer above.[23,24] The degree of the temperature evolution inside the metal depends on several material related properties such as the optical absorption within the wide spectrum range of the xenon flash pulse, the thermal conductivity, the specific heat capacity, the enthalpy of fusion or vaporization. Taking all these parameters into account the expected maximum temperature on a metal surface for a given flash energy can differ significantly from metal to metal. In a recent study by the authors using numerical calculations, it was found that metals such as Pt, Ti, or Cr develop higher temperatures during the xenon flash treatment than Al or Au due to their more advantageous material properties, making them

more suitable candidates for the required metallisation layer in the photonic curing process.[21] Tests using each of these materials yielded optimal results when using a chromium base layer, which was then made the standard for further tests.

Here, we describe the deposition of high-quality In_2O_3 layers from $\text{In}(\text{NO}_3)_3$ precursors on three different substrates, including borosilicate glass, polyimide (PI), and polyethylene naphthalate (PEN), and study their surface morphology and electronic properties. Thin films prepared by a classic thermal anneal are compared to In_2O_3 layers treated with different numbers of optical flashes with a duration of 1.6 ms. The surface of the resulting thin films is characterised using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). This enables the exploration of the influence of the substrate and the post-processing steps on the morphology, surface chemistry, and electronic structure of this technologically important metal oxide semiconductor grown via photonic sintering in ambient air. The results presented here indicate the significant change in properties caused by this film and synthesis route modification, proving photonic curing's potential for flexible device fabrication.

2. Materials and Methods

An indium nitrate precursor solution was made by dissolving 60 mg mL^{-1} indium nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.99%, Sigma-Aldrich) in 2-methoxyethanol (99.8%, Sigma-Aldrich) under constant stirring at room temperature. Borosilicate glass, polyimide (PI), and heat-stabilized polyethylene naphthalate (PEN) substrates with thicknesses of 1.1 mm, 125 μm , and 125 μm , respectively, were ultrasonically cleaned in deionised water and 2-propanol for 10 min each, with an additional 10 min of acetone cleaning for glass samples. The PEN substrates were covered with an additional 4 μm buffer layer of polyimide (HD-PI 2555) which was spin coated at 500 rpm for 5 s, followed by 1500 rpm for 30 s, and annealed overnight at 200 °C on a hotplate in nitrogen. All substrates were sputtered with 60 nm of chromium and irradiated with UV-ozone for 15 min to remove organic residues, hence improving surface wetting. The spin-coating of the pre-prepared indium nitrate solution on the substrates was carried out at 4000 rpm for 30 s followed by 5 min of sample drying at 130 °C (herein referred to as the “bake” step) to remove unwanted solvent. This spin coating/baking process was repeated to deposit the desired thickness of indium on the substrate surface, ready for further processing.

Four separate processing routes were explored for each substrate along with an untreated control sample. These tests were designed to compare traditional annealing techniques to photonic curing carried out using a Speedotron xenon flash lamp system (105 CC light unit, 4803CX LV power supply). To achieve this, three of the prepared samples were flashed 10, 20 and 40 times at energies per flash pulse (provided by the manufacturer) of 4.80 kJ, 4.80 kJ and 4.38 kJ, for glass, PI and PEN/PI, respectively. The flashes were 1.6 ms in length and pulsed at a rate of 0.125 Hz onto the sample stage 1 cm from the lamp; this distance was increased to 15 cm for PEN/PI samples to prevent cracking of the metallization layer. Although, non-uniformities of the light intensity across the sample were not considered, the treated substrate was always mounted using identical geometry and position, hence minimising intensity fluctuations. Thermally treated samples were annealed using a precision hotplate for one hour at 250 °C for glass and PI substrates and at 200 °C for PEN/PI samples due to the substrate's lower glass transition temperature. The surface morphology of the samples was investigated using an Agilent 5500 AFM in intermittent contact mode. XPS

spectra of the metal oxide films after different processing steps were collected on a Thermo Scientific K-Alpha+ X-ray photoelectron spectrometer operating at 2×10^{-9} mbar base pressure. The system incorporates a monochromated, microfocused Al K_{α} X-ray source ($h\nu = 1486.6$ eV) and a 180° double focusing hemispherical analyser with a 2D detector. The X-ray source was operated at 6 mA emission current and 12 kV anode bias. Data was collected at 20 eV pass energy for core level and 15 eV pass energy for valence band spectra using an X-ray spot size of 400 μm . A flood gun was used to minimize sample charging. Data were aligned assuming the C 1s binding energy to be 284.8 eV. All produced data were analysed using the Avantage software package.

