CrossMark

Photo-electrochemical water splitting in silicon based photocathodes enhanced by plasmonic/catalytic nanostructures

T. Han[a,b], S. Privitera[a,*], R.G. Milazzo[a], C. Bongiorno[a], S. Di Franco[a], F. La Via[a], X. Song[b], Y. Shi[b], M. Lanza[b], S. Lombardo[a]

[a] Istituto per la Microelettronica e Microsistemi (IMM), Consiglio Nazionale delle Ricerche (CNR), Zona Industriale, Ottava strada 5, 95121 Catania, Italy
[b] Institute of Functional Nano & Soft Materials, Soochow University, 199 Ren-Ai Road, Suzhou 215123, China

ARTICLE INFO

ABSTRACT

Photoelectrochemical water splitting is a promising method to produce H_2 by making use of solar energy. In this paper we report on a photocathode made by p-type crystalline Si covered with an n-type 3C-SiC polycrystalline film, acting as protective layer and transparent emitter. The photoelectrodes exhibit a saturated photocurrent above 30 mA cm^{-2}. No decay is observed after 9 h under constant current stress at 1 kW m^{-2} with AM1.5G spectrum illumination. Improvement of the photocurrent value is achieved by covering the 3C-SiC emitter with Au or Pt nanoparticles. Under suitable metal nanoparticles deposition conditions, compared to the samples without nanoparticles, two major effects are observed: first the onset potential is considerably reduced, and second, higher saturated photocurrent is found, up to 38 mA cm^{-2}, i.e. with a 27% increase. Optical and microstructural studies on the nanoparticles provide insights on the origin of the observed effects.

1. Introduction

Using sunlight to split water into hydrogen and oxygen recently raised considerable interest to produce sustainable and clean fuels alternative to fossil fuels. Photo-electrochemical (PEC) water splitting was initially studied in wide band gap semiconductors (e.g. TiO_2, $SrTiO_3$, $KTaO_3$, RuO_2 or 4H-SiC) [1–5] to achieve sufficient photovoltage to split water. However, most of the wide bandgap semiconductors only operate under ultraviolet (UV) light, which accounts for only ca. 4% of the total solar energy [6]. Therefore such approaches imply an inherently low photocurrent. To increase photocurrent, photoelectrodes with the ability to work under visible light are highly desirable, since visible light contributes to almost half of the incoming solar energy. For example, metal sulphides [7,8], and selenides [9,10] are considered promising for water splitting by visible light. Silicon is also a very attractive material because of its earth-abundance and prevalence in the electronics and PV industries. In particular, using crystalline silicon junctions would take advantage of the very advanced technology, low cost, and high photovoltaic efficiency (25.6% on crystalline Si solar cell) [11]. However, the realization of a silicon based PEC device must overcome the inherent corrosion of this semiconductor in electrolytes with high basic pH [12], which are required in high efficiency electrolyzers. For this reason, initially, the stand-alone water-splitting PEC cell configurations based on silicon photoelectrodes used

wires [13] or conductive oxide [14,15] to physically shield the silicon from the electrolyte and to connect the semiconductor to the hydrogen and/or oxygen generating electrodes. More recently, catalysts comprising earth-abundant materials have been integrated with silicon solar cells, obtaining almost stable production for 10 h, but with current density on the order of 4 mA cm^{-2} [16]. Tunnelling oxide layers have also been recently explored to stabilize silicon photoelectrodes covered with metals [17–23]. The metal layers act as catalytic films and improve the photoelectrode endurance, but since metals are not transparent, they can remarkably reduce the amount of light arriving into the semiconductor. There is therefore a trade-off between stability and maximum photovoltaic (PV) current [23]. To overcome those limits another approach is to cover silicon based photoelectrodes with wide band-gap semiconductors such as $BaTiO_3$ [24], TiO_2 [19,20,22,25,26] and Al_2O_3 [27], or with ultra-thin 2D semiconductors such as MoS_2 [28,29], reaching current density up to 25 mA cm^{-2}, as reported in a recent paper [29].

