

Chemically Sprayed Fluorine-Doped Zinc Oxide Thin Films Deposited from $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$: Effect of the Molarity and Substrate Temperature on the Physical Properties

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Fluorine-doped zinc oxide thin films, ZnO:F , were deposited by the chemical spray pyrolysis technique using zinc acetylacetonate, $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$, and ammonium fluoride as precursors. The molar concentration in the starting solution and the substrate temperature, T_s , were varied in order to obtain transparent and conductive films. For molarities higher than 0.3 M, growth rate values on the order of 3.5 nm/s were obtained. As the molarity increases, the resistivity ρ decreases up to a minimum value in the order of $10^{-2} \Omega \text{ cm}$ for films deposited from a 0.4 M starting solution and $T_s = 475^\circ\text{C}$; for higher molarities an increase in ρ is observed. The preferential growth direction is affected by the molarity and T_s , showing a switching of the (101) planes obtained for the lowest molarities (0.1 and 0.2 M) and $T_s < 475^\circ\text{C}$ to the (002) preferential growth for molarities higher than 0.1 M and all the substrate temperatures used. The mobility and the carrier concentration were varied from 1 to $3 \text{ cm}^2/\text{Vs}$ and 4×10^{20} to $5 \times 10^{20} \text{ cm}^{-3}$, respectively. From scanning electron micrographs, small grain size is evidenced, which can give rise to a high density of trapping states in the grain boundaries. Films were uniform, pinholes-free, with a transmittance in the visible in the order of 85%.

1. Introduction

Zinc oxide thin films, ZnO , doped with some group III elements and fluorine, F, can be applied as transparent conductive electrodes in amorphous silicon thin film solar cells and as a window layer [1, 2], among others.

ZnO thin films have been deposited by several techniques such as reactive evaporation [3], sputtering [4], chemical vapor deposition [5], chemical spray [6] and sol-gel techniques [7]. The chemical spray technique has the advantages of being cheap, safe and easy handling [8]. In addition, highly conductive and transparent chemically sprayed ZnO thin films, competing well with those obtained by the physical deposition techniques, have been reported [9–16]. Henceforth we are interested in chemically sprayed ZnO thin films.

Although the effect of some deposition parameters on the physical properties of ZnO thin films have been reported for films obtained by the chemical spray technique, a complete knowledge is still far from being reached. For instance, a beneficial effect of the acidity and the aging of the starting solution on the resistivity and the surface texturing in ZnO films has been observed in our laboratory [17]. Due to the lack of more

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detailed information, we think that an improvement in the transport properties, structure and surface morphology of ZnO thin films should occur when different zinc compounds are used as precursors. This is not a new idea, as distinct zinc compounds have been tried before, and as a result, it has been found that zinc acetate yield superior quality films as compared with nitrate and chloride salts [18]. This is the reason why most of the reports on chemically sprayed ZnO thin films are based on zinc acetate. However, to the best of our knowledge in the professional literature, chemically sprayed fluorine-doped zinc oxide thin films, ZnO:F, deposited from zinc acetylacetonate, $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$, have not been reported. This organometallic compound has the advantages of no incorporate anionic impurities into the film, which can degrade the efficiency and sensitivity of gas sensors, and is easily soluble in a mixture of water, methanol and acetic acid. Transparent, uniform and pinhole-free films are obtained at a substrate temperature T_s as low as 425 °C, as has been confirmed in our laboratory. The price of the zinc acetylacetonate, being higher than that of zinc acetate is the only disadvantage.

In addition, the work of Sato et al. [19] on chemically vapor deposited ZnO thin films gives an experimental support to zinc acetylacetonate as they reported superior quality films with low resistivity even for undoped films. Moreover, based on the outstanding work of Viguie and Spitz [20], in which chemical spray is a special case of CVD process, we expect an enhance in the properties of films deposited from zinc acetylacetonate as compared with those obtained from zinc acetate.

In this work the electrical, structural and optical characteristics of chemically sprayed ZnO:F thin films as a function of the molarity and substrate temperature are reported. Because our main goal, in this work, is to obtain semiconductor thin films to manufacture transparent electrodes, which require both lowest resistivity and highest transparency in a wide range of the solar spectrum, we are interested in optimizing the deposition conditions in order to obtain highly conductive and transparent ZnO:F thin films.

