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On the photo-induced electrical conduction related to gas sensing of the Sb:SnO_2/TiO_2 heterostructure

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ABSTRACT

In this work, changes on the electrical properties as function of the temperature and gas addition on the surface of the 4at%Sb:SnO_2/TiO_2 heterostructure are investigated. This heterojunction privileges the gas sensor application at temperatures nearer to the ambient temperature, when compared to existing devices, which is more efficient when sensitized with monochromatic light of specific wavelength. The results point that the conduction mechanism, under the thermally activated trapping influence, is occurring preferentially in the TiO_2 layer, since the activation energy of the deepest level is 56 meV, comparable to donors from TiO_2. Besides, an increase of the photo-current decaying rate was noticed when using the excitation of a He-Cd laser under O_2 atmosphere and room temperature, compared to films with a sole TiO_2 layer. Samples showed a high resistance variation (up to 40 times) with the addition of gas at temperatures higher than 330 K, that can be attributed to the electron trapping by the oxygen molecules adsorbed on the sample surface. A model that describes such trap-states and the conduction mechanism within the samples is proposed. This way, this work can be valuable to the better understanding of the effects and rules on the electrical behavior of this heterostructure, in order to apply this material as a gas sensor device.

1. Introduction

Nowadays gas sensors based on semiconductors present growing interest [1–4] but have some disadvantages concerning the relatively high operating temperature and high power consumption [5]. To overcome such obstacles, several reports about the use of photoactivation of metal oxide semiconductor sensors have been published, in order to increase the gas sensitivity. Some of these works present the use of UV light to improve the gas sensitivity [4,6–8], and this illumination is an alternative to modulate and activate the sensor signal value [9]. On the other hand, the use of semiconductor heterostructures may improve even further the gas sensing properties, by means of the charge transfer from one material to another. Such heterostructures may also be improved through the UV illumination, by means of the creation of incomplete bonding on the sensor's surface, enabling the adsorption of more gas molecules [10,11].

Interesting properties may be achieved from different heterostructures, and a very high variety of heterostructure applications have been reported in recent years, such as electrodes for supercapacitors [12], high energy density supercapacitors [13], and gas sensing devices [14–16]. In the case of gas sensor application, the formation of heterostructures enhances the sensing properties, as the use of SnO_2:Zn_2SnO_4 nanowires (NW) [16] that causes an improvement of about 1.5 times in efficiency to sense ethanol, compared with sole SnO_2 NW. Such improvement occurs in the principal mechanism for ethanol sensing [17], attributed to the dehydrogenation of ethanol with the addition of Zn_2SnO_4 to SnO_2. The use of n-ZnO/n-In_2O_3 presents up to 6 times improvement on methanol sensing compared to sole In_2O_3, ruled by the electron transfer effect at the heterostructure interface [15].

The junction of two materials forming a heterostructure creates a potential barrier at the interface, originated from the valence and conduction bands discontinuities of both semiconductors, after the thermodynamic equilibrium is reached [18]. The electrons tend to migrate from one material to another, according to the elec-

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tron affinity of the material [18,19]. Considering the SnO_2/TiO_2 (tin dioxide / titanium dioxide) heterostructure, the equilibrium condition leads to electron transfer from the SnO_2 to TiO_2, due to the higher electron affinity of the TiO_2 [18,20]. The improvement of gas sensing properties in this heterostructure under illumination, compared to sole materials, occurs due to the photo-excitation of electrons in the exposed TiO_2 layer, that along with the transferred electrons from the SnO_2 layer, at the formation of the junction, increases the concentration of charges exposed on the surface, which act as adsorption centers for gas molecules [11]. The photo-excitation must be done by an UV-light source, with higher energy than TiO_2 bandgap, and, after photo-excitation, electron transfer from TiO_2 to SnO_2 also may occur but due to the potential barrier at their interface this transference may be limited [10].

TiO_2 is a semiconductor with wide bandgap of about 3.3 eV [21]. The n-type conductive nature of TiO_2 comes from interstitial Ti^{3+} and oxygen vacancies [22]. The presence of oxygen vacancies in this oxide facilitates the gas adsorption through stronger bonding between the film surface and the gas molecules, with desorption temperature of about 410 K [23,24]. Improved gas sensitivity of TiO_2 can be achieved by growing the films in the (101) and (001) (hkl) planes of the anatase structure [23,25,26]. Tin dioxide (SnO_2) is also a wide bandgap semiconductor, that presents high transparency in the visible region, and high thermal stability [27,28]. The n-type conductivity nature of SnO_2 also originates from oxygen vacancies and interstitial tin atoms [29]. Thin films obtained through sol-gel related techniques present low conductivity related to the small crystallites and consequently high grain boundary scattering that decreases considerably the electron mobility [30,31]. On the other hand, when donor-doped with Sb^{5+} ions an increase of electron density occurs in the semiconductor [31], which raises the conductivity.

In this work, the investigation of electrical characteristics of the 4at%SnO_2/TiO_2 heterojunction under photo-excitation is carried out at gas and room atmospheres. Different temperatures and their influences on the photo-induced decay rate are also evaluated and are related to deep level defects in the semiconductor layers. Concerning the improvement of the gas sensing properties, the illumination of the heterojunction, with well-established excitation energy, contributes to increase on the adsorption centers on the surface of the TiO_2 exposed layer. The investigation presented in this work contributes to the understanding of the gas sensing mechanisms, and to the improvement in the Sb:SnO_2/TiO_2 heterostructure under different atmospheres, temperatures and light excitation.

