Preparation of Highly Transparent (at 450–800 nm) SnO$_2$ Homojunction by Solution Method and Its Photoresponse

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Abstract: High-quality SnO$_2$:Si films and SnO$_2$:10 at.% Ga films were prepared by the solution method. The roughness of films is below 1.08 nm, and possess exceptional transparency (>75%) and decent semiconductor properties. Based on this, the SnO$_2$:Si/SnO$_2$: Ga homojunctions with different Si doping concentrations were prepared. It is found that the conductivity of the SnO$_2$:Si thin film gradually increases, and the rectification characteristics of the homojunction are optimized with increasing Si doping content. The SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homogeneous junction has the best performance, the turn-on voltage is as low as 5.6 V, and it also exhibits good unidirectional conductivity. The photoresponse of the SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction under the lights of red, yellow, and purple was explored respectively. The result shows that the device responds strongly to purple light. Compared with the test results in the dark environment, the device current increases by two orders, which is expected to be applied in the field of near-ultraviolet detection.

Keywords: solution method; SnO$_2$; homojunction; highly transparent; photoresponse

1. Introduction

In recent years, with the rapid development of optoelectronic technology, transparent optoelectronic devices have been widely used in many fields due to their excellent optoelectronic properties, such as solar cells [1], light emitting diodes [2,3], photodetectors [4,5], and so on. The highly transparent PN junction is the basic component of many transparent optoelectronic devices. Therefore, the development of low-cost, high-performance transparent PN junctions is the key to the popularization of transparent optoelectronic devices. Transparent semiconductor oxide (TSO) has both excellent transparency and conductivity, which is an excellent material for preparing transparent PN junctions. The current mainstream TSO materials mainly include tin oxide (SnO$_2$), zinc oxide (ZnO), indium oxide (In$_2$O$_3$), etc. However, indium is a precious metal, which is expensive and toxic, limiting its market size; ZnO has poor stability and is not resistant to acid and alkali corrosion, which limits its application; SnO$_2$ is non-toxic, environmentally friendly, low-cost, stable and its mechanical wear resistance is good. At the same time, the optical band gap is 3.67 eV and the transparency is excellent. Based on these, SnO$_2$ has attracted the attention of scholars. Taking advantage of the excellent UV
response characteristics of SnO2. Gao et al. [6] prepared a high-performance UV photodetector based on the SnO2/TiO2 core-shell structure heterojunction, with a response rate as high as 0.6 A/W, and rise and decay times as low as 0.02 and 0.004 s. The wide optical band gap and low $E_{CB}$ of SnO2 make it the preferred material for preparing efficient electron transport layers. Park et al. [7] used SnO2:Li to prepare effective electron transporting layers in perovskite solar cells (PSCs), which effectively promoted electron injection and transfer, and reduced charge recombination. Sathyamoorthy et al. [8] prepared a thin film diode based on a transparent SnO/SnO2 PN junction with the thermal evaporation deposition, which exhibits rectification characteristics, proving the feasibility of preparing a PN junction diode with tin oxide.

Generally, there are oxygen vacancies and intrinsic defects in tin oxide, causing tin oxide to exhibit n-type semiconductor properties, but the density of defects is not controlled, resulting in the electrical and optical properties of SnO2 being difficult to meet the requirements of devices. Doping can effectively overcome this problem to achieve the regulation of its electrical and optical properties [9]. Tsay et al. [10] prepared the SnO2 semiconductor thin film by Ga doping, when the Ga doping concentration is 10 at.%, the conductivity type of the film is changed from n-type to p-type, and when the doping concentration is 5 at.%, the film’s transmittance is better than that of pure SnO2 film. In addition, Singh et al. [11] successfully prepared Sb, Zn co-doped SnO2 n-type semiconductor thin films with a transmittance of more than 60% by the spray pyrolysis method. Among these many doping elements, the Si element has the advantages of being resourceful, low-cost, non-toxic and environmentally friendly. At the same time, the radius of Si$^{4+}$ (0.4 Å) is slightly smaller than Sn$^{4+}$ (0.69 Å), which make it easy to replace tin ions without causing lattice distortion. Si doping can effectively regulate the electrical properties of SnO2 thin films, and then regulate the current response of the SnO2 homojunction. In addition, Si doping is also conducive to the increase of the lattice parameters and the stabilization of the electrochemical impedance [12], improving the photoelectric performance and stability of the film. Therefore, SnO2:Si was selected to prepare the PN junction in this paper.

