# On tuning the preferential crystalline orientation of spray pyrolysis deposited indium oxide thin films

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## ABSTRACT

In the present work we investigated the change of preferred crystalline orientation of indium oxide thin films prepared by ultrasonic spray technique on glass, single crystalline Si (400) and KCl single crystal substrates heated at 500 °C. The structural analysis suggests that films deposited on glass and Si wafer substrates are polycrystalline with a preferred grain orientation along the (222) plane. However, films deposited on KCl single crystal substrate, exhibit preferred (400) orientation. The films deposited on KCl substrates have larger grain size than the ones deposited on the other substrates. The electrical characterization indicated that films deposited on KCl substrates have lower resistivity of $0.8 \times 10^{-3}$ $\Omega$ cm. While films prepared on glass substrates exhibit higher resistivity in the order of 33 $\Omega$ cm. This discrepancy is explained in terms of oxygen diffusion from the films towards the KCl substrate.

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## 1. Introduction

During the last decades, an increasing interest has been paid to the transparent conducting oxides (TCO) thin films due to their interesting properties such as high optical transparency and large electrical conductivity. Therefore, TCO thin films are considered as serious candidate for numerous applications namely: photovoltaic devices, transparent windows; liquid crystal displays (LCD), light emitting diode (LED), solar cell, gas sensors and anti-reflecting coatings [1]. Among these TCO films, indium oxide has been less investigated by comparison to the commonly used zinc and tin oxides thin films. Technical and scientific literature outlined that the structural and electrical properties of indium oxide thin films are close related to the preferential growth orientation [2–5], the used growth process [6] and doping [7].

Actually, the diffraction plane intensity is altered by the oxygen concentrations and films stoichiometry variation. Several studies revealed that decreasing the oxygen concentrations in In2O3 films suppresses the intensity of the (222) plane and stimulates the (400) orientation of the $In_2O_3$ films [8–10]. In order to control the preferred growth orientation of the sprayed $In_2O_3$ thin films as a function of films oxygen concentration, we have deposited $In_2O_3$ films on KCl single crystal substrate which is voracious to the $O_2$ molecular. Moreover, $In_2O_3$ thin films were deposited on glass and single crystalline Si (400) wafer substrates in order to investigate films optical properties and composition.

## 2. Experimental procedure

0.1 M of indium chloride $InCl_3$ (Merk, 99.9) is dissolved in methanol and sprayed onto glass, Si wafer and KCl single crystal substrates. The substrates were chemically cleaned before the deposition. The precursor solution was sprayed, in atmospheric pressure, on heated substrates ($T_S$ = 550 °C) placed at 5 cm from the nozzle, the deposition time was fixed at 4 min. The solution flow rate is controlled by (Syringe pump PHOENIX D-CP) and fixed at 25 ml/h. The FT-IR investigation was performed with a Thermo-Nicolet equipment in the 900–400 $cm^{-1}$ range.

The films structural properties were analyzed by X-ray diffraction (XRD) with D8 ADVANCE Diffractometer using a Cu K$\alpha$ radiation ($\lambda$ = 1.5405 Å). The electrical resistivity was determined using four probes method.

## 3. Results and discussion

The XRD patterns of $In_2O_3$ thin films grown on the glass (labeled $In_2O_3$/glass), single crystalline Si (400) (labeled $In_2O_3$/Si) and KCl single crystal (labeled $In_2O_3$/KCl) substrates are shown in Fig. 1. The XRD pattern of $In_2O_3$/glass exhibits a preferential orientation peak with low intensity located at 2$\theta$ = 30.76° representing (222) reflection plane of $In_2O_3$ cubic structure. However, $In_2O_3$/Si film exhibits several peaks located at 29.61°, 30.76°, 33.06°, 35.76°, and 51.31 , corresponding to (211), (222), (321), (400) and (440) planes of cubic phase respectively, with a preferential orientation along the [111] direction. In addition, we observed a Si single crystal a peaks at 69.54° corresponding to the (400)