2. Experimental Procedure

The molarity of the starting solution ranged from 0.1 to 0.5 M in steps of 0.1 M. For each case the corresponding quantity of zinc acetylacetonate was dissolved in a mixture of deionized water, methanol and acetic acid (volume proportion of 300:150:550, respectively). Ammonium fluoride dissolved in deionized water with a 1.6 M concentration was used as dopant. Sodocalcic glass plates were used as substrates. The substrates were placed on a tin molten bath, whose temperature was measured with a chromel–alumel thermocouple coated with a stainless steel jacket. As a result of the spray, a thermal shock is unavoidable; for this reason the thermocouple is placed just near the surface in order to obtain the best control of the bath temperature through an electronic control backed by a SCR power unit. A temperature variation of less than $\pm 5^\circ\text{C}$ was present for each substrate temperature.

Four-point probe technique was used to measure electrical resistivity with the appropriate geometric corrections. Hall effect measurements were performed using the van der Pauw arrangement. The structural characterization was performed by X-ray diffraction using a Siemens D500 diffractometer and K_α radiation from Cu ($\lambda = 1.534 \text{ \AA}$). The morphology was observed through scanning electron microscopy with a JEOL-35 SEM equipment. Transmittance spectra were obtained from 350 to 1000 nm in a spectrophotometer UV–VIS, Shimadzu 2401 PC.

3. Results

3.1 Growth rate

Figure 1 shows the growth rate as a function of the molarity of the starting solution for films deposited at $T_s = 475^\circ\text{C}$. The growth rate increases linearly, in two distinct regions, showing two slopes as is evident from Fig. 1. The growth rate for films deposited with a 0.3 M solution is higher than two times those corresponding for films deposited from a 0.1 M starting solution. An additional increase in the molarity, higher than 0.3 M, gives rise to a decrease in the growth rate, however, its dependence on the molar concentration is linear, at least up to 0.5 M, which corresponds to the highest molarity used in this work. The growth rate value for films deposited with a 0.5 M solution was around of 3.5 nm/s. Figure 1 shows that for lower molarities the mass transport commands growth rate, whereas for higher molarities the limiting mechanism is the diffusion of the reactants on the surface [21]. The highest growth rate values here obtained confirm that zinc acetylacetonate compete well with zinc acetate.

3.2 Electrical results

Figure 2 shows the resistivity as a function of the substrate temperature for four different molar concentrations of the starting solution. It is evident from Fig. 2 that the resistivity decreases as the molar concentration increases. In fact, highest resistivity values are obtained when a 0.1 M starting solution is used, remaining practically constant with T_s , in the order of $1 \times 10^{-1} \Omega \text{ cm}$, for $T_s > 475^\circ\text{C}$. The lowest resistivity value, in the order of $10^{-2} \Omega \text{ cm}$, was obtained for films deposited from a 0.4 M starting solution and $T_s = 475^\circ\text{C}$. It is worthy to mention that the lowest resistivity value reported in this work ($10^{-2} \Omega \text{ cm}$) is one order of magnitude lower than the value reported for ZnO films obtained from zinc acetate ($1 \times 10^{-1} \Omega \text{ cm}$) [22]. A further increase in the molarity (higher than 0.4 M), leads to a slight increase in the resistivity, as can be observed in

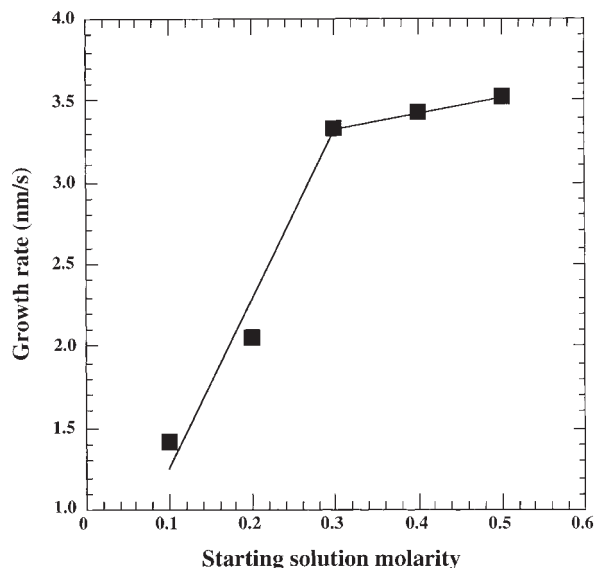


Fig. 1. Growth rate variation with the starting solution molarity for ZnO:F thin films deposited at $T_s = 475^\circ$

