Analysis of Nitrogen-Implanted Tin Oxide Films used in Dye-Sensitised Solar Cells

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Nitrogen was implanted in SnO_2:F film using ion energies between 10 and 40 keV and ion dose range $10^{14} – 10^{16}$ cm^{-2}. The microstructure of the film was modified by the ion implantation giving an amorphous region of various thicknesses. The amount of N was found to increase with increasing ion dose and energy. A maximum concentration of 5% N was measured in the highest ion dose and energy implanted sample.

1. Introduction

Dye-sensitised photoelectrochemical solar cells provide a technically and economically credible alternative to present day p-n junction photovoltaic devices [1]. The fundamental constraint on more widespread use of these cells is the current low energy conversion efficiency. There are several sources within the cell which are believed to limit the cell efficiency. The presence of reverse diode bias at TiO_2/electrolyte or TiO_2/substrate interfaces will tend to increase the probability of recombination of electrons with various ionised species and can be the cause of the low efficiency of the cell. Considerable gain in performance was reported when thin interfacial layers are present in heterojunction solar cells consisting of wide-band-gap semiconductors intimately contacted to a narrow-band-gap semiconductor [2].
In this work the TiO_2/substrate interface was modified by ion implantation resulting in changes in the surface composition, morphology, chemical bond structure and microstructure. Defects and lattice imperfections can be produced through ion implantation and this can cause a reduction in the optical band gap of the implanted film which may promote tunnelling at an interface by narrowing the depletion layer through increasing carrier concentration near the interface [3, 4]. The goal of the project is to reduce heterojunction effects at the interface between the TiO_2 and the SnO_2:F layers by varying the amount of the implanted species as well as the composition, microstructure and thickness of the implanted layer. Transmission Electron Microscopy (TEM) was used to investigate the microstructure of the implanted samples, including film thickness and crystalline properties. The distribution and amount of nitrogen were analysed using Secondary Ion Mass Spectroscopy (SIMS) and Photoelectron Spectroscopy (XPS) depth profiling.

2. Experiment

SnO_2:F samples were mounted in a chamber and implantation was performed over the pressure range $2 \times 10^{-6} – 6 \times 10^{-6}$ Torr. Nitrogen gas was ionised using a Freeman ion gun and a N^+ ion beam was selected using a magnetic field ion mass analyser at each accelerating voltage used. The ion current was measured using a Faraday cup in the chamber. The samples were implanted at normal incidence using ion energies between 10 and 40 keV and the sample current was maintained between 1 to 5 μA. Uniformity of the implanted samples was assured by sweeping the sample across the ion beam. Different samples having ion doses in the range $10^{14} – 10^{16}$ cm^{-2} were produced.

3.   Results

Fig. 1 shows TEM cross-sectional images of two SnO_2:F samples implanted with N at 10 keV and 40 keV for ion dose of 10^{16} cm^{-2}. The implanted layer has a thickness of about 30 nm and 110 nm for the 10 keV and 40 keV ion energies, respectively. In the implanted region a distinct amorphous layer can be observed at the surface of a polycrystalline region. It is suspected that implantation enhanced diffusion that could result in partial annealing of the amorphous region leading to the polycrystalline grains [5].
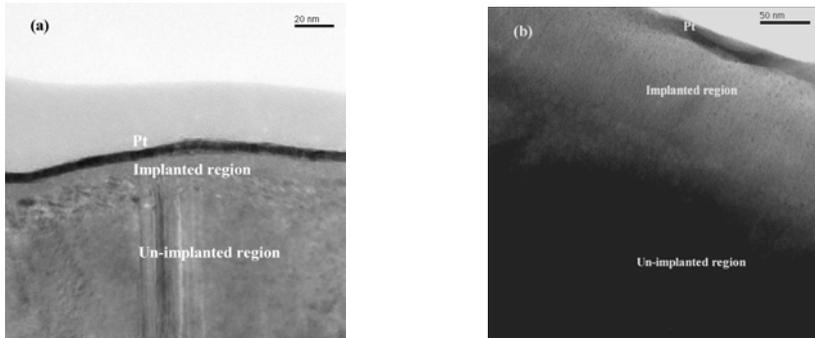

Fig. 1 Cross-sectional TEM image of N$^+$ implanted SnO_2:F films implanted at ion energies of (a) 10 keV and (b) 40 keV. Both films have ion dose of 10^{16} cm^{-2}.

