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Optoelectronic properties of SnO_2/p-Si heterojunction prepared by a simple chemical bath deposition method

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Abstract: The SnO_2 film was successfully deposited on Si wafer by a simple chemical bath method to fabricate n-SnO_2/p-Si heterojunction structure photoelectric device. The self-made chemical bath system is very cheap and convenient. The structural, optical and electrical properies of the SnO_2 film were studied by XRD, SEM, XPS, PL, UV-VIS spectrophotometer and Hall effect measurement. The current-voltage (*I-V*) curve of SnO_2/p-Si heterojunction device was tested and analyzed in detail. SnO_2/p-Si heterojunction shows a prominent visible-light-driven photoelectrical performance under the low intensity light irradiation. Great photoelectric behavior was also obtained.

Key words: SnO_2 film, chemical bath method, heterojunction, current-voltage (*I-V*) characteristics

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简易化学水浴法制备 SnO_2/p-Si 异质结光电性能

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摘要:通过一种简易化学水浴法将 SnO_2 薄膜沉积在晶硅衬底上以制备 n-SnO_2/p-Si 异质结光电器件,这种自制的化学水浴装置非常便宜和方便.采用 XRD、SEM、XPS、PL、紫外-可见光分光光度计和霍尔效应测试系统表征了 SnO_2 薄膜的微结构、光学和电学性能,对 SnO_2/p-Si 异质结的 *I-V* 曲线进行测试并分析,获得明显的光电转换特性.

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关 键 词:SnO_2 薄膜;化学水浴法;异质结;*I-V* 曲线

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Introduction

Semiconductor heterojunctions have established themselves as the most suitable candidates for optoelectric devices[1-3]. Tin oxide (SnO_2) is an important optoelectronic semiconductor with wide direct band gap of 3.6 ~ 3.9 eV, which has received enormous attention in recent years. It has attracted considerable attention because of significant applications in the field of optoelectronic devices, such as solar cells, photodiodes, transparent electrodes and photo transistors. There are many merits for SnO_2, such as abundance in natural resource, low cost and non-toxicity. A variety of techniques have been used to fabricate SnO_2 thin films, such as magnetron sputtering[4-8], PLD[9-12], ultrasonic spray method[13-15], sol-gel[16] and so on. Among these techniques, the chemical bath method is simple, low cost, convenient and fast for large area deposition of polycrystalline SnO_2 films.

In the present study, a polycrystalline SnO_2 film was prepared by a simple chemical bath deposition method on a p-type single crystal Si wafer for making an n-SnO_2/p-Si heterojunction structure photoelectric device. The characterizations of the SnO_2 polycrystalline film were carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL), ultraviolet-visible (UV-Vis) spectrophotometer and Hall effect measurement. The current-voltage (*I-V*) characteristics of the n-SnO_2/p-Si heterojunction were measured by a Agilent 4155C semiconductor parameter analyzer.

1 Experiment

The starting material was a p-type texturized silicon substrate with a boron-doping concentration corresponding to a resistivity of 1Ω · cm. The thickness of the wafer used was 300 μm and the crystal orientation was (100). The wafer was prepared by a standard cleaning procedure, then it was dipped into a 10% HF solution for one minute to remove the native oxide layer and a texturized. Finally, the wafer was dried in a flow of nitrogen.

SnO_2 thin film was deposited on a Si substrate by a simple chemical bath method to fabricate the n-SnO_2/p-Si heterojunction. The details of the procedure are as follows. Firstly, four tin chloride and hexamethylenetetramine ($(CH_2)_6N_4$, HMT) were dissolved in distilled water by a thermostatic magnetic mixer at 85℃ for 10 min. The Molar ratio of four tin chloride and hexamethylenetetramine was 1∶1, and the concentration of four tin chloride was 0.1mol/L. Then, the texturized Si substrate was vertically placed into the solution and heated at 85℃ for 3 hours to grow the polycrystalline SnO_2 film. The sample taken out of the reaction bath was washed with distilled water and dried with nitrogen. Figure 1 shows the schematic diagram of the polycrystalline SnO_2 film chemical bath deposition system. The thickness of SnO_2 film is about 200 nm.

