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Research Article

Properties of SnO_2:F thin films prepared by using HF or NH_4F after exposure to atmosphere

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Abstract: Nanocrystalline fluorine doped tin oxide (SnO_2:F) thin films were produced by the spray pyrolysis technique (SP) on glass substrates at a substrate temperature $T_s = 450$ °C. The hydrated stannous chloride ($SnCl_2.2H_2O$) was used as a precursor and ammonium fluoride (NH_4F) was used as the doping compound for one set of films, and hydrofluoric acid (HF) was used as the doping compound to produce another set of films. After exposure to atmosphere for about one month, a comparison between the compositional, morphological and optical properties of the films obtained by using the two doping compounds was performed by using scanning electron microscope (SEM) observations, X-ray energy dispersive spectroscopy (EDS) and transmittance measurements. Both sets of films are found to be oxygen rich, but the films prepared by using NH_4F have higher oxygen content. SEM images showed that the films prepared by using HF have larger grain size, and EDS analysis showed that these films have higher fluorine to oxygen ratio. In addition, the films prepared by using HF have lower transmittance and higher direct optical bandgap energy. These results are interesting for the use of SnO_2:F as a fore contact in CdS/CdTe solar cells.

***Keywords**: Transparent conducting oxides, Spray pyrolysis, Doping, CdS/CdTe solar cells,*

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1. INTRODUCTION

Tin dioxide is an n-type, wide bandgap semiconductor (about 3.5 eV) and in the form of thin films, it is a transparent conducting material, characterized by high optical transmission (80-90%) [1]. The transparent-conducting thin films of this oxide are used as electrodes in a variety of optoelectronic devices, as heat mirror coatings in 'smart windows' for buildings, in automobile and airplane windshields, in incandescent light bulbs, in flat-plate and concentrating solar collectors. Tin oxide and zinc oxide, in thin film configuration are technologically important materials because of their applications in photovoltaic cells [2]. Fluorine doped tin oxide (SnO_2:F) is the most widely used transparent-conducting oxide material especially as a fore contact in CdS/CdTe solar cells.

Among various dopants for SnO_2, fluorine is often preferred, because fluorine doping results in films with high transparency and good conductivity [3]. By exploring the literatures, it was found that different sources of fluorine were used to produce SnO_2:F thin films, among which are ammonium fluoride (NH_4F) and hydrofluoric acid (HF) are the most used. Some researchers used NH_4F [2, 4-7] and others used HF [3, 6-8] for doping SnO_2 films. Gordillo et al.[7] used both of NH_4F and HF and showed that the resistivity of thin films obtained by using HF was lower than that of similar films obtained by using NH_4F by a factor of 2.2. They also found that the films obtained by using HF have more random orientations. Elangovan and Ramamurthi [9] used $SnCl_2$ and NH_4F and produced SnO_2:F thin films by the spray pyrolysis technique, where they studied the optoelectronic properties of the films to be used as window materials in solar cells. Riveros et. al. [10] used $SnCl_2$ and HF to prepare SnO_2:F thin films by the same technique and studied their optical and structural properties. According to our knowledge just Gordillo et al. [7] used both of NH_4F and HF and made a comparison between the produced films and this study was performed in 1994. In reference [11] we performed a comparison between films produced by using both of these compounds and showed that the films prepared by using HF have lower resistivity by a factor of more than 67, higher transmittance, higher bandgap energy, lower Urbach tail width than the films produced by using NH_4F and they are less capacitive. In reference [12] we produced SnO_2:F/CdS structures by the same technique and used both of NH_4F and HF to dope SnO_2 films, where it was found that SnO_2:F/CdS structures made by doping SnO_2 with HF have better crystallization, more ordered crystal growth, smaller content of complex compounds which decompose to CdS, larger grain size and sharper absorption edge.

