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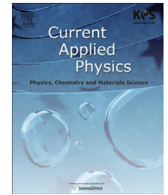

Surface photovoltage characterizations of Si nanopillar arrays for verifying field-effect passivation using a SiN_x layer

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ABSTRACT

The surface photovoltage (SPV) characteristics of periodic nanopillar (NP) arrays formed on Si wafers were investigated. The NP arrays exhibited broadband omnidirectional antireflection effects with Mie resonance. Kelvin probe force microscopy (KPFM) revealed that the positive fixed charges in SiN_x layers induced band bending at the Si surface and increased surface photovoltage (SPV) at the NP top surface. Estimated SPV values, determined by the amount of surface band bending, were similar in NPs and planar counterparts. This finding suggests that field effect passivation by the dielectric layer coating could help improve photovoltaic performance of nanostructure-based Si solar cells and that KPFM may be a useful tool for the investigation of surface electrical properties of Si nanostructures.

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1. Introduction

Surface nanopatterns of semiconductor materials enable broadband antireflection (AR) effects due to their beneficial optical properties, such as a graded refractive index, multiple scattering, and Mie resonance [1–10]. Such AR effects have led to extensive studies on nanostructure-based optoelectronic devices. The large refractive index and indirect bandgap of Si seriously limit optical absorption [2–10]. Therefore, nanostructured Si absorbers have great potential in high efficiency solar cells. However, nanostructured Si solar cells often suffer from high levels of surface recombination due to defects on the extended surface area. Strategies to overcome electrical loss are crucial to improve photovoltaic (PV) performance [4,5].

Surface photovoltage (SPV) – changes in the surface potential under illumination – originates from the photo-excitation of carriers and subsequent redistribution of net charges. SPV measurements are important for investigating electrical properties of semiconductor surfaces, including diffusion length, surface state density, and recombination processes [11]. SPV techniques have been widely used in conventional planar Si solar cells. However, few studies have focused on SPV characterization of light-trapping Si nanostructures [11]. To achieve very high spatial resolution, Kelvin probe force microscopy (KPFM) can be used for SPV measurements of Si nanostructures [12]. KPFM has been successfully used for nanoscopic characterization of light-induced charge transfer in a nanowire-based photoelectrochemical system [13], polycrystalline inorganic thin film solar cells [14], organic/inorganic nanostructure solar cells [15], and bulk heterojunction devices [16].

In this study, we investigated the SPV characteristics of Si nanopillar (NP) arrays that exhibit broadband omnidirectional AR effects. NP arrays with diameters of 140, 210, and 280 nm were fabricated using e-beam lithography and subsequent dry etching. The SPV of bare NP arrays was almost zero, indicating negligibly small surface band bending. Coating of SiN_x layers on the array increased the SPV, because positive fixed charges in the SiN_x layer accumulated photo-excited carriers at the SiN_x/Si interface. This finding suggests that field effect passivation by dielectric layer deposition could suppress recombination loss at nanopatterned Si surfaces. Our results indicate that KPFM measurements could be useful for examining the surface electrical properties of nanostructure-based Si solar cells.

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2. Experimental

KPFM measurements were conducted using an atomic force microscopy (AFM) system (XE-100, Park Systems) inside a glove box, as shown in Fig. 1(a). Illumination with a 5-mW red (in the web version) laser module (wavelength: 635 nm) generated electron–hole pairs in samples. As illustrated in Fig. 1(b), *p*-type Si usually exhibits downward surface band bending and the minority carrier electrons (majority carrier holes) drift to the surface (quasi-neutral region) under illumination [11]. The electrons accumulated at the surface will fill the surface states and the surface will be negatively charged with respect to the bulk region. Such redistribution of charge carriers reduces the band bending, resulting in alteration of the surface work function. SPV is defined as difference between the surface work function in dark (W_{dark}) and light (W_{light}), i.e., SPV $= W_{dark} - W_{light}$. It can be noted that SPV is negative in the case of Fig. 1(b).

In the band diagrams of Fig. 1(b), E_{vac}, E_c, E_f, and E_v indicate the vacuum level, the conduction band minimum, the Fermi level, and the valence band maximum of Si, respectively. An AC bias voltage, $V_{ac}\sin(\omega t)$, and a DC bias voltage, V_{dc}, are applied to the tip. The blue solid lines (the gray dashed lines) describe the band diagrams under illumination (in the dark). The difference in E_{vac} at the sample surface and the tip indicates that the electrostatic force between the tip and sample exists. When V_{dc} is equal to difference between the work function of the tip, W_t, and the work function of the sample, such electrostatic force can be nullified. Calibration of W_t using a proper reference allows us to estimate the sample work function (W_{dark} and W_{light}). In our experiments, conductive Pt-coated Si cantilevers (NSG10/Pt, NT-MDT) were used for both surface work function (W_S) and topography measurements. Immediately after each measurement, the work function of the tip was calibrated with a highly ordered pyrolytic graphite (HOPG, SPI Supplies) reference sample. After the glove box was purged with N_2 for at least 3 h, the samples were baked at 100 °C for 30 min to dehydrate them. Subsequent measurements were performed in dry N_2 gas.