In this work we have used n-type 3C-SiC/p-type Si heterojunction as photocathode. We investigated a 3C-SiC polycrystalline layer deposited by chemical vapour deposition (CVD) on crystalline Si. SiC acts as both Si protective layer and PEC cell emitter. The absorber material is the p-type crystalline Si substrate. Many are the reasons to employ 3C-SiC on Si. First, SiC is a very stable material under harsh environments. Second, among the SiC various polytypes, the 3C-SiC can be grown
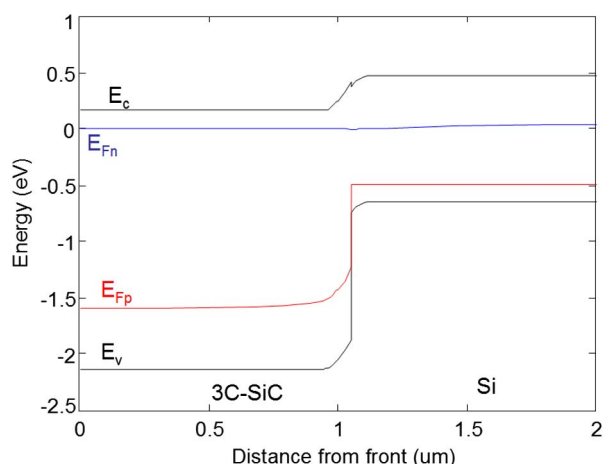
Fig. 1. Energy-band diagram of n-type 3C SiC/p-type Si heterojunction PV cell calculated using the PC1D simulation tool under 1 sun of AM 1.5G illumination.

Fig. 2. (a) SEM micrograph of the n-doped 3C-SiC layer deposited on Si(1 0 0). (b) 3C-SiC polycrystalline layer on Si(1 0 0) observed in cross section by TEM. The thickness is 1 μm.

(amorphous, polycrystalline or even epitaxial) on Si at a relatively low CVD deposition temperature. Third, the band alignment of 3C-SiC (4.0 eV electron affinity [30] and 2.3 eV band gap) may enable the formation of an effective heterojunction solar cell on Si, as it suppresses the minority carrier injection from the Si substrate (both when it works as photocathode, thanks to the 1 eV barrier for holes injected from Si into SiC, and when it works as photoanode, thanks to the 0.2 eV barrier to the injection of electrons into the SiC layer).

As an example, Fig. 1 shows the energy-band diagram of an n-type 3 C-SiC/p-type Si heterojunction solar cell forward biased under illumination at $1 \, kW \, m^{-2}$ with AM 1.5G spectrum. The band diagrams have been calculated using the a computer program called PC1D that solves the fully coupled differential equations for the quasi-one-dimensional transport of electrons and holes in semiconductor devices [31]. E_C and E_V denote the conduction band and valence band, respectively. E_{Fn} and E_{Fp} denote the quasi-electron and quasi-hole Fermi levels under illumination. The E_C and E_V band offsets at the SiC/Si heterojunction as above described are evident.

About 3C-SiC/Si photovoltaic cells, previous studies showed that n-type Al-doped ZnO (AZO)/n-type 3 C SiC/p-type (1 0 0) oriented crystalline Si heterojunction cells have good electrical characteristics, although the open circuit voltage is quite low, because of a low minority carrier lifetime [32].

Moreover, in this paper we also studied the effect of integrating noble metal nanoparticles on the 3C-SiC film surface to investigate the catalytic effects on the H_2 production. Recently, noble metal (such as Au, Ag or Pt) nanostructures have been extensively studied for improving the photoactivity of wide bandgap semiconductors [33–37]. In this paper we show that, under suitable conditions of metal nanoparticle deposition, evidence for photocurrent enhancement can be obtained with a Si based photocathode covered by 3C-SiC. The enhancement is attributed to plasmonic effects.

