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Effects of electron beam irradiation on tin dioxide gas sensors

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Abstract. **In this paper, the effects of electron beam irradiation on the gas sensing performance of tin dioxide thin films toward H_2 are studied. The tin dioxide thin films were prepared by ultrasonic spray pyrolysis. The results show that the sensitivity increased after electron beam irradiation. The electron beam irradiation effects on tin dioxide thin films were simulated and the mechanism was discussed.**

Keywords. **Electron beam; irradiation; gas sensor; tin dioxide.**

1. Introduction

The theory, fabrication and application of semiconducting gas sensors, has been well developed in the last thirty years. However, their limited selectivity and sensitivity are still problematic. The usual methods to improve gas sensing properties of SnO_2 gas sensors are doping metal, metal ion, metal oxides etc (Heng *et al* 2003; Mittal *et al* 2004; Wurzinger and Reinhardt 2004). Microstructure is an important factor that influences gas sensing properties. There are reports to enhance the gas sensing performance of gas sensors by ultraviolet (Camagni *et al* 1996; Comini *et al* 2000, 2001) and plasma (Srivastava *et al* 1998; Chaturvedi *et al* 2000) irradiation to modify the surface structure, which will greatly increase sensitivity of tin dioxide gas sensors. In this paper, electron beam irradiation was used to improve the gas sensing properties of SnO_2. The effect of electron beam irradiation on the SnO_2 gas sensors is studied in this paper and the performance of SnO_2 gas sensors can be improved notably.

2. Experimental

Tin dioxide thin films were prepared by ultrasonic spray pyrolysis, described in detail earlier (Jiao *et al* 2003). The electron beam irradiation was performed by a GJ-2 electron accelerator, working at 1·75 MeV, 2 mA. The irradiation doses were controlled by irradiation for different times.

The gas sensitivity, S, is denoted by R_a/R_g, where R_a and R_g stand for the resistances of the samples in air and H_2 gas, respectively. The resistance of the sample was measured in a gas chamber with an inside stirring fan. The sample was heated and a thermoregulator controlled its temperature.

3. Results and discussion

The sensing curves before and after 1000 kGy electron beam irradiation of SnO_2 thin film gas sensors to H_2 are shown in figure 1. The response of SnO_2 thin film to H_2 increased after electron irradiation. The sensitivity of SnO_2 gas sensor to 100 ppm H_2 is 11·5 before irradiation and 37·5 after irradiation, ~3 times higher, which proves that the electron beam irradiation will increase gas sensing properties.

The relationship between sensitivity of SnO_2 sensor to 50 ppm H_2 and electron beam irradiation doses are shown in figure 2. The sensitivity increases with the raise of elec-

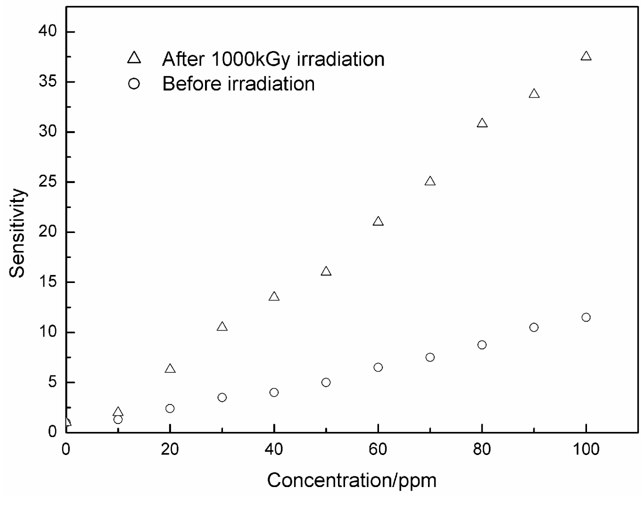

Figure 1. The sensitivity of SnO_2 gas sensor to H_2 before and after 1000 kGy electron beam irradiation.