2. Experimental details

Sol–gel production of TiO_2 was accomplished by hydrolysis and condensation of titanium (IV) isopropoxide using a high molar ratio of water:alkoxide (200:1), isopropanol as co-solvent, HNO_3 as catalyst, and Triton X-100 as surfactant [32,33]. Initially 2.6 ml of Nitric acid was added to 185 ml of deionized water and 57 ml of isopropanol, followed by dropwise addition of 15 ml of titanium (IV) isopropoxide alkoxide, under stirring and heating at 85 °C during 4 hours. The concentration of solution was performed by evaporating the solvent and dispersants at 100 °C until reach a volume of 50 ml, which was followed by the addition of the surfactant under stirring for 30 min. Colloidal suspension of 4 at% Sb:SnO_2 was obtained through an aqueous solution of Sn^{4+} (0.5 M) obtained by dissolution of $SnCl_4 \cdot 5H_2O$ in deionized water mixed to a solution of Sb obtained by dissolution of SbF_3 in deionized water. Hydrolysis of Sn^{4+} and Sb^{5+} ions were promoted by addition of NH_4OH. The obtained suspension was submitted to dialysis against distilled water for elimination of chloride and fluoride ions [30,34].

The films depositions were carried out by dip-coating on soda lime substrate, previously cleaned with piranha solution at H_2SO_4:H_2O_2 ratio of 70:30, with immersion/emersion speed of 10 cm/min. The semiconductors films were obtained in a single deposition of each material. Firstly, the 4at%Sb:SnO_2 layer was deposited, followed by a calcination at 80 °C for 10 min, and a thermal annealing at 500 °C for 2 h. Then, the TiO_2 was deposited, as the top layer semiconductor, with same calcination and annealing processes. The final thicknesses of these films are approximately 380 nm and 360 nm, for 4at%:SnO_2 and TiO_2 respectively, as reported in a recent work with the same deposition parameters [35]. Aluminum electrodes were deposited paralelly on the TiO_2 surface, using shadow masks, through thermal evaporation at pressure of about 10^{-6} torr. The thickness (t) and width (W) of Al deposited was $t = 100$ nm and $W = 10$ mm, and length (L) between electrodes $L = 5$ mm. The final assembly of the sensor device is shown as inset of Fig. 2.

Structural, optical, and electrical characterizations were performed accordingly with the descriptions below. X-ray Diffraction (XRD) was carried out in a Rigaku diffractometer (Model D / Max - 2100 / PC) operating with CuK_α radiation (1.5405 Å) and Ni filter for attenuation of K_β radiation and scanning rate of 2°/min, in 2θ mode with fixed incident angle of 1.5°. Data were analyzed with the software Match (Crystal Impact), and the average crystallite size (τ) was estimated by Scherrer equation $\tau = K^*\lambda/\beta^*cos(\theta)$, where K is a shape factor with typical value of 0.9; λ is the wavelength of the X-ray; β is the broadening at half maximum intensity peak, and θ is the Bragg angle [30]. Optical transmittance and absorbance were performed in a Perkin Elmer spectrophotometer (Lambda Model 1050 UV / VIS / NIR) in the range 200–3300 nm. Photocurrent decay was performed under vacuum conditions in different temperatures (120–300 K), and under O_2 atmosphere at room temperature. The photoexcitation was performed with He-Cd Laser, $\lambda = 325$ nm and power of 200 mW, during 90 s, with the laser beam directed to the region between electrodes. Although the laser energy is higher than the bandgap of both oxide semiconductors, it is inside the spectra region of high absorption of the TiO_2 film (top layer) that works as a filter to higher energies than its bandgap. Therefore, most of the light energy is absorbed by this top layer and light with only energy lower than the TiO_2 bandgap (3.3 eV) achieves the Sb:SnO_2 bottom layer, which is then, lower than its direct (3.8 eV) bandgap. A fixed applied voltage V = 2 V was set during the photoexcitation under room and O_2 atmospheres. For measurements with O_2 atmosphere, the gas was injected in the system at the end of the photoexcitation, to assure the same excitation conditions as under low pressure atmosphere.

3. Results

Results on structural and optical properties of the Sb:SnO_2/TiO_2 film were obtained by XRD and UV–vis measurements, shown in Fig. 1, to obtain information about the optical properties and bandgap, as well as the crystalline phase and crystallite size of the sample. These properties are important factors that affect directly the electrical character in oxide semiconductors. The XRD presented in Fig. 1(a) shows that the most intense diffraction peak is attributed to plan (101) of anatase TiO_2 (JCPDS-ICDD 2003, file #089-4921). Although the thermal annealing occurred at 500 °C, which is below the necessary temperature for TiO_2 anatase/rutile phase transition [33,36], the figure shows diffraction peaks related to the planes (110) and (211) of TiO_2 rutile phase (JCPDS-ICDD 2003 file # 089-4920). In spite of the low thermal annealing temperature, TiO_2 rutile phase may occur by two different mechanisms: the thermally activated transition phase, or the ordered structural induction. The first mechanism is associated with the formation of