Journal of Alloys and Compounds 616 (2014) 155–158

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Letter

Ultrahigh responsivity UV detector based on TiO_2/Pt-doped TiO_2 multilayer nanofilms

Guohua Liu [a], Min Zhang [a], Dezhong Zhang [b], Jingran Zhou [b,*], Fanxu Meng [c,*], Shengping Ruan [a,*]

[a] *State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, China*
[b] *College of Electronic Science and Engineering, Jilin University, Changchun 130012, China*
[c] *Jilin University of Chemical Technology, Jilin 132022, China*

ARTICLE INFO

Article history:
Received 5 July 2014
Received in revised form 18 July 2014
Accepted 18 July 2014
Available online 30 July 2014

Keywords:
Pt-doped TiO_2
Schottky barrier height
Thin films
UV detector

ABSTRACT

High-response UV detector based on TiO_2/Pt-doped TiO_2 (PT) multilayer nanofilms with Au interdigitated electrodes was fabricated. PT film was used as the main light sensitive layer of the detector. By introducing a sufficiently thin TiO_2 film as an interfacial modified layer between Au electrodes and the PT film, the Schottky barrier height was effectively reduced, leading to the remarkable enhancement in the device photoresponse properties. At 5 V bias, a photocurrent of 191.77 μA and an ultrahigh responsivity of 3194 A/W were obtained under 260 nm UV illumination (15.8 $\mu W/cm^2$). The rise and the recovery time were 60.12 ms and 579.9 ms, respectively. The effects of Pt doping on TiO_2 film and device performance were also systematically investigated. These experimental results demonstrate the potential prospects of noble doping in fabricating high-response UV detectors.

1. Introduction

TiO_2 UV detectors (TUDs) are popular for ultraviolet detection and have attracted considerable attention in astronomy, military and civil applications since TiO_2 has been demonstrated as an excellent matrix material due to its low cost, intrinsic visible-blindness, outstanding photoelectronic properties and biocompatible characteristics [1–5]. Varies structures, including metal–semiconductor–metal (MSM) [6,7], heterojunction [8,9], Schottky [10,11] and metal–insulator–metal (MIS) [12,13], have been investigated for the TUD fabrication. Among them, MSM TUDs exhibit obvious advantages for its ease fabrication, low dark current and good compatibility with modern optoelectronic integrated circuits [14–16]. It is well-known that an MSM TUD consists of two back to back Schottky barriers and the Schottky barrier height (SBH) between TiO_2 and metal electrodes plays an important role in device performance [17,18]. The higher the SBH is, the more difficult the electrons transport across the space charge region and are collected by the electrodes. Thus the photoresponse properties, including the photocurrent, responsivity and time response characteristics, would be limited, which may impede the TUDs' further development toward civilian facility applications especially operating in harsh environment, such as fire alarm and electronic spark detection.

In order to reduce the restrictions of SBH on the photoresponse properties, a TiO_2/Pt-doped TiO_2 (PT) multilayer nanofilms UV detector is proposed in this letter. PT film (150 nm) was used as the main light sensitive layer of the detector due to its smaller contact electric potential difference with Au electrodes. By introducing a sufficiently thin TiO_2 film (30 nm) as an interfacial modified layer between Au electrodes and the PT film, the SBH was further reduced. The detector exhibited high photocurrent, high responsivity and fast response time. Besides, it is worth noting that noble metal Pt doping in TiO_2 thin films, which can facilitate the charge transport and improve light absorption characteristics, has firstly been used in UV detection filed.