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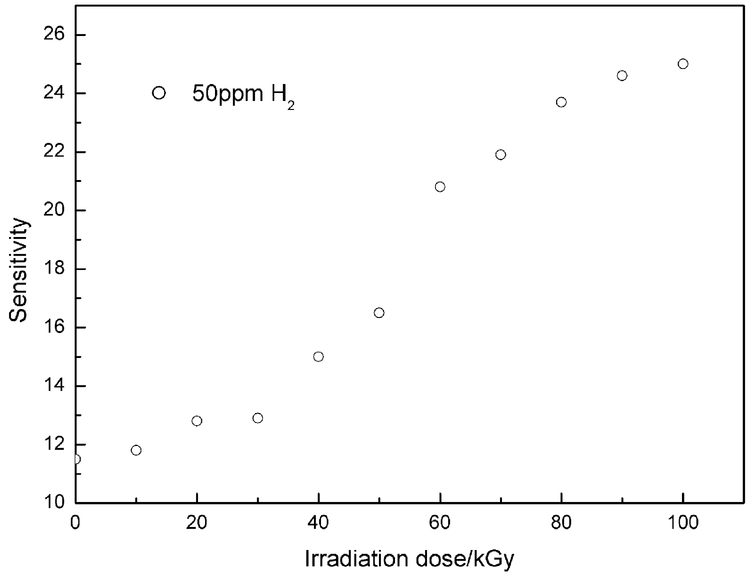

Figure 2. The relationship between sensitivity of SnO_2 sensor to 50 ppm H_2 and electron beam irradiation doses.

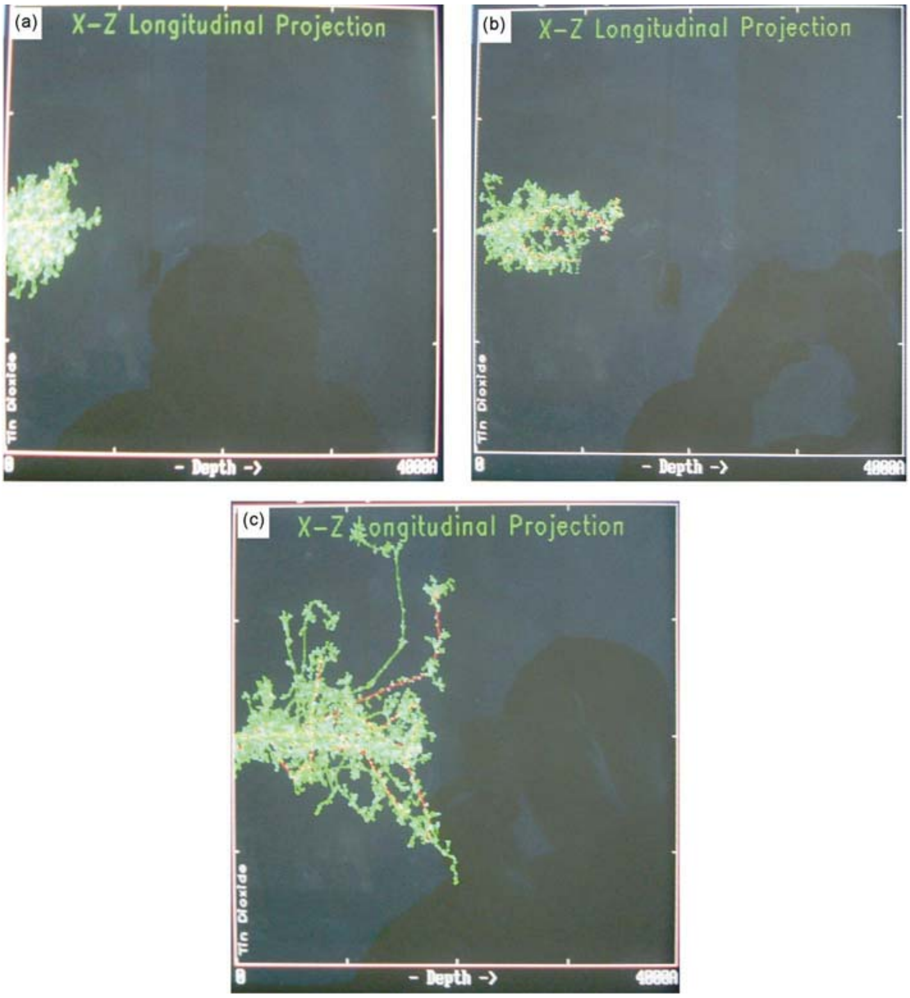

Figure 3. The simulated results of electron beam injecting effects under various irradiation doses: (**a**) 200 kGy, (**b**) 400 kGy and (**c**) 800 kGy.

tron irradiation dose. Under low irradiation dose, <300 kGy, the sensitivity of SnO_2 thin film shifts slightly, from 300–850 kGy, the sensitivity increases greatly, at 850 kGy and it reaches 24·8. Then the sensitivity reaches maximum and remains stable while continuing to increase irradiation doses.