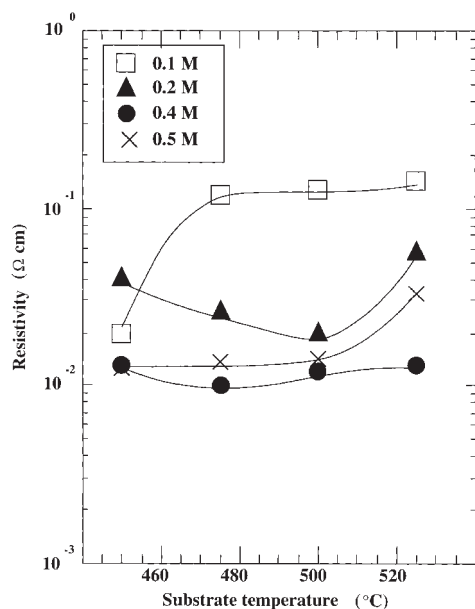


Fig. 2. Electrical resistivity as a function of the substrate temperature for ZnO:F thin films deposited from four different molarities

the Fig. 2 for films deposited with a 0.5 M starting solution. Moreover, Fig. 2 indicates that the optimum substrate temperature is located between 475 and 500 °C, for films deposited with 0.2 and 0.4 M starting solutions. The mechanisms generally invoked in order to explain the variation of the resistivity against the substrate temperature are two. The first one is based on microstructural changes, namely an increase in the grain sizes and a good crystallinity are obtained as T_s is increased. The second mechanism takes into account the presence of zinc excess and oxygen vacancies, due to an incomplete oxidation of zinc during the growth process, which produces a stoichiometry deviation. The resulting effect is to decrease the resistivity. An increase in T_s not only enhances the stoichiometry but also increases the diffusion of alkaline impurities coming from the substrate. Both processes leading to an increase in the resistivity of the films.

It is noted that the lowest resistivity value here reported does not match with that routinely obtained for chemically sprayed indium-doped ZnO thin films. Two factors should be taken into account in order to explain this behavior. The first one is the high volatility of fluorine compounds at high substrate temperatures, decreasing the incorporation of fluorine into the film, which in turn increases the resistivity. From this one could think that a direct consequence of increasing the fluorine concentration of the starting solution is a lowering of the resistivity. Unfortunately this is not successful at all, as we have confirmed. So, the second factor becomes relevant. It is referred to the role of chemical species into the starting solution, which in turn enhance the incorporation of fluorine into the ZnO matrix. We have obtained the best results when the solution has been aged for two days. Films with a resistivity value one order of magnitude lower than those deposited with a fresh solution of zinc acetate were obtained. The starting solution is affected by several factors: the chemical species dissolved, the kind of solvent, the temperature, the acidity and the aging time, among others. These factors have to be considered in order to command the transport and structural properties of chemically sprayed thin films. The study of the effect of the pH of the starting solution on the chemical species have been reported by Smith [23], based on zinc acetate, however, a similar study on zinc acetylacetonate has not been reported. The understanding of the role of each one of the starting solution parameters is a necessary condition in order to decrease the resistivity of ZnO:F thin films.

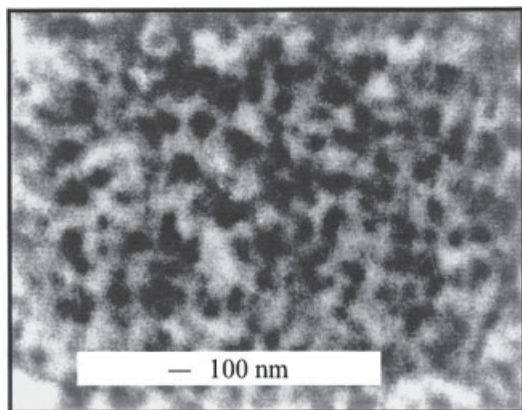


Fig. 3. Scanning electron micrograph for a typical film deposited at $T_s = 475^\circ\text{C}$ from a 0.4 M starting solution

The mobility and the carrier concentration values as a function of the substrate temperature were obtained by Hall effect measurements. The mobility values ranged from $1\text{--}3\text{ cm}^2/\text{Vs}$ and the carrier concentration varied from 4×10^{20} to $5 \times 10^{20}\text{ cm}^{-3}$. The low mobility values can be due to a high density of defects located on the grain boundaries because the films obtained by the chemical spray technique present a rough surface and small grain size.

