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A resonant nuclear reaction analysis of fluorine in thin CdO films

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The resonant nuclear reaction (RNR) technique has been used for determining the fluorine content in CdO thin films prepared by spray pyrolysis. The gamma rays observed were from the nuclear reaction ^{19}F(p,$\alpha\gamma$)^{16}O, which presents a resonance at 340 keV bombarding energy. From the excitation curves the dependence of the fluorine content in the films on the wt % of NH_4F in the starting solution was observed. In order to understand the doping process, the RNR study was complemented with the other techniques of chemical and electrical analysis such as energy dispersive spectroscopy and the Hall effect.

Keywords: Transparent conducting oxides TPCO fluorine CdO.

Se usa la técnica (RNR) Reacción Nuclear Resonante para determinar el contenido de fluor en películas delgadas de CdO obtenidas por Rocio Pirolítico. Se observaron los rayos gamma provenientes de la reacción nuclear ^{19}F(p,$\alpha\gamma$p^{16} O, que presenta una resonancia a una energía de bombardeo de 340 keV. De las curvas de excitación se obtiene la dependencia de contenido de fluor en las películas con el porcentaje en peso de NH_4F presente en la solución inicial. Para entender el proceso de contaminación, el estudio de RNR se complementó con otras técnicas de análisis químico y eléctrico, como espectroscopía de dispersión de energía y efecto Hall.

Descriptores: Oxidos conductores transparentes TCO, CdO con fluor.

PACS: 78.20.Jq

1. Introduction

Transparent conducting oxides (TCO) have found a great variety of applications as transparent electrodes for crystal displays, light-emitting diodes and solar cells. Cadmium oxide (CdO) is particularly interesting and could be a promising material for optoelectronic applications. It is the most ionic IIB-VI compound and the only TCO from this group which crystallizes in the rocksalt structure. Moreover, CdO has the highest electrical conductivity but the lowest optical gap among all undoped TCOs. This last property has limited its use in optoelectronics. However, in the last few years, CdO thin films with improved optical and electrical properties have been obtained by means of doping with fluorine (CdO:F) [1] and tin (CdO:Sn) [2]. In general, the doping process is achieved by substitution of the cation by an appropriate chemical element. In the case of fluorine, however, the substitution of the anion (oxygen) has also been proposed. Furthermore, it has been observed that the changes in the electro-optic properties with fluorine doping are associated with the increase in carrier concentration. It is known that structural defects such as oxygen vacancies and/or metal interstitial atoms act as donors; therefore a change in the stoichiometry of the oxide when doping with fluorine might be involved in the change of the electro-optic properties of the material. The doping of TCO is at present an important subject for research [3].

It should be pointed out that the lack of precise information on the fluorine content of the deposited films has been a serious obstacle to reaching a definite conclusion on the doping mechanism. In this context, the present work deals with the precise determination of the fluorine content in fluorine-doped CdO films. Spray pyrolysis is used as the deposition technique since it is simple, inexpensive and suitable for mass production [3]. The fluorine content is studied as a function of parameters such as substrate temperature, impurity salt concentration in the spraying solution (wt %), and thickness.

Fluorine is difficult to detect and measure by standard techniques of chemical analysis such as Auger electron spectroscopy and X-ray spectroscopy. In the present work we have used Resonant Nuclear Reaction (RNR) analysis for this purpose.

2. Experimental details

The films were prepared by spray pyrolysis starting from a 0.1 M solution of cadmium acetate dissolved in a (1:1) mixture of methanol and distilled water. A standard pneumatic method was used for spraying the solution on a Corning glass substrate placed on a planar oven with a tin/lead bath. The bath was used to increase and homogenize the heat transfer to the substrate. The substrate temperature was measured and controlled within $\pm 3^{\circ}$C by a thermocouple connected to a temperature controller. The nitrogen flow rate (5 l/min) and the nozzle-substrate distance (25 cm) were kept constant, while three different substrate temperatures (190, 210 and 230°C) and two different solution flows (5 and 3 ml/ min) were used. The fluorine doping was achieved by adding different amounts in weight percent (wt %), ranging from 2% to 8 %, of ammonium fluoride (NH_4F) to the spraying solution. The film thickness was determined as part of the RNR analysis.