3. Results and Discussion

For the present study, three substrates, all coated with a Cr layer to aid photonic curing, were selected to prepare thin films of In_2O_3 , based on the initial exploration of film preparation. Borosilicate glass was chosen as the substrate for the reference samples based on it being a widely used, rigid, transparent substrate for opto-electronic applications. Polyimide (PI) was chosen as the first polymer substrate due to its comparatively high glass transition temperature (T_g), in the region of 380 to 410 $^\circ\text{C}$. This property makes it resilient to thermal expansion at the temperatures created by the flash-lamp, which cause complications such as cracking and film delamination. The films deposited on PI withstood high energy pulses without showing signs of cracking or delamination, allowing complete conversion to the oxide to take place. However, PI is far from an ideal flexible substrate due to its high cost and tinted nature, limiting its potential in optoelectronic devices. Alternatively, PEN would be a better substrate, due to its low cost, high optical transparency, and high melting/glass transition temperature, relative to other cost-effective polymeric substrates such as polyethylene terephthalate or polycarbonate. However, photonic curing treatment on PEN substrates showed significant directional surface cracking of the Cr metallization layer. Decreasing the energy of the flashes and increasing the lamp-to-substrate distance did reduce this cracking, although it was also found to inhibit full precursor conversion due to the resulting lower temperature. It can be concluded that this heavily directional cracking was due to the large difference in thermal expansion coefficient between the Cr layer and PEN. Above a polymer's glass transition temperature polymer chains begin to move freely over one another, this leads to a drastic increase in thermal expansion coefficient. [25,26] PEN has a glass transition temperature of as low as 120 $^\circ\text{C}$, which is well below the temperatures created at the surface of the Cr film. It is therefore unsurprising that directional cracking occurred as the PEN substrates will have expanded considerably once this temperature was exceeded, fracturing the Cr coating. Modification of the substrate was hence carried out to minimise these thermal stresses. This was achieved by the application of a 4 μm PI intermediate layer, which buffered the expansion of the underlying majority PEN substrate from the Cr layer above. Higher energy pulses could then be applied to the substrate allowing full precursor conversion without Cr cracking.

After careful selection of the three substrates and optimisation of the photonic curing parameters based on these initial macroscopic observations, In_2O_3 thin films could be manufactured without any cracking or delamination. Once this was achieved the surface morphology of the films was investigated using AFM. Figure 1 shows AFM images of the Cr and In_2O_3 films deposited on all substrates and after different processing steps. Figure 2

gives an overview of the resulting root mean square (RMS) roughness along with the height distribution for the films on each substrate material. The AFM results of the Cr layers have been included to indicate the substrate quality beneath the oxide thin film. As shown in Figure 2, the roughness of this Cr layer was found to be comparable on the two polymer substrates, whilst slightly higher on glass. This discrepancy however is not retained across further process steps and the roughness of all samples after the initial deposition and low temperature baking of the In_2O_3 films increased to a similar value. During the following annealing step, samples typically exhibited a decrease in surface roughness due to changes in morphology and M-O-M network formation. This trend was not however shown for the thermally annealed PEN/PI sample which was found to increase in roughness after the annealing step, as is shown in Figure 1 and 2 (a) and (d). This can be attributed to the fact that the thermal treatment is very close to the upper processing limit of the PEN substrate which might have an effect on the dimensional stability and thus also on the morphology. [27] Alternatively, photonic curing was shown to successfully reduce surface roughness in all samples, with 20 and 40 flashes showing even lower RMS roughness values than their thermally annealed counterparts. This flattening effect is also displayed in the height distribution diagrams of Figure 2, which show sharper peaks with less broadening and shifts of the height distributions towards lower values for all photonicallly cured In_2O_3 films compared to the baked and thermally treated films. A noticeably high roughness is found for the thermally annealed film on PEN/PI, which is higher than the as-deposited roughness. After 40 flashes all films showed a particularly low roughness of 0.7 nm or below. This is of particular importance for device applications, as high surface roughness values can have a detrimental effect on device performance.

In order to study the surface chemistry and electronic structure of the thin films, X-ray photoelectron spectroscopy (XPS) was used. The chemical conversion of the precursor material $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ to In_2O_3 can be represented by the following chemical reactions [28]:

As shown in Equations 1-3, thermal decomposition is accompanied by a reduction of the NO_3^- and OH^- content. The degree of this reduction can give important information about the quality of the resulting metal oxide films and their impurity levels. By using XPS the overall relative atomic % (rel. at.%) ratios could be extracted from the peak fits to the total areas of the In, O and N core levels for photonicallly and thermally annealed In_2O_3 on glass, PI and PEN/PI as presented in Figure 3. It can be seen that a reduction of the N content of the In_2O_3 sol-gel layers on all substrates was already achieved after 10 flashes, although this was less significant on PEN/PI. Here, an increase in the number of flashes decreased the N content to a comparable level of sol-gel films on glass and PI substrates, which in turn did not show any further reduction with increasing number of flashes. Nevertheless, small amounts of N are still present in all photonicallly treated substrates, even after 40 flashes, but the values are comparable to those found in thermally annealed samples. In addition, an almost stoichiometric composition of 2:3 of In to O is found on all substrates after 40 flashes which indicates the formation of In_2O_3 .

