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Solution processed highly sensitive visible-light photodetectors based on α-Fe_2O_3/p-Si heterojunctions

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ABSTRACT

High-sensitive visible-light photodetectors based on α-Fe_2O_3 thin films on p-Si substrates with a responsivity as high as 2×10^3 A/W have been fabricated and characterized. The solution-processed devices exhibit a rapid rise/decay time (<1 ms) and a high ratio of photocurrent to dark current (~1.3×10^4) under 12.5 mW/cm^2 illumination at 403 nm. The superior performances can be attributed to the interface with a suitable energy band structure of the α-Fe_2O_3/p-Si heterojunction and the role of fast transport channel for photogenerated holes the p-Si substrates played. A stable, reversible, and rapid photoresponse at visible wavelengths, along with the simple, low-cost, and large-scale fabrication of the photodetectors, clearly demonstrates the possibility of industrial mass-production for commercial and military applications.

1. Introduction

α-Fe_2O_3 (hematite) is an important semiconductor material in the fields of catalyst [1,2], gas sensors [3], environmental protection [4], and magnetic storage media [5]. Because of its ample abundance, environmental compatibility, chemical stability, and capability to absorb visible light (band gap, E_g = 2.0 eV), it has been extensively studied for photoelectrochemical splitting of water to produce hydrogen [6–8]. However, poor minority charge carrier mobility (0.2 cm^2 V^{-1} s^{-1}) [8] and ultrafast recombination of the photogenerated carriers (on the order of 10 ps) [9] limit its promising applications in photocatalysts, photodetectors and photovoltaic cells [10].

So far as we know, few studies have been reported on the light detection with α-Fe_2O_3. Until recently, a photodetector based on an individual α-Fe_2O_3 nanobridge between two Au electrodes was reported [11]. The device showed a fast response time of <20 ms and on/off ratio of >12 times under 0.5 mW/cm^2 illumination at a wavelength of 490 nm. It is believed that difficulty to separate and facility to recombine electron–hole pairs in α-Fe_2O_3 are the main limitations. Further enhancement of the photoresponse performances is desirable for practical applications.

Here, we report the fabrication of α-Fe_2O_3 thin film-based photodetectors and their photoresponse properties. The photodetectors exhibit a rapid, reversible, and high-sensitive response to visible light. An extremely high responsivity of 2×10^3 A/W and a high ratio of photocurrent to dark current of ~1.3×10^4 were demonstrated under 12.5 mW/cm^2 illumination at 403 nm. The samples were stable under ambient conditions since no degradation of photoresponse performances was observed when the samples were stored in air for over four months. It is worth noting that the α-Fe_2O_3 thin film was directly spin-coated on p-type silicon substrates. Therefore, the α-Fe_2O_3 thin film-based photodetectors are compatible with the traditional silicon semiconductor technology and can be easily integrated on a single chip.

2. Experimental procedure

The α-Fe_2O_3 thin film based photodetectors were fabricated by using a chemical solution deposition method. The substrates were boron-doped p-Si with a resistivity of 100 Ω cm (boron doping concentration: about 1.33×10^{14} cm^{-3}). Prior to use, the p-Si substrates were cleaned through a standard cleaning process. There was a native SiO_2 layer with about 5 nm on the silicon substrate surface. The chemical solution was synthesized using iron nitrate as raw materials and 2-methoxyethanol and acetic acid as co-solvent. In brief, iron (III) nitrate ([$Fe(NO_3)_3 \cdot 9H_2O$]) was mixed into the 2-methoxyethanol solvent while a proper amount of acetic acid was added as co-solvent. The final precursor solution was adjusted to 0.2 M. Spin-coating of the solution was performed at 3000 rpm for 20 s on p-type Si substrates, followed by baking on a hot plate to remove organics. In order to increase film thickness, the above spin-coating and baking procedure was repeated different times. Finally, the thin films were annealed at 600 °C for 1 h. The thickness of the thin film obtained by repeating twice the spin-coating and baking procedure

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was about 40 nm measured by stylus profilometer (Ambios XP-200 Plus).

The phase purity was studied by Raman spectrum (Renishaw inVia Laser Micro-Raman Spectrometer). The UV–visible absorption spectra of α-Fe_2O_3 films spin-coated on fused silica substrates were measured using a Shimadzu UV-3150 in the wavelength range 350–650 nm. To characterize the electrical properties, platinum top electrodes were sputter-deposited on the surfaces of the thin films through a shadow mask and Ag paste was painted on the naked Si substrate as bottom electrode. *I–V* measurements were carried out using a Keithley 236 in air at room temperature. A set of calibrated light emitting diodes was used as illumination source.