The electron beam injecting effects into SnO_2 surface layer were simulated and are shown in figure 3. It can be seen that stronger irradiation will inject deep inside the layer and at 200 kGy, the affected depth is about 100 nm (1000 A in image), at 400 kGy the electron beam reached a depth of 150 nm and at 800 kGy, it reached 200 nm. Furthermore, electron beam will not only cause defects in depth, but also in a wider area in the same layer.

According to traditional gas sensing mechanism, polycrystalline metal oxide semiconductor material is composed of grains with different orientations. There are double potential barriers between every grain boundaries, which control the conductance of bulk materials. Electron irradiation can affect transport across these grain boundaries by increasing the density of free carriers throughout the material, decreasing the intergrain barrier height by changing the intergrain states charge, and increasing the probability of tunneling through the intergrain barriers by decreasing the depletion layer widths in the adjacent grains.

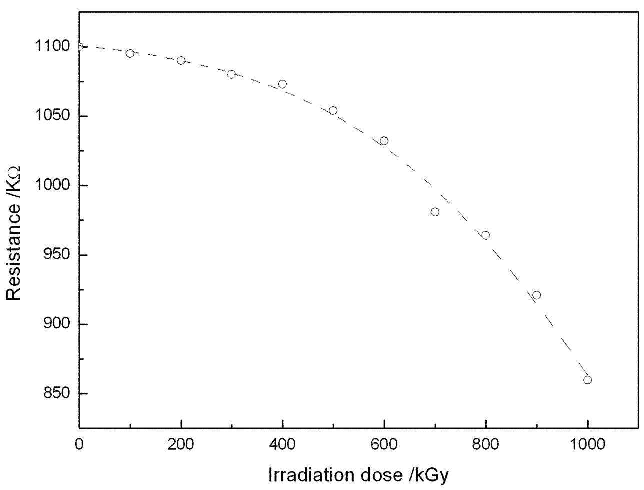

Figure 4. The resistance shift of SnO_2 thin film after electron beam irradiation.

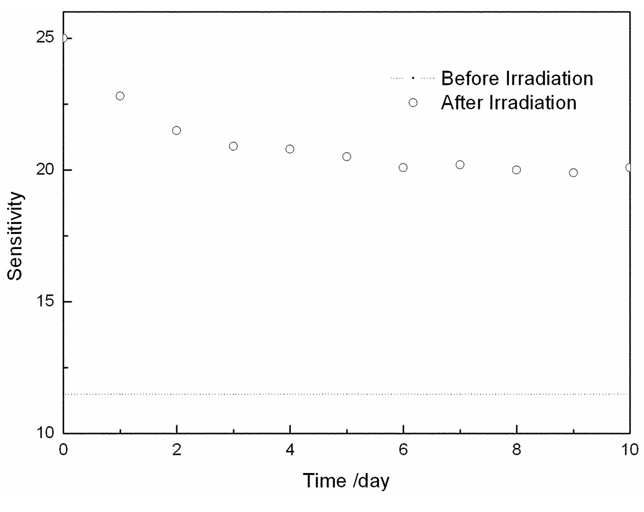

Figure 5. The sensitivity evolution of SnO_2 sensor electron beam irradiation.

The resistance shift of SnO_2 thin film after electron beam irradiation is shown in figure 4. The resistance of SnO_2 thin film decreases slowly at low irradiation dose, but decreases rapidly under high irradiation dose. The electron beam irradiation will not change the chemical composition of the semiconductor, but produces structural defects. The electron beam irradiation changes the occupancy of the defects by electrons and holes, changes the concentration of the adsorption centres of each given type and the capacity of adsorption on the surface of the semiconductor, these factors caused the decrease of resistance of SnO_2 thin film.

Figure 5 shows the sensitivity evolution in several days after electron beam irradiation. The highest sensitivity was obtained just after irradiation and decreases with time. But it will reach a stable value after 4 or 5 days, and still much higher than the sensitivity before irradiation, shown as dashed line in the figure.

4. Conclusions

The ultrasonic spray pyrolysis prepared tin dioxide thin film gas sensors were treated by electron beam irradiation. The results show that the bulk resistance decreased and the sensitivity to H_2 increased after irradiation. The sensitivity increases more rapidly under high doses of irradiation than under low doses of irradiation. The electron beam irradiation effects were simulated and the mechanism was discussed.

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