Figure 4 shows the In 3d and O 1s core levels of films deposited on the three substrates after the different processing steps. The In 3d core levels, particularly for the glass and PI substrates, show some slight changes in peak position and width. This is due to varying contributions from fully converted In_2O_3 as well as from unconverted $\text{In}(\text{NO}_3)_3$ and $\text{In}(\text{OH})_3$, which is formed after initial baking. This difference is more obvious in the O 1s core level as the different chemical environments can be distinguished clearly. In all cases, the O 1s core level is dominated by the In_2O_3 feature at 529.8 eV. The films deposited on glass and PI show that the initial bake does not convert all of the nitrate to hydroxide. A high binding energy (BE) feature at 532.3 eV can be assigned to nitrate environments still present in the films, following similar O 1s binding energies in other nitrates.[23–25] Independent of substrate, a large feature at 531.2 eV from unconverted $\text{In}(\text{OH})_3$ is found after the initial bake. After flashing, no contribution from nitrate is found throughout, and the presence of hydroxide is significantly reduced, in agreement with previous studies.[21,22] Table 1 summarises the ratios of the different O contributions for all samples, determined from peak fit analysis to the O 1s core level. Representative peak fits for the PI samples are shown in the Supplementary Information, Figure S1. The conversion after photonic curing is the same as after thermal annealing, with glass and PI samples giving comparable conversion rates, whilst the PEN/PI samples show lower conversion rates. This is due to the fact that in the PEN/PI case, the photonic curing was carried out with a lower energy and a larger lamp-to-substrate distance in order to avoid cracking of the Cr metallisation on the substrate. In this regard, further improvement of the buffer layer, by optimising the material system or film thickness, could allow higher flash energies to be used resulting in a better conversion rate of the sol-gel layers. The observations made from the core level spectra are further confirmed by the results from valence band measurements (see Figure 5). After the bake the glass and PI samples show a significant shift of the valence band edge away from the Fermi energy E_F , due to the influence of nitrate and hydroxide species. In addition, intense features around 10–12 eV are indicative of these species. After photonic curing and thermal annealing, the valence band shifts towards E_F , giving separations between the valence band maximum VB_{max} and E_F of around 2.5 eV (see Table 2 for a summary of all values). The position of VB_{max} was determined by linear fitting. The PEN/PI samples show a slightly different structure in the valence states compared to the other samples, due to the higher amount of hydroxyl groups remaining in the film.

4. Conclusions

This work presents the successful fabrication of In_2O_3 thin films deposited on three different substrates, including two flexible, thin polymers. The use of a buffer layer is shown to be successful in reducing strain on the metal layer allowing the use of polymers less thermally resistant compared to polyimide. Photonic curing is employed as an alternative to thermal annealing, giving excellent surface roughness and precursor conversion rates. Through XPS analysis, direct relationships between the surface chemistry and the electronic structure of the thin films are shown, which in turn can be correlated to the process conditions. The presented work clearly shows the relationship between surface morphology and chemistry and the photonic processing parameters crucial for the application of In_2O_3 in opto-electronic devices.

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Table 1. Relative contributions from different species to the O 1s core level derived from peak fit analysis in rel. at.%. For the bake sample the ratio given is $O_{In_2O_3}:O_{-OH}:O_{NO_3}$, whilst for all other samples the ratio given is $O_{In_2O_3}:O_{-OH}$ as no NO_3 contribution could be detected.

	bake	10 F	20 F	40 F	anneal
glass	30:38:32	79:21	77:23	73:27	75:24
PI	38:43:19	62:38	73:27	74:26	73:27
PEN/PI	48:33:19	54:46	55:45	64:36	65:35

Table 2. Separation between the valence band maximum VB_{max} and the Fermi energy E_F in eV derived from XPS measurements for In_2O_3 thin films deposited on glass, PI, and PEN/PI after different processing steps.

	bake	10 F	20 F	40 F	anneal
glass	2.96	2.42	2.41	2.56	2.48
PI	2.89	2.42	2.45	2.38	2.39
PEN/PI	2.80	2.51	2.58	2.75	2.57

Figure 1. AFM images ($1 \times 1 \mu m^2$) of the Cr layer and In_2O_3 thin films deposited on glass, PI, and PEN/PI after different processing steps. All images include the values for the root mean square (RMS) roughness.

Figure 2: Analysis of AFM measurements of the Cr layer and of In_2O_3 thin films deposited on glass, PI, and PEN/PI after different processing steps, including (a) root mean square roughness, and (b)-(d) height distributions.

Figure 3: Relative atomic ratios of In, O and N of thin films deposited on (a) glass, (b) PI, and (c) PEN/PI after different processing steps, determined from peak fits to the respective XPS core level spectra.

Figure 4: XPS core level spectra for In_2O_3 thin films deposited on glass, PI and PEN/PI after different processing steps, including (a)-(c) In 3d, and (d)-(f) O 1s.

Figure 5: XPS valence band spectra for In_2O_3 thin films deposited on (a) glass, (b) PI, and (c) PEN/PI after different processing steps. The dotted line represents the Fermi energy E_F .