Nuclear Instruments and Methods in Physics Research B45 (1990) 115–118
North-Holland

A STUDY OF FLUORINE IN TIN OXIDE FILMS *

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Fluorine-doped tin oxide films are used as transparent conducting electrodes in solar cells. Films grown by chemical spraying were studied using the $^{19}F(p, \alpha\gamma)^{16}O$ reaction at the 340 keV resonance, by observing the emitted gamma rays in a 5.08 cm × 5.08 cm NaI(Tl) detector. The film thicknesses, fluorine distributions, and relative fluorine concentrations were determined from excitation curves, and the dependence of these properties on the substrate temperature during deposition was studied. The film thickness increases, and the fluorine concentration decreases, with increasing deposition temperature. Increasing the deposition time gives rise to a loss of surface fluorine.

1. Introduction

There has been recent interest in $SnO_2:F$ thin films due to a combination of special electrical, mechanical, and optical properties. The films present good adherence to different substrates and they are chemically resistant. Their refraction index, good electrical conductivity, and high optical transmittance in the visible region makes them well suited for contacts in amorphous silicon solar cells [1,2].

The fluorine doping, which strongly affects the conductivity, is carried out during the film preparation, using several different techniques. One of these, chemical spraying, has the advantage of great simplicity. Using this technique the films may be produced over large areas and there is an excellent uniformity and reproducibility. Determining the fluorine content and distribution is desirable in order to correlate these with the physical properties of the films. Several previous attempts to determine these quantities using conventional analytical methods have presented experimental difficulties. The resonant nuclear reaction method provides a useful probe in this case.

2. Experimental method

In the conventional chemical spraying technique [3] a solution of $SnCl_4$ is used, with a known amount of HF added in order to provide the fluorine. It is sprayed onto a heated Pyrex or silicon substrate using nitrogen gas as a carrier. The spraying conditions used here are typical of those in which the best electrical and optical properties suitable for photovoltaic applications are obtained.

The fluorine was measured using the nuclear reaction $^{19}F(p, \alpha\gamma)^{16}O$ in the vicinity of the well known, high cross section, 2.4 keV wide resonance at a proton energy of 340 keV. The proton beam from the Instituto de Física 700 kV Van de Graaff accelerator was used. The 6.14 MeV gamma rays plus first and second escape peaks were measured in a 5.08 cm × 5.08 cm NaI(Tl) detector placed, as close as possible, directly behind the target and inside a lead shielding. The target was surrounded by a Faraday cup for best beam integration. For each sample an excitation curve was measured in steps of approximately 1 to 2 keV, taking care to advance only in one direction, in order to avoid hysteresis effects in the analyzing magnet. Typically, with 20 μC per point, at a current of 100 nA, a profile takes a couple of hours in running.

As is well known, the excitation curve is an indication of the fluorine profile. Gamma rays produced when the bombarding energy is equal to the resonance energy come from the surface. As the bombarding energy increases, the gamma rays come from deeper within the target. The shape of the excitation curve was calculated using the usual expression (see, e.g., ref. [4]). In the computer program used, the fluorine concentration as a function of depth may be changed for each calculation. The Breit–Wigner shape on zero background was used for the resonance (width 2.4 keV); the beam energy spread was assumed Gaussian of width 1 keV. The proton energy at any given depth was obtained from the

* Work supported in part by Consejo Nacional de Ciencia y Tecnología.

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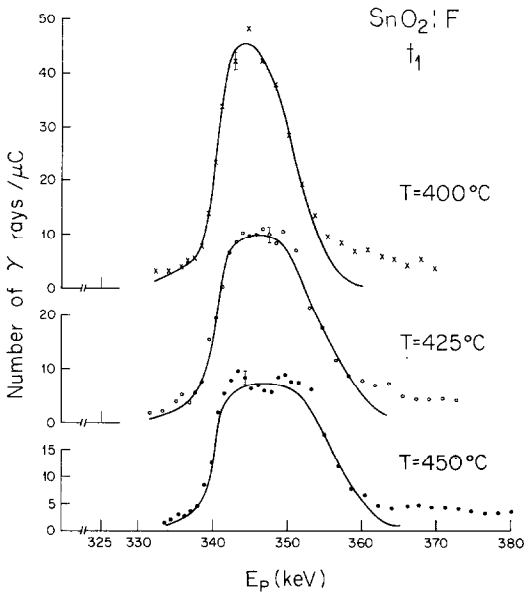

Fig. 1. Excitation curves of fluorine in SnO_2 films measured with the $^{19}F(p, \alpha\gamma)^{16}O$ reaction. The films were grown at substrate temperatures of 400, 425 and 450 °C, for a short deposition time t_1. The full curves, which were calculated as described in the text, are fits to the experimental points.

