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Influence of Charge Carriers Concentration and Mobility on the Gas Sensing Behavior of Tin Dioxide Thin Films

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Abstract: In order to investigate function of carrier behavior on gas-sensing properties, tin oxide-based films with different carrier concentration and mobility were obtained, by magnetron sputtering from the powder target, which was followed by further oxygen-management through the annealing treatment. The microstructure, surface morphology, electrical properties and gas sensitivity were characterized by XRD, Raman spectrum, photoluminescence spectrum, atomic force microscope, the hall effect system and electrochemical workstation, respectively. The results showed that all SnO₂-based films had a tetragonal rutile phase with (101) preferred orientation. The introduction of fluorine and regulation of oxygen vacancies tuned carrier concentration from 10¹⁵/cm³ to 10²¹/cm³ and mobility from 10² cm²/V·s to 10^{−1} cm²/V·s. The decreasing carrier concentration as well as increasing mobility had a positively important function to improve the sensitivity of SnO₂-based films. The air-annealed SnO₂ film with lowest carrier concentration had a maximum sensitivity of R = 5.0, while vacuum-annealed SnO₂:F film with the highest carrier concentration being the minimum sensitivity. This puts forward a novel reference for the design and application of SnO₂-based gas sensing films.

Keywords: SnO₂ film; fluorine doped; carrier concentration; carrier mobility; gas response

1. Introduction

With the requirement of environmental protection and safety, the dangerous, toxic, harmful, flammable and explosive gases need to be detected and regulated, which greatly promoted the development of gas sensor technology. Among many semiconductor materials, tin oxide (SnO₂) has been the mainstream of research owing to good chemical stability, fast response/recovery, high sensitivity, low cost and a wide variety of gas responses [1–3].

Many studies focus on the synthesis of SnO₂-based with different nano sizes and morphologies to improve their adsorption properties, and in turn improve the gas response. By preparing different sizes of SnO₂:F nanorod film with spray pyrolysis method, Cho et al. [4] found that nanorod film with a long length of about 370 nm showed relatively higher sensitivity, but a slow gas response and recovery time. Chao et al. [5] reported that the SnO₂ nanotubes consisting of 5–10 nm nanoparticles still achieved sensitivity of 16.1% and response time of 20 s, even though under a low-concentration 9.7 ppb NO₂ at room temperature. Zhang et al. [6] synthesized SnO₂ hollow spheres of different sizes

to increase the specific surface area of the sensor, and obtained that the sensitivity to 5–100 ppm NO₂ is 8–12.2 times that of solid particles.

Moreover, in order to further improve the sensitivity and selectivity of different nanostructure, many elements including noble metal were doped to increase the active adsorption sites of the sensor. Yin et al. [7] explored the preparation of dual sensors with (Pd, Fe)-modified SnO₂ and Pt-loaded SnO₂ for improving the gas selectivity, which could detect and calculate the respective concentrations of CO and H₂ in the mixed gas. Jin et al. [8] studied that SnO₂-based nanostructure by 2.5% doped Cu reached sensitivity of 221 for 500 ppm acetone and increased selectivity between acetone and ammonia, and the corresponding response and recovery times are 9 s and 6 s, respectively. Additionally, Mahdavian et al. [9] and Prades et al. [10] further clarified the interaction of SnO₂-based sensors with different kinds of target gases and through simulation calculations.

As a matter of fact, the sensitivity of resistance-typed gas sensor is derived from the change with the resistance of the material [1], which was explained by the molecular reaction model [11] and the grain boundary barrier model [12]. Based on such models, the current researches focused the enhancement of conductance change ΔG by controlling Δn and $\Delta \mu$ of SnO₂-based materials, and ignored the effect of initial electrical conductance characteristics about the carrier concentration n_0 and mobility μ_0 .

Here, the SnO₂-based dense films with a single preferential orientation were prepared by RF magnetron sputtering to exclude the influence of other factors on carrier transport, in which carrier concentration and mobility were jointly regulated by fluorine doping and oxygen management with annealing. That met the need to study the effect of initial carrier concentration and mobility of SnO₂-based films on gas response. Exploration of function on carrier behavior in gas-sensing SnO₂-based films would provide a simple and effective criterion for the design and application of sensor in the future.

2. Materials and Methods

In this work, SnO₂ film was prepared by a pure SnO₂ powdered target, as described in references [13,14]. The fluorine in SnO₂:F film was introduced by mechanically mixing the SnF₂ powder (99.99%) and the SnO₂ powder (99.99%) at an atomic ratio of 1:40. In detail, the glass substrate was dried after a series of ultrasonic cleaning. After the background vacuum of the system was as low as 3×10^{-3} Pa, 99.99% argon was introduced to make the operating pressure to 1.0×10^{-1} pa. The gas-sensing films were deposited in a radio frequency (RF, AE600X) magnetron sputtering for 1 h, with a target power of 200 W and a substrate-target separation of 100 mm.

The as-prepared SnO₂-based films were annealed at air atmosphere and vacuum of 2.5×10^{-3} Pa by rapid thermal processing equipment (RTP-500V) with a rate of 1 °C/s, respectively. Samples were stayed at 110 °C and 200 °C for 5 min to remove adsorbed residues on the surface of the films, and then were kept heating at 400 °C for 1 h. Particularly, annealing at 400 °C may adjust the oxygen vacancy as well as reduce interstitial defects to regulate carrier concentration and mobility. Meanwhile, annealing at 400 °C prevents re-crystallization of the SnO₂-based films to maintain the same columnar crystalline structure as the as-prepared samples. In addition, annealing beyond 400 °C can be dangerous to damage the glass substrate to deteriorate structure and property of film.

