Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2008, Article ID 395490, 4 pages
doi:10.1155/2008/395490

Research Article

Enhancement of Ammonia Sensitivity in Swift Heavy Ion Irradiated Nanocrystalline SnO_2 Thin Films

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Received 12 July 2008; Accepted 24 September 2008

Recommended by Rakesh Joshi

Swift heavy ion irradiation is an effective technique to induce changes in the microstructure and electronic energy levels of materials leading to significant modification of properties. Here we report enhancement of ammonia (NH_3) sensitivity of SnO_2 thin films subjected to high-energy Ni^+ ion irradiation. Sol-gel-derived SnO_2 thin films (100 nm thickness) were exposed to 75 MeV Ni^+ ion irradiation, and the gas response characteristics of irradiated films were studied as a function of ion fluence. The irradiated films showed *p*-type conductivity with a much higher response to NH_3 compared to other gases such as ethanol. The observed enhancement of NH_3 sensitivity is discussed in context of ion beam generated electronic states in the SnO_2 thin films.

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1. INTRODUCTION

Tin oxide (SnO_2) is a material widely used for gas sensing applications because of its suitable properties such as natural off-stoichiometry, chemical and thermal stability, and ease of processing [1]. Tin oxide-based gas sensors have been successfully designed to detect a variety of toxic and hazardous gases and vapors for applications ranging from domestic leak detections to industrial process control. However, because of stricter environmental regulations and process control requirements, gas sensors with higher sensitivity and selectivity are in continuous demand; hence efforts are on to tailor the properties of sensing materials such as tin oxide to achieve better gas response properties.

Swift heavy ion irradiation, in which an energetic ion beam is allowed to pass through a material, is a very effective technique to induce changes in microstructure and electronic energy levels, and has been used to tailor properties of various metallic, semiconducting, and insulating thin films [2]. When a high-energy ion beam passes through a material, it loses its energy in two distinct pathways; namely, nuclear and electronic energy losses. The nuclear energy loss dominates at lower energies, whereas higher energy beam results in electronic excitation of the target material. By suitable control of the irradiation parameters such as energy and fluence of the ion beam, it is therefore possible to tailor various properties of the target material. Ion irradiation technique has been used to tailor the structure-property relationships in several metal oxide systems; for tin oxide, however, studies have so far been limited only to variation of microstructure in powders [3, 4], and nanocrystallization in thin film [5]. An attempt to modify the gas sensing properties of tin oxide thin films by ion irradiation had resulted only in the baseline stabilization [6].

In this work, we report on the effect of 75 MeV Ni^+ ion irradiation on gas sensing properties of sol-gel-derived SnO_2 thin films. Gas sensing experiments using ammonia and ethanol on irradiated films revealed a much greater enhancement of sensitivity for ammonia with respect to ethanol. Furthermore, in comparison to unirradiated films, the irradiated films showed *p*-type conduction. The observed enhancement of gas sensitivity and selectivity to ammonia has been discussed in context of ion beam-induced changes in the material.

2. EXPERIMENTAL

SnO_2 thin films were deposited from a solution containing 10 gm of $SnCl_4 \bullet 5H_2O$ dissolved in 80 mL of 2-propanol. Thorough mixing was ensured by refluxing the solution

with magnetic stirring arrangement for 6 hours at 80°C and then the resultant solution was left for ageing for another 6 hours. This solution was then filtered through a Whatman filter paper to obtain a clear solution free of any particulate. The final solution was coated onto Corning 7059 glass by dip coating system at speed of 10 cm/min^2 for depositing one layer of the film. Each deposited layer was dried at 200°C for 15 minutes before deposition of the next layer. Final sintering of the films was carried out at 600°C after deposition of a required number of layers to obtain a desired thickness. Thickness of the deposited films was estimated by an Ambios surface profilometer and was approximately 1000 Å. These films were irradiated at room temperature by using 75 MeV Ni^+ ions at two different fluences, namely, 1×10^{11} and 1×10^{12} ions/cm^2. During the irradiation, pressure inside experimental chamber was at 1.5×10^{-6} mbar. Structural analysis of the films was done with the help of a Philips "XPert" model glancing angle X-ray diffractometer (GAXRD) in the 2θ range of 20°–60°. Microstructural characterization was performed using Technai G20-Stwin (200 KeV) high-resolution transmission electron microscope (HRTEM). For HRTEM studies the films were ultrasonically dispersed in ethanol and taken on the carbon coated grids. Gas sensing experiments were performed with an indigenously designed gas-sensing setup attached with mass flow controllers for precise measurement of gas flows at ppm level. Change in resistance of the films was measured as a function of temperature through a computer interfaced digital multimeter (DMM).

