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COMMUNICATIONS

Fabrication and characterization of $Si/SiO_2/TiO_2/ZnO$ heterostructures from sputtered and oxidized Ti-film

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The present work reports the fabrication of p-Si/SiO_2/TiO_2 and p-Si/SiO_2/TiO_2/ZnO heterostructures deposited by RF sputtering on p-Si substrate. The structural properties of the heterostructures were characterized by X-ray reflectivity and SIMS depth profiling. The electrical and optical properties of the heterostructures were investigated by $I-V$, C-V measurements and VIS spectroscopy, respectively. The measurements reveal that $I-V$ characteristics in dark show semiconductor-insulator-semiconductor (SIS) structure properties. The $I-V$ characteristics under illumination exhibit changes with significant increase of photocurrent due to photoassisted tunnelling and injection through SiO_2/TiO_2 interlayer.

K e y w o r d s: SIS heterostructures, thin films, Ga-doped ZnO, TiO_2, Si, SIMS, $I-V$ characteristics, spectroscopy

1 Introduction

ZnO and TiO_2 heterostructure-based thin films have found wide applications in electronic and optoelectronic areas, including solar cells, gas sensors, memory devices, and ultraviolet photodetectors [1, 2]. There are low cost and widely available materials with unique electrical and optical properties. Titanium oxide (TiO_2) is a wide bandgap (3.03 eV, rutile; 3.20 eV, anatase) semiconductor, which can be of p- or n-type conductivity and has excellent chemical stability. In addition, the electron affinity of TiO_2 (5.1 eV, anatase) is larger than that of other semiconductors, such as ZnO (4.35 eV) and Si (4.05 eV). Thus, large band offset could be obtained in Si/TiO_2 hetero-junction larger than those of Si/ZnO heterojunction, which would be advantageous to control the electrical transport of carriers [2]. Various techniques have been used to prepare TiO_2 films, one of them can also be thermal oxidation of sputtered titanium film [3]. The insulating material SiO_2, is also being used as a promising buffer layer to improve not only the crystalline quality of TiO_2 (ZnO) films but also the optical and electrical properties of p-Si heterojunction [4, 5, 6, 7]. The origins of semiconductor-insulator- semiconductor (SIS) structure potential superiority are the suppression of majority carrier tunneling in the high potential barrier region of SIS structures, and the existence of thin interface layer, which minimizes the amount and impact on interface states. This paper reports on the structural, electrical and optical properties of p-Si/SiO_2/TiO_2 and p-Si/SiO_2/TiO_2/ ZnO heterostructures deposited on silicon dioxide covered p-Si(100) substrates from sputtered and oxidized Ti films and Ga-doped ZnO layer, respectively.

2 Experimental procedure

The thin Ti layers were deposited on silicon dioxide covered p-Si(100) substrates to fabricate top TiO_2 layer (sample A) and covered by nanocrystalline Ga-doped ZnO layer (sample B). The particular layers were deposited in one cycle using metal Ti target 150 mm in diameter and ceramic ZnO:Ga_2O_3 target 100 mm in diameter. Thin Ti layer (2 to 6 nm) was deposited using pure Ar pressure of 1.3 Pa in the sputtering chamber, sputtering power of 150 W and subsequently oxidized in oxygen atmosphere in the sputtering chamber at 200 °C during 2 hours. Consecutively the ZnO layer (50 nm) was deposited at room temperature on the formed TiO_2 layer. The complete structures after deposition were annealed in forming gas at 400 °C for 10 minutes. To confirm the presence of a titanium dioxide layer and to investigate the oxidation state of the titanium layer X-ray diffraction and reflectivity measurements were carried out for structure analyse using Bruker D8 DISCOVER diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW (40 kV/300 mA). Reflectivity curves were

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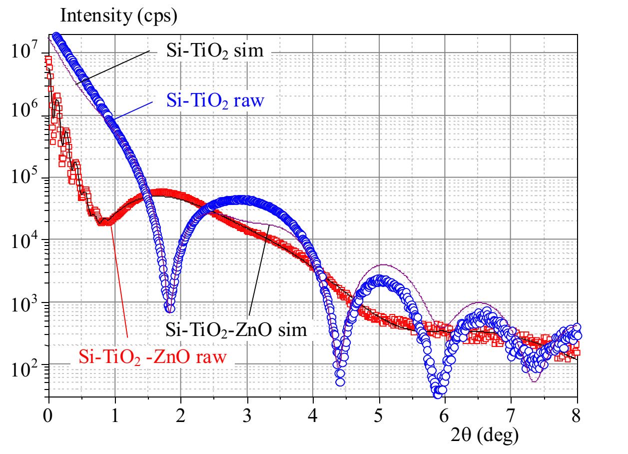