The parameters including film thickness and deposition rate were obtained through the Profilometry (Alpha-step D-100, Shanghai, China). The micro-crystal structure and electronic band structure were characterized by glancing angle XRD with an incident angle of 0.3° (X-ray diffraction, X'Pert Pro, Almelo, Netherlands, Cu-K α), Raman spectra (LabRam HR 800, Paris, France) with an excitation wavelength of 532 nm, steady state photoluminescence (PL, FLSP-920, Edinburgh, England) using a 310 nm excitation light and UV-vis light spectrophotometry (Cary 5000/6000i, Beijing, China) with a measuring range of 300–900 nm. Surface morphology and roughness was observed using a field-emission scanning electron microscope (FESEM, Sigma HD, Oberkochen, Germany) at 5 kV and an atomic force microscope (AFM, CSPM5500, Guangzhou, China) by contact mode. Electrical properties

including carrier concentration and mobility were recorded at the hall effect measurement system (HALL 8800, Taiwan, China).

The gas response measurements of the films directly assembled and connected to the electrochemical workstation (CHI660B, Chenhua Instruments Inc., Beijing, China) through Al_2O_3 sheet and Pt wire, were carried out in an electric furnace device equipped with a gas mass flow apparatus. At a constant voltage of 5 V, the “current (I)–time (t) curve” was measured at different temperatures for 2000 ppm different target gases (H_2 , CO and CH_4) in the air ambient. According to Ohm’s law, the resistance was derived from the fixed voltage and the tested current. Response of the films in the paper is defined: $R = R_a/R_g$, in which R_a and R_g are the resistance values before and after the introduction of the target gas, respectively. The response and recovery time are the consumed time that the resistance value reached or returned to 90% of the previous resistance [15].

3. Results and Discussion

3.1. Composition and Microstructure

3.1.1. X-ray Diffraction

The XRD patterns of the as-prepared and annealed SnO_2 -based films are shown in Figure 1a. The diffraction peaks of all films are consistent with standard PDF cards (P42/mnm, (136), JCPDF 01-070-4177), and corresponding diffraction planes are (110), (101) and (200), which are from the tetragonal rutile structure SnO_2 intensity ratio of (101) peak to other peaks in XRD patterns is higher than that of the standard non-oriented SnO_2 powder samples from the above mentioned PDF file, suggesting that all films are the (101) preferred orientation, which is due to the lack of oxygen and the low relaxation ability during sputtering in a pure Ar atmosphere [14,16]. The film with a single orientation effectively simplifies the study of carrier transport on gas-sensing properties.

Besides the original diffraction peak of SnO_2 after doping with F, no impurity peaks were observed, and the lattice of the SnO_2 after doping remains unchanged, indicating that fluorine atoms is effective doped in SnO_2 solid solution. F atom similar with the oxygen atom in size replaces the position of oxygen in the crystal lattice, and plays a role of shallow donor [17]. It provides more carriers to conduction band. In addition, the F doping changes surface energy of different crystal plane, which strengthen the intensity of the preferential (101) peak and suppresses the intensity of (200) peak.

As shown in Figure 1a, the diffraction peak of the SnO_2 film after vacuum annealing is much more diffused than that of as-prepared film, which can be explained by the extraction of oxygen atoms under low partial pressure and high temperature. Loss of lattice oxygen releases a large number of carriers to increase conductance. In contrast, the oxygen vacancies in original samples are effectively filled by the atmosphere oxygen during the air-annealing process, which reduce carrier concentration. Meanwhile, the lattice in films is much more perfect to increase the intensity of the (101) peaks as shown in Figure 1a. Particularly, the introduction of fluorine further reduces the intensity of the (101) peak after vacuum annealing, indicating that de-oxidation occurred to a greater extent, because the coulomb force of the bound lattice in SnO_2 is weakened by substitution of F [18]. While the atmosphere oxygen is sufficient under air-annealing, the appearance of (110) orientation suppress (101) preferred orientation to some extent.