3. RESULTS AND DISCUSSION

Figure 1 shows the glancing angle XRD patterns of unirradiated and irradiated SnO_2 thin films. All peaks in the spectra correspond to the standard rutile phase with polycrystalline structure. It is observed that, in comparison to unirradiated film, the relative intensities of all peaks increase in irradiated films. Furthermore, the intensities of XRD peaks also increase with increase in ion fluence, implying that SHI beam irradiation enhances crystallinity of the SnO_2 thin films. A careful examination of the XRD patterns further reveals that the relative intensity of (110) peak in the irradiated films increases at a faster rate as compared to the intensities of the other peaks, which implies that irradiation of Ni ions also enhances the preferred orientation of the SnO_2 thin films. Increase of crystallinity along the (110) plane plays a crucial role in enhancing gas-sensing properties of SnO_2 thin films, which is discussed later.

Figure 2 compares the HRTEM images of unirradiated and irradiated SnO_2 thin films. In the unirradiated film (Figure 2(a)), the crystallites appear randomly oriented, a characteristic feature of sol-gel-derived thin films. With the ion irradiation, however, the crystallite boundaries gradually disappear and enhancement of crystallinity is observed. At higher fluence (Figure 2(c)), the crystallites show preferred orientation along (110) planes, which confirms XRD observations reported in the last paragraph.

Gas sensing experiments performed on unirradiated SnO_2 films with 1000 ppm ammonia and ethanol gases are

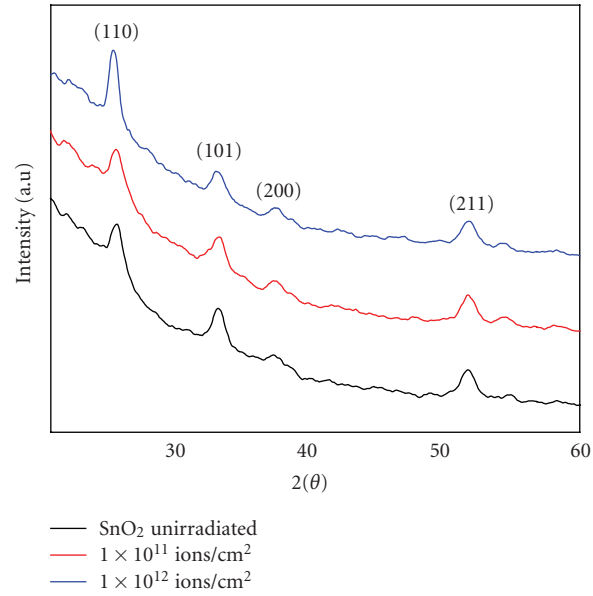

Figure 1: Glancing angle XRD patterns of unirradiated and irradiated SnO_2 thin films.

shown in Figure 3, and Figure 4 compares the responses of irradiated (with 10^{12} ions/cm^2) films under similar conditions. Here it is worth mentioning that unirradiated films show decrease of resistance when exposed to ammonia and ethanol, both reducing gases, due to normal n-type behavior; however, the irradiated films show increase of resistance under similar conditions indicating p-type conduction resulting from ion irradiation. The sensitivity factors are calculated by the equation:

$$s = ((R_g - R_a)/R_a)\%, \quad (1)$$

where R_g and R_a represent resistance in the presence of gas and air, respectively; the values of s for unirradiated and irradiated films at different temperatures are tabulated in Table 1. For the unirradiated films, the values of sensitivity "s" in ammonia and ethanol gases at 300°C are 284 and 87, respectively, while for irradiated films they increase to 516 and 115, respectively, for 1×10^{11} ions/cm^2, and to 882 and 142, respectively, for 1×10^{12} ions/cm^2. This implies that irradiation of SnO_2 thin films by high-energy ion beam, for example with a fluence of 1×10^{12} ions/cm^2, results in a 213% (284 to 882) increase in its ammonia sensitivity, while only 63% (87 to 142) increase in sensitivity for ethanol is observed under similar conditions. Such an enhancement of ammonia sensitivity can be explained in terms of the surface chemistry modifications due to ion beam irradiation.

The XRD data shown in Figure 1 shows an enhancement of crystallinity along the (110) plane resulting from Ni^+ ion irradiation, which also indicates preferred surface orientation of the irradiated SnO_2 thin films. Such a (110) surface of SnO_2 consists of two types of oxygen vacancies: the bridging oxygen vacancies created by removal of oxygen ions from the top layer of an ideal (110) surface, and the "in-plane" oxygen vacancies created by removal of oxygen