The objective of this work is to compare the properties of SnO_2:F films prepared by using HF and NH_4F as sources of fluorine after exposure to atmosphere. It was found all of the films are oxygen rich. But it is found that films prepared by using NH_4F as a doping source contain more oxygen. SEM micrographs revealed that the films prepared by using HF have better crystallization and larger grain size. EDS analysis showed that the films produced by using HF have higher fluorine to oxygen ratio and hence they have higher direct optical bandgap energy.

2. EXPERIMENTAL PROCEDURE

To prepare the precursor solution for SnO_2:F thin films the hydrated stannous chloride $SnCl_2.2H_2O$, and ammonium fluoride NH_4F (BDH Chemicals. Ltd Poole England) or hydrofluoric acid HF (40%) were used. Methanol was used as the reducing agent and HCl was added to increase the transparency of the solution. Two different solutions were prepared by using 45 ml of methanol CH_3OH (MAY AND BAKER LTD DAGENHAM ENGLAND), 5 ml of distilled water and 1 ml of HCl. The first solution was made from 5.03×10^{-3} moles of $SnCl_2.2H_2O$ and 4.73×10^{-3} moles of NH_4F. The ratio of fluorine ions to tin ions in this solution was 0.94 which is approximately the same as that used by Gordillo et al. [7] at which they got the smallest resistivity and highest transmittance. The set of films prepared from this solution is called NH_4F-films. The second solution was made by dissolving 5.01×10^{-3} moles of $SnCl_2.2H_2O$ with 5.71×10^{-3} moles of HF. The ratio of fluorine ions to tin ions in the solution was 1.14 which is also approximately the same as that of Gordillo et al. [7] at which they got the smallest resistivity and highest transmittance. The set of films prepared from this solution is called HF-films. Both sets of films were produced at the substrate temperature $T_s = 450^\circ C$. The substrates were glass micro slides of the dimensions $2.5 \times 6 \times 0.1\ cm^3$ that were ultrasonically cleaned with methanol for at least 15 min. The experimental set-up used in this work has been described elsewhere [13]. The carrier gas was nitrogen and the optimum carrier gas pressure was about 5 kg/cm^2.

The transmittance of the films was measured at room temperature in the wavelength range $\lambda = 290 - 1100 nm$ by using a double beam Shimadzu UV 1601 (PC) spectrophotometer. The film thickness was estimated from interference maxima and minima in the transmittance curves by using the way described by Alvin [14]. For films with transmittance that doesn't show such maxima and minima, Lambert law for absorption in a semiconductor was used to estimate the thickness. This is done by deducing the absorption coefficient (α) for films with known thickness at a certain wavelength (i.e. λ = 310 nm) which lies below the cut-off wavelength of SnO_2. The thickness of the films was estimated by using this value of α and transmittance of each film at the afore-mentioned wavelength. Both of the SEM micrographs and EDS measurements were taken by a FEI scanning electron microscope (Inspect F 50), which was supplied by X-ray energy dispersive spectroscopy (EDS) apparatus.

3. RESULTS AND DISCUSSION

The interdiffusion processes taking place at the CdS/CdTe interface during CdTe deposition at high temperature and/or CdCl2 heat treatment have largely been realized to significantly affect the device performance. There is 10% lattice mismatch between CdS and CdTe, which should generate a large density of defects [4], and produces strain at the CdS/CdTe interface [9]. Intermixing at the CdS/CdTe interface is expected to reduce the effect of lattice mismatch, and then it relieves strain, reduces the number of interfacial states, and reduces the number of recombination centers [20]. In addition, a graded layer is formed at the interface [4,20] in which a gradual bandgap is produced in the interfacial region. As explained in sub-section 2.2.1, this bandgap varies with composition x according to quadratic relations Eq.(2) and Eq.(3) due to the optical bowing parameter of the CdTe-CdS alloy system. This results in a narrowing of the absorber-layer bandgap, and hence a higher long wavelength quantum efficiency of the solar cell. Intermixing at the CdS/CdTe interface also passivates (at least partially) the grain boundaries and improves the carrier lifetime in the absorber, and it may reduce the dark recombination current.