Resonant nuclear reaction (RNR) analysis [4] was used to measure the fluorine profiles. It consists in bombarding the sample with projectiles at energies near an isolated resonance in a reaction with the element to be detected. In the present case, a proton beam from the Instituto de Física 700 kV Van de Graaff accelerator was used to excite the $^{19}F(p,\alpha\gamma)^{16}O$ nuclear reaction, which presents a resonance at 340 keV bombarding energy [5]. The 6.14 MeV gamma rays and two escape peaks from the reaction were detected in a 7.5 × 7.5 cm NaI(Tl) scintillation detector. The resonance, which corresponds to a discrete level in the compound nucleus ^{20}Ne, has a width of 2.4 keV and its shape resembles a typical Breit-Wigner shape superposed on a slowly increasing background. Since the resonance energy is characteristic of this particular reaction, and no competing reactions with Cd, O, or other possible contaminants appear in the energy interval covered, the identification of the F is unambiguous.

The experiment consists in varying the energy of the incident protons, starting with a value just below the resonance, and increasing it in small steps of 1 keV. By counting the gamma rays produced at each step, an excitation curve is obtained which is related to the F concentration profile. When the proton energy is the same as the resonant energy (340 keV), the gamma ray counts correspond to F at the surface. As the proton energy is increased above 340 keV, the resonance takes place deeper within the bulk, at a depth d which depends on the stopping power of the sample material for protons. Therefore the energy scale of the excitation curve can be transformed to a depth scale in units of mg/cm^2. In our experiment, typical values were 20 μC per point at a current of 100 nA. With these values, there is no F loss during bombardment; this was verified on one sample by running the excitation curve forward and backward at the same point.

A computer program [6] calculates gamma ray counts as a function of proton energy, given an assumed F concentration profile, the shape of the resonance, the stopping power, and the behavior of the proton energy straggling. By successive approximations, experimental excitation curves can be fitted with a concentration profile. The numerical values of the profiles were obtained by comparing the excitation curves with corresponding curves obtained from an LiF standard where the fluorine concentration is known. In order to convert mg/cm^2 to units of length, the density was taken as 8.15 g/cm^3, the value for pure crystalline CdO.

The chemical composition was determined by means of a Noran EDS system coupled to a JEOL C1020 SEM Microscope. Carrier concentration and mobility were determined from resistivity and Hall coefficient measurements made with a standard Van der Pauw configuration and a magnetic field of 0.56 T, using silver paint for contacts.

3. Results and discussion

The excitation curves for samples prepared at 190, 210 and 230° are shown in Figs. 1a, 1b, and 1c, respectively. In each figure, curves corresponding to 2, 4, 6 and 8 wt % of NH_4F in solution are shown. The corresponding total fluorine concentration was measured and is reported in Fig. 2 as a function of the wt % of NH_4F in solution. It should be noted that:

i) the trend in the total fluorine concentration is to decrease with increasing temperature, indicating some evaporation, and