2. Experimental details

In the experiment, 6 ml tetrabutyl titanate [$Ti(OC_4H_9)_4$] was dissolved in 90 ml ethanol (C_2H_5OH), followed by additions of 8 ml acetic acid (CH_3COOH), 8 ml acetylacetone and 8 ml deionized (DI) water. The mixture was kept stirring until transparent orange red TiO_2-sol formed. Then, 8 g of 2 wt.% H_2PtCl_6 aqueous solution and 10 ml TiO_2-sol were mixed under 70 °C water-bath condition and kept stirring to form transparent brown PT-sol. The PT-sol was subsequently smeared on a cleaned quartz substrate by spin coating at a rate of 3000 rpm for 20 s. The process was repeated for another four times. Then the sample was annealed at 600 °C for 2 h in a muffle furnace to form nanocrystalline PT film. The thickness of the film measured by a XP-2 profilometer was 150 nm. To prepare TiO_2/PT multilayer (TPM) nanofilms, TiO_2-sol was directly spun cast on the PT film and annealed under the same conditions to form a thin TiO_2 film (30 nm). As a comparison, pure TiO_2 and

---

* Corresponding authors. Tel.: +86 431 85168240x8219; fax: +86 431 85168270.
E-mail addresses: zhoujr@jlu.edu.cn (J. Zhou), fxmengjlu@gmail.com (F. Meng), rspjlu@163.com (S. Ruan).

http://dx.doi.org/10.1016/j.jallcom.2014.07.147
0925-8388/© 2014 Elsevier B.V. All rights reserved.

pure PT films were also prepared in the same way. The thicknesses of the samples were all about 180 nm. Au interdigitated electrodes with the same finger width and spacing of 20 μm were fabricated on the three film samples to form MSM TUDs using photolithography, radio frequency magnetron sputtering and lift-off techniques. The total active area of the devices was 0.38 mm^2.

The X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements are performed using a Shimadzu XRD-6000 diffractometer and a British photoelectron spectrometer (VG ESCA LAB MKII). A Shimadzu UV-1700 Pharma Spec UV spectrophotometer was used to obtain the UV–Vis absorption spectra. The current–voltage (*I–V*) characteristics and photoresponse spectra of the devices were measured using a Keithley 2601 source meter together with a UV power meter. 30-W deuterium lamp and a monochromator were combined to provide the monochromatic light.

3. Results and discussion

XRD was used to examine the crystal structures of the TiO_2 and PT films (Fig. 1(a)). The reflection peaks show that the TiO_2 film is composed of anatase phase and small amount of rutile phase. As for the PT film, an obvious shift to lower angles of the anatase TiO_2 peaks is observed, which implies that parts of Pt atoms substitute Ti atoms in TiO_2 lattice to form oxidized state Pt (Pt^{4+}) [19,20]. Meanwhile, the appearance of diffraction peaks of Pt (JCPDS NO. 04-0802) also indicates the existence of metallic Pt (Pt^0). In addition, the embedded Pt atoms increase the interplanar distance and expand the cell volume, which is conducive to the formation of anatase TiO_2 with larger lattice constants. Therefore the TiO_2 crystalline structure was completely transformed into pure anatase phase after Pt doping. To further determine the chemical state of the Pt elements incorporated in the as-prepared TiO_2 thin film, XPS measurements were carried out and showed in Fig. 1(b). The survey XPS spectra clearly exhibit the existence of Pt 4f, Pt 4d and Pt 3d peaks in the PT film. Fig. 1(c) shows the high-resolution spectra of the Pt 4f core level. Deconvolution of the Pt 4f region shows the presence of two pairs of doublets. The most intense doublet with binding energies of 73.383 (Pt $4f_{7/2}$) and 76.629 eV (Pt $4f_{5/2}$) is attributed to Pt^{4+} that embedded into TiO_2 lattice. Peaks at 71.18 (Pt $4f_{7/2}$) and 74.67 eV (Pt $4f_{5/2}$) could be assigned to metallic Pt [21–24]. Similar results are also obtained according to the Pt 4d and Pt 3d core level spectra. The XPS spectra clearly demonstrate the existence of Pt^0 (20.29%) and Pt^{4+} (79.71%) in the PT film, which is consistent with the XRD analysis. Fig. 1(d) shows the UV–Vis absorption spectra for the TiO_2, PT and TPM films, which are of the same thicknesses. It can be seen that Pt doped samples have stronger absorption intensity and broader detection range. We can control the light absorption edge of the TPM film at the UVA cutoff edge (400 nm) by modulating the doping concentration of Pt.