At present, the preparation of films generally relies on vacuum methods, such as magnetron sputtering [13,14], electron beam deposition [15], chemical vapor deposition [16], etc. However, the vacuum method has strict requirements on the air tightness of equipment, high maintenance costs, high operation levels and high energy consumption. In comparison, the solution method has many advantages, such as: low cost, simple operation, low requirements for equipment, and so on. All these advantages are in line with the mainstream concepts of environmental protection, greenness and energy conservation, as well as being conducive to long-term development. Besides, the solution method is suitable for large-area film production and suitable for large-scale production in factories.

Otherwise, in our previous research [17], the X-ray photoelectron spectroscopy (XPS) characterization shows that the atomic ratio of SnO2 in the SnOx film, which is annealed at 100 °C by solution method is 94.49%. It can be deduced from this that the composition of the film samples annealing at 300 °C is mostly SnO2 in this research. Based on this, the $n$-type and $p$-type transparent SnO2 films were prepared by Si doping and Ga doping, and a highly transparent SnO2 homojunction was prepared by the solution method. The effects of different Si doping concentrations on the structure and performance of the homojunction were emphatically studied, and the current response of the device under different frequencies of light was further discussed.

2. Materials and Methods

The SnO2 precursor solution was prepared with 0.564 g of tin chloride dihydrate (SnCl2·2H2O, Aladdin reagent, analysis pure 98%) and 5 mL of ethylene glycol methyl ether (CH3OCH2CH2OH, Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China, analysis pure 98%). Then, the solution was stirred at room temperature for 48 h to make it mix well.

An appropriate amount of tetraethyl silicate solution (SiC8H20O4, Aladdin reagent, density: 0.933 g/mL, M = 228.33) was added into SnO2 precursor solution to prepare the SnO2: Si precursor
solution with the atomic ratio of Si/Sn of 5%, 10%, and 15%, respectively. Similarly, Gallium (III) Nitrate Hydrate \( \text{Ga(NO}_3\text{)}_3 \cdot x\text{H}_2\text{O} \) Macklin, analysis pure 98%) and SnO\(_2\) precursor solution were used to prepare a 10 at.% Ga-doped SnO\(_2\) solution.

Glass substrates (1 cm × 1 cm) were treated with a plasma with a power of 120 W for 10 min, then 50 mL of SnO\(_2\):Si precursor solutions with different doping concentrations were added dropwise to the glass substrate respectively, and then spun coating by homogenizer (model: KW-4A) at 5000 rpm for 12 s. This process was repeated three times to obtain a wet film, and then the film was annealed at 100 °C for 10 min for curing, and then annealed at 300 °C for 1 h to obtain SnO\(_2\):Si films with different Si concentrations. The same process was used to prepare SnO\(_2\):10 at.% Ga thin films. The above process was also used to sequentially prepare the SnO\(_2\):10 at.% Ga film and SnO\(_2\):Si film with different doping concentrations on the ITO substrate (1 cm × 1 cm) in turn, and the 80 nm aluminum electrode was prepared on SnO\(_2\):Si film by the thermal evaporation method, then, the tin oxide homojunction was successfully prepared. The structure diagram of the homojunction is shown in Figure 1.

![Figure 1. Schematic structure of the PN junction.](image)

The morphology of SnO\(_2\):10 at.% Ga thin films and SnO\(_2\):Si thin films prepared on glass substrates was characterized using atomic force microscope (AFM) (BY3000, Being Nano-Instruments Ltd., Guangzhong, China). The transmittance of SnO\(_2\):10 at.% Ga thin films and SnO\(_2\):Si thin films prepared on glass substrates was measured with ultraviolet-visible spectrophotometer (Shimadzu UV-2600, Shimadzu Corporation, Shimadzu, Japan). Time-resolved microwave photoconductive decay (μ-PCD) (LTA-1620SP, KOBELCO, Kobe, Japan) technology was used to test the semiconductor properties of SnO\(_2\):10 at.% Ga thin films and SnO\(_2\):Si thin films prepared on glass substrates. The electrical performance of all thin film samples and the homojunction of tin oxide, as well as the current response of the homojunction under different frequency light excitation were studied through the semiconductor parameter analyzer (Agilent 4155C, Dongguan nuozhan electronic instrument co. Ltd., Dongguan, China).