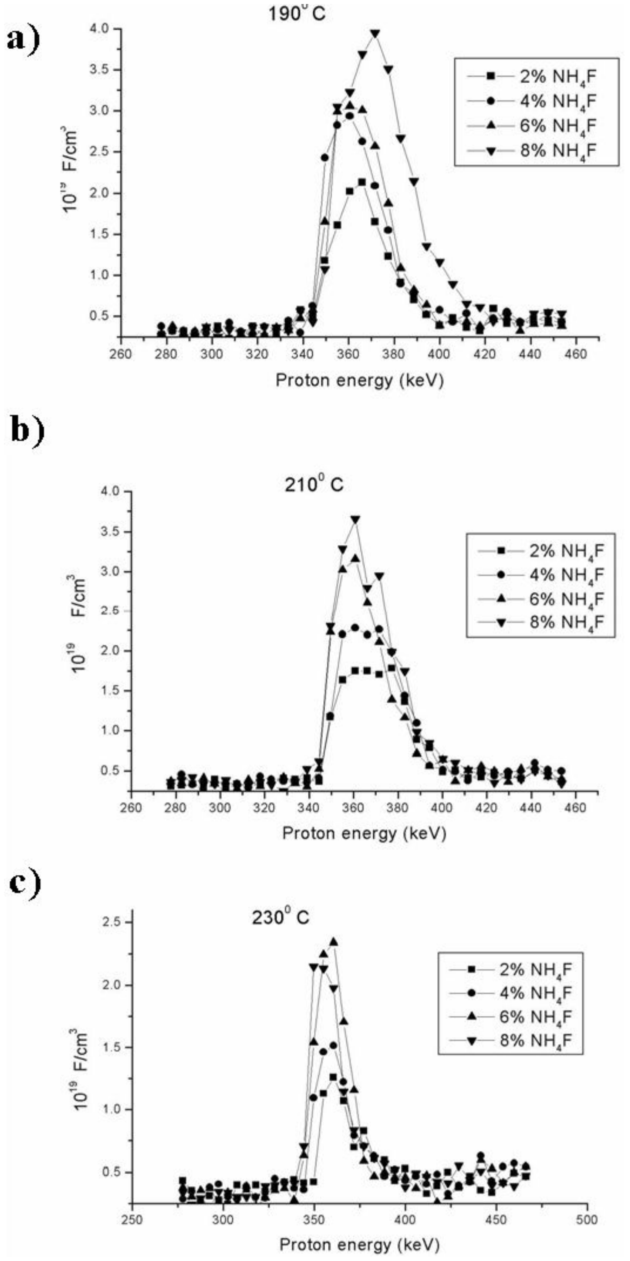

FIGURE 1. Fluorine distribution curve for samples of CdO prepared with starting solutions of 2, 4, 6 and 8 wt % of NH_4F and at three different substrate temperatures: a) T_s = 190°C, b) T_s = 210°C, c) T_s = 230°C

TABLE I. Variation of the. [O]/[Cd] % atomic ratio and calculated fluorine concentration in solution with the weight % of NH_4F in solution.

$[NH_4F]$ %	[O]/[Cd] at. % ratio	[F] solution 10^{21} cm^{-3}
0	0.97	
2	0.92	0.75
4	0.87	1.10
6	0.82	2.00
8	0.74	2.50

TABLE II. Calculated fluorine concentration in the film and the increase in electron concentration when doping as a function of the weight % of NH_4F in solution.

$[NH_4F]$ %	[F] 10^{21} cm^{-3}	Δn 10^{20} cm^{-3}
2	1.03	4.45
4	1.94	5.26
6	2.90	5.26
8	4.88	5.26

TABLE III. RNR fluorine concentration and Hall electron concentration in CdO films prepared at different temperatures and from solutions with different NH_4F content.

$[NH_4F]$ %	T = 190°C		T = 230°C	
	[F] 10^{19} cm^{-3}	n 10^{20} cm^{-3}	[F] 10^{19} cm^{-3}	n 10^{20} cm^{-3}
2	5.1	6.3	1.9	4.2
4	7.1	13.7	3.1	5.9
6	8.4	13.7	5.5	6.1

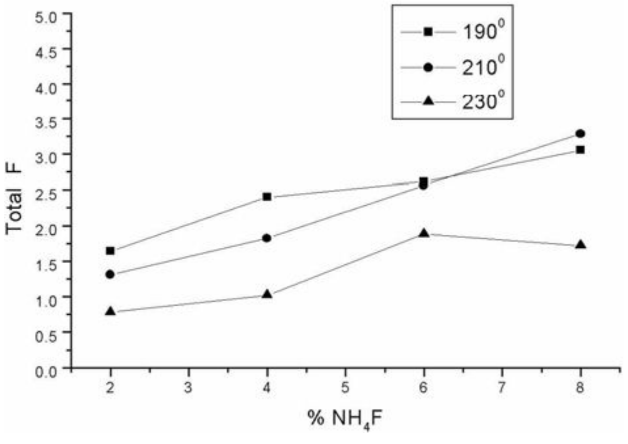

FIGURE 2. Measured total fluorine content as a function of the NH_4F wt % in the starting solution and substrate temperature.

ii) as expected, the total fluorine concentration an increases with increasing wt % of NH_4F in solution.

In order to study the fluorine doping mechanism in our films, the cadmium and oxygen concentration must be measured. This was done by means of Energy Dispersive Spectroscopy. For this study, the samples deposited at 210°C were selected. In Table I, the O/Cd atomic fraction is reported. The fluorine concentrations in this table were calculated from the wt % of NH_4F in the starting solution. The first conclusion from this table is that the films are not stoichiometric. The oxygen concentration is lower than that of the cadmium and this difference increases with a growing fluorine concentration in the solution. This result could be related reaching the oxygen atom substitution by fluorine. Indeed, their atomic radii are very similar (R_{at} (F) / R_{at} (O) = 0.9729). Of course, another possible reason could be the presence of interstitial cadmium. At the same time, it should be noted than the fluorine concentration is two orders of magnitude higher that that measured by means of RNR. Therefore, we can conclude that the effectiveness of the doping process is less that 50 % and decreases with the increase in wt % of NH_4F in solution.

The results of the RNR measurements can be complemented with the electrical measurements of electron concentration in order to obtain additional insight into the doping process. In Table II, the calculated concentration of fluorine atoms in the films is presented, assuming that the non-stoichiometry of films is due exclusively to the oxygen substitution by fluorine atoms. The increase in electron concentration as a result of the fluorine doping is also reported.

From these results, two observations should be mentioned:

i) the solution concentration of fluorine atoms is not enough to replace all oxygen atoms, and

ii) the experimentally obtained fluorine concentration is lower, about one order of magnitude, than the increase in electron concentration in the films with doping.

