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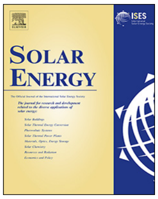

Ultra-low reflective black silicon photovoltaics by high density inductively coupled plasmas

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ABSTRACT

Photovoltaics (PV) as a renewable source of energy has received renewed interest in the immediate provision of sustainable energy to meet market demand in recent years. A key challenge in clean energy research is to ensure that the technology not only provides a sustainable energy source during device operation, but is also environmentally sustainable during the manufacturing phase of the device lifecycle. Plasma sources have been conventionally employed in numerous surface nucleation and nanostructure growth processes due to highly controllable process parameters that enable precise control of material properties at the nanoscale. However, these processes usually employ toxic feedstock as a means to obtain favourable PV characteristics, such as nanotexturing. In this work, an inductively coupled plasma (ICP) system in a cascading cluster configuration setup was employed for fabrication of highly efficient nanotextured PV cells. A 2-step process was developed to use a high density N_2 discharge for high density plasma immersion ion implantation (HD-PIII) in group V doping of c-Si samples for high quality junction formation. Subsequently, an Ar + H_2 discharge was utilized for the simultaneous nanotexturing of the surface as well as passivation of surface defects through intense hydrogenation from the plasma generated radical flux. The resulting black silicon (b-Si) PV cells fabricated through this process typically have ultra-low reflectance of $< 1.8\%$, V_{oc} of ~ 540 mV, and J_{sc} of ~ 24 mA $\times$ cm^{-2}. In-situ plasma diagnostics were also performed to enable a truly deterministic method for obtaining optimal material properties based on plasma parameters instead of process parameters, which may vary for different reactor geometries.

1. Introduction

Since the advent of the industrial revolution, the global energy market has flourished rapidly, and the demand for energy sources has increased exponentially (Lan et al., 2016; Amaro e Silva et al., 2018). One of the drivers which have catalysed this growth is a rapid increase in the energy demand associated with the manufacturing and use of personal electronic devices, in addition to the already flourishing industrial sectors which draw large quantities of energy in order to deliver their product or service (Hussein, 2015). With the increase in the demand for energy for day-to-day operations, it is projected that the global energy demand might soon overwhelm the global energy supply given the current energy sources, available consumables, and technological capabilities (Kumar et al., 2018; Pleßmann et al., 2014; Levchenko et al., 2016). Moreover, the development of industries and power plants that fuel technological progress have resulted in significant environmental pollution and toxic by-products from numerous combustion processes in fossil fuel-based power plants, and chemical pollutants released to large bodies of water in manufacturing processes (Gu et al., 2018; Bilgen, 2014; Fang, 2012). Therefore, in order to meet the energy needs of the future, academics and clean energy research facilities are hard pressed to meet two main demands, namely sustainable energy generation capabilities, as well as environmentally friendly processes and manufacturing lines (Nejat et al., 2015; Bazaka et al., 2015; Han et al., 2013).

Crystalline silicon (c-Si) based photovoltaics (PV) still exerts dominance in the energy market due to its mature technological research infrastructure, excellent cross-compatibility with numerous electronic devices, as well as rapid ability for employment in large scale commercial facilities and modules (Creutzig et al., 2017; Masuko et al.,

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2014), including applications for satellites (Levchenko et al., 2018a, 2018c). Advancement in fabrication techniques based on plasma processes allow for homogeneous PV characteristics over wide areas (Mariotti et al., 2016). Popular plasma processes for fabrication of PV devices include the growth of thin-films for optical management and defect passivation (Peck et al., 2017; Jacob et al., 2012) plasma based reactive ion etching for surface modification (Xu et al., 2014; Levchenko et al., 2013), sputtering for deposition of electric contacts (Gwamuri et al., 2016), as well as ion implantation for controlled doping and impurity incorporation (Michel et al., 2015), and other processes (Ahmad et al., 2013; Bazaka et al., 2017), including self-organization (Levchenko et al., 2018b). However, one of the concerns involving plasma fabrication remains the nature of the feedstocks, where many of the conventional precursors and processing gases considered hazardous and toxic. For example, in doping and thin film growth for light management and passivation, hazardous gases such as SiH_4, B_2H_6 and PH_3 are often employed (Lim et al., 2017; Rider et al., 2007; Baranov et al., 2018a).

Therefore, the focus of this investigation was to incorporate environmentally friendly feedstocks into a low-frequency inductively coupled plasma (LF-ICP) for the fabrication of efficient PV cells. LF-ICP allows for low temperature processing of materials, where a high density of dissociation of feedstock is required for production of reactive species involved in surface-plasma reactions. LF-ICP processes have previously been demonstrated in both theoretical and experimental studies to achieve high levels of uniformity over large areas (Shin et al., 2015; Baranov et al., 2018b), with adequate control over the processes through the real-time monitoring of plasma parameters while modifying the input processing parameters (Kirner et al., 2013). A back-to-back process in a single LF-ICP chamber was developed utilizing gaseous feedstocks of N_2, Ar and H_2. Apparently, single processing environment was significant advantages in relation to purity and price (Baranov et al., 2017).