3. Results and Discussion

3.1. Film Morphology

Figure 2 shows the AFM images of the SnO\(_2\):Si and SnO\(_2\):10 at.% Ga thin films at 5 μm × 5 μm scale. As can be seen in those images, there are no obvious physical defects such as cracks and holes on the surface of all films. All films are smooth and flat, which can effectively ensure the normal operation of the homojunction. The root mean square roughness (Sq) of the SnO\(_2\):10 at.% Ga film is as low as 0.93 nm, which provides good conditions for the growth of the upper SnO\(_2\):Si film. The roughness of SnO\(_2\):Si films is lower than that of pure SnO\(_2\) film, implying that a proper amount of Si doping is beneficial to improve the surface morphology of SnO\(_2\) film; the particles and bumps on the surface of the film grow with increasing Si doping concentrations, which finally causes greater roughness of the SnO\(_2\):Si film.
When the Si doping concentration is 5 at.%, the transmittance of the thin film is the best, exceeding 78%, which indicates that a proper amount of Si doping will help improve the transparency of the SnO$_2$ film. Then, as the doping concentrations continue to increase, the transmittance decreases. However, in the near-ultraviolet band (300–450 nm), the transmittance of the SnO$_2$:Si film is significantly reduced, indicating that there is a strong absorption effect of light in this band. As the spectral wavelength decreases, the transmittance of SnO$_2$:Si films show a gradually decreasing trend, which is attributed to the increased absorption of light in near-ultraviolet band.

![AFM images of SnO$_2$:Si films and SnO$_2$:Ga film](image)

**Figure 2.** The AFM images of SnO$_2$:Si films and SnO$_2$:Ga film: (a) Sq = 1.32, (b) Sq = 0.74, (c) Sq = 0.93, (d) Sq = 1.08, (e) Sq = 0.93.

### 3.2. Optical Characterization

The optical transmittance spectra (300–800 nm) of four concentrations of Si in the SnO$_2$:Si films are illustrated in Figure 3. All films have excellent transparency and the transmittance in the visible region exceeds 75%. The transmittance values of the films at the wavelength of 560 nm are shown in Table 1. When the Si doping concentration is 5 at.%, the transmittance of the thin film is the best, exceeding 78%, which indicates that a proper amount of Si doping will help improve the transparency of the SnO$_2$ film. Then, as the doping concentrations continue to increase, the transmittance decreases. However, in the near-ultraviolet band (300–450 nm), the transmittance of the SnO$_2$:Si film is significantly reduced, indicating that there is a strong absorption effect of light in this band. As the spectral wavelength decreases, the transmittance of SnO$_2$:Si films show a gradually decreasing trend, which is attributed to the increased absorption of light in near-ultraviolet band.

![Optical transmittance spectrum of SnO$_2$:Si films with different doping concentrations.](image)

**Figure 3.** Optical transmittance spectrum of SnO$_2$:Si films with different doping concentrations.
Table 1. Optical parameters of SnO$_2$:Si thin films with different Si doping concentrations.

| Si Doping Concentrations | Transmittance (at 560 nm) (%) | Band Gap (eV) |
|--------------------------|-------------------------------|--------------|
| 0 at.%                   | 83.1                          | 3.60         |
| 5 at.%                   | 84.6                          | 3.61         |
| 10 at.%                  | 80.4                          | 3.56         |
| 15 at.%                  | 82.8                          | 3.58         |