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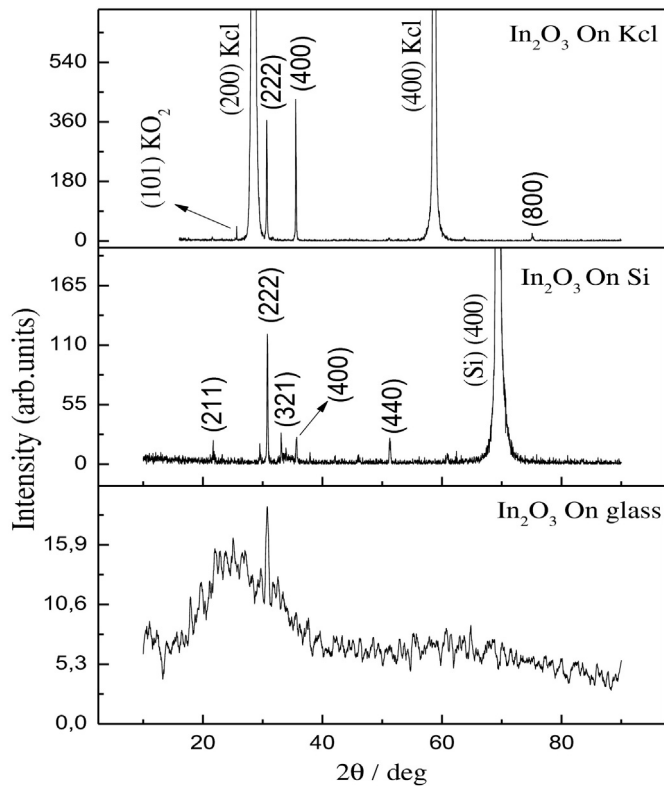  E-mail address: ab_attaf@univ-biskra.dz (A. Attaf).

Fig. 1. XRD diffraction pattern of In$_2$O$_3$ thin films deposited on glass, single crystalline Si (4 0 0) and KCl single crystal substrates.



Fig. 2. Substrate effect on the film texture.

plane (JCPDS 27-1402 file). However, in the case of In$_2$O$_3$/KCl film, we noticed the presence of two main peaks located at $2\theta = 30,69°$ and $35,55°$ assigned to (222) and (400) planes of In$_2$O$_3$, respectively. Beside these peaks we noticed the emergence of a small peak located at $75,11°$ and identified as (800) plane diffraction. Moreover, we observed a KCl peaks at $2\theta = 28,42°$ and $2\theta = 58.74°$ corresponding to the plan (200) and its harmonics (400) respectively (JCPDS 41-1476 file). Peak located at $25,65°$ assigned to (101) KO$_2$ plan (JCPDS 39-0697 file) is also present. It is worth noting that KO$_2$ phase originates from the reaction between O$_2$ molecular and KCl substrate; this is due to the high degree of solubility of O$_2$ molecular in KCl single crystal substrate heated at 550 °C [11]. To investigate the dependence of structural properties on the used substrate, we studied the variation of (222) and (400) diffraction peak intensity (see Fig. 2). The increase in intensity of diffraction peaks of In$_2$O$_3$/Si and In$_2$O$_3$/KCl films confirms their crystallinity enhancement. This is due to the high crystalline quality of these substrates which enhances the nucleation of condensed In$_2$O$_3$ atoms [12]. However, it is interesting to note that the peak intensity increase is more pronounced in In$_2$O$_3$/KCl film than in In$_2$O$_3$/Si one. This can be attributed to the topography of KCl single crystal substrate which supports the nucleation process. It well knows that the nucleation density and the average nucleus size depend on a number of parameters such as the flow rate, temperature, topography and the substrate chemical nature. Also, it was observed that there is a shift in the position of the In$_2$O$_3$/glass and In$_2$O$_3$/Si peaks towards higher Bragg angle. This indicates a lattice compression due to mechanical stresses in these films.