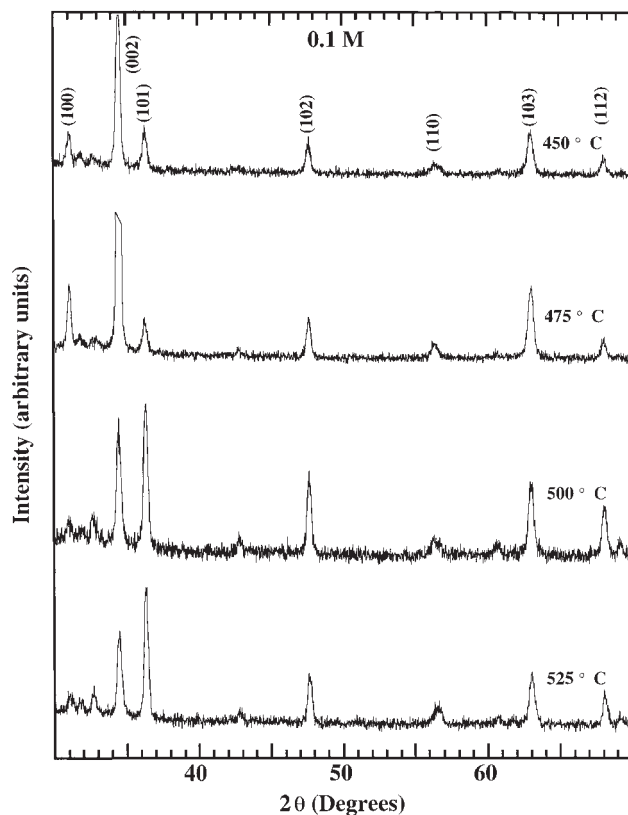


Fig. 4. X-ray diffractograms of ZnO:F thin films grown from a 0.1 M starting solution and several substrate temperatures

3.3 Morphology

Figure 3 shows the surface morphology of a typical film deposited at 475 °C from a 0.4 M solution. The surface looks very uniform, covered by small grains with a diameter on the order of 100 nm. This grain size is lower than that usually reported for highly conductive ZnO:In thin films. It can be argued that fluorine “poison” the ZnO inhibiting the film growth. This can also be a key factor that limits the lowering of the resistivity, due to the low mobility values presented and a high density of the trapping states located on the grain boundaries. A large grain size technology for ZnO:F thin films still remains to be developed.

3.4 Structural properties

Figures 4 to 8 show the X-ray diffraction spectra of ZnO thin films deposited at different substrate temperatures and molarities. Films are polycrystalline in all the cases, fitting well with a hexagonal wurtzite structure. Films deposited with a 0.1 M solution show a (002) preferential growth for $T_s = 450$ and 475 °C, whereas a switching to the (101) preferential growth is observed for films deposited at 500 and 525 °C (see Fig. 4). This change is associated with a variation of the c -axis orientation, which is normal to the substrate for the [002] direction, and it is 58° with respect to the

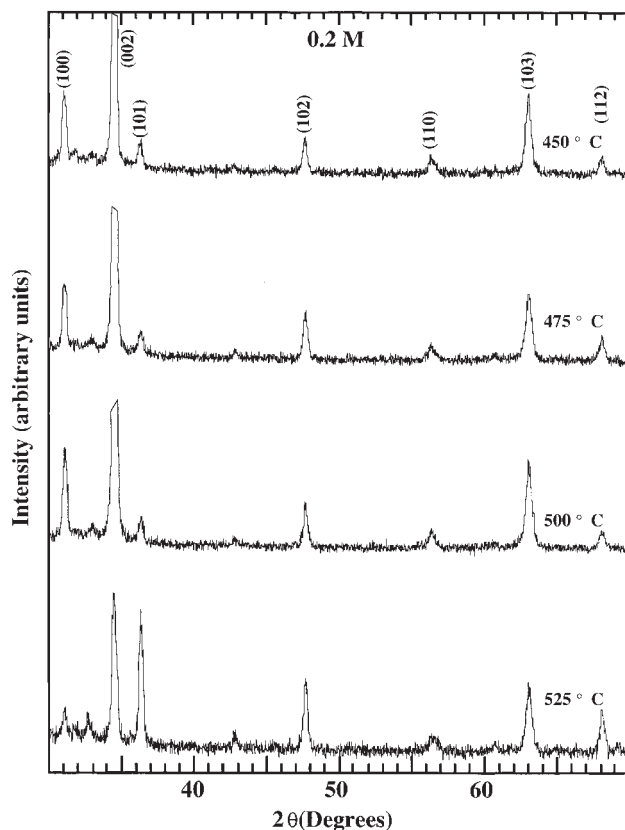


Fig. 5. X-ray diffractograms of ZnO:F thin films grown from a 0.2 M starting solution and several substrate temperatures