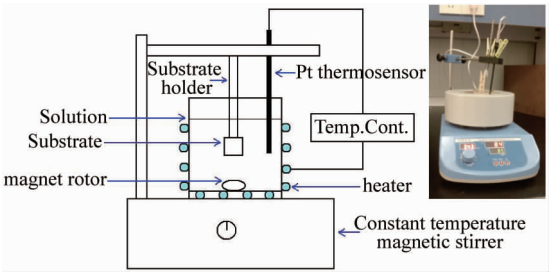

Fig. 1 Schematic diagram of the polycrystalline SnO_2 film chemical bath deposition system

图 1 多晶 SnO_2 薄膜简易化学水浴制备系统

Finally, by rod coating, Ag paste was deposited on the back and top sides of SnO_2/p-Si heterojunction. The area of the device is 0.25 cm^2.

The thickness of SnO_2 film was measured by step profiler (XP-2). The crystallinity, crystal structure, and growth orientations were investigated by X-ray diffraction (XRD). Surface morphology of the SnO_2 film was analyzed with scanning electron microscopy (SEM). The chemical composition was examined by XPS. Photoluminescence (PL) spectra was measured at room temperature. Optical properties of the SnO_2 film were measured by a UV-VIS spectrophotometer in the wavelength rang from 300 nm to 900 nm. The electrical properties of the film were characterized by Hall effect measurement unit (Accent HL5500pc) at room temperature. The current-voltage (*I-V*) characteristics of the device were measured by an Agilent 4155C semiconductor parameter analyzer.

2 Results and discussion

2.1 Microstructural, optical and electrical properties of SnO_2 films

Crystallinity and structural information of as deposited SnO_2 film were estimated by X-ray diffraction analysis. X-ray diffraction spectra of the SnO_2 film deposited by chemical bath method are presented in Fig. 2(a). The sample shows a polycrystalline phase. The dominant peak located at 31.7° is attributed to the SnO_2 (111) diffraction[17]. The result indicates that the SnO_2 film prapared by chemical bath method has a cubic phase structure with its dominant orientation strongly along the (111) direction perpendicular to the Si substrate surface. This indicates that the SnO_2 film via a simple chemical bath deposition method is polycrystalline in nature and highly textured along the (111) plane. The average grain size corresponding to (111) peak was cal-

culated by the Scherrer equation, which is expressed as follows:

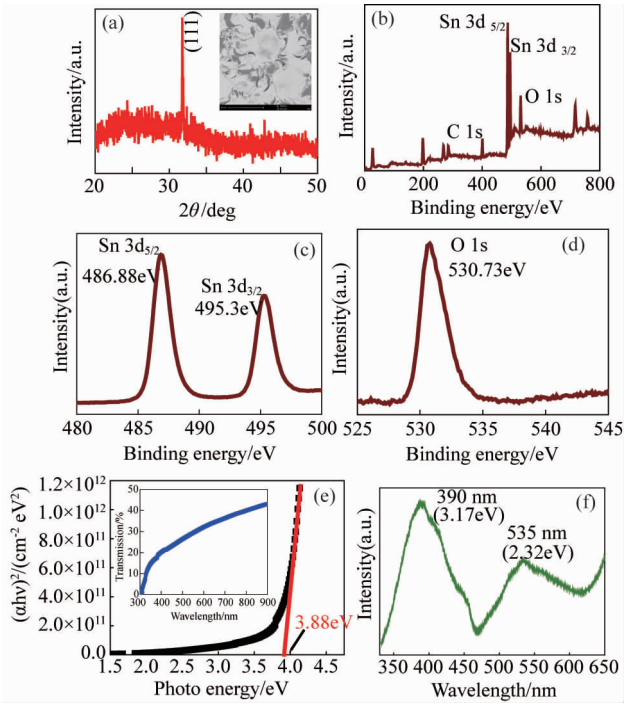

Fig. 2　Microstructural and optical properties of SnO_2 films. (a) XRD spectra of the SnO_2 film, (b) XPS survey spectra of the SnO_2 film, (c) Sn 3d narrow scan XPS spectra, (d) O 1s narrow scan XPS spectra, (e) The $(\alpha h\nu)^2$ vs $h\nu$ plot of SnO_2 film, (f) Photoluminescence spectra of the SnO_2 film

图 2　SnO_2 薄膜的微结构和光学特性. (a) SnO_2 薄膜 XRD 谱, (b) SnO_2 薄膜 XPS 全谱图, (c) Sn 3d 的精细 XPS 谱, (d) O 1s 的精细 XPS 谱, (e) SnO_2 薄膜的 $(\alpha h\nu)^2$ vs $h\nu$ 曲线, (f) SnO_2 薄膜的 PL 谱

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad , \quad (1)$$

where λ, θ and β are the X-ray wavelength (1.540 56 Å), the Bragg diffraction angle, and the FWHM of SnO_2-(111) diffraction peak, respectively. The grain size of the SnO_2 film was about 85 nm. Figure 2(a), sinset shows SEM image of the SnO_2 film. The SEM image indicates that the deposited film has a soft surface.