4. CONTROLLING CDS/CDTE INTERDIFFUSION

In CdS/CdTe thin film solar cells, alloy formation has both beneficial and detrimental effects on device performance depending on how the alloys are formed, their composition and their compositional distribution. The proper amount of interdiffusion is necessary for a superior efficiency solar cell [8]. However, diffusion of CdS into CdTe is a faster process than that of CdTe into CdS, and is more difficult to control, especially for cell structures with ultra-thin, <100 nm, CdS films. Diffusion of CdTe into CdS has unwanted effects: It can reduce the transmissive properties of the window, and the CdS film thickness will be reduced, which can be beneficial for window transmission, but can result in lateral junction discontinuities. Non-uniform consumption of CdS can be mitigated by heat treatment of the CdS layer prior to CdTe deposition to increase CdS grain size, density, sharpen the CdS optical transmission edge, and to form oxides, which reside on grain surfaces and penetrate grain boundaries. In this case, CdS consumption can be limited by reducing grain boundary diffusion, CdCl2 and O2 vapor concentrations and treatment temperature.

A viable processing route that can be established for minimizing CdS consumption and deterioration of the device performance is utilizing uniform CdTe1-xSx alloy absorber layers in place of pure CdTe [7,29,30] to prevent deterioration of the solar cell related to interdiffusion and current losses. But it is found that this directly-deposited alloy layer is not fundamentally detrimental to device performance [19]. Duenow et al. [29] found that devices that received no CdCl2 treatment performed poorly, while devices containing the alloy layer that received a CdCl2 HT after the CdTe deposition in many cases showed comparable performance to devices without the alloy layer.

$$NH_4F \rightarrow NH_3 + HF \tag{1}$$

$$NH_3 + HCl \rightarrow NH_4Cl \tag{2}$$

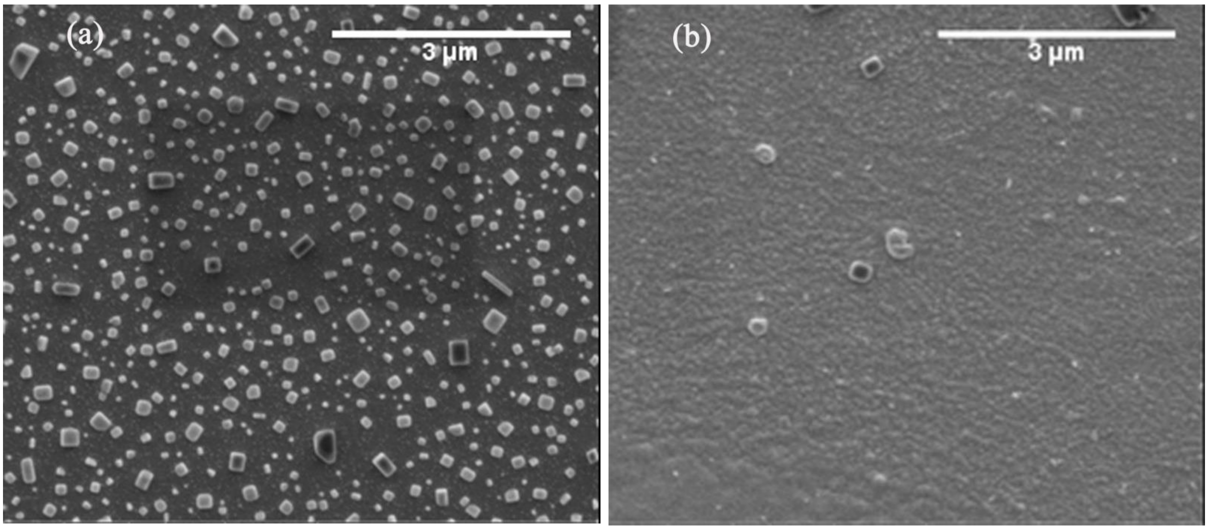

Figure 1. Two SEM micrographs of SnO_2:F thin films. a) NH_4F-film. b) HF-film.

where NH_4Cl decomposes at elevated temperatures [15]. These results are consistent with the results obtained by Dhere et al .[16] who produced SnO_2 films by chemical vapor deposition using tin tetrachloride and tetramethyltin precursors and found that the morphology of these films is strongly influenced by the type of precursor used for deposition.