Thus we can conclude that the substitution process of oxygen by fluorine atoms should be accomplished with the creation of new oxygen vacancies (V_o^{++}) which are usually considered as donors. It could explain the observed values of the

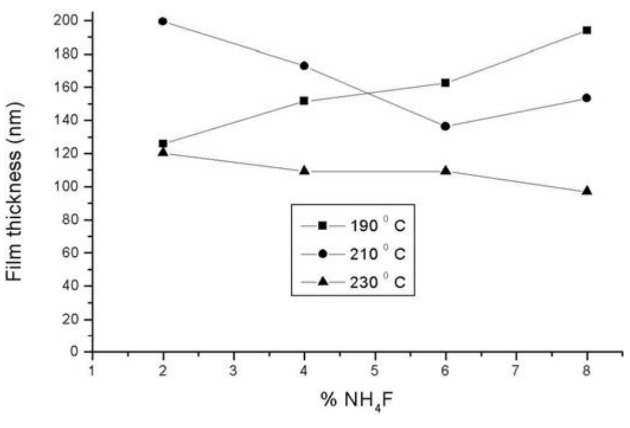

FIGURE 3. Film thickness *vs* wt % NH_4F in solution, for different substrate temperatures.

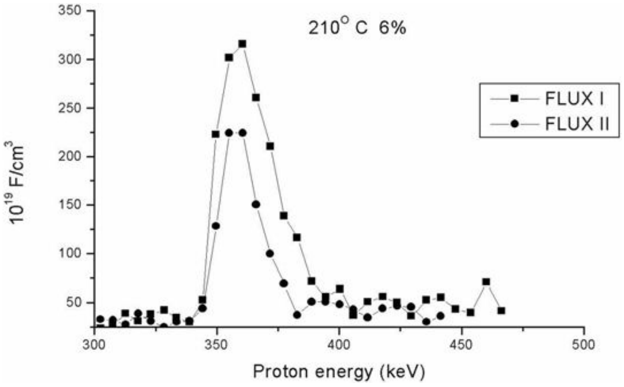

FIGURE 4. Distribution of fluorine in CdO:F films prepared at 210°C using different solution fluxes (Flux I=5 ml/min, Flux II=3 ml/min) and starting from solutions with 6 wt % NH_4F.

increase in electron concentration with doping. At the same time, it seems that this last process is less intense as the wt % of NH_4F in solution increases, since a saturation of the electron concentration is observed in the films. The presence of cadmium interstitials, which act as donors, could also explain the higher values of the electron concentration increase with respect to the fluorine concentration in the film.

The same analysis can be used to explain the results of the electron concentration in films obtained at 190 and 230°C. In Table III, the measured fluorine concentration and electron concentration in films deposited at 190 and 230°C are presented. It should be observed that the rapid saturation of carrier concentration in films obtained at 190°C can be attributed to the better fluorine incorporation in these films.

Figure 3 depicts the thickness, as measured from the excitation curves, of films obtained at different temperatures starting from solutions with different concentrations of fluorine. The thickness is deduced from the difference between energies at half maximum at the leading and trailing edges. The film thickness increases with % NH_4F in solution at 190°, but decreases at 210° and is almost constant at 230°. The variation of the thickness (about 80 nm) observed when changing the concentration of NH_4F in the starting solution is not easy to understand. It is known that the deposition rate of films obtained by the spray solution depends on many factors, the temperature and the solution PH being among the most important. It seems that the effect of the NH_4F concentration in solution on the kinetics of film deposition decreases with an increasing temperature in the same way that the fluorine incorporation in the films decreases. In any case, it should always be taken into account that in the spray pyrolysis technique it is hard to control the thickness in the first few minutes when the temperature is not well controlled, so a systematic error is always present.

Finally, Fig. 4 shows the excitation curves obtained from CdO thin films deposited at 210°C starting from a solution with 6 wt % of NH_4F and varying the solution Flux. Flux I corresponds to 5 ml/min while Flux II corresponds to 3 ml/min. It can be seen that the higher the flux, the higher the fluorine concentration that is obtained.

4. Conclusions

The resonant nuclear reaction technique has been revealed as a very suitable and sensitive technique for determining light chemical elements such as fluorine, which are difficult to detect by other standard techniques of chemical analysis. The study made in this paper on the CdO thin films doped with fluorine allows us to identify the doping mechanism. The substitution of oxygen by fluorine atoms is the main mechanism but it should be accompanied by the formation of cadmium interstitial or oxygen vacancies in order to explain the electrical properties of the film. On the other hand, the RNR study allows us to optimize the solution flux and to better control the film thickness.

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