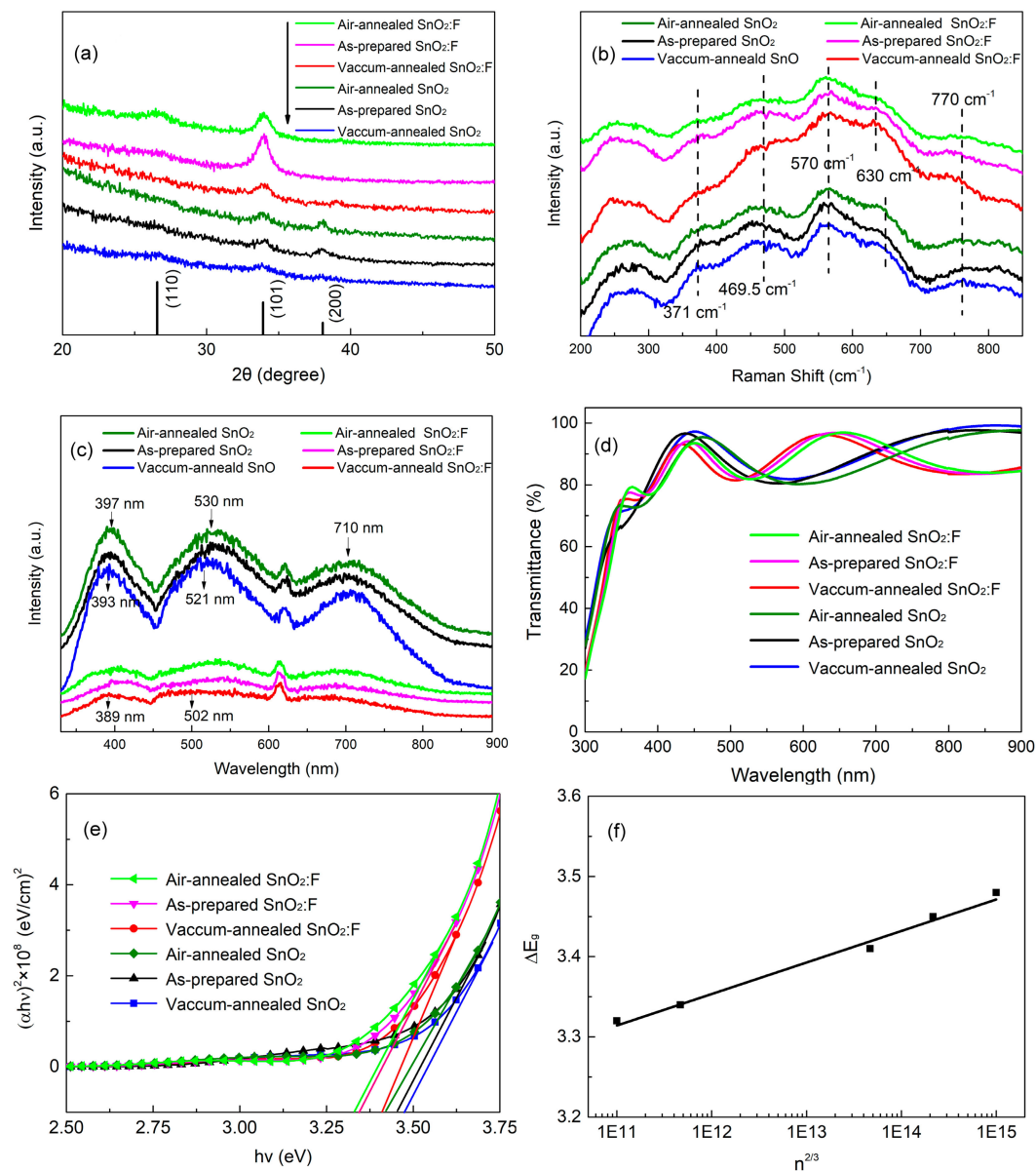


Figure 1. (a) The XRD patterns, (b) the Raman spectra, (c) the photoluminescence (PL) spectra, (d) transmittance spectra, (e) the optical band gaps of SnO₂-based films as-prepared and annealed at different annealing ambient and (f) the proportional relationship between the 2/3 power of carrier concentration and band gap width.

3.1.2. Raman Spectra

The structural information of SnO₂-based films including oxygen vacancies could be detected by Raman spectra [19] as shown in Figure 1b. All samples showed the Raman characteristic vibration of pure phase SnO₂ with rutile structures [20], containing E_g (~470 cm⁻¹), A_{1g} (~630 cm⁻¹) and B_{2g} (~775 cm⁻¹). Conforming to the Matossi's constant, the peak of 371 cm⁻¹ is closely related to the local lattice disorder, and the peak at 570 cm⁻¹ originates from the plane oxygen vacancies, which the greater the relative intensity is, the higher the concentration of the oxygen vacancies is [21].

The integral intensity of the air-annealed SnO₂ film at 570 cm⁻¹ is weaker than that of the as-prepared film, as well as the intensity of A_{1g} reflecting the reverse vibration of the Sn–Sn and O–O in the c-axis plane is higher. It indicates that air-annealed films have much less oxygen vacancies. By contrast, de-oxidation of the vacuum-annealed SnO₂ film produces more oxygen vacancies due to

the relatively higher intensity of the peak at 570 cm^{-1} . The similar change of oxygen vacancies is also presented in F doped SnO_2 films before and after annealing.

The F atom replacing the lattice oxygen affected the vibration of the original Sn–O bond, and the intensity of all Raman peaks is reduced to some extent after doping. A_{1g} mode of SnO_2 :F films have a lower wavenumber compared with undoped samples. It illustrates that the oxygen vacancies in the sample are increased after doping F [21], which reflects the weakened Sn–O binding ability. This also shows that the generation of oxygen vacancies in vacuum annealing is further enhanced by F doping.

3.1.3. Photoluminescence Spectra

As shown in Figure 1c, the photoluminescence (PL) spectra of all samples showed fluorescence emission peaks appear at $\sim 397\text{ nm}$, $\sim 530\text{ nm}$ and $\sim 710\text{ nm}$. However, the emission peaks at 620 nm are due to the second-order emission peak of the excitation light that is not filtered out. The UV emission peak near 397 nm (about 3.26 eV) attributed to carrier recombination from the conduction band to the valence band. Moreover, as shown in Figure 1d,e, the optical bandgap width by Tauc extrapolation is about 3.3 eV , which is almost the same as the PL result, and smaller than the band gap (3.6 eV) of SnO_2 in the other study [22]. It implies that our SnO_2 -based films have more charge carriers whose transport behavior could be expected to be tunable. The peak of $\sim 530\text{ nm}$ (2.34 eV) reflects the defect energy level in samples, which is related to the formation of oxygen vacancy [23]. In addition, the peak at 710 nm is usually related to surface defects at grain boundaries [24].

