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Structural, electrical and photovoltaic characterization of Si nanocrystals embedded SiC matrix and Si nanocrystals/*c*-Si heterojunction devices

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Abstract

Thin films of Si nanocrystals (Si NCs) embedded in a silicon carbide (SiC) matrix (Si-NC:SiC) were prepared by alternating deposition of Si-rich silicon carbide ($Si_{1-x}C_x$) and near-stoichiometric SiC mutilayers ($Si_{1-x}C_x$/SiC) using magnetron cosputtering followed by a post-deposition anneal. Transmission electron microscopy and Raman spectroscopy revealed that the Si NCs were clearly established, with sizes in the range of 3–5 nm. Optical studies showed an increase in the optical band gap after annealing from ~1.4 eV (as-deposited) to ~2.0 eV (annealed at 1100 °C). *P*-type Si-NC:SiC/*n*-type crystalline silicon (*c*-Si) heterojunction (HJ) devices were fabricated and their electrical and photovoltaic properties were characterized. The diode showed a good rectification ratio of 1.0×10^4 at the bias voltage of ± 1.0 V at 298 K. The diode ideality factor and junction built-in potential deduced from current–voltage and capacitance–voltage plots are ~1.24 and 0.72 V, respectively. Illuminated *I–V* properties showed that the 1-sun open-circuit voltage, short-circuit current density and fill factor of a typical HJ solar cell were 463 mV, 19 mA/cm^2 and 53%, respectively. The external quantum efficiency and internal quantum efficiency showed a higher blue response than that of a conventional *c*-Si homojunction solar cell. Factors limiting the cell's performance are discussed.

Keywords: Si nanocrystals; Silicon carbide; Heterojunction; Photovoltaics; Solar cell

1. Introduction

Over the past decade, materials consisting of silicon nanocrystals (Si NCs) embedded in a dielectric matrix have been the subject of intense research in the field of optoelectronics [1,2]. Low dimensional Si NCs efficiently emit light even at room temperature due to quantum confinement effects, thus potentially allowing optoelectronic functions to be incorporated into Si integrated circuit technology. Recently, Si NCs have also attracted interest in relation to fabrication of "all-Si" tandem cells for third generation photovoltaics [3,4]. Si NC materials may allow the fabrication of higher band gap solar cells that can be used as tandem elements on top of a conventional Si cell. It is possible that band gap for tandem elements and sufficient carrier mobility can be achieved by optimizing Si-NC size, spacing and barrier height between matrix and Si NCs [4,5]. Although Si NCs embedded in a silicon oxide or silicon nitride have been widely investigated [6,7], Si NCs in a SiC matrix (Si-NC:SiC) are of particular interest as the low barrier height of SiC relative to SiO_2 and Si_3N_4 is conducive to carrier transport [8]. However, experimental investigations on Si-NC:SiC films are few [9] and the electrical and photovoltaic properties of devices based on these films are not reported yet.

In this work, Si-NC:SiC films were prepared by alternating deposition of substoichiometric and near-stoichiometric silicon carbide mutilayers ($Si_{1-x}C_x$/SiC) by magnetron cosputtering followed by a post-deposition anneal. The use of $Si_{1-x}C_x$/SiC multilayers instead of a single $Si_{1-x}C_x$ layer is expected to give better control over

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Si-NC size as the Si NCs are constrained by the thickness of the Si-rich layer. This was found to be the case for Si NCs in the SiO_2 and Si_3N_4 matrix analogues studied in Refs. [3,6]. We present the results of structural studies by transmission electron microscopy (TEM) and Raman spectroscopy. The chemical composition depth profile has been determined by X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). The optical band gap energy (E_{gopt}) at room temperature was determined by the Tauc's equation. Heterojunction (HJ) devices of *p*-type Si-NC:SiC on *n*-type crystalline silicon substrates [(*p*)Si-NC:SiC/(*n*)*c*-Si)] were fabricated. The study of the (*p*) Si-NC:SiC/(*n*) *c*-Si HJs is useful to evaluate the electrical material quality of the Si-NC:SiC films, and to investigate the design parameters required for their application in photovoltaic devices. Additionally, it also is useful to builds on the understanding of properties for this kind of HJs because it is of considerable interest as wide band gap emitters or window regions in bipolar transistors [10] and photodetectors [11]. The electrical properties of the devices were characterized by dark current–voltage (*I–V*) and capacitance–voltage (*C–V*) measurements. The photovoltaic properties were evaluated by illuminated *I–V*, quasi-steady-state open-circuit voltage (*Suns-*V_{oc}), and quantum efficiency measurements. Factors limiting the cell's performance are discussed.