Fig. 1. X-ray reflectivity measured and simulated curves of samples A and B

measured with the beam width of 0.1 mm in the angular range 0 - 9 deg and 0 - 12 deg of 2θ, respectively. The samples were analyzed using SIMS instrument (Ion-TOF, SIMS IV) to get the full profile information about their structures. Primary liquid metal ion gun Bi^+ operated at 25 keV and Cs^+ ion sputtering operated at 1 keV in dual beam mode was used for depth profiling. Formation of electrical contacts and fabrication of the device was realized by thermal evaporation of Al electrode on the back side of Si substrate and semi-transparent thin Au film on SiO_2, TiO_2 and ZnO top layers, respectively. The samples were cleaved to 1×1 mm^2 sized chips and mounted on socket for electrical and optical measurements. The $I-V$ curves were measured using Agilent 4155C parametric analyser in dark and under light using illumination of tungsten lamp focused by microscope on the sample surface with different intensities. The capacitance $(C-V)$ measurements were done using Agilent 4284A Impedance Analyzer (20 Hz to 1 MHz). Standard UV-vis-NIR spectroscopy system was utilized for spectral measurements.

3 Experimental results and discussion

The reflectivity curves of p-Si/SiO_2/TiO_2 and p-Si/SiO_2/TiO_2/ZnO structures were analyzed using the software LEPTOS 3.04 provided by Bruker Company as shown in Fig. 1. Theoretical curves were calculated for a simple model comprising the Si substrate, thin interlayer ≈ 2 nm thick SiO_2 and TiO_2 layers (5.2 nm for sample A and 3.5 nm for sample B) including 50 nm ZnO top layer to fit the measured reflectivity curves.

These parameters are in a good relation with measured SIMS depth profiles as shows in Fig. 2 and Fig. 3. The traces of Ti, TiO and SiO_2 with total thickness $\sim$6 nm were resolved at the Si substrate interface for sample A (Fig. 2). The overlapping TiO_2 and SiO_2 traces indicate an inter-diffusion during oxidation of Ti. Similarly the depth profile of sample B (Fig. 3) shows overlapping TiO, SiO_2 and ZnO traces at Si and ZnO interface with a total thickness of $\sim$8 nm. In the case of sample B due to the mass interference the trace of TiO_2 and ZnO cannot be resolved.

In Figure 4 there are shown the measured semi-log plots of $I-V$ characteristics in dark and under white light illumination for samples A and B in comparison with reference pSi/SiO_2 sample. The $I-V$ characteristics of pSi/SiO_2/Au sample show properties similar to MOS structure described in [7], where such behaviour is owing to the injection of minority carriers into the depletion region of junction. The ohmic behavior of the IV characteristics at low voltages is due to existing background doping or thermally generated carriers. As the applied voltage is larger than 0.2 V, the $I-V$ characteristics follow a power law $I \propto V_n$, which is generally attributed to a space-charge-limited current (SCLC) for a single-carrier injection. For voltage higher than 1 V the current is limited by the resistivity of the emitter and top layers. The presence of TiO_2 considerably increases space-charge limited current.

The $I-V$ characteristics under illumination exhibit changes with significant increase of photocurrent mainly