The optical band gap ($E_g$) values are calculated from the extrapolation of linear line portion of the plot of $(\alpha h\nu)^2$ versus $(h\nu)$, as shown in the Figure 4 for the prepared films. The absorption coefficient $(\alpha)$ and incident photon energy $(h\nu)$ are linked by the following equation [18]:

$$(\alpha h\nu)^2 = A(h\nu - E_g),$$

where $A$ is the constant and $E_g$ is the optical band gap. The calculated band gaps of 0 at.%, 5 at.%, 10 at.% and 15 at.% Si-doped SnO$_2$ films are 3.60, 3.61, 3.56, and 3.58 eV respectively. The optical band gap width of 5 at.% Si-doped SnO$_2$ is larger than that of pure SnO$_2$, which may be caused by the Burstein-Moss effect [19]. With an increasing Si doping level, the carrier concentration of SnO$_2$:Si film increases, and the rise in the Fermi level in the semiconductor causes the band gap to increase. However, when the doping concentrations continue to increase, the band gap becomes narrower, which may be due to the multibody interaction between free carriers or between free carriers and ionized impurities [20,21].

At the same time, the optical transmittance spectrum of the SnO$_2$:10 at.% Ga thin film was measured, and the optical band gap of the SnO$_2$:10 at.% Ga thin film is 3.54 eV, calculated by Equation (1), as shown in Figure 5. It is observed that the SnO$_2$:10 at.% Ga film also has high transparency in the visible light range, and the transmittance exceeds 71.4%.

![Figure 4](image-url)  
**Figure 4.** The $(\alpha h\nu)^2$ versus $h\nu$ plots of SnO$_2$:Si films for different doping concentrations.

![Figure 5](image-url)  
**Figure 5.** (a) Optical transmittance spectrum of SnO$_2$:10 at.% Ga films; (b) The $(\alpha h\nu)^2$ versus $h\nu$ plots of SnO$_2$:10 at.% Ga films.
3.3. Characterization of Semiconductor Properties of Thin Films

The semiconductor properties of the films were tested by μ-PCD. The shallow localized states, mid-gap states, and the deep localized states of semiconductor oxide have a great influence on the carrier concentration and mobility [22,23]. Shallow localized states can be evaluated by D values, and a high D value indicates low density of shallow local defects; mid-gap states can be evaluated by mean peak value, and a high peak value indicates low density of mid-gap defects; in addition, the deep localized states can be reflected by the fast decay time (that is, the minority carriers lifetime [24]) in the thin-film photoconductivity test [25–28].

The photoelectric response curve of the SnO$_2$:Si thin films is shown in Figure 6, and the mean peak value, D value and minority carrier lifetime of the thin films are extracted from the light response curve, as shown in Table 2. Compared with the shorter rapid decay time (0.05 μs) [25] reported previously, all SnO$_2$:Si films have a longer rapid decay time (≥0.424 μs), indicating the density of deep localized states is at a lower level. Furthermore, with the increase of the Si doping concentration, the mean peak value gradually increases, which means that the increase of the Si doping level is beneficial to suppress the generation of mid-gap states. At the same time, the D value of the SnO$_2$:10 at.% Si film and SnO$_2$:15 at.% Si film in SnO$_2$:Si films is relatively large, which indicates that the density of shallow localized defects is low at this time; for a PN junction, it is beneficial to reduce the carrier surface recombination probability, and make the formation of space charge area more favorable. Taken together, the SnO$_2$:15 at.% Si film may be more suitable as the n-type layer of the PN junction.

![Photoelectric response curve of SnO$_2$:Si thin films](a) Pure SnO$_2$, (b) SnO$_2$:5 at.% Si, (c) SnO$_2$:10 at.% Si, (d) SnO$_2$:15 at.% Si.

**Figure 6.** Photoconductivity responses of SnO$_2$:Si thin films: (a) Pure SnO$_2$, (b) SnO$_2$:5 at.% Si, (c) SnO$_2$:10 at.% Si, (d) SnO$_2$:15 at.% Si.
3.4. Characterization of SnO$_2$ Homojunction with Different Si Doping Concentrations

The electrical characteristics of the SnO$_2$:10 at.% Ga and SnO$_2$:Si thin films with different Si doping concentrations were tested by the semiconductor parameter analyzer. As shown in Figure 7, the I-V curves of all samples have a good linear relationship. The current magnitude of SnO$_2$:10 at.% Ga and pure SnO$_2$ thin film reaches $10^{-5}$ at 5 V. From the Figure 7a, it is established that Si doping can effectively improve the electrical conductivity of SnO$_2$ thin film, and current magnitude of the film reaches $10^{-4}$ at 15 at.% Si doping concentration. In the literature of Tsay et al. [10], the SnO$_2$:10 at.% Ga thin film subjected to post-annealing at 300 °C is p-type conductive.