The effective introduction of F atoms makes the photoluminescence intensity significantly lower compared to undoped SnO_2 film, which is similar to the result of the references [22]. Doped F in the crystal lattice makes it more difficult for the carrier in the excited state back to the ground state and the luminescence intensity is lower. Moreover, more oxygen vacancies in F-doped films deduced from XRD and Raman analysis should be responsible for the decrease of the photoluminescence intensity [25]. Meanwhile, besides a certain amount of oxygen vacancies and other lattice defects, the introduction of fluorine causes the impurity band to further expand, resulting in an increase in the electron transition range, which leads to the broadening PL peak of the SnO_2 :F films.

From Figure 1c, both introduction of F atoms and increase of oxygen vacancies make peaks at $\sim 397\text{ nm}$ and $\sim 530\text{ nm}$ blue-shifted, corresponding to the increase of optical band gap. For degenerate semiconductor, there would be a relationship of Equation (1) between band gap width ΔE_g (BM) variation and carrier concentration n for the Burstein–Moss effect [26].

$$\Delta E_g = \frac{h^2}{2} \left(\frac{1}{m_v^*} + \frac{1}{m_c^*} \right) (3\pi n)^{\frac{2}{3}}. \quad (1)$$

In which m_v^* and m_c^* are the effective masses of electron in the conduction band and the valence band, respectively, and h is the Planck constant. As shown in Figure 1f, the band gap variation ΔE_g of SnO_2 -based samples is basically proportional to the $2/3$ power of their carrier concentration, which satisfies with the Equation (1). It could be deduced that the Burstein–Moss effect may be available to our degenerate SnO_2 -based films. Subsequently, the band gap becomes wider as the carrier concentration increases in this study. The co-operation of F atoms or oxygen vacancies would make the film have higher carrier concentration, which is illustrated from blue-shift of F-doped SnO_2 film in Figure 1c and the increase of band gap in the vacuum-annealed samples in Figure 1e.

3.2. Surface Morphology

As seen in Figures 2 and 3, the cross-sectional SEM presents the films consisting of columnar crystalline with diameters about 100 nm , which is consistent with the typical microstructure of magnetron sputtered SnO_2 -based films. The top SEM together with three-dimensional AFM morphology of samples shows that the surfaces of films are dense and smooth. The morphology difference between SnO_2 and SnO_2 :F films originated from the variant etching ability due to the introduction of fluorine in the sputtering process. It is obvious that the as-prepared SnO_2 -based films

have a roughness of only about 4.1 nm in Figure 2 and Table 1. Furthermore, the film surface is smoothed by the rounded top of the column grain during the annealing process. Moreover, the film annealed under ambient air has the lowest roughness owing to the supplement of oxygen. In addition, it can also be seen from Figure 3a,e to Figure 3c,f that the image contrast of the surface morphology gradually becomes unobvious, which is due to the smoother sample surface and the lower electrical conductivity deteriorated by the introduction of oxygen.

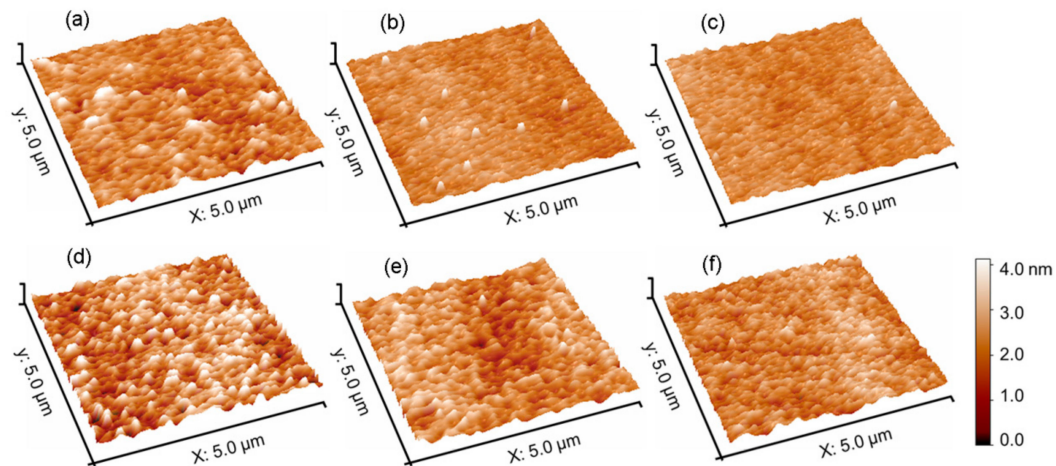


Figure 2. Atomic force microscope (AFM) morphologies of (a) as-prepared SnO_2 film, (b) vacuum-annealed SnO_2 film, (c) air-annealed SnO_2 film, (d) as-prepared $\text{SnO}_2:\text{F}$ film, (e) vacuum-annealed $\text{SnO}_2:\text{F}$ film and (f) air-annealed $\text{SnO}_2:\text{F}$ film.