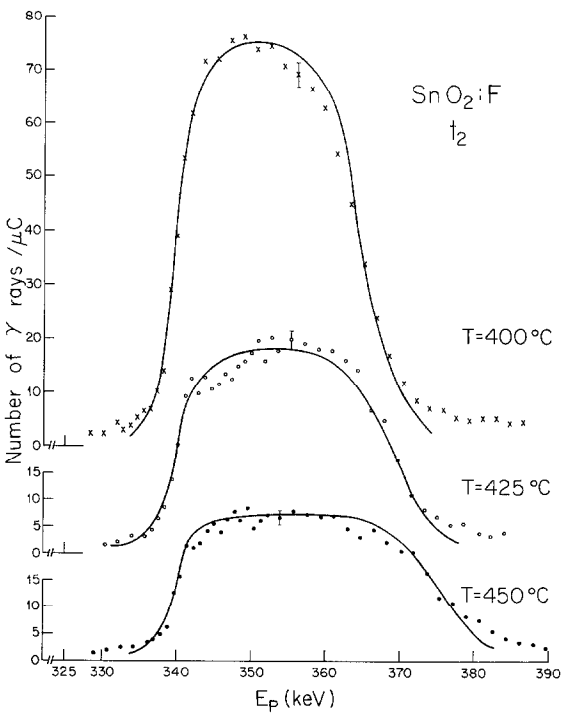

Fig. 2. Experimental and calculated excitation curves measured on samples grown for a longer time t_2. A loss of surface fluorine is observed at the higher temperatures.

formula of Montenegro et al. [5] and the Bragg rule was used for adding stopping cross sections in compound targets. An expression for the proton straggling was obtained based on ref. [5]. By integrating these quantities over the appropriate energy and depth intervals, excitation curves were calculated for comparison with the experimental curves.

3. Results

Fluorine has been identified as an impurity which improves the electrical properties of SnO_2 films without degrading the optical transmittance. However, a large amount of F can alter the crystalline structure. In consequence, it is very important to determine its concentration as precisely as possible. In the results presented here, the overall efficiency of the system was not determined accurately, so only relative values are reported. However, the resonant nuclear reaction technique offers the advantage of determining not only the relative impurity concentration from sample to sample, but also its distribution as a function of depth for each case.

Fluorine profiles were obtained for doped SnO_2 samples grown under different conditions. Two batches of samples were prepared, each one spanning different regions of thickness. The first one, of short deposition time t_1, covered from 77 to 91 nm, as measured with an ellipsometer; the second, of a longer time t_2, covered from 150 to 250 nm. Each batch consisted of samples grown at 400, 425 and 450 °C substrate temperatures; the HF concentration in the solution was kept constant at 8% for all the samples.

Figs. 1 and 2 show the experimentally measured excitation curves for the six samples studied. The curves drawn in the figures were calculated as described, assuming stoichiometric SnO_2, by adjusting the ordinate with an arbitrary constant. The FWHM of each fluorine

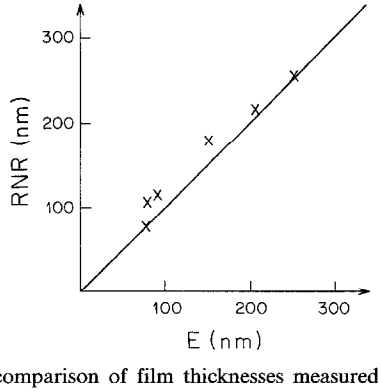

Fig. 3. A comparison of film thicknesses measured using the resonance nuclear reaction technique (RNR) and those using an ellipsometer (E). They agree within an average of 13%.