The scanning electron microscope (SEM) images of the detector and the TPM nanofilms are displayed in Fig. 2. Fig. 2(a) shows the surface structure of the TPM detector. The Au interdigital electrodes with 20 μm finger width and spacing can be clearly seen. Fig. 2(b) shows the top view of the TPM nanofilms, whose surface is uniform and compact. Inset shows the corresponding cross sectional image. It can be seen that the TiO_2/PT interface is easy to distinguish and the thickness of TiO_2 layer and PT layer is about 30 nm and 150 nm, respectively.

The structure of the MSM TPM detector is illustrated in Fig. 3(a). Since comparing with TiO_2, PT has larger work function ($q\phi_{s2}$) and lower Fermi level (E_{F2}), the contact electric potential difference ($q\psi_2$) and SBH [$q\phi_{b2} = q\psi_2 + (E_{C2} - E_{F2})$] between PT and Au electrodes are much smaller, as shown in Fig. 3(b) and (c). Therefore PT film is used as the main light sensitive material of the detector. On the other hand, the relatively high Fermi level of TiO_2 represents a higher electron occupied energy level. Once the thin TiO_2 film and PT film touch each other, the electrons in TiO_2 would transfer into PT to maintain the flattening of the Fermi level. Thus a thin space charge layer is finally formed and its electric field direction ($E_{TiO2/PT}$) is opposite to that of the built-in electric field (E_{MS}) between PT and Au electrodes, consequently leading to a further reduction of the SBH (Fig. 3(d)). The photocurrent of the device is improved thereby, which is responsible for the high photoresponsivity.

The *I–V* characteristics of the devices in dark and under 260 nm UV illumination (15.8 μW/cm^2) are shown in Fig. 4(a). At 5 V bias, the TiO_2 device gets the lowest photocurrent of 6.42 μA, and the

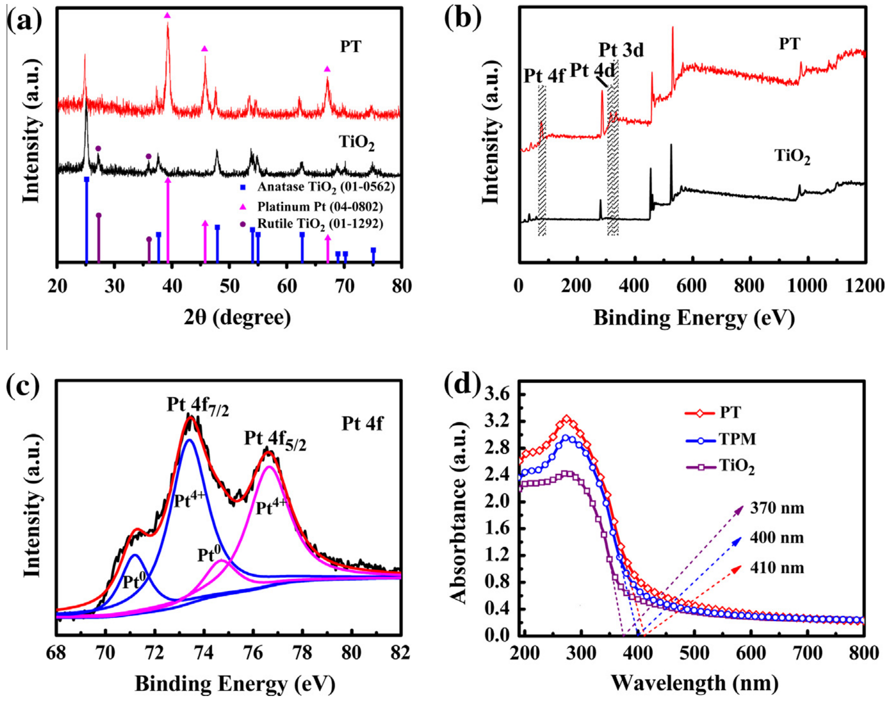

Fig. 1. (a) XRD patterns of TiO_2 and PT films. (b) Survey XPS spectra of TiO_2 and PT films. (c) High-resolution XPS spectra of Pt 4f core level. (d) UV–Vis absorption spectra of TiO_2, PT and TPM films.