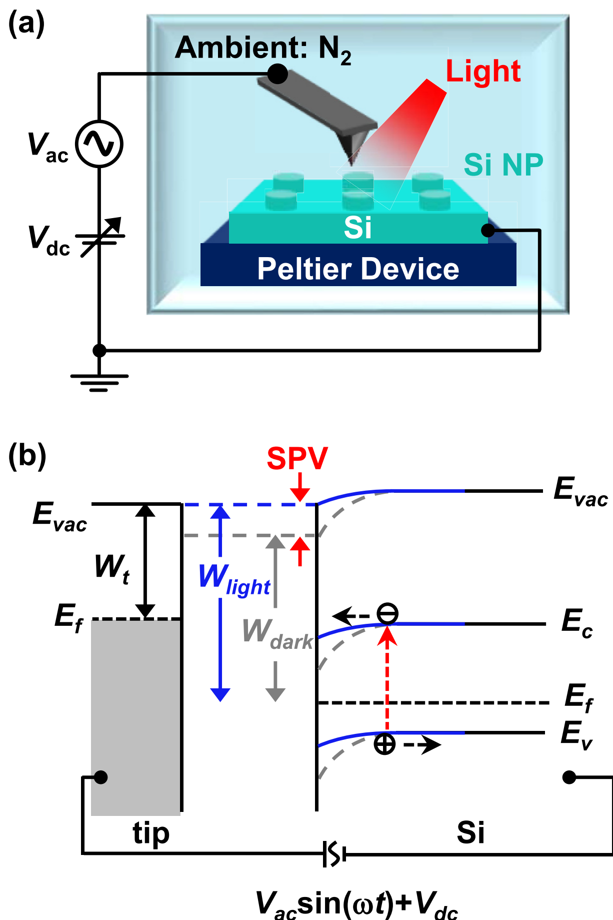

Fig. 1. (a) Schematic illustration of SPV measurement setup using a KPFM system with a glove box. (b) Energy band diagrams to explain the principle of SPV measurements of *p*-type Si surface using KPFM.

Square arrays of Si nanopillars (NPs) were fabricated with three different diameters (*D*) (140, 210, and 280 nm) and a fixed height (100 nm) and period (700 nm), as shown in Fig. 2(a), (b), and (c). A 4-inch Si wafer (*p*-type, doping concentration: 10^{17} cm^{-3}, Topsil) was coated with a 165-nm-thick chemically amplified negative tone resist (NEB, Sumitomo Chemical) and exposed using a 100-kV electron beam lithography system (JBX9300FS, JEOL). After exposure, the electron beam resist was developed using a developer (AZ300MIF, AZ Electronic Materials). The Si wafer with the resist pattern was then etched using deep reactive ion etching (AMS200, Alcatel). The fabricated NP arrays were examined using field emission scanning electron microscopy (SEM) (S-4800, HITACHI).

Optical scattering cross-section spectra of Si NPs ($D = 140$, 210, and 280 nm) on a Si substrate were calculated using finite-difference time-domain (FDTD) simulations (Lumerical FDTD Solutions), as shown in Fig. 2(d). The scattering cross-section, normalized to the geometrical cross-section, was larger than unity in the wide wavelength range. Spinnelli et al. reported that a cylindrical NP on an Si substrate exhibited broadband Mie resonance, leading to a large cross-section [7]. With increasing particle size, a red shift of the Mie resonance mode occurs and the number of modes increases. This explains the phenomena shown in Fig. 2(d). The 140-nm-diameter NP had a broad peak at ~600 nm and the 210-nm-diameter NP had a split two-peak feature. The scattering cross-section of the largest NP ($D = 280$ nm) was almost twofold that of the geometrical one, up to a wavelength of 1000 nm.

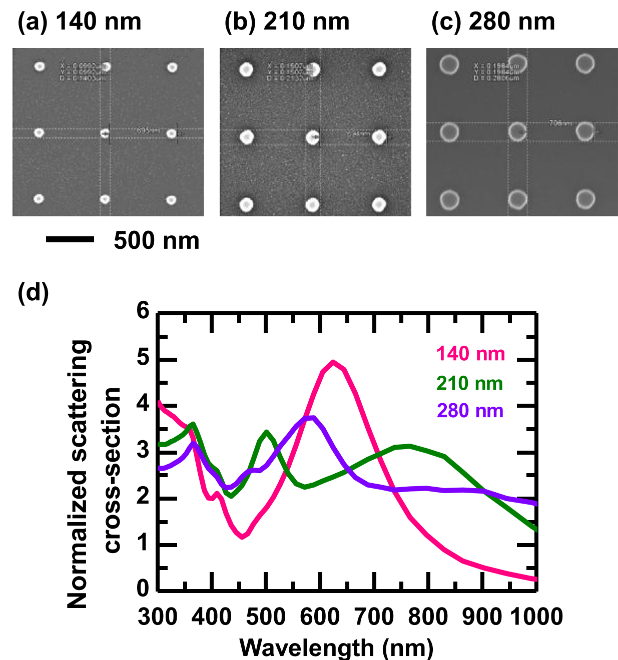

Fig. 2. SEM images of Si NP arrays with diameters of (a) 140 nm, (b) 210 nm, and (c) 280 nm; (d) scattering cross-section normalized to the geometrical cross-sections of Si NPs with three different diameters on Si substrates.

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