The most import feature in the XRD analysis is the change in the preferential growth orientation with the used substrate nature. For the In$_2$O$_3$/KCl film the texture changes from the [111] direction to [100] direction. Despite that the later has a higher surface free energy in the bixbyite structure [13]. This can be attributed to the low oxygen concentration in the film texture. Oxygen molecules have a high degree of solubility in heated KCl single crystal substrate [11], this prevents the incorporation of oxygen in the growing film structure. Thereafter, the
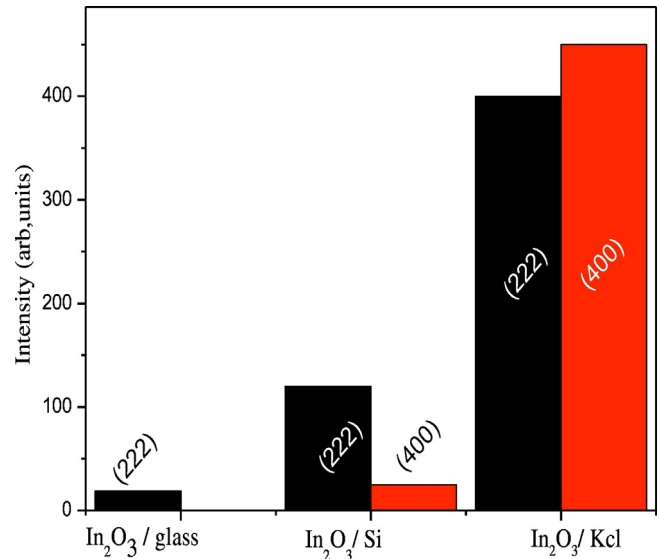
lack of oxygen causes the preferential growth along (400) plane according to Thilakan et al. [4] and Shigesato .and Paine [5] results. The same behavior of In$_2$O$_3$ films texture was observed with film thickness variation, it was discussed, in earlier work, in terms of oxygen variation [14].

The average grains size D of In$_2$O$_3$ is estimated using Scherer's formula [15]:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where $\theta$ is the Bragg's angle and $\beta$ is the full width at half maximum (FWHM) of the peak, $\lambda$ is the X-ray wavelength.

The strain ($\epsilon$) values of In$_2$O$_3$films are calculated by the following formula [16]:

$$\epsilon = \frac{\beta\cos\theta}{4} \qquad (2)$$

The dislocation density ($\delta$) is calculated using the formula [17]:

$$\delta = \frac{1}{D^2} \qquad (3)$$

The crystallite size, strain and dislocation density of (222) and (400) planes are reported in Table 1. As can be seen, the average crystalline size of In$_2$O$_3$/KCl film and In$_2$O$_3$/Si films are large, they are in the order of 70 and 62.5 nm respectively. While, In$_2$O$_3$/glass films have a relatively low crystallite size of 18 nm. The observed large crystallites size is probably due to the nucleation centers rise when using KCl and Si substrates. Moreover, In$_2$O$_3$/KCl and Si/In$_2$O$_3$ films exhibit a lower strain and dislocation density. This can be attributed to films crystallinity improvement. However, the calculated value of lattice constant a = 10.161 Å in the case of In$_2$O$_3$/KCl film is slightly greater than the reported value 10.118 Å for pure indium oxide. This increase in the lattice parameter may be related to oxygen deficiency [18,19] due to the solubility of O$_2$ molecules in KCl network. This result is consistent with XRD analysis.

The FT-IR spectral analysis of In$_2$O$_3$/KCl and In$_2$O$_3$/Si films is shown in Fig. 3. the FT-IR spectral analysis of In$_2$O$_3$/KCl film shows several peaks located, respectively, at 420, 471, 594, 612, 672 and 874 cm$^{-1}$, these peaks are assigned to In—O and In—In vibration modes. Similar results have been reported by other researchers [20,21]. The In—O stretching mode is found at 420, 594, 612 and 672 cm$^{-1}$. The observed band at 471 cm$^{-1}$ attributed to the In—In stretching mode. Whereas, the band located at 874 cm$^{-1}$, is the absorption characteristic of In—O