2. Materials and methods

2.1. Photoelectrode fabrication

n-type 3C-SiC polycrystalline layers were grown by hot-wall chemical vapor deposition (CVD) as detailed in [38] on (1 0 0) p-type 6″ Si wafers with resistivity 1.5–4 Ohm cm. Trichlorosilane (TCS) has been employed as silicon precursor, ethylene as carbon precursor and hydrogen as gas carrier. 3C-SiC film thickness was 1 μm, determined by cross-sectional transmission electron microscopy (TEM), as shown by the micrograph in Fig. 2. The n-type doping was achieved by introducing nitrogen in the CVD chamber. A multi-step process was adopted in
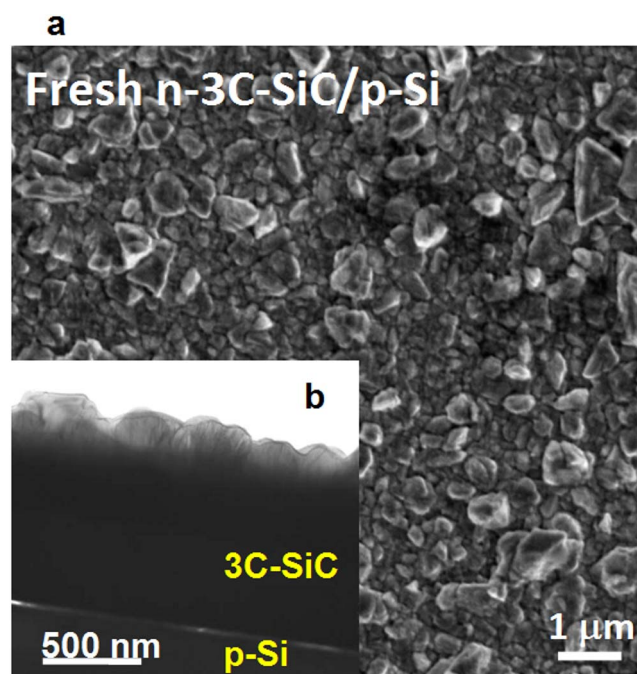
order to minimize the formation of voids at the Si/SiC interface. The back surface field (BSF) contact to the Si substrate was obtained by depositing boron doped amorphous Si on the back of the wafer and with rapid thermal annealing at 1100 °C [32].

Some of the 3C-SiC/Si samples were covered by a layer of Au or Pt nanoparticles (NPs). Pt NPs were deposited by magnetron sputtering while Au NPs were deposited by galvanic displacement using an Au NPs solution of 1 mM Potassium gold (III) chloride ($KAuCl_4$ 99.995% pure from Sigma-Aldrich) in 4.8 M HF [39]. Two different sets of samples were fabricated. The first, indicated in the following as Au NPs 1, was obtained by a single immersion in the Au solution for 240 s and then rinsed in deionized water. The second (Au NPs 2) was obtained by immersion for 60 s in the Au solution, followed by rinsing in deionized water. This procedure was repeated for three times, obtaining a total immersion time in the Au solution of 180 s.

2.2. PEC characterization of the photocathodes

The photoelectrodes were characterized using a PTFE cylindrical container with a $0.5 \, cm^2$ circular aperture at its bottom face, through which the 3C-SiC/Si photoelectrode was placed. The back-contact to the sample was an Al substrate. The electrolyte for PEC water splitting was 1 M KOH. The samples were illuminated at 1 SUN, i.e. $1 \, kW \, m^{-2}$ with AM1.5G spectrum, with a L.O.T. QuantumDesign solar simulator with a high-pressure 150 W Xe short arc lamp. The light intensity was calibrated using a crystalline silicon solar cell as reference. PEC measurements were performed in a three-electrode system with a Pt wire as counter electrode and a saturated calomel electrode (SCE, saturated KCl solution) as reference. To bias the electrodes and measure voltages and currents a Keithley 4200A-SCS parameter analyzer equipped with 8 SMUs was employed. The activity and stability of the samples was analyzed by current-voltage (I-V) characteristics and voltage-time (V-t) measurements at constant current.

2.3. Materials characterization

The morphology and structure of the photoelectrodes before and after the PEC tests have been characterized by Scanning Electron