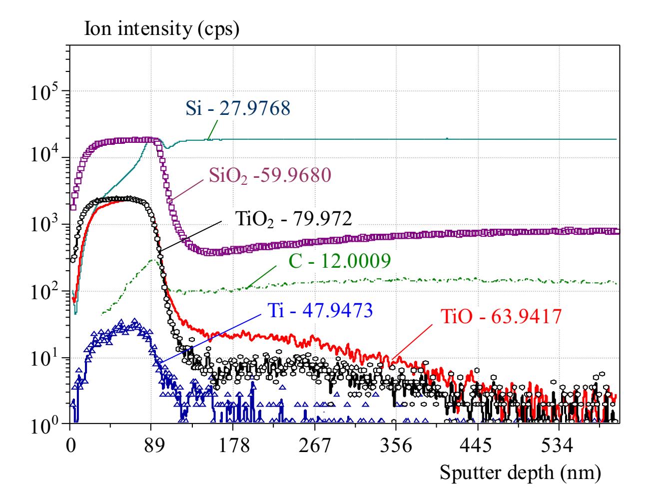

Fig. 2. SIMS depth profile of sample A

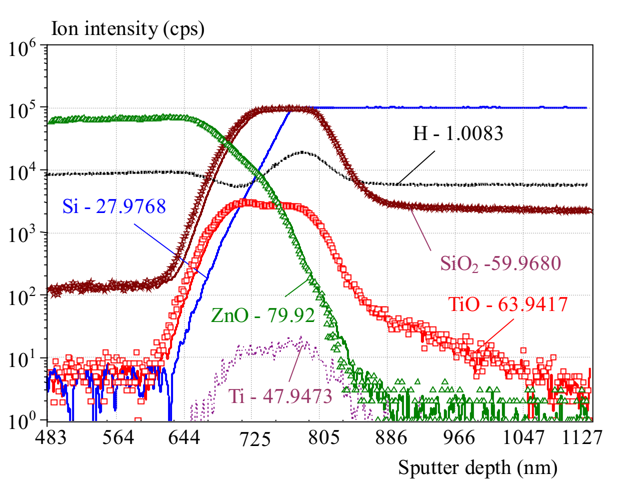

Fig. 3. SIMS depth profile of sample B

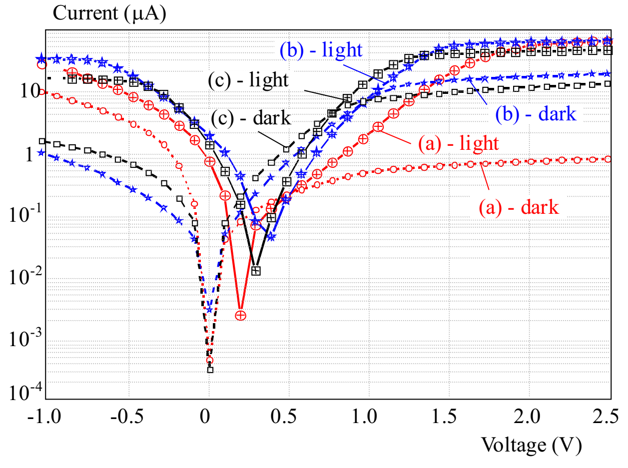

Fig. 4. Measured semilog plot of $I-V$ characteristics in dark and under illumination of sample A and B in comparison with pSi/SiO_2 sample

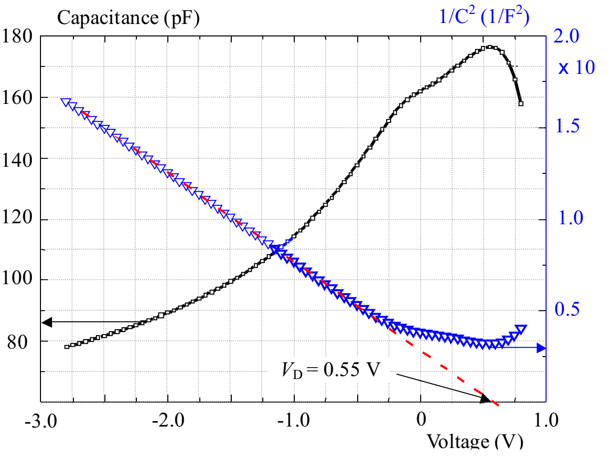

Fig. 5. Dark $C-V$ and C^{-2} characteristics versus voltage variation 1 MHz of sample A

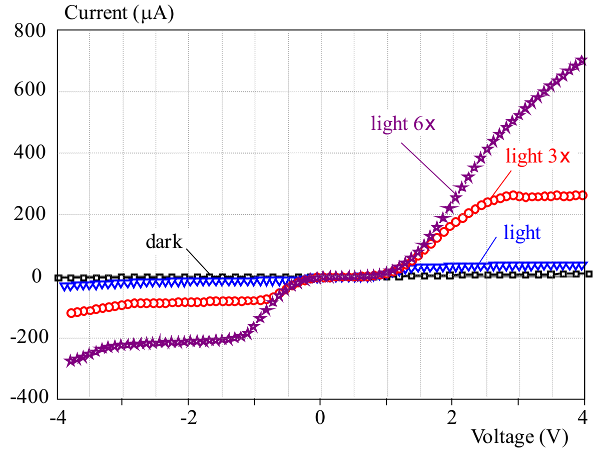

Fig. 6. $I-V$ characteristics comparison in dark and under different illumination of sample B