The first process is a high density plasma immersion ion implantation (HD-PIII) process involving a pure N_2 discharge. The high density ICP discharge produces a dense flux of N^+ ions that are extracted from the discharge through an applied bias on the processing stage, and accelerated towards a p-type c-Si substrate where it gets implanted into the lattice. This implantation process results in a shallow conductivity type conversion (and therefore, junction formation) on the surface due to the group V doping of atomic N. The junction depth as well as the dose of the impurity incorporation can be further tuned through the variation of the magnitude of the applied bias on the processing stage. This enables the formation of a high quality pn junction with tuneable electronic properties with an environmentally friendly feedstock of N_2 as opposed to conventional methods of fabrication which requires toxic PH_3 in plasma based processes, and copious amounts of chemicals and deionised water for washing in wet chemical processes.

Following the formation of the pn junction through N_2HD-PIII, optical losses on the surface are greatly reduced through a plasma dry etch (PDE) process involving Ar + H_2 feedstocks. This process has been well documented previously in its ability to produce dense high aspect ratio nanostructures (Lim et al., 2016). Optical losses have been shown to be reduced from a high of > 30% to < 1.8% after surface texturing with high aspect ratio nanocones (Xu et al., 2011). The nanostructure profile is a result of the effects of the plasma-generated radicals of Ar and H on the c-Si through physical and chemical processes. For example, the large flux of energetic Ar on the c-Si surface causes a physical etch removal of atomic Si, whereas the role of the H covering the surface of the substrates serves to saturate dangling bonds, and to promote the regrowth and re-deposition of sputtered material, leading to more stabilized and high aspect ratio nanostructure formation (Xu et al., 2009; Levchenko and Ostrikov, 2009; Kumar et al., 2012). Additionally, it has also been widely reported that the PDE process causes simultaneous conductivity type conversion in p-type c-Si substrates (Zhou et al., 2010). This conductivity type conversion results from two main processes, namely the creation of oxygen-related thermal donors (OTD), and hydrogen-related shallow thermal donors (HSTD) that would be covered in greater detail in the results and discussion section.

This two-step process has been performed back-to-back in the same ICP reactor, and a precise control of the process parameters utilizing a real-time control and feedback suite allows for the pumping in of different feedstocks at different times and variation of other process parameters for seamless transition in a process chain (such as the substrate bias and applied RF power). This scalable production of b-Si PV cells has already been demonstrated to be successful in reactors of similar configurations (Xiao and Xu, 2011). This work also incorporates in-situ plasma diagnostics during process optimization to enable real-time feedback for precise process controllability through monitoring of the plasma parameters during the discharge, and tailoring the input parameters through computerized automated systems to enable high levels of consistent repeatable experimental outcomes.

The goal of this work was to optimize scalable plasma processes for the fabrication of highly efficient nanotextured PV materials via environmentally friendly plasma processing methods. This has been achieved to a large degree of success, and the preliminary characterization of the completed cells fabricated in the lab has demonstrated ultra-low reflectivity of < 1.8%, and highly promising indicative V_{oc} and J_{sc} of 540 mV and 24 mA cm^{-2}, respectively, which offer great promise for further increment with the incorporation of field effect passivation films that would be the focus of future work.

2. Experimental methods

A hybrid processing technology was used to ensure the best results; below we describe the processing stages in detail.

2.1. Sample preparation

Prior to processing, p-type c-Si samples (of resistivity = 5.0 Ω cm) measuring 1.5 × 1.5 cm were first prepared through an elaborate laser slicing process, and a dry plasma cleaning process utilizing a $SF_6 + O_2$ discharge which removes the saw damage and surface impurities on the samples. This has been well documented in previous works, where it was also demonstrated how the plasma treatment could be applied in conventional plasma-based processes (Huang et al., 2016; Levchenko et al., 2018d). The ICP reactive ion etch process was performed with 1.7 kW of applied power and −50 V as substrate bias. The pressure was maintained at 2.0 Pa, and a flow percentage of 16% O_2 in the $O_2 + SF_6$ feedstock was used throughout the 15 min process via precision mass flow controllers. Following the ICP reactive ion etch, the feedstocks for the HD-PIII process was introduced into the ICP chamber, and the PV fabrication process followed.

2.2. Plasma processing facility

The LF-ICP reactor used in this work is part of a multi-chambered nano-fabrication cluster used to process full PV cells in various adjacent processes as has been documented previously (Huang et al., 2016). The setup of the LF-ICP reactor used for the HD-PIII and PDE processes is shown in Fig. 1, whereby a N_2 discharge in H-mode is shown in Fig. 1(a), and an internal view of the process through the radial optical diagnostic port is shown in Fig. 1(b). A high density inductive plasma is generated with the aid of power coupled through a planar RF coil, from an RF generator and matching network system. A dielectric lid separates the discharge and the RF coil, and the reactor is sealed with a vacuum grade O-ring. The ICP chamber is evacuated by a 2 stage rotary and turbomolecular pump suite enabling a base pressure of < 10^{-4} Pa. Gaseous feedstocks are introduced into the chamber through gas inlets located radially at the top of the reactor for high degree of dissociation near the RF antenna. The dissociated species are then accelerated towards the processing stage, which is outfitted with a heating element