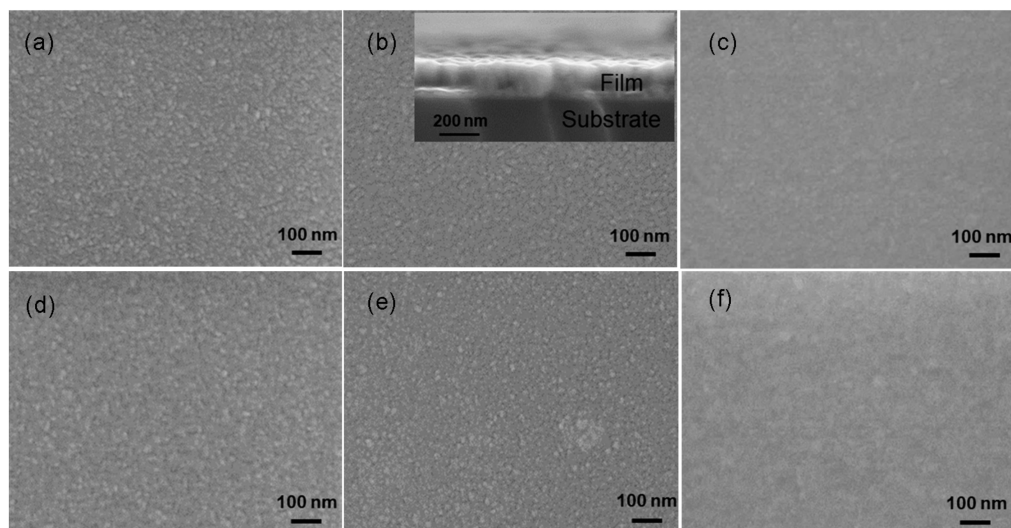


Figure 3. SEM morphologies of (a) vacuum-annealed SnO_2 film, (b) as-prepared SnO_2 film, (c) air-annealed SnO_2 film, (d) vacuum-annealed $\text{SnO}_2:\text{F}$ film, (e) as-prepared $\text{SnO}_2:\text{F}$ film and (f) air-annealed $\text{SnO}_2:\text{F}$ film, and the inset in Figure 3b is a cross-section view.

Table 1. Electrical parameters of as-prepared and annealed SnO₂-based films.

Samples	<i>d</i> nm	<i>v</i> nm/min	ρ Ohm·cm	<i>n</i> cm ³	μ cm ² /V·s	<i>R</i> nm
Air-annealed SnO ₂	—	—	2.88×10^1	1.8×10^{15}	1.2×10^2	4.0
As-prepared SnO ₂	171.6 ± 3.2	2.86	1.34	7.0×10^{16}	7.0×10^1	3.7
Vacuum-annealed SnO ₂	—	—	4.77×10^{-1}	2.0×10^{19}	2.7×10^{-1}	3.2
Air annealed SnO ₂ :F	—	—	2.35×10^{-2}	2.1×10^{19}	1.3×10^1	4.2
As-prepared SnO ₂ :F	249.6 ± 4.8	4.16	3.78×10^{-3}	1.2×10^{20}	6.1	3.8
Vacuum-annealed SnO ₂ :F	—	—	1.97×10^{-3}	5.9×10^{21}	5.3×10^{-1}	3.5

Note: *d*—thickness, *v*—sputtering rate, ρ —resistivity, *n*—carrier concentration, μ —carrier mobility, *R*—roughness.

3.3. Electrical Properties

The oxygen vacancies of SnO₂ as an N-type semiconductor may play an important role in its electrical transport properties, by forming an impurity level to release free electrons to conduction band. Through oxygen introduction in air-annealing and oxygen extraction in vacuum-annealing, the number of oxygen vacancies could be simply regulated in a wide range, and in turn change carrier concentration from $10^{15}/\text{cm}^3$ to $10^{19}/\text{cm}^3$ as shown in Table 1. However, the carrier mobility decrease from $10^2 \text{ cm}^2/\text{V}\cdot\text{s}$ to $10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$ results from scattering of lattice distortion owing to the increase of oxygen vacancy. It is well known that resistivity ρ , carrier concentration *n* and mobility μ have the relationship $\rho = 1/nq\mu$. The resistivity of SnO₂ mainly depends on the carrier concentration and mobility. As can be seen from the data in Table 1, resistivity and carrier concentration show a positive correlation regardless of mobility. Therefore, the effect of carrier concentration on resistivity is stronger than that of mobility.

F-doped is also another way to adjust the electrical properties of SnO₂-based materials by increasing the carrier concentration. According to equation $\text{O}_o + \text{F} \rightarrow \text{F}' + \text{e}^- + 1/2\text{O}_2(\text{g})$, fluorine occupies the position of the oxygen atom and releases a free electron [27]. By comparing between two kinds of the air-annealed films, it can be seen that the merely F-doped action can effectively increase the carrier concentration by four orders of magnitude whereas mobility changes from $1.2 \times 10^2 \text{ cm}^2/\text{V}\cdot\text{s}$ to $1.3 \times 10^1 \text{ cm}^2/\text{V}\cdot\text{s}$. Furthermore, electrical transport properties of SnO₂-based films are synergistically improved by fluorine atoms and oxygen vacancies, and the carrier concentration of vacuum-annealed SnO₂:F film can reach $5.9 \times 10^{21}/\text{cm}^3$ from $2.0 \times 10^{19}/\text{cm}^3$ of undoped SnO₂ film. It is worth mentioning that the films with similar carrier concentration and different mobilities were obtained to explore carrier transport behaviors as seen in the third and fourth line in Table 1. So far, different carrier behaviors in the films by fluorine doping and oxygen management may be used to discuss gas response.