Figure 2 also displays SEM micrographs of the same films, but with higher magnification. The NH_4F-film appears less compact and it consists of smaller density of smaller grains, while the HF-film appears more compact and it consists of a larger density of larger grains. To estimate the grain size, a random set of crystallites was chosen in each figure, and the sizes were measured and displayed on each micrograph. The average grain size in the NH_4F-film is 20.04±3.75 nm, while that of the HF-film is 63.92±7.94 nm. So both films are nanocrystal line but a larger grain size was obtained by using HF rather than NH_4F as a doping compound.

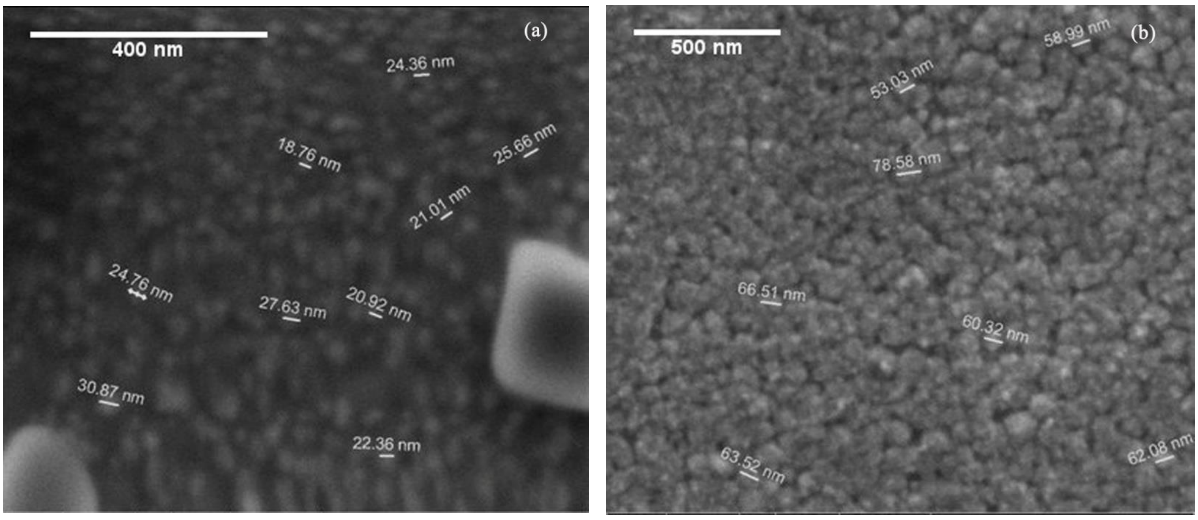

Figure 2. Two SEM micrographs of SnO_2:F thin films showing the grain size for a random set of grains. a) NH_4F-film. b) HF-film.

To explore the composition of the films, the analysis of X-ray energy dispersive spectroscopy (EDS) was performed and the spectra are shown in Figure 3 for both types of films. The results of the compositional analysis are inserted in table 1. From the inspection of table 1, it is found that both sets of films are rich in oxygen, taking into account the large error in the measurements of oxygen concentration. This is because the EDS system cannot give accurate measurements for light elements including oxygen. The ratio of oxygen to tin in the NH_4F-film is 8.47, but in the HF-film it is 2.56. The stoichiometric ratio of oxygen to tin in SnO_2 is 2, so both films are rich in oxygen, where the films were exposed to air for about one month. Usually SnO_2 films are deficient in oxygen which makes them n-type, but when exposed to air, oxygen will be adsorbed on the surface, and the data in table 1 shows that a stronger oxygen adsorption had taken place in the NH_4F-films. When the films are rich in oxygen then the density of the defects such as O^-, O_2^- and Sn deficiency is large, and hence it is larger in the NH_4F-films than that in the HF-films. These defects reduce the density of free charge carriers (electrons) in the films and reduce their conductivity.