The chemical binding states and surface composition of the SnO_2 film were studied by XPS. Figure. 2(b) shows the X-ray photoelectron spectroscopy (XPS) survey scan of SnO_2 film on p-type texturized CZ silicon. The sample contains Sn, O, and traces of C. The Sn $3d_5/2$ and Sn $3d_3/2$ peaks shown in Fig. 2(c) are present at 486.88 eV and 495.3 eV, respectively, with a peak splitting of 8.42 eV, which confirms the presence of Sn^{4+}. Narrow scan XPS spectra of O 1s state of the sample is shown in Fig. 2(d). The O 1s peak observed at 530.73 eV for the SnO_2 film prepared by chemical bath method in the work can be attributed to the chemisorbed oxygen. This result agrees with XRD analysis.

The band gap of SnO_2 film was determined from the measured transmittance spectra. Figure 2(e) shows the $(\alpha h\nu)^2$ vs $h\nu$ plot of SnO_2 film on glass substrate, which was calculated by a UV-VIS spectrometer. The inset of Fig. 2(e) shows the transmittance curve of SnO_2 film. The average transmittance of the SnO_2 film is about 30% in the visible region of light. The absorption cofficient α were obtained using $\alpha = (1/d)\ln(1/T)$, where d is the film thickness and T is the transmittance[18]. The optical band gap, E_g, of the film was calculated using the relation $\alpha h\nu = (h\nu - E_g)^{1/2}$, where $h\nu$ is the photon energy. The optical bandgap is determined by extrapolating the linear part of the $(\alpha h\nu)^2$ curve towards the $h\nu$ axis. In order to evaluate the energy band gap of SnO_2 film, the plot of $(\alpha h\nu)^2$ vs $h\nu$ was shown in Fig. 2(e). The band gap energy (E_g) value of SnO_2 film is 3.88 eV.

Figure 2(f) shows room-temperature PL spectra of the as-grown polycrystalline SnO_2 film on glass substrate, where the excited wavelength is 325 nm (He-Cd laser). An intensive ultraviolet (UV) emission peak at 390 nm (about 3.17 eV) and a weak-broad visible emission shoulder at 535 nm (about 2.32 eV) are observed. The UV emission band could be related to oxygen vacancies of the SnO_2 film[19], while the weak-broad visible emission basically originates from some defects in the sample.

Electrical properties of the SnO_2 film were determined from the Hall effect measurement. It is an n-type semiconductor. The resistivity is 13.67 Ω · cm. The electron concentration and mobility are 1.087×10^{17} atom/cm^3 and 4.201 cm^2/V · s, respectively.

Table 1　Electrical parameters of SnO_2 film

表 1　SnO_2 薄膜的电学性能参数

Material	ρ/(Ω · cm)	n/(atom/cm^3)	μ/(cm^2/V · s)
SnO_2	13.67	1.087×10^{17}	4.201

2.2　*I-V* characteristics

The linear current-voltage (*I-V*) behaviors between the two Ag electrodes on the surface of the SnO_2 film are shown in Fig. 3. The inset shows the schematic of the test structure. It indicates a good ohmic contact. The distance between the two Ag electrodes on the film is 1 cm.