3.4. Gas-Sensing Properties

3.4.1. Temperature-Dependent Electrical Properties

Both the introduction of fluorine and the increase of oxygen vacancy in films increase the carrier concentration and decrease the resistivity as described in Section 3.3. This is also testified by the response of the initial current in the I–T curves of samples from room temperature to 300 °C at a heating rate of 0.043 °C/s, as presented in Figure 4a,b. The adsorbed oxygen on the film surfaces is desorbed from room temperature to 300 °C, and the bound electrons by the adsorbed oxygen returns to the samples results in increasing carrier concentration all the time, and in turn leading to the increase of conductance, as described in literature [28]. Meanwhile, the lattice scattering to electrons always keeps increasing in the samples with an increase of temperature, and then causes the decrease of conductance. Therefore, the opposite effect of the increasing carrier concentration and enhancing lattice scattering results in a critical transition temperature (T_c) for I–T curves of different films. Before the T_c , the effect of increasing carrier concentration is more significant than that of lattice scattering. After the T_c , the role of lattice scattering becomes dominant to hinder carrier transport.

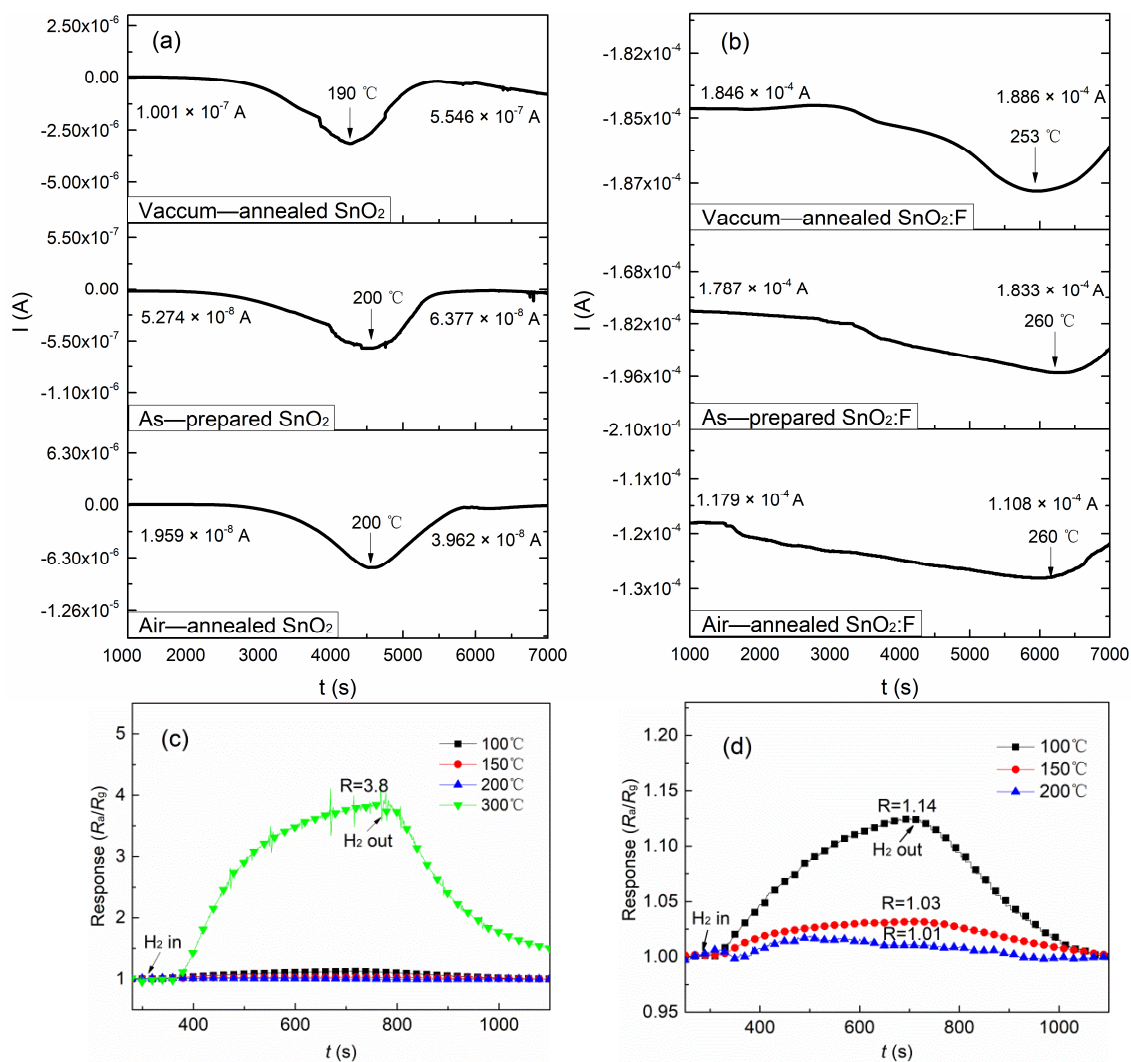


Figure 4. The current–temperature curves of (a) as-prepared and annealed SnO₂ films, (b) as-prepared and annealed SnO₂:F films, and (c) H₂ response of as-prepared SnO₂ films at different temperatures, (d) magnified view at 100–200 °C in (c).