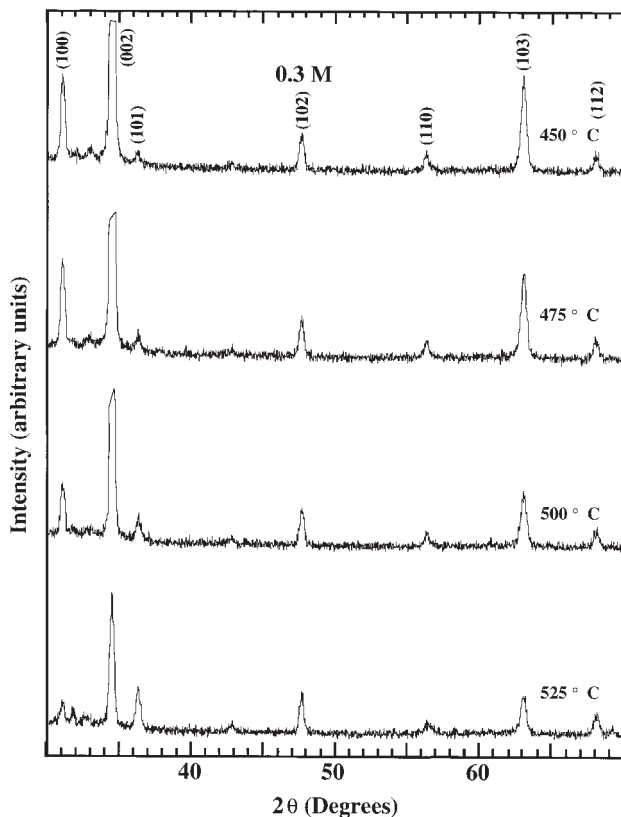


Fig. 6. X-ray diffractograms of ZnO:F thin films grown from a 0.3 M starting solution and several substrate temperatures

normal of the plane for the [101] direction [24]. For films deposited from a 0.2 M solution the (002) preferential growth commands up to 500 °C, however, for films deposited at $T_s = 525$ °C a similar contribution of the (101) signal is observed (see Fig. 5). For films deposited from 0.3, 0.4 and 0.5 M starting solutions the (002) preferential growth commands at all substrate temperatures employed in this work (see Figs. 6 to 8).

3.5 Optical properties

The films are transparent, uniform and pinhole-free. The transmittance increases as the substrate temperature increases due to an enhancement in the crystallinity and a high structural homogeneity of the films. Figure 9 shows the variation of the refractive index n of ZnO:F thin films as the substrate temperature is varied, for the different molarities used. The refractive index presents an almost constant value, except for films deposited from a 0.5 M solution, where the refractive index values decrease as the substrate temperature increases. Slight variations of the band gap values E_g as a function of the substrate temperature for all the molarities used were observed. The E_g values calculated were in the 3.35–3.40 eV range.