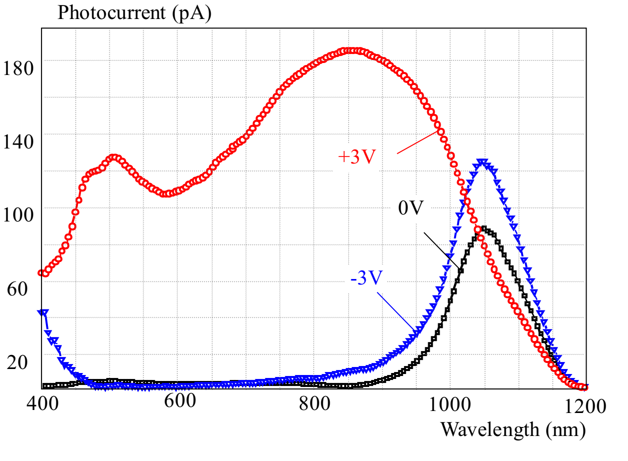

Fig. 7. Spectral characteristics comparison of sample B at 0 V and ($\pm$3 V)

for samples including TiO_2 interlayer due to photoassisted tunnelling together with increased built in potential polarity $\sim$ 0.4 V showing short circuit current $\sim$ 1 A. This points out the SiO_2/TiO_2 interface shift due to the hole-blocker and results in dark and photocurrent characteristics variation. Figure 5 shows the room temperature $C^{-2}-V$ measurement of the $pSi/SiO_2/TiO_2$ heterojunction conducted at 1 MHz. It can be seen clearly from the figure that, at the low voltage region, the capacitance of the heterojunction decreases sharply with the increase of reverse bias voltage and increases with the higher forward bias voltage. This phenomenon demonstrates that in the sample is obvious a space charge region. The intersection of the $C^{-2}-V$ characteristics with the voltage axis shows built-in potential V_D $\sim$0.5 V.

In Figure 6 the measured $I-V$ characteristics under dark and different intensities of white light illumination for sample B are shown. The $I-V$ characteristics exhibit significant increase of photocurrent, higher than 200 μ A caused by increased intensity of illumination at both, forward and reverse bias. This is generally explained by considering that the phototransistor effect results from the light-induced carriers generation at heterojunction interfaces and their injection through depletion layer under high electric field.

The spectral characteristics of sample B (Fig. 7) revealed broadening and switching effects in spectral photoresponse dependent on bias voltage (-3, 0, 3 V). The reverse bias shows higher sensitivity near Si band edge (1050 nm), while only small amount of photo-generated carriers at TiO_2 /ZnO layer (400 nm) were transported. The forward biased structure shows typical heterojunction broad spectral characteristic (400 - 1000 nm), where photogenerated carriers in ZnO layer prevail. Another argument is that the TiO_2 layer and its interface shifts shift the built in voltage and change the photocurrent characteristics due to the hole-blocker, and these properties make it attractive for multicolor photodetector applications.

4 Conclusions

In the presented work we have successfully fabricated a p-Si/SiO_2/TiO_2 and p-Si/SiO_2/TiO_2/ZnO heterostructures deposited on silicon dioxide covered p-Si(100) substrates from sputtered and oxidized Ti films and Ga-doped ZnO layer. The $I-V$ characteristics under illumination exhibit significant increase of photocurrent for samples including SiO_2/TiO_2 interlayer due to photo-assisted tunnelling. The barrier heights of the samples were determined from both $I-V$ and $C-V$ characteristics, and are nearly in the same range 0.4 to 0.5 V.
The investigated structures show short circuit currents ~ 1 μA under illumination and there is a significant increase of photocurrent higher than 200 μA caused by increased intensity of illumination at both bias polarities. The electrical and optical properties of the SIS heterojunction with pSi/SiO_2/TiO_2 SIS heterostructures indicate their suitability for optoelectronic device applications as well as attractiveness for use in multicolor photodetectors.

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