2. Experimental procedure

Si wafer and quartz plate substrates were used simultaneously for different measurement purposes. The Si wafer substrates were used for structural and electrical performance measurements, and the quartz plates were used for optical measurements. The Si and quartz substrates were cleaned by standard wet chemistry cleaning procedures. The Si wafers were additionally dipped in 5% HF solution for 10 s to remove the surface native oxide before being immediately loaded into the sputtering system vacuum chamber. The amorphous $Si_{1-x}C_x$/SiC (x∼0.1–0.15) multilayers were deposited by magnetron cosputtering from Si and SiC targets using a computer-controlled AJA ATC-2200 sputtering system. The SiC target was boron-doped, with the intention that boron would be incorporated in the multilayer films. The thickness of individual layers was typical ∼6 nm ($Si_{1-x}C_x$) and ∼2.5 nm (SiC) and the total emitter thickness was ∼160 nm. Prior to sputtering, the chamber was evacuated down to a pressure of $\sim 5 \times 10^{-7}$ Torr, subsequently the chamber was filled with Ar gas to a working gas pressure of 2 mTorr. The argon flow was maintained at 20 sccm during deposition. All the samples were not intentionally heated during the deposition process. Following deposition the samples were annealed at 1100 °C for 9 min in a conventional furnace in a N_2 ambient.

The structures of the Si-NC:SiC films were investigated by cross-sectional TEM (JEOL-3000F, operating at 300 kV). Depth profiling of the films' chemical composition was conducted by XPS (Fisons ESCALAB 220i-XL) and SIMS. The SIMS analysis was done by a 25 kV Bi^+ TOF-SIMS IV (time of flight SIMS) system, ION-TOF with sputtering of 0.5 kV Cs^+ ions at a 45° incident angle. The beam currents were 1 pA and 30 nA for the analysis gun and sputtering gun, respectively. Raman spectra were measured by micro-Raman spectroscopy (Renishaw, RM2000) in a backscattering configuration, with a 50× optical microscope objective. The laser beam was provided by an Ar ion laser with a wavelength of 514.4 nm. A double-beam UV/visible/IR spectrophotometer (Varian Cary 5G) and an attached integrating sphere (Labsphere, RSA-CA-50) were used to measure transmission and reflection spectra. The dark *I–V* characteristics of the diodes were measured by an automatic measuring system comprised of a DC voltage–current source/monitor (Advantest, TR6143) and a computer. The measured devices were held on a vacuum chuck whose temperature was controlled by a temperature controller. A copper casing was used to cover the sample holder to prevent environmental light from influencing the recorded data. *C–V* measurements were performed by an impedance analyzer (HP4194) at a frequency of 100 kHz. The spectral response was determined through measurement of the spectral dependence of the external quantum efficiency (EQE) and internal quantum efficiency (IQE) over the wavelength range of 300–1200 nm. The 1-sun *I–V* curves of the solar cells were measured under approximated standard test conditions (AM1.5G spectrum, 100 mW/cm^2, 298 K). The pseudo *I–V* curves without the influence of the series resistance were extracted by means of the quasi-steady-state open voltage measurements (abbreviated "*Suns-*V_{oc}" in this work).

3. Results and discussion

3.1. Film characterization

3.1.1. Structural and compositional properties

The presence of Si NCs in the annealed films was confirmed by TEM observations. Fig. 1 shows a typical cross-sectional TEM view of an as-deposited sample. In the lower left corner of Fig. 1 is an inset of the high resolution TEM image of the sample annealed at 1100 °C for 9 min. The as-deposited film contains two uniform amorphous phases with a clear layered structure due to the density difference between $Si_{1-x}C_x$ and SiC materials. After annealing, we can clearly see lattice fringes (see the inset) that are dispersed in amorphous matrix, indicating the formation of NCs after annealing. A measurement of the lattice fringes of the high-resolution TEM image demonstrates the NCs are composed of Si atoms because the lattice fringes, at 3.1 Å, correspond to Si {1 1 1} lattice planes. The Si-NC size obtained from the TEM micrographs is in the range of 3–5 nm. Fig. 2 shows a typical Raman spectrum of the Si-NC:SiC film on a quartz substrate formed by annealing at 1100 °C [curve (a)]. The