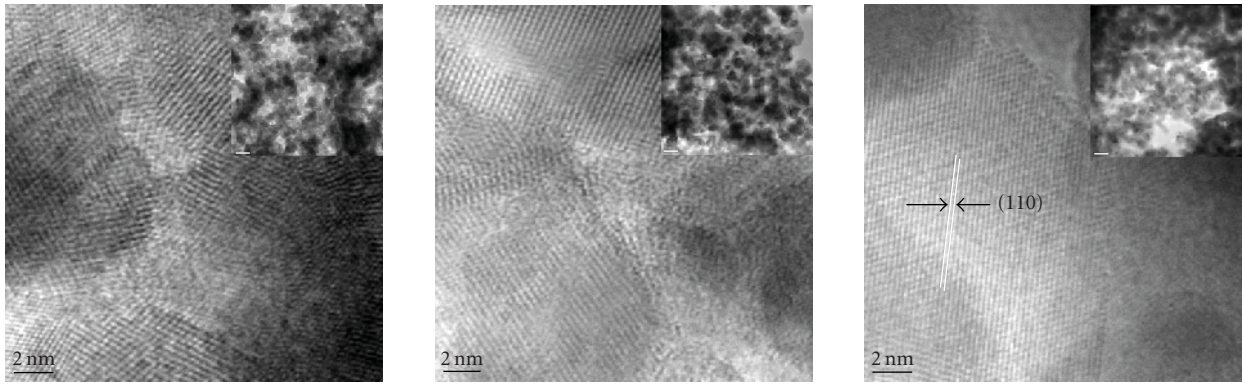

Figure 2: High-resolution TEM images of SnO_2 thin films: (a) unirradiated, (b) irradiated with 10^{11} ions/cm^2, and (c) irradiated with 10^{12} ions/cm^2.

Table 1: Sensitivity factors of unirradiated and irradiated SnO_2 thin films for ammonia and ethanol at different temperatures.

Ni^+ ion irradiation fluence	Temperature 200°C (sensitivity %)		Temperature 250°C (sensitivity %)		Temperature 300°C (sensitivity %)	
	NH_3	C_2H_5OH	NH_3	C_2H_5OH	NH_3	C_2H_5OH
Unirradiated	52	5	98	32	284	87
1×10^{11} ions/cm^2	68	15	103	53	516	115
1×10^{12} ions/cm^2	122	27	649	73	882	142

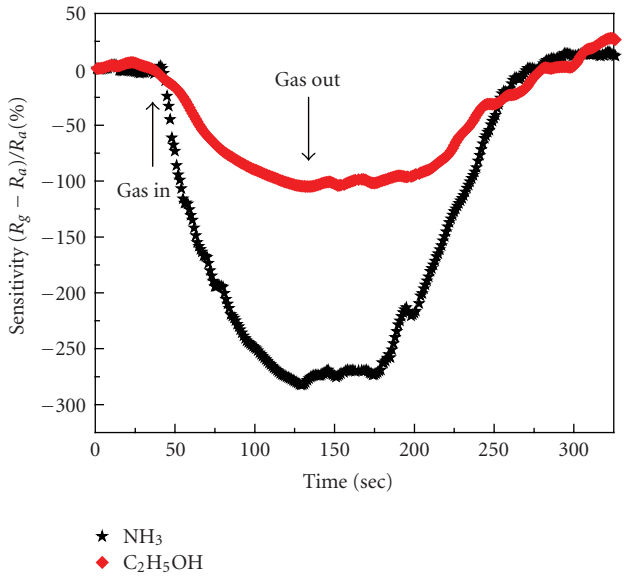

Figure 3: Gas sensing behavior of unirradiated SnO_2 thin films at 300°C, exposed to 1000 ppm ammonia (NH_3) and ethanol (C_2H_5OH) vapors.

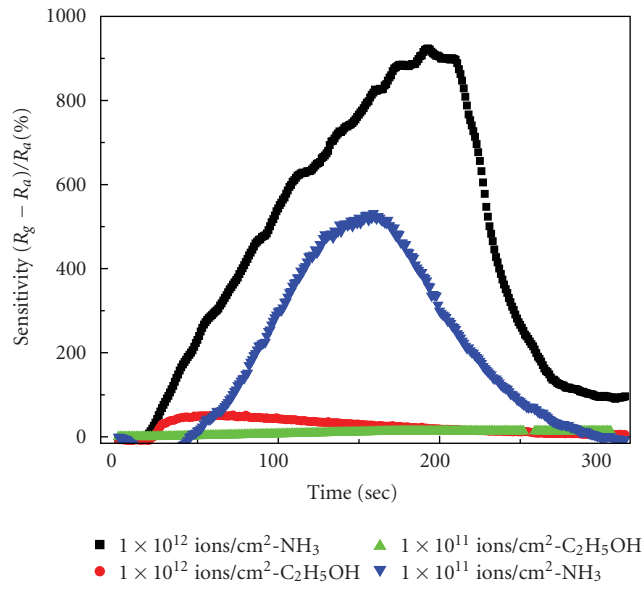

Figure 4: Gas sensing behavior of SnO_2 thin films irradiated with 1×10^{11} ions/cm^2 and 1×10^{12} ions/cm^2, exposed to 1000 ppm ammonia (NH_3) and ethanol (C_2H_5OH) vapors at 300°C.