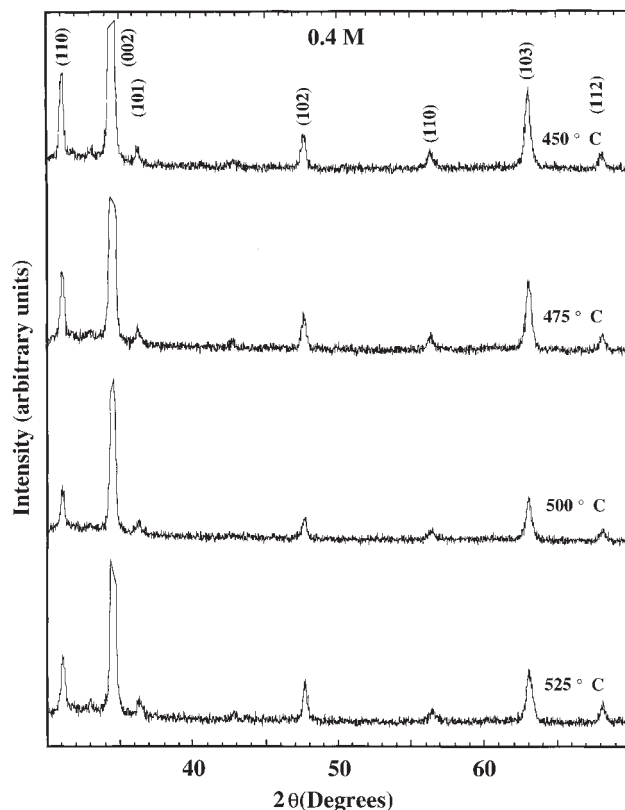


Fig. 7. X-ray diffractograms of ZnO:F thin films grown from a 0.4 M starting solution and several substrate temperatures

4. Conclusions

The characterization obtained of conductive and highly transparent ZnO:F thin films deposited from zinc acetylacetonate and ammonium fluoride was reported. These compounds lead to films with resistivity, mobilities and carrier concentrations values of $1 \times 10^{-2} \Omega \text{ cm}$, $1\text{--}3 \text{ cm}^2/\text{Vs}$ and 3×10^{20} to $5 \times 10^{20} \text{ cm}^{-3}$, respectively. The increase in the molarity of the starting solutions decreases the resistivity of the ZnO:F films. These results show that films deposited from zinc acetylacetonate are better than films deposited from zinc acetate, however, still more detailed work concerning starting solution is necessary in order to further decrease the resistivity. The electrical resistivity, refractive index, transmittance and band gap values obtained make these films potentially adequate for applications in thin film solar cells.

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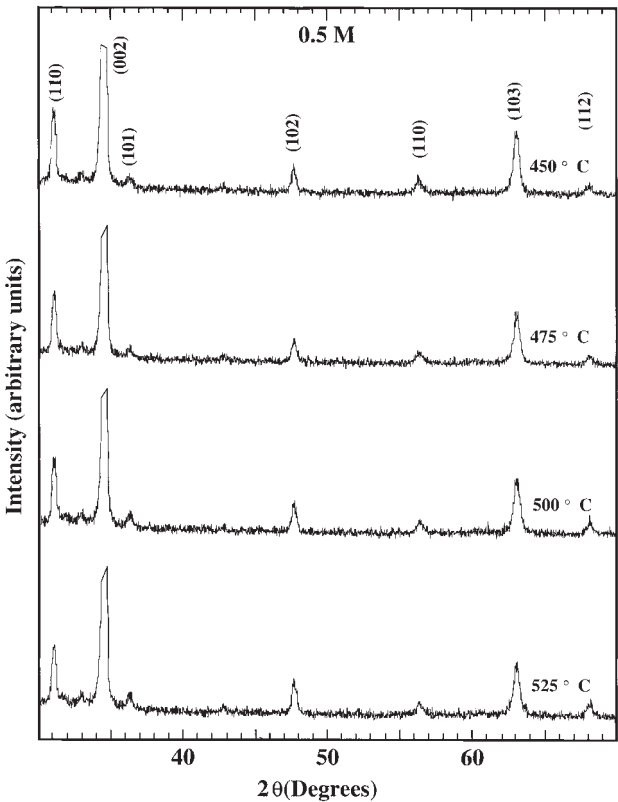


Fig. 8. X-ray diffractograms of ZnO:F thin films grown from a 0.5 M starting solution and several substrate temperatures

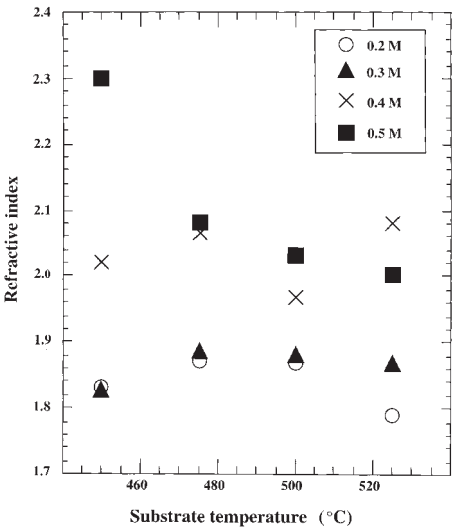


Fig. 9. Variation of the refractive index with the substrate temperature of ZnO:F thin films deposited from solutions with different molarities

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