Fig. 2a shows the SIMS depth profile of a sample implanted at 10 keV for an ion dose of 10^{16} cm^{-2}. The sample was etched until the intensity of N became almost zero, which is about 200 nm of thickness. A peak in N intensity can be observed at a thickness of 23 nm. Fig. 2b shows a skewed gaussian distribution of N at 10 keV obtained using a SRIM-2000 simulation by assuming the density of SnO_2 to be 3.34 g/cm^3. In the figure an intensity maximum located at about 35 nm may be observed and this peak is close to the result obtained from SIMS analysis (Fig. 2a). The calculated ion ranges for the 10 keV and 40 keV samples were 35 nm and 120 nm, respectively, which are in good agreement with the experimental results (Fig. 1).
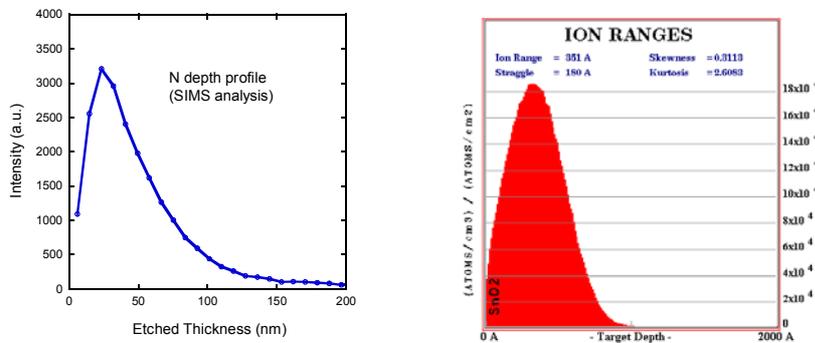

Fig. 2 Depth profile of N implanted SnO_2:F film obtained by (a) SIMS analysis and (b) SRIM-2000 simulation.

The relative intensity of N at the surface of the film decreases with increasing ion dose and a given ion energy. Fig. 3a shows the N/Sn intensity ratio of SnO_2:F film implanted at 10 keV and various ion doses. This result can be attributed to the effect of sputtering (surface erosion) from the films during implantation. When samples were exposed to the ion beam for long periods of time the erosion of earlier implanted N species from the surface of the film at a given energy can be higher resulting in the relative decrease in N/Sn. Fig. 3b shows the N/Sn intensity ratio as a function of etched thickness for different implantation energies having an ion dose of 10^{14} cm^{-2}. From the figure it can be observed that the relative intensity of N decreases with increasing implantation energy. Using SRIM-2000 simulations, the sputtering yield of Sn was found to decrease with increasing ion energy for a given number of ions. The sputtering rate of Sn bombarded by nitrogen decreases by 0.65 times as the implantation energy increases from 10 keV to 40 keV. The sputtering (erosion) of earlier implanted N during implantation can also be expected to increase with increasing implantation energy.
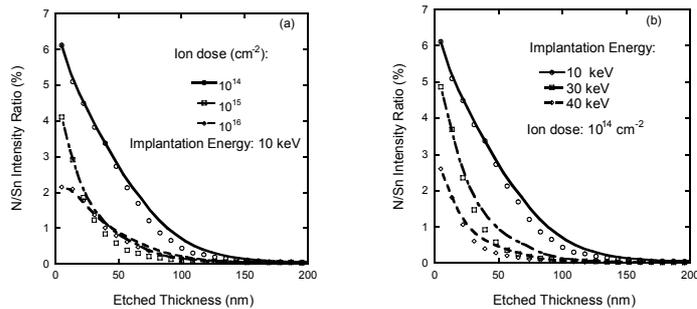
Fig. 3 N/Sn intensity ratio (%) of N implanted SnO_2:F film obtained using SIMS depth profile at various values of (a) ion dose, and (b) implantation energy.

The concentration of N for a given ion dose was found to increase with increasing implantation energy as shown in Fig. 4. A maximum N concentration of about 5% was obtained when the SnO_2:F film was implanted at 40 keV. By annealing the implanted samples defects induced by the ion implantation can be removed. It was observed that with increasing annealing temperature the content of N in the film decreased. The concentration of a sample with an ion dose of 10^{16} cm^{-2} (implanted at 10 keV) decreased to zero after annealing at 500°C for 1 hour (Fig. 4). The decrease of N content after annealing might be related to the number of defects removed from the film.
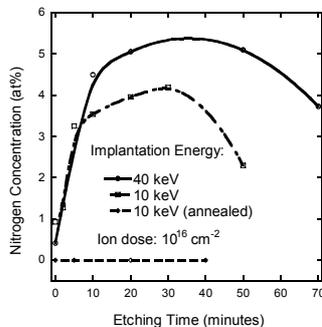

Fig. 4 Depth profile of N obtained by XPS for 10 keV and 40 keV implanted samples having ion dose of 10^{16} cm^{-2}. A sample implanted at 10 keV and annealed at 500°C for 1 hour is also included.

In summary, the surface of SnO_2:F film was modified by ion implantation. The overall results showed an increase of N concentration in the film with increasing ion dose and energy. From a previous study of the implanted film change in optical and electrical properties have been reported [6]. The effect of this modified heterojunction layer on the performance of dye-sensitised titania solar cells could have a significant effect which will be investigated.

References
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