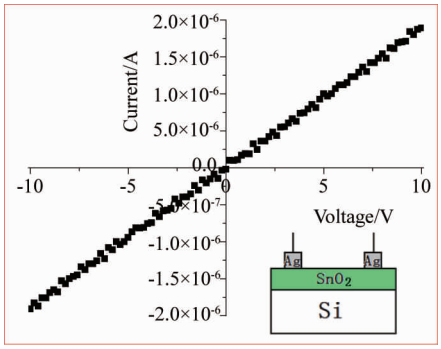

Fig. 3　*I-V* characteristics of Ag ohmic contacts to the SnO_2 film

图 3　Ag 电极与 SnO_2 薄膜欧姆接触的 *I-V* 曲线

Figure 4 shows a typical *I-V* characteristic of the

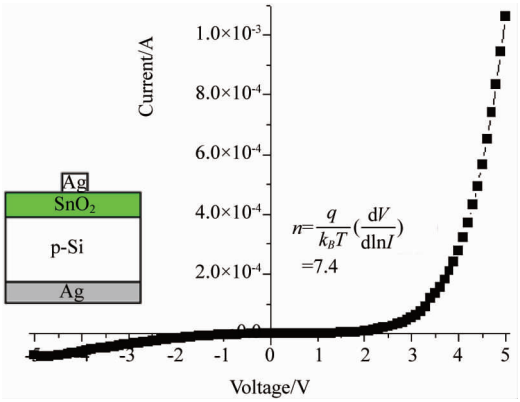

Fig. 4 *I-V* curve of the SnO_2/p-Si heterojunction in dark
图 4 无光照 SnO_2/p-Si 异质结 *I-V* 曲线

SnO_2/p-Si heterojunction device measured in dark. The inset in Fig. 4 shows the heterojunction device structure. The *I-V* curve of device shows a rectifying behavior. A small leakage current is observed in the reverse bias region, but the forward current is much higher than the reverse current. And the value of I_F/I_R (I_F and I_R stand for forward and reverse current, respectively) reaches to 14.46. In general, the equation of the diode is

$$I = I_0(e^{\frac{qV}{nk_BT}} - 1) \quad , \quad (2)$$

where n is the ideality factor given by . The value of n is found to be 7.4. While the value n of AZO/SiO_2/p-Si SIS heterojunction prepared by RF magnetron sputtering is 24.42[20]. The results indicate that the SnO_2/p-Si heterojunction has good diode characteristics. The p-n heterojunction is formed at the interface of the p-Si wafer and n- SnO_2 thin film.

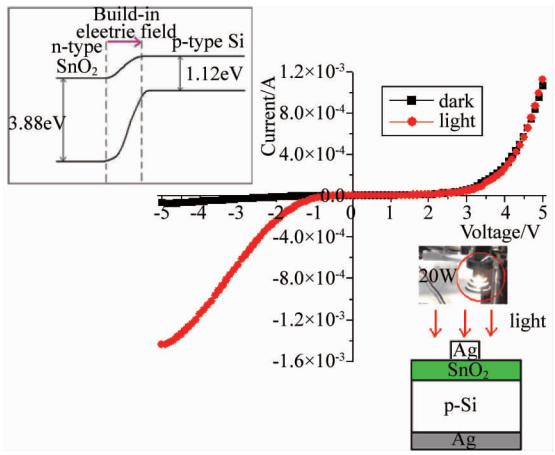

Fig. 5 *I-V* characteristic of the SnO_2/p-Si heterojunction in dark and in light (20 W halogen lamp)
图 5 SnO_2/p-Si 异质结无光照及光照(20W 卤钨灯)条件下 *I-V* 曲线

The photo *I-V* characteristic of the SnO_2/p-Si heterojunction device was measured under illumination by a 20 W halogen lamp as shown in Fig. 5. Typical good rectifying and photoelectric behavior are observed for the device. Under the reverse bias, the photocurrent is much larger than the dark current. For example, when the reverse bias is -5 V, the dark current is only 7.33×10^{-5} A, while the photocurrent reaches to 1.44×10^{-3} A under the 20 W halogen lamp illumination. The photocurrent gain is as high as 19.65, because the visible light can be absorbed in the p-Si substrate to generate many electron-hole pairs. Then the electron-hole pairs can be effectively separated by the strong electric field in the interface. Consequently, a large photocurrent is obtained under the reverse bias.

3 Conclusion

The SnO_2 film was successfully deposited on a Si wafer by a simple chemical bath method to fabricate an n-SnO_2/p-Si heterojunction-structured photoelectric device. The self-made chemical bath system is cheap and convenient. The structural, optical and electrical properies of the SnO_2 film were studied by XRD, XPS, UV-VIS spectrophotometer and Hall effect measurement. The *I-V* curves of SnO_2/p-Si heterojunction devices show good rectifying behaviors. This indicates that the p-n heterojunction is formed at the interface of n-type SnO_2 film and p-type Si substrate. A high photocurrent is obtained under a reverse bias. The results indicate that the SnO_2/p-Si heterojunction are promising for low cost visible-light photodiodes for various applications.