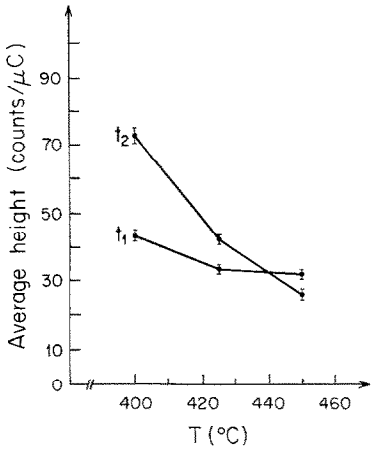

Fig. 4. Average fluorine concentration taken from the relative heights of the excitation curves, measured as a function of substrate temperature during deposition. The two curves correspond to the two different deposition times.

distribution was used to determine the corresponding film thickness in nm, by comparison with the calculated curves and assuming a density of 6.95 g/cm^3 for SnO_2. These thicknesses are compared with ellipsometer measurements in fig. 3; the average deviation is 13%. The good agreement is an indication that the fluorine is present in all of the SnO_2 film. On the other hand, the measured high-energy fall-off corresponds to the calculated fall-off (which includes straggling) in all cases, indicating that the fluorine did not penetrate the substrate. The stability of the fluorine at the interface improves the quality and performance of the electronic devices.

Various shapes of excitation curves are observed, most of which show an almost constant fluorine concentration over the film thickness. This confirms the high quality of the films obtained using the chemical spray method, even though the growth mechanisms are rather complex. In the thicker films (larger deposition time) there is an indication of loss of fluorine from the surface.

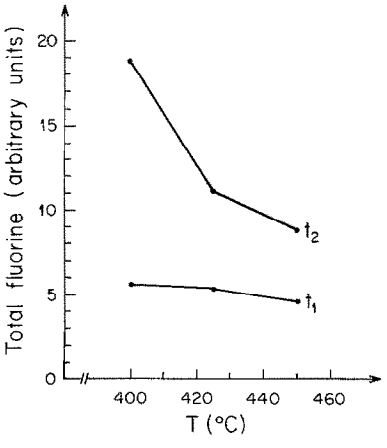

Fig. 5. Total fluorine content in the films, taken from the area under the excitation curves, measured as a function of substrate temperature, for the two deposition times.

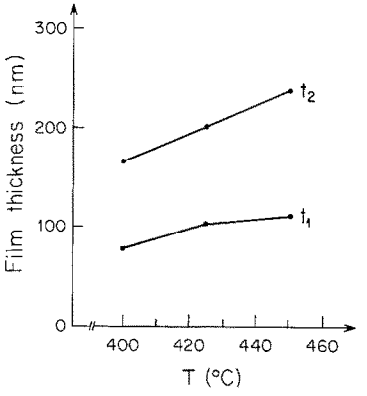

Fig. 6. Film thickness measured as a function of substrate temperature, for different deposition times.

Depending on substrate temperature during deposition, certain trends were observed. With increasing temperature the fluorine concentration per unit depth, obtained from the relative heights of the excitation curves, diminishes as shown in fig. 4. The total fluorine content of the film, calculated from the area under the excitation curve, also diminishes, as indicated in fig. 5. On the other hand, the film thickness, as measured from the FWHM of the profile, grows with increasing temperature, as shown in fig. 6.

The decrease in the fluorine concentration at high substrate temperatures is in agreement with the smaller conductivity observed in films grown above 450 ° C [6], indicating a smaller number of donors at these temperatures. A more detailed study is in progress to determine the correlation between fluorine concentration as measured by the nuclear reaction method and its effect on the electrical properties.

4. Conclusions

The nuclear resonance method for profiling fluorine has been shown to be a sensitive probe when applied to doped tin oxide films, used as transparent contacts. Microscopic film properties such as thickness, distribution of fluorine, and relative fluorine concentration, may be correlated with such preparation parameters as substrate temperature and duration of film deposition.

The authors gratefully acknowledge the help of Mr K. López in the accelerator operation and maintenance.

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