![Figure 7](image)

Figure 7. (a) The I-V characteristics of SnO$_2$:Si films with different doping concentrations; (b) The I-V characteristics of SnO$_2$:10 at.% Ga film.

Table 2. The results of μ-PCD test of SnO$_2$:Si films.

| Thin Films | Pure SnO$_2$ | SnO$_2$:5 at.% Si | SnO$_2$:10 at.% Si | SnO$_2$:15 at.% Si |
|------------|-------------|-----------------|-----------------|-----------------|
| Mean peak(mV) | 36.3 | 14.5 | 17.0 | 58.6 |
| D value | 0.321 | 0.234 | 0.276 | 0.260 |
| Minority carrier lifetime (µs) | 0.528 | 0.547 | 0.424 | 0.626 |

Figure 8 shows the I-V characters of homojunctions prepared based on SnO$_2$:10 at.% Ga and SnO$_2$:Si characterized by semiconductor parameter analyzer. It can be found that the prepared devices exhibit homojunction electrical properties, proving that the SnO$_2$:Si thin film is n-type conductive.

As shown in Figure 8, as the Si doping concentration increases, the rectification characteristics of the homojunction are significantly optimized. When the Si doping concentration is 15 at.%, the rectification characteristic of the homojunction is the best, showing a good unidirectional conduction characteristic. Moreover, the turn-on voltage of is 8.0, 6.4, 5.6 V respectively for 5 at.%, 10 at.%, 15 at.% Si-doped SnO$_2$:Si/SnO$_2$:10at.% Ga homojunction, as the Si doping concentration increases, the turn-on voltage of the homojunction decreases. It shows that Si doping is beneficial to improve the working performance of the SnO$_2$ homojunction, and makes the homojunction exhibit more obvious rectification and unidirectional conduction characteristics.

When a forward bias voltage is applied, the electrons and holes inside the homojunction move to the space charge region, then the space charge region is narrowed, and the electron-hole pair recombination generates a current. In this process, the difference in the conductive properties of the n-type and p-type thin films will have a reverse blocking effect on the current [29]. Among all homojunctions, the SnO$_2$/SnO$_2$:10 at.% Ga homojunction has the largest response current (on the order of $10^{-5}$ A), which is likely to be related to the same magnitude of conductivity of the SnO$_2$ and SnO$_2$:10at.% Ga thin films. The SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction exhibits the best rectification characteristics, which may be related to the minority carrier lifetime of the SnO$_2$: Si thin film. Generally, the longer the minority carrier lifetime, the better the rectification characteristics of the
homojunction. In Table 2, when the Si doping concentration is 15 at.%, the minority carrier lifetime of the SnO\textsubscript{2}:Si film is the longest (0.626 μs), which confirms the presumption very well. In addition, as the Si doping concentration increases, the conductivity of the SnO\textsubscript{2}:Si film increases, and the rectification characteristic of the homojunction shows an optimization of synchronization. This may be due to the increase of the difference in conductivity between the SnO\textsubscript{2}:Si film and the SnO\textsubscript{2}:Ga film, which leads to an imbalance in the carrier concentration of both sides, and a large number of carriers are injected into the SnO\textsubscript{2}:Ga film, leading to this phenomenon.

![Graphs showing I-V characteristics](image)

**Figure 8.** The I-V characters of SnO\textsubscript{2}:Si/SnO\textsubscript{2}:10 at.% Ga homojunction with different Si doping concentrations: (a) undoped, (b) 5 at.%, (c) 10 at.%, (d) 15 at.%.  