ions from the tin containing lattice plane [7]. During the ion irradiation process, samples are kept in an ultrahigh vacuum ambience that promotes oxygen desorption, especially from the top layer resulting in the formation of "bridging" oxygen vacancies. Such oxygen vacancies may also result from the thermal spikes created in the samples during ion irradiation. The formation of bridging oxygen vacancies lowers the coordination number of the surface tin cations from an initial value of six to four, which, in turn, reduces their charge state from Sn^{4+} to Sn^{2+}. The four- coordinated Sn^{2+} ions are known to be more acidic compared to Sn^{4+} cations, which promotes a higher chemisorption of ammonia, a strongly basic gas, on the surface of the irradiated films [8]. Hence the sensitivity of high-energy ion irradiated SnO_2 thin films

toward ammonia is significantly enhanced compared to that for any other gas such as ethanol. Furthermore, the four coordinated Sn^{2+} ions create a local SnO—like environment at the surface and near surface region of the irradiated SnO_2 thin films, which results in *p*-type conductivity observed in the gas sensing experiments [9].

4. CONCLUSIONS

The present study shows that structural and gas sensing properties of SnO_2 thin films are significantly modified by 75 MeV Ni^+ ion irradiation. The crystallinity of the irradiated films is enhanced along the (110) plane that also affects the gas sensing characteristics. Gas sensing experiments with ammonia and ethanol reveal a significant enhancement of sensitivity for ammonia over ethanol that is attributed to acidic nature of the irradiated SnO_2 surfaces. Formation of bridging oxygen vacancies during the ion irradiation process converts the six coordinated Sn^{4+} cations into four coordinated Sn^{2+} cations; the latter have more acidic character than the former. This promotes a stronger chemisorption of ammonia molecules on the surface of the ion irradiated SnO_2 thin films.

ACKNOWLEDGMENT

The authors acknowledge the support of Nano Science Unit (at IIT Delhi) of NSTI, DST, Government of India for carrying out the HRTEM investigations.

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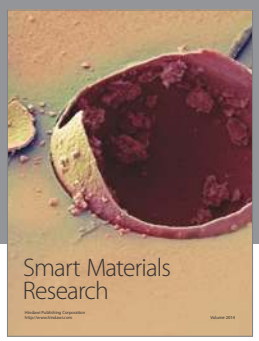

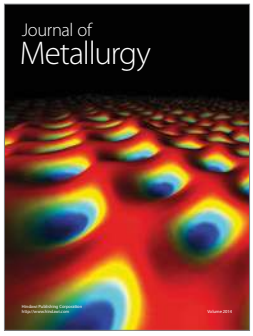

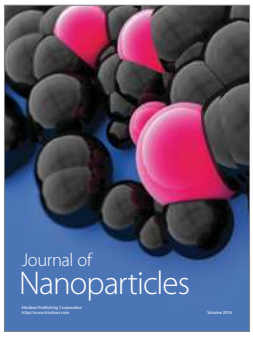

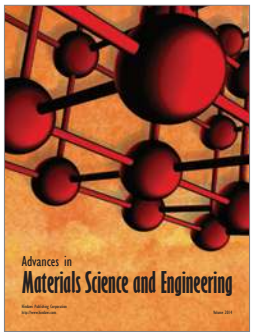

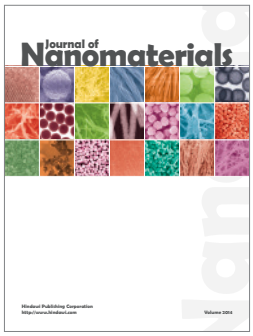

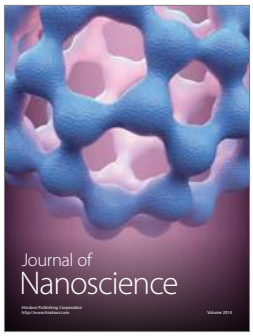

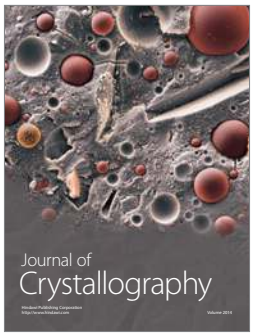

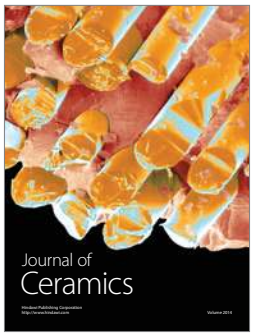

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