**Table 1**
Evaluated data of In$_2$O$_3$ films deposited on different substrates.

| Substrates | Preferred orientation | Intensity (au) | Crystallite size (nm) | Resistivity ($\Omega$ cm) | Film thickness (nm) | Strain ($\varepsilon$) $* 10^{-3}$ | Dislocation density ($\delta$) $* 10^{14}$ lines/m$^2$ | Lattice constant (Å) |
|---|---|---|---|---|---|---|---|---|
| Glass | (222) | 19.27 | 18 | 33 | 255 | 2.85 | 26 | 10.087 |
| KCl single crystal | (400) | 426.7 | 70 | $0.8 * 10^{-3}$ | 290 | 0.42 | 2.04 | 10.161 |
| Si single crystal | (222) | 119.4 | 62.5 | / | 280 | 0.64 | 2.56 | 10.083 |

bending vibrations. However, in the case of In$_2$O$_3$/Si film we observe two peaks located at 558 and 610 cm$^{-1}$. These correspond to In—O stretching modes. The presence of In—In vibration mode, in In$_2$O$_3$/KCl film spectrum, is attributed to the oxygen deficiency in the film network. This result confirms the oxygen concentration decrease in In$_2$O$_3$/KCL films and supports the XRD results.

The In$_2$O$_3$/KCl film showed lower value of electrical resistivity ($\rho$) than the In$_2$O$_3$/glass film (see Table 1.). This is owing to the large grain size of In$_2$O$_3$/KCl film, an increase in grain size leads to reduced grain boundary scattering and thus a decrease in electrical resistivity [22]. In addition, the oxygen concentrations in the crystal have important impacts on the electronic properties of In$_2$O$_3$. As suggested above, from XRD analysis; the oxygen lack observed in films network when using KCl substrate, is then accompanied by oxygen vacancies formation. The latter causes a decrease in films electrical resistivity due to the free carriers concentration enhancement in In$_2$O$_3$/KCl films [23, 24]. On the other hand, the low electrical resistivity of In$_2$O$_3$/KCl is probably due also to the decrease in the dislocation density in this film [7].

## 4. Conclusions

Effect of substrates nature on the crystalline structure and electrical properties of sprayed In$_2$O$_3$ films were investigated. X-ray diffraction reveals a polycrystalline nature for all films with a preferred orientation along to (222) for the film deposited on glass and Si wafer substrates. However, in the case of the KCl single crystal substrate we found that the preferred plane orientation is along (400) plane. The preferential orientation change from (222) to (400) plan is explained in terms of the decrease of oxygen concentration in the film structure due to the solubility of the oxygen molecules in KCl substrate. The (400)-plane textured In$_2$O$_3$/KCL film exhibits the lowest resistivity of $0.8 \times 10^{-3}$ $\Omega$ cm due to the enhancement of free carrier concentration caused by increasing oxygen vacancies in this film.
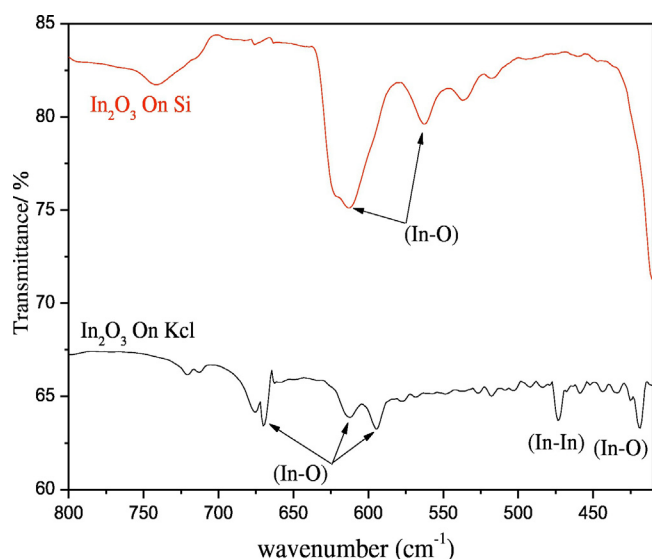


**Fig. 3.** FT-IR spectra of KCl/In$_2$O$_3$ film and Si/In$_2$O$_3$ film.

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