For the samples with high carrier concentrations, lattice scattering is more difficult to become the dominant factor, which requires higher temperature to enhance the scattering ability to reduce mobility of carriers. Therefore, the critical temperatures 260 °C of SnO₂:F films with more free carriers is higher than 200 °C of SnO₂ films. Additionally, the vacuum-annealed films with more oxygen vacancies and larger lattice distortion have enough lattice scattering capacity in lower temperatures than present at lower T_c compared to other samples as shown in the top of Figure 4a,b.

Figure 4c,d illustrates the response of the as-prepared SnO₂ film to H₂ at different detecting temperature. Under the weak chemical reactivity between the target gas and the adsorbed oxygen below 200 °C [1], gas-sensing response decrease with the increasing temperature, in which the increasing number of re-bound electrons seems to be an unfavorable factor. The enhanced lattice scattering ability as well as the strong chemical reactivity above 200 °C would result in the higher gas response with the increasing temperature, which account for the highest sensitivity at 300 °C. It suggests that low mobility may have a positive impact on the improvement of gas sensitivity properties.

3.4.2. Dependence of Gas-Sensing Properties on Carrier Behavior

In order to further confirm the influence of carrier behavior on the gas response, the H₂ response curves of SnO₂-based films with different carrier concentration and mobility were tested as shown

in Figure 5a. It has been clearly seen that the H_2 response of the films increases with the decrease of carrier concentration. The air-annealed SnO_2 film with a carrier concentration of $10^{15}/cm^3$ has a maximum responsivity of $R = 5.0$, while the vacuum-annealed $SnO_2:F$ film with a carrier concentration of $10^{21}/cm^3$ has a responsivity of only $R = 1.003$. Likewise, the effect of carrier concentrations on the gas response is also reflected in CO and CH_4 in Figure 5b. Excessive carrier concentration can deteriorate the gas-sensitive properties of the material, which seems to be a possible cause of the lack of gas sensitivity of metallic materials.

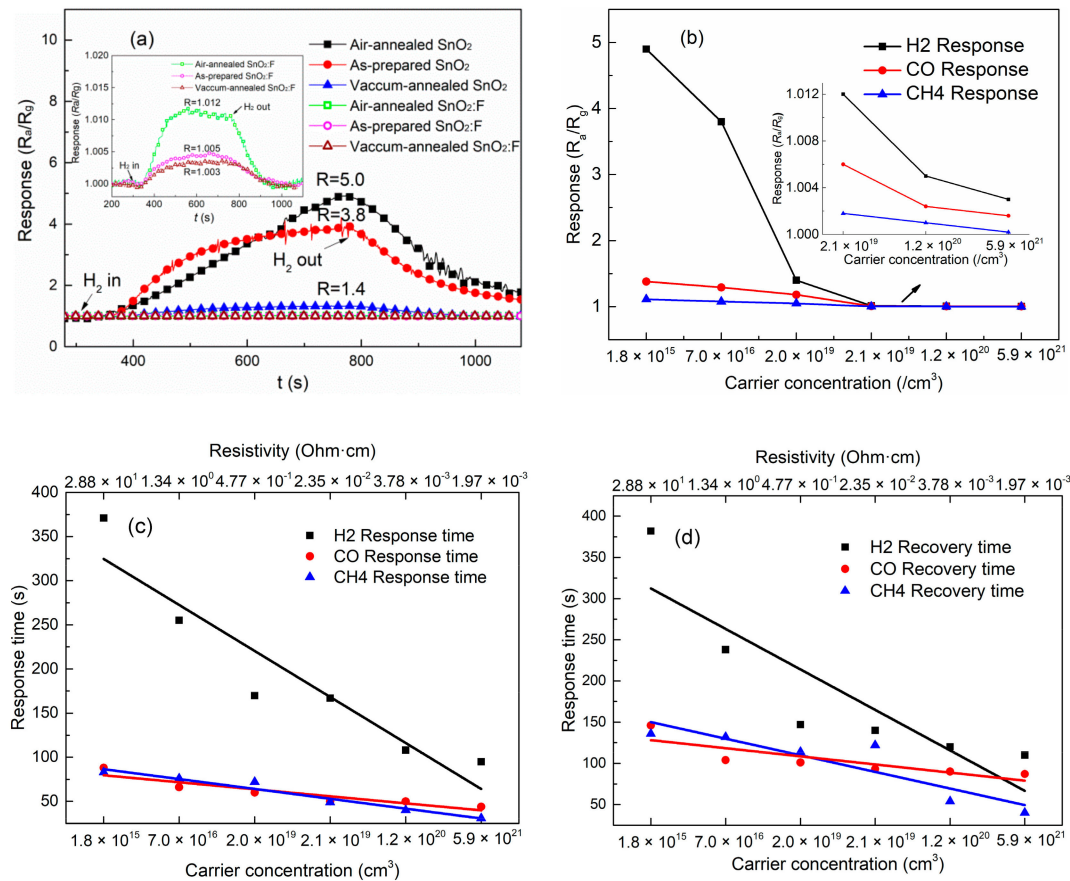


Figure 5. (a) H_2 response of different SnO_2 -based films, (b) dependence of the H_2 , CO and CH_4 response of films on carrier concentration, and dependence of the H_2 , CO and CH_4 response time (c) and recovery time (d) of films on carrier concentration.