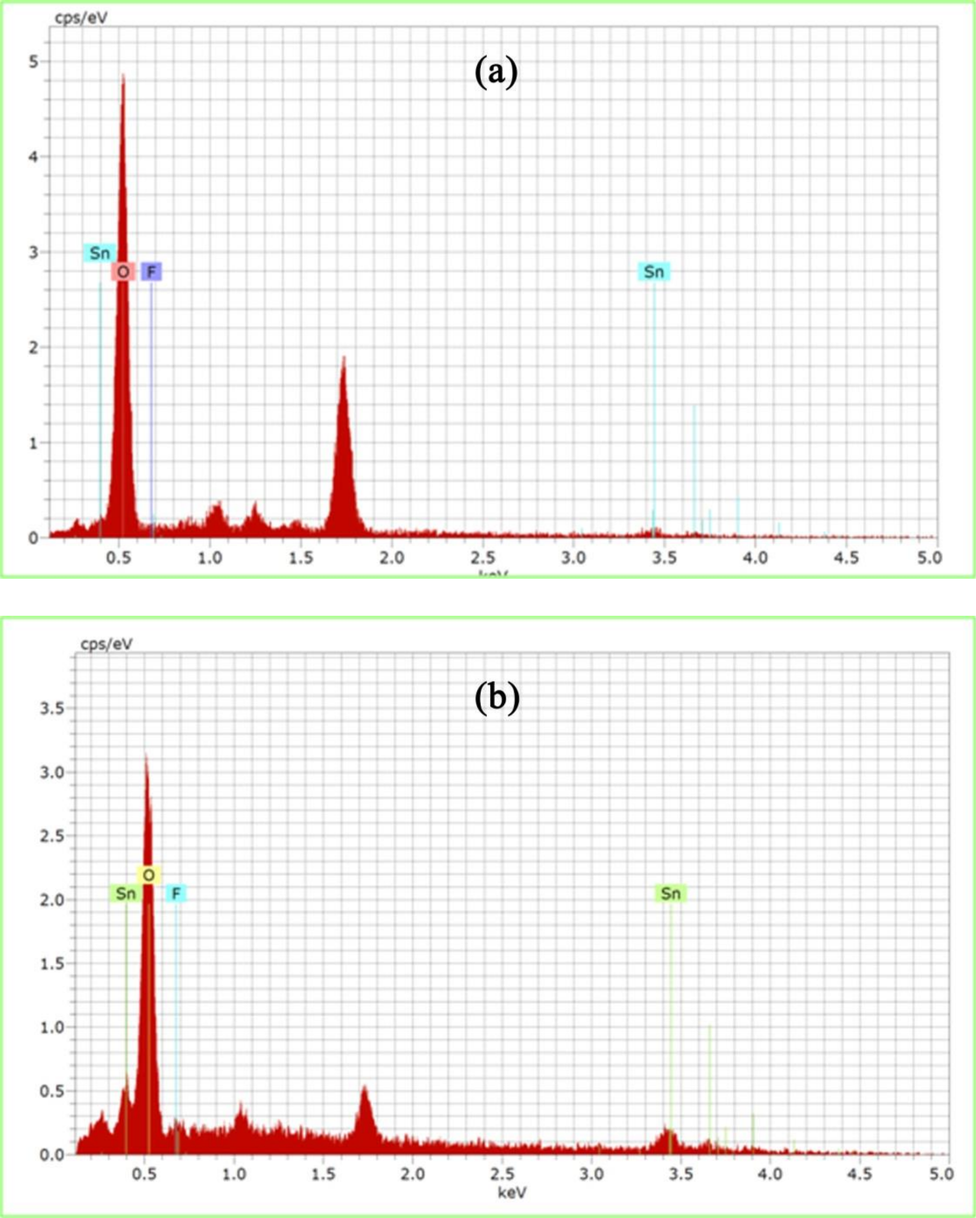

Figure 3. EDS spectra of two SnO_2:F thin films. a) NH_4F-film. b) HF-film.

