Materials Letters 115 (2014) 45–48

Contents lists available at ScienceDirect

Materials Letters

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

Rapid thermal-treated transparent electrode for photodiode applications

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ARTICLE INFO

Article history:
Received 23 August 2013
Accepted 2 October 2013
Available online 14 October 2013

Keywords:
Transparent electrode
Indium-tin-oxide (ITO)
Oxidation reaction
Rectifying contact
Photodiodes

ABSTRACT

We demonstrate a high performing and cost-effective photodiode with a low thermal budget. A quality heterojunction photoelectric device provided extremely high photo-responses. Transparent conductive indium-tin-oxide (ITO) film was coated on a Si substrate at a room temperature and then, rapid thermal treatment was done at 300 °C for 10 min. This heterojunction (ITO/Si) spontaneously provides a rectifying junction that shows high photo-response values of 1920%, 3240%, and 2800% at wavelengths of 350 nm, 600 nm, and 1100 nm, respectively. Thermal treatment affects the solid-state oxidation reaction of ITO and Si and control the formation of an interfacial layer.

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1. Introduction

Transparent conductors are mostly used as ohmic contact layers of front or back transparent electrodes for photoelectric devices. However, a transparent layer can be uniquely applied as a rectifying junction [1] to a semiconductor, which also enables a transparent conductor to work as an electrode [2]. This may be a promising approach for cost-effective photoelectric applications, including solar cells [3] and photodiodes [4,5].

Indium-tin-oxide (ITO) has been widely used as a transparent conductor due to its excellent electrical conductivity and a high optical transparency. However, a high processing temperature induces cost burden and limits the use of ITO in flexible electronics [6]. Thus, a crucial issue is the fabrication of a high quality ITO film with a low thermal budget.

Herein, we present a high-response photodiode of an ITO film-embedding Si heterojunction device. Rapid thermal treatment was effective to form a quality rectifying junction. An interfacial layer, between the ITO film and the Si substrate, is substantially affected by thermal treatment, which treatments are crucial for the performances of photodiodes.

2. Experimental procedure

ITO films were deposited on p-type Si and glass substrates by DC sputtering. A DC power source (3.70 W/cm^2) was applied to a 4-inch ITO target (In_2O_2 containing 10 wt% SnO_2) at room temperature (RT). Rapid thermal annealing (RTA) was subsequently performed for 10 min under vacuum condition. ITO films on glass samples, processed in the same manner as their Si counterparts, were used to measure the optical properties of the ITO films with a UV spectrophotometer (Scinco, Neosys-2000).

A transmission electron microcope (TEM, JEM-ARM200F, JEOL) was employed to investigate the cross-sectional structures. The depth profile and content of the elements were measured by secondary ion mass spectroscopy (SIMS, Cameca, magnetic sector ims7f). A quantum efficiency measuring system (McScience, K3100) was used to measure the quantum efficiencies of the temperature-dependent ITO film devices.

3. Results and discussion

We prepared 200 nm-thick ITO films at room temperature, 300 °C and 600 °C (hereafter referred to as ITO-RT, ITO-300 °C, and ITO-600 °C). Fig. 1(a–f) are TEM images of interfaces between an ITO film and a Si substrate. Due to the identical deposition conditions, all ITO films have the same thickness on the Si substrate (Fig. 1a–c).

For an as-deposited ITO film, TEM clearly shows mixed structures of crystalline and amorphous phases. The interplanar distance was measured and found to be 0.29 nm, which is consistent with a cubic (222) plane of ITO (Fig. 1d). Scale bar was calibrated for precision using a single crystalline Si (111) plane. After RTA process, an ITO film was well crystallized. Fig. 1(e) is for ITO-300 °C, showing crystalline ITO film growth along the (222) plane

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0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.10.017