Based on the reference [29,30], the conductance of SnO_2 -based films is given:

$$G = n_0 e \mu A, \quad (2)$$

where n_0 is the initial carrier concentration, e is the electronic charge, μ is the mobility and A is related to the surface area of the columnar crystalline. The variety of A between different films is very small according to the surface morphology analysis. When a target gas is introduced during a gas sensing test, a change of conductance in the SnO_2 -based films will result from the change of carrier concentration Δn :

$$\Delta G = \Delta n_0 e \mu A. \quad (3)$$

Particularly, as can be seen from the data in Table 1, resistivity and carrier concentration show a positive correlation regardless of mobility. The effect of carrier concentration on resistivity is much

stronger than that of mobility. Considering the dominant effect of carrier concentration on conductance during the gas-sensing test, Equations (2) and (3) are still effective to obtain Equation (4):

$$R = \Delta G/G \sim \Delta n_0/n_0. \quad (4)$$

Δn_0 , the number of carriers return to the films due to desorption of adsorbed oxygen reacted by target gas, is constant at given conditions for different films. It means that the sample with low carrier concentration n_0 would have larger $\Delta n_0/n_0$, and in turn lead to higher gas sensitivity R .

The air-annealed SnO₂ with the low carrier concentration and high mobility has a higher sensitivity to hydrogen, which is more due to that the prominent contribution of low carrier concentration covers the negative role of high mobility. The third and fourth line in Table 1 shows that when the carrier concentration is similar, the mobility decreases from $1.3 \times 10^1 \text{ cm}^2/\text{V}\cdot\text{s}$ to $2.7 \times 10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$, and the gas response increases from $R = 1.012$ to $R = 1.4$, and the sample with low mobility has a relative high gas sensitivity. Although there is only a small increment of the sensitivity value of SnO₂-based films by decreasing mobility, it seems that the depressed carrier mobility is still helpful for improving gas sensitivity. Furthermore, the effect of mobility on gas sensitivity was also confirmed in the detection of the other two target gases (CO and CH₄). All these indicate that carrier concentration is regarded as a primary factor on gas-sensing properties, while mobility is a secondary factor.

Moreover, the films with the higher carrier concentration have the better electric conductance, resulting in the deeper equivalent depth (D_q) in film to conduct an electron through a cross-section. However, Debye depth (D_e), conductance affected zone of the adsorbed gases, is almost invariable. It indicates that higher carrier concentration would cause lower D_e/D_q , which is proportional to the sensitivity R . On the whole, we can regulate gas response of SnO₂-based films by controlling the carrier concentration as well as mobility.

3.4.3. Response/Recovery Time

The excessive carrier concentration is not beneficial to the gas sensitivity of SnO₂-based films, whereas it has a positive impact to shorten the response/recovery time as presented in Figure 5c,d that shows the response time and recovery time of H₂, CO, and CH₄ as a function of carrier concentration and resistivity. For SnO₂-based films, the response/recovery time of three kinds of target gases decreases with the increasing carrier concentration and the decreasing of resistivity. That is because high conductance from higher carrier concentration and mobility can effectively improve electron transport to speed up the response of the gas-sensing films to the target gas.

Among three kinds of target gases, CO and CH₄ have shorter response/recovery time in spite of their low sensitivity, which may derive from that of the atom configuration of the preferential (101) crystal plane in SnO₂ films is advantageous to absorb CO and CH₄. In addition, the prepared thin films seem to be quite selective to hydrogen. This is mainly due to that H₂ compared with another target gas has more optimal adsorption sites on the SnO₂-based materials like O_{Bridging}, O_{Plane}, Sn_{5c} and Sn_{6c} [31]. In addition, when each of the H₂ and CO molecules is adsorbed, the electron losses are 0.08 e and 0.06 e, respectively. H₂ provides more equivalent electrons than CO, the higher conductivity of the SnO₂ sensor, making the higher change in conductance of the SnO₂ sensor [32]. In view of the above, we could consider combining response/recovery time with sensitivity to selectively identify target gases.

4. Conclusions

The gas-sensing SnO₂-based films with a single preferential orientation were prepared by RF magnetron sputtering. The content of oxygen vacancies in SnO₂-based films was changed by the annealing by different ambient, which tuned the carrier concentration from $1.8 \times 10^{15}/\text{cm}^3$ to $2.0 \times 10^{19}/\text{cm}^3$ and carrier mobility from $1.2 \times 10^2 \text{ cm}^2/\text{V}\cdot\text{s}$ to $2.7 \times 10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$. The introduction of fluorine continually increased carrier concentration to $5.9 \times 10^{21}/\text{cm}^3$.

Below about 200 °C, H₂ sensitivity of SnO₂ films decreased in the process of rising temperature, whereas the H₂ sensitivity reached a maximum at 300 °C. Samples with low carrier concentration had higher gas response properties. Compared to almost unresponsive vacuum-annealed SnO₂:F film with highest carrier concentration, the air-annealed SnO₂ film with lowest carrier concentration had a maximum sensitivity of $R = 5.0$. In addition, vacuum-annealed SnO₂ film with lower mobility had higher sensitivity than air-annealed SnO₂:F film, considering their similar carrier concentration. By contrast, the films with low sensitivity presented a short response/recovery time.

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