Table 1. The results of the EDAX analysis for the NH_4F-film and the HF-film.

Element	For NH_4F-film Norm. C [Wt.%]	Error [%]	For HF-film Norm. C [Wt.%]	Error [%]
O	88.47	28.4	71.03	23.1
F	1.08	1.3	1.17	1.8
Sn	10.44	5.0	27.80	11.5

Also depending on table 1 it is found that the ratio of fluorine atoms to tin atoms -which is always defined as the doping ratio- in the NH_4F-films is 10.3%, but in the HF-films it is 4.21%. Although this ratio is larger in the NH_4F-films, but it will not result in a higher conductivity of these films, because the ratio of fluorine atoms to oxygen atoms in the NH_4F-films is 1.22%, but in the HF-films it is 1.65%.

It is known that fluorine replaces oxygen in the films which results in the increase of the free charge carriers (electrons) and because [F]/[O] in the HF-films is larger it is expected that they will have larger conductivity.

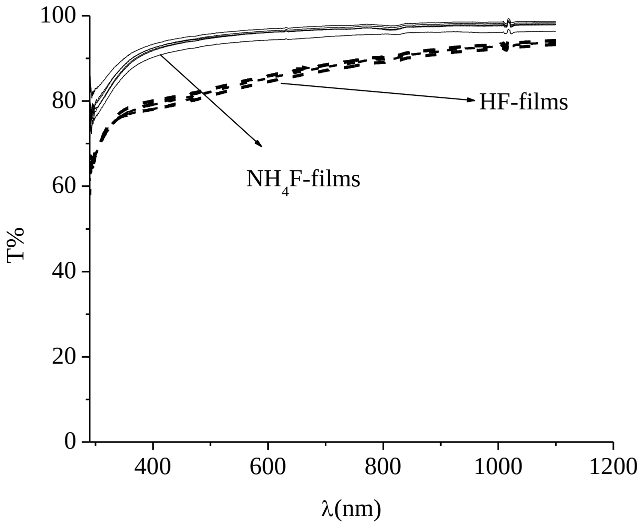

Figure 4. Transmittance of two sets of both types of SnO_2:F thin films.

Fig.4 depicts the transmittance curves for the two sets of films of approximately the same film thickness (about 100 nm), where the NH_4F set consists of four films deposited at the same time, and the HF-set consists of three films deposited at the same time too. The transmittance of the NH_4F-films is larger than that of the HF-films on the whole wavelength range, which may be related to the higher fluorine content of these films, and the larger density of free charge carriers in the HF-films as explained before, which results in higher absorption and lower transmittance. The position of the absorption edge is deeper in the short-wavelength side in the case of the HF-films, which means that they have higher optical bandgap edge, which is due to the increase in the absorption related to the larger density of free charge carriers (electrons in the case of SnO_2:F) in these films.

By assuming a direct transition, the optical bandgap energy was estimated from the plot and linear fit of $(\alpha h\nu)^2$ against hν shown in Fig.5 for both sets of films, where α is the absorption coefficient, *h* is Planck's constant and ν is the frequency of the radiation. The values of the direct bandgap energy E_d were found from the intercepts with the energy axis and the average values are 3.543 ± 0.015 eV and 3.608 ± 0.055 eV for the NH_4F-films and the HF-films respectively. The larger value of E_d of the HF-films is due to the larger density of free charge carriers in these films. These values are smaller than the values that we found in other works [11,16,17], but are in good agreement with the value of $E_g = 3.57$ eV reported for single crystal SnO_2 [2]. The lower optical bandgap energy for these films is related to the smaller number of free charge carriers due to excess oxygen in the films which is due to the long exposure to atmosphere.