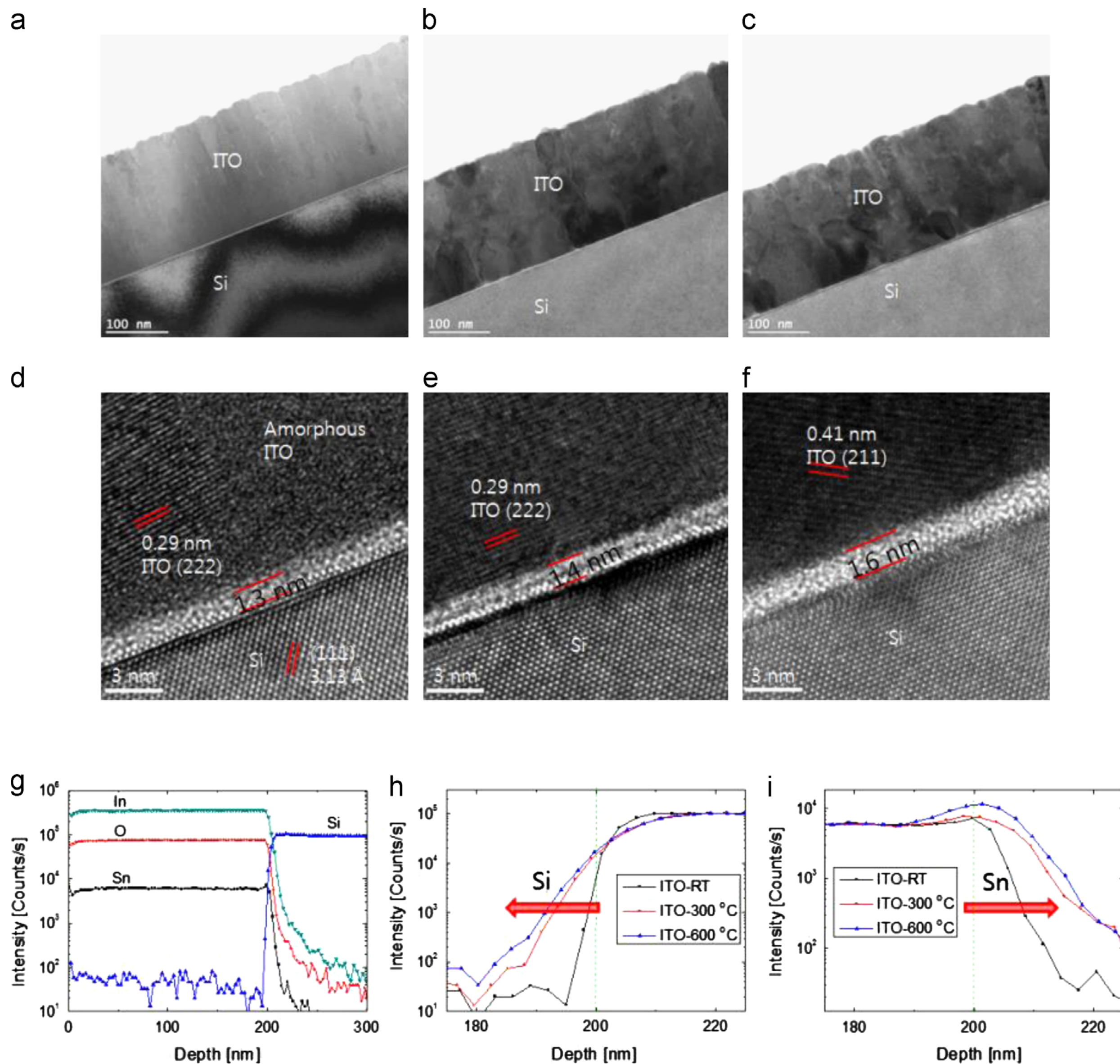

Fig. 1. (a–c) Low-magnitude TEM images. (d–f) High-magnitude TEM images. (a)–(d) are for ITO-RT, (b)–(e) are for ITO-300 °C, and (c)–(f) are for ITO-600 °C. (g–i) Depth profiles. (g) is for ITO-RT, (h) shows Si signals and (i) shows Sn signals of ITO-RT, ITO-300 °C, and ITO-600 °C.

with a lattice space of 0.29 nm. Fig. 1(f) is an image of ITO-600 °C, having a lattice space of 0.41 nm along the (211) plane.

It is interesting to observe the increase of thickness of an interface layer as a function of the applied RTA temperature. ITO-RT shows an interface thickness of 1.3 nm, which is thicker than the usual 0.2–0.6 nm native oxide layer. This is attributed to the formation of a SiO_x layer by the implantation of negatively charged oxygen ions into the Si during the ITO deposition [4]. After RTA processes, the interface grew to 1.4 nm for ITO-300 °C and to 1.6 nm for ITO-600 °C.

To investigate the interface transition, SIMS depth profiles were performed. For the ITO-RT sample, uniform distributions of In, O, and Sn atoms were found through the 200 nm-thick ITO film, as shown in Fig. 1(g). At a depth of 200 nm, abruptly changed signals were detected. A Si signal appeared above the interface, as shown in Fig. 1 (h). Different from the ITO-RT case, noticeable Si transitions toward ITO were found from ITO-300 °C and ITO-600 °C samples. In contrast, Sn signals were propagated into the Si substrate for ITO-300 °C and ITO-600 °C samples, as shown in Fig. 1(i). Both transition intensity and penetration depth of Si and Sn tend to be enhanced according to an increased RTA-temperatures. This clearly shows the solid-state oxidation reaction of Si to ITO [4]. Limited Si diffusion occurs through the SiO_x and Si continuously finds oxygen at an interface, incurred by the decomposition of SnO_2 [1], resulting in the growth of the SiO_x layer.

Fig. 2(a) is the electrical resistivity of ITO films. As-deposited ITO-RT film has a resistivity of 8.56×10^{-3} Ω cm. The high resistive value was caused by insufficient activation of the impurity dopant (Sn^{4+}) at RT. Sn^{4+} atoms replace In^{3+} atoms in the In_2O_3 lattice and one substitutional replacement donates an electron to increase the carrier concentration, reducing the resistivity [7]. A proportional reduction of resistivity was achieved as annealing temperature increases. RTA processed at 300 °C reduced the resistivity value by 4.97×10^{-4} Ω cm. A further reduction was achieved at 600 °C–2.92×10^{-4} Ω cm. In comparison, the resistivity of a similar thick-ITO film, grown with substrate heating at 600 °C during 30 min of sputtering, showed a value of 2.39×10^{-4} Ω cm. This clearly indicates that the RTA process is an effective method to reduce the thermal budget, while maintaining a comparable performance.

Fig. 2(b) shows optical transmittance profiles. Excellent transparency was achieved from ITO-600 °C, showing an average

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