3. Results and discussion

Fig. 1(a) shows the α-Fe_2O_3 film-based photodetector structure. The Raman spectrum of the α-Fe_2O_3 film is shown in Fig. 1(b) to confirm phase purity. The α-Fe_2O_3 belongs to the D^6_{3d} crystal space group. Typical Raman bands are two A_{1g} modes (225 and 498 cm^{-1}) and five E_g modes (247, 293, 299, 412 and 613 cm^{-1}) [12]. In this work, all the peaks exhibit a slight red shift due to quantum size effect [12,13], while the 498 cm^{-1} band is overlapped by the Raman peak of silicon (520 cm^{-1}). In addition, α-Fe_2O_3 is a weak anti-ferromagnetic material at room temperature [14]. The peak at 1308 cm^{-1} is assigned to a two-magnon scattering which distinguishes α-Fe_2O_3 from other iron oxides, such as Fe_3O_4 [12]. Fig. 1(c) shows UV–visible absorption spectrum of the α-Fe_2O_3 film spin-coated on fused silica substrate. The α-Fe_2O_3 film exhibits an absorbance onset around 590 nm and a small peak around 400 nm corresponding to 2.1 eV and 3.1 eV, respectively. Fig. 1(d) shows the photocurrent spectral response at −10 V bias of the α-Fe_2O_3 thin film based photodetector. The spectrum shows a wide-band response in the range from 380 to 630 nm, and a maximum photoresponse at 403 nm. We also measured the photocurrent of the film when illuminated from the bottom of Si substrate. It was observed that the photocurrent was only about 1% of the corresponding value in Fig. 1(d), confirming that the photocurrent mainly originates from the photogenerated carriers formed in the α-Fe_2O_3 thin film, Fig. 2(a) shows the typical *I–V* characteristics of the α-Fe_2O_3 film based photodetector both in the dark and under 12.5 mW/cm^2 light illumination (λ = 403 nm). Up to −15 V, a small dark current (<6 nA) flows in the photodetector, which is favorable for fabricating low-consumption photodetectors. The current increases by 4 orders of magnitude under illumination (at an average light intensity of 12.5 mW/cm^2). Both of the *I–V* curves in the dark and under illumination follow an exponential rise when bias voltage varies from 0 to −1.0 V and are saturated at higher bias. It is noteworthy that even for zero external bias ('photovoltaic mode'), a significant photocurrent of ~27 nA is generated while a small current (~0.9 nA) flows in the photodetector, which indicates that the separation of photogenerated electron–hole pairs takes place in the depletion region by a built-in field. Fig. 2(b) shows the incident optical power dependence of the photocurrent. The photocurrent of the photodetector increases from 5.7 μA to 79.8 μA as the average power intensity is increased from 1.045 mW/cm^2 to 12.5 mW/cm^2. It is found that the photocurrent (I_{pc}) can be expressed by a linear relationship:

$$I_{pc} \propto P \quad (1)$$

where *P* is the average power of illumination. The linear relationship is a result of the simple process of electron–hole generation and recombination in the α-Fe_2O_3 film. Fig. 2(c) and (d) shows a rapid, stable, and reversible photocurrent response to turn-on and turn-off of the illumination. Both of the rise time and decay time of the photodetector are less than 1 ms.

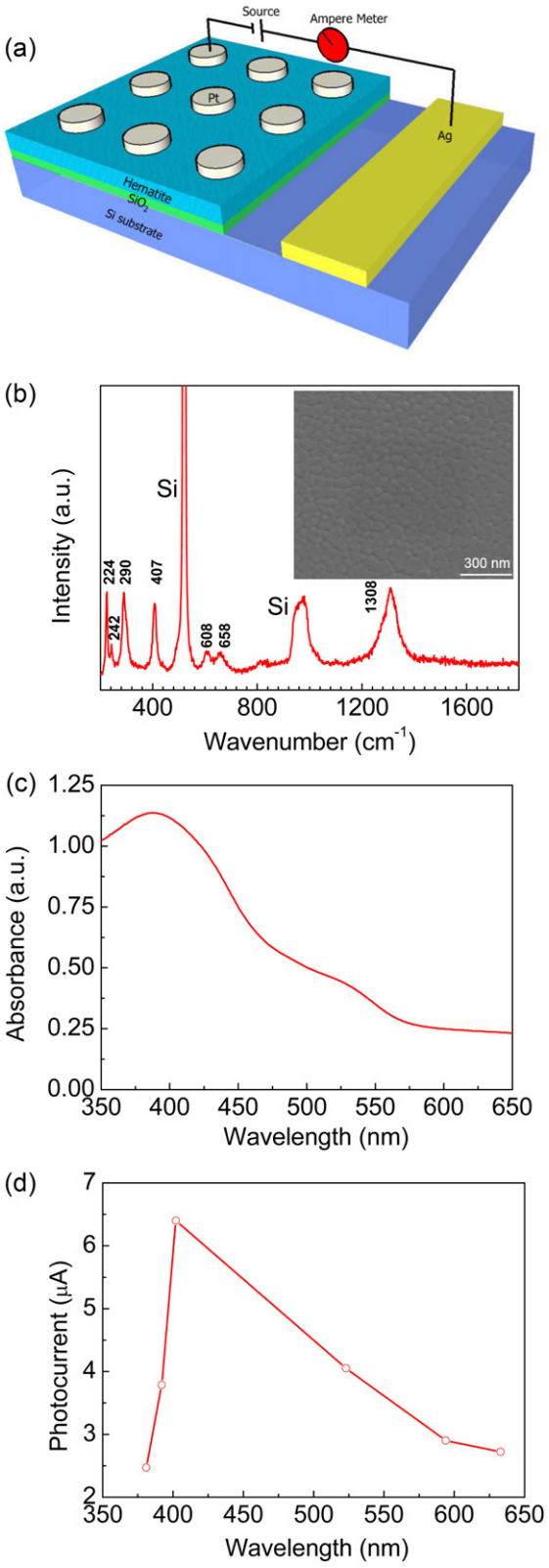

Fig. 1. (a) Schematic of the α-Fe_2O_3 thin film-based photodetector structure (not to scale), (b) Raman spectrum of the α-Fe_2O_3 film on p-Si substrate, and SEM image (inset) of the film surface, (c) UV–visible absorption spectrum of the α-Fe_2O_3 film on fused silica, and (d) Photocurrent spectral response of the α-Fe_2O_3 film-based photodetectors, and all the photocurrents were measured at an average intensity of 1 mW/cm^2 at 403 nm under −10 V bias.