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References

[1] Yuan X, Tang L, Liu S S, *et al*, Arrayed van der waals vertical heterostructures based on 2D GaSe grown bymMolecular beam epitaxy [J], *Nano Letters*, 2015, **15**(5):3571 - 3577.
[2] Liu S S, Yuan S, Wang P, *et al*. Controllable growth of vertical heterostructure $GaTe_xSe_{1-x}$/Si by molecular beam epitaxy[J]. *ACS Nano*, 2015, **9**: 8592 - 8598.
[3] Yuan X, Tang L, Wang P, *et al*, Wafer-scale arrayed p-n junctions based on few-layer epitaxial GaTe[J]. *Nano Research*, 2015, **8**(10): 3332 - 3341.
[4] Korotkov R Y, Ricou P, Farran A J E. Preferred orientations in polycrystalline SnO_2 films grown by atmospheric pressure chemical vapor deposition[J]. *Thin Solid Films*, 2006, **502**(1-2):79 - 87.
[5] Ruske M, Bräuer G, Pistner J. Properties of SnO_2 films prepared by DC and MF reactive sputtering[J]. *Thin Solid Films*, 1999, **351**(1-2):146 - 150.
[6] Leng D, Wu L L, Jiang H C[J]. Preparation and properties of SnO_2

film deposited by magnetron sputtering[J]. *International Journal of Photoenergy*, 2012, 2012:235971.

[7] Gui T L, Hao L, Wang J M. Structure and features of SnO_2 thin films prepared by RF reactive sputtering[J]. *Chinese Optics Letters*, 2010, **8**:1671.

[8] Chowdhuri A, Haridas D, Sreenivas K. Mechanism of trace level h_2s gas sensing using rf sputtered sno_2 thin films with cuo catalytic overlayer[J]. *International Journal on Smart Sensing and Intelligent Systems*, 2009, **2**(4):540 - 548.

[9] Cachet H, Bruneaux J, Folcher G. n-Si/SnO_2 junctions based on macroporous silicon for photoconversion[J]. *Solar Energy Materials and Solar Cells*, 1997, **46**(2):101 - 114.

[10] Chen Z W, Lai J K L, Shek C H. Nucleation and growth of SnO_2 nanocrystallites prepared by pulsed laser deposition[J]. *Applied Physics A*, 2005, **81**(5):959 - 962.

[11] Chan y Díaz E, Duarte-Moller A, Camacho J M. SnO_2 thin films grown by pulsed Nd:YAG laser deposition[J]. *Applied Physics A*, 2012, **106**(3):619 - 624.

[12] Zhao S Q, Zhou Y L, Wang S F. Effect of ambient oxygen pressure on structural, optical and electrical properties of SnO_2 thin films[J]. *Rare Metals*, 2006, **25**(6):1 - 4.

[13] Serin T, Serin N, Karadeniz S. Electrical, structural and optical properties of SnO_2 thin films prepared by spray pyrolysis[J]. *Journal of Non-Crystalline Solids*, 2006, **352**(3):209 - 215.

[14] Sánchez-García M A, Maldonado A, Castañeda L. Characteristics of SnO_2:F thin films deposited by ultrasonic spray pyrolysis: Effect of water content in solution and substrate temperature[J]. *Materials Sciences and Applications*, 2012, **3**(10):690 - 696.

[15] He B, Xu J, Xing H Z. Observation of nanospherical n-SnO_2/p - Si heterojunction fabricated by ultrasonic spray pyrolysis technique[J]. *Surface Review and Letters*, 2013, **20**(5):1350052.

[16] Gu Z T, Liang P H, Liu X L. Characteristics of Sol-Gel SnO_2 films treated by ammonia[J]. *Journal of Sol-Gel Science and Technology*, 2000, **18**(2):159 - 166.

[17] Song J, Cai M Z, Dong Q F. Structural and electrochemical characterization of SnO_x thin films for Li-ion microbattery[J]. *Electrochimica Acta*, 2009, **54**(10):2748 - 2753.

[18] He B. Influence of substrate temperature on structural, electrical and optical properties of ito thin films prepared by rf magnetron sputtering [J]. *Surface review and letters*, 2013, **20**:1350045.

[19] Hera Y C, Wu J Y. Low-temperature growth and blue luminescence of nanoblades[J]. *Applied Physics Letters*, 2006, **89**:043115.

[20] He B, Zhong Q M, Xu J. Structural, electrical and optical properties of AZO/SiO_2/p-Si SIS heterojunction prepared by magnetron sputtering[J]. *Optica Applicata XL*, 2010, **40**(1):14 - 24.