### 3.5. Current Response of SnO\textsubscript{2} Homojunction under Different Frequency Lights

The small localized states density of the film can greatly reduce the possibility of photo-generated carriers and defects recombination, as well as provide a favorable environment for the movement of photo-generated carriers. Combined with Figure 8, since the performance of the SnO\textsubscript{2}:15 at.% Si/SnO\textsubscript{2}:10 at.% Ga homojunction is the most excellent, it was selected as the sample for the optical response test. By controlling the center distance and angle between the light and the homojunction, the illuminance is uniformly 1200 ± 100 lx, and the three colors of light are irradiated to the surface of SnO\textsubscript{2}:15 at.% Si/SnO\textsubscript{2}:10 at.% Ga homojunction as the excitation source, as shown in Figure 9.
Figure 9. Schematic diagram of a sample illuminated by a light source.

Figure 10 shows the spectrum of light of different colors used in the experiment. The red light is mainly centered at a wavelength of 630 nm; the band of yellow light is mainly distributed from 550 to 700 nm, with the peak at 650 nm; the purple light is centered at a wavelength of 420 nm.

Figure 10. The images of different colors of lights and its wavelength distributions: (a,b) Red light, (c,d) Yellow light, (e,f) Purple light.

The I-V characteristics of the homojunction under the above condition are plotted in Figure 11.
In a dark environment, the response current is of the order of $10^{-9}$, and the response current of the homojunction excited by red, yellow, and purple light is significantly improved by a maximum of two orders of magnitude. With the increase of the frequency of light, the response current of the homojunction gradually increases. This may be due to the increase of the concentration of photo-generated carriers, which increases the probability of carriers moving to the space charge region to a certain extent and reduces the on-resistance of the homojunction. The excitation of the purple light increases the response current of the homojunction by two orders of magnitude, which is due to: (1) the SnO$_2$: Si film has a significantly stronger absorption of purple light than red and yellow light; (2) the energy of purple light is higher than that of red and yellow light, resulting in a significant increase in photocarrier concentration. In addition, the turn-on voltage of the homojunction under the purple light excitation is significantly reduced to 5.0 V, and the homojunction shows more excellent rectification characteristics. The open circuit voltage ($V_{OC}$) is about 1.5 V and the short-circuit current ($I_{SC}$) is about $1.23 \times 10^{-10}$ A in this analysis. Compared with the UV detector based on p-NiO/n-ZnO structure prepared by Zhang et al. [30], which shows the performance that the photogeneration current increases to dark current about twice with ultraviolet light illumination and the $V_{OC}$ is about 0.43 V, the SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction in this research shows better photodetector performance. Besides, the SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction has weak light response to the red and yellow light bands, which is conductive to enhancing the reliability of the photodetector. The above experimental results show that the SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction has the potential to be used as a near-ultraviolet detector.

4. Conclusions

In this paper, a high-quality transparent SnO$_2$:Si film was prepared by the solution method, and the effect of Si doping concentrations on the structure and properties of the SnO$_2$ film was studied. It was found that: (1) a proper amount of Si doping can reduce the film roughness to as low as 0.74 nm (SnO$_2$:5 at.% Si); (2) a proper amount of Si doping can improve the transparency of the film, up to 84.6% at 560 nm for SnO$_2$:5 at.% Si film; the absorption of light in the near-ultraviolet region enhances for SnO$_2$:Si film with increasing Si doping concentrations; (3) the $\mu$-PCD test shows that the mean peak and D value of SnO$_2$:15 at.% Si is high, indicating that the localized states density of thin film is small and has good semiconductor performance; (4) as the Si doping concentration increases, the conductivity of the film improves. Based on the preparation of high-quality SnO$_2$: Si thin films, the SnO$_2$:Si/SnO$_2$:10 at.% Ga homojunctions with different Si doping concentrations were prepared by the solution method in this paper. Research shows that: Si doping can optimize device performance, SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction shows the best performance, the turn-on voltage is as low as 5.6 V, and it has good rectification characteristics. The photoresponse characteristics of SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction under different frequency light was studied. The response to purple light (420 nm) is strong and the current increases by two orders of magnitude than the results.
tested in the dark environment, indicating that SnO$_2$:15 at.% Si/SnO$_2$:10 at.% Ga homojunction has the potential for applications in near-ultraviolet detectors.

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