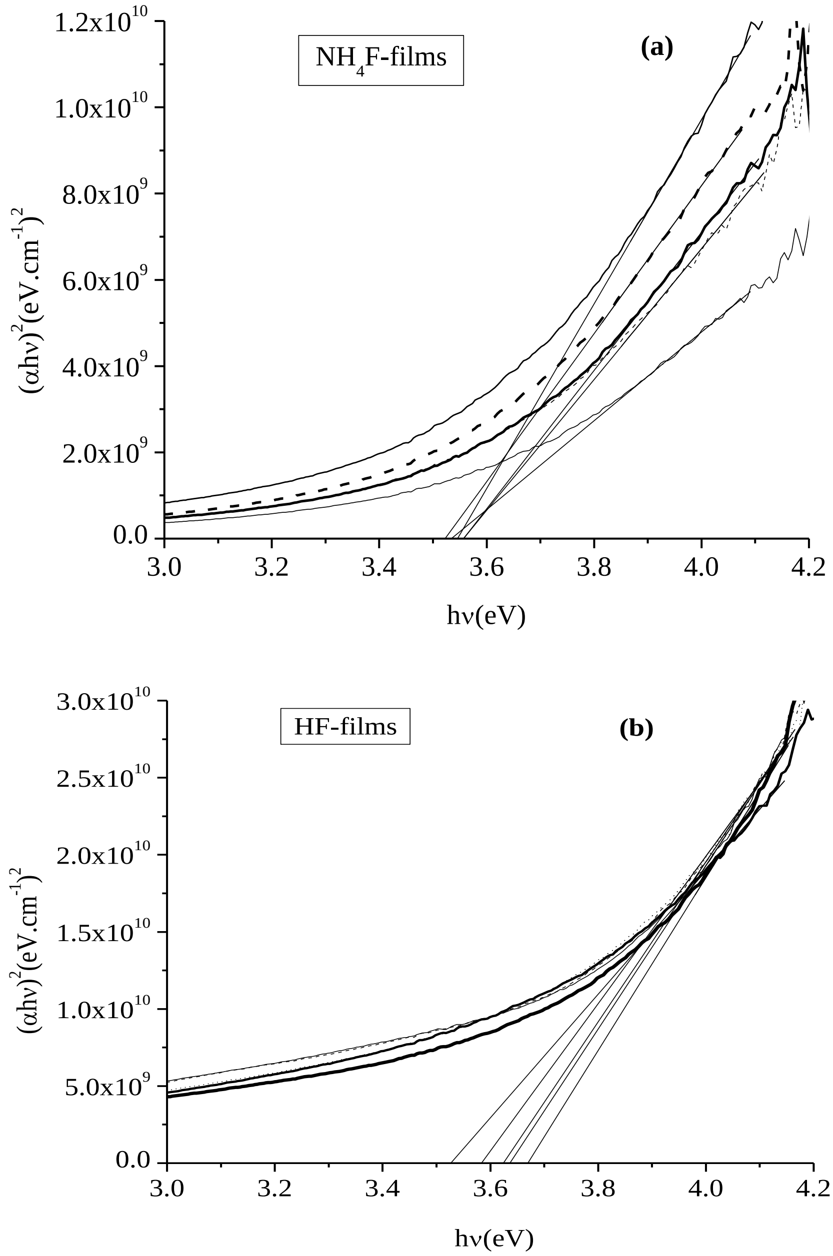

Figure 5 The plot of $(\alpha h\nu)^2$ against hν for two SnO_2:F thin films. a) NH_4F-film. b) HF-film.

5. CONCLUSION

SnO_2:F thin films were produced by the SP technique by using two doping compounds: NH_4F and HF. The comparison between the two sets of films showed that the HF-films have larger grain size, larger transmittance and larger direct bandgap energy. The films are rich in oxygen due to long exposure to atmosphere, but the NH_4F-films are the richer, which make them less conductive than the HF-films. From these findings we conclude that the HF-films are better for the use as fore-contacts in the CdS/CdTe solar cells.

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