Solar Energy Materials and Solar Cells 171 (2017) 98–105

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Rapid fabrication of antireflective pyramid structure on polystyrene film used as protective layer of solar cell

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ARTICLE INFO

Keywords:
Light trapping effect
Antireflection
Pyramid
Solar cell
Microinjection compression molding

ABSTRACT

A promising strategy is proposed for facilely and successively replicating randomly arranged pyramids on an etched silicon wafer to polystyrene (PS) surface. First, a nickel mold insert with negative pyramids is fabricated via combining electroless plating and subsequent electroplating with an etched silicon wafer as a template. Then, by using microinjection compression molding with the nickel mold insert as a template, the pyramids on the insert are accurately transcribed to the PS surface. The pyramids on the PS replica surface have the hemlines of about 1–7 μm and heights of about 1–4 μm. The PS replica surface exhibits a reflectance of about 5% in the wavelength range of 400–900 nm and an enhanced transmittance. That is, it exhibits an enhanced light trapping effect, which originates from a combination of staggered arrangement and dense distribution of the pyramids with arc-shaped top and different sizes. Especially, a thin film solar cell covered with the PS replica exhibits increased power conversion efficiency enhancement of up to 7.9% under normal incidence comparing to that covered with the PS counterpart. The solar cell covered with the PS replica also shows an excellent photovoltaic performance over a wide range of incident angles (0–70°). The proposed fast and efficient replication strategy can be an excellent candidate for developing antireflective protective layers without complicated procedures and expensive materials.

1. Introduction

Suppressing reflection of light and improving its transmission are crucial in developing high-performance photovoltaic devices, especially solar cells [1]. Two main means used for reducing reflection losses at the air-substrate interface are antireflection coating and surface texturing [2], which can impart a surface with antireflective property. For solar cells, they can increase the short circuit current and boost the conversion efficiency [3]. Compared to antireflection coatings, texturized surface exhibits better durability and mechanical stability due to its monolithic structure and homogeneous material. Many efforts have been devoted to fabricate the structured antireflective surfaces possessing the quasi-omnidirectional, broadband antireflective properties. Different micro/nanostructured arrays, such as nanopillar [4,5], nanocone [6], micropyramid structure [7–9], V-groove [10], nanowire [11,12], and micro-lenses [13,14], have been artificially created. Among the antireflective structures developed, pyramid structure has been intensively applied in light trapping to increase the conversion efficiency of solar cell through its light trapping effect [15–17]. Texturing pyramids on silicon wafers by alkaline etching is an established technique. However, this approach is not suitable for thin film solar cells where the thickness of active region is only several microns or even hundreds of nanometers. It also requires significant amount of material loss to achieve superior reflection properties, resulting in high cost. Moreover, as an essential element of solar cell for protecting it from external shocks and corrosion [18], the protective layer also reflects a fraction of incident light. In practical applications, glass or polymer based protective layer reflects normal incident light from 4% to more than 6.5% from air-substrate interface [19]. Since the conversion efficiency of solar cells relies on efficiently transmitted energy, reflection losses from protective layer are notably disadvantageous.

Although glass and metals are still the most commonly used as top- and bottom-sealing substrates for solar cells, great efforts have been expended to develop polymeric and biopolymeric supporting substrates [20–26] for solar cells. Griffini et al. [20] developed an organic-inorganic hybrid coating material as luminescent downshifting host matrix, simultaneously enhancing the efficiency and durability of flexible organic photovoltaic devices. Especially, polymeric thin layers with patterned surfaces can impart solar cells with multifunctional properties when acting as their supporting substrates. Patterning micro/

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http://dx.doi.org/10.1016/j.solmat.2017.06.013
Received 5 May 2017; Received in revised form 8 June 2017; Accepted 10 June 2017

nanostructures on the external side of polymer-based solar cells results in their hydrophobic/superhydrophobic properties and so self-cleaning effect [21,23–25]. More interestingly, using structured surfaces of polymeric protective layer to enhance light absorption [22–26] is a vogue topic nowadays. Besides being used as supporting substrates for solar cells, polymeric and biopolymeric materials can be used in electrolytes and photoanodes [27,28].

Polymers with high transmittance are recently emerging as a favorable alternative especially for flexible solar cells, due to their flexibility and affordable cost. Replacing glass with polymeric layer can provide a more durable mechanical protective layer and eliminate glass breakage. There are a few techniques reported for fabricating polymer-based protective layers that can suppress surface reflection, such as hot embossing [24,29], UV imprint [23,30–32], and sol-gel process [22,25,33,34]. Lee et al. [24] fabricated a solar cell protective film with a moth-eye anti-reflection structure by hot-embossing to suppress the reflection of incident light, resulting in a total increase of 3.9% in accumulated electric energy of the solar cell. In hot-embossing process, polymer is heated to above its glass transition temperature yet below its melting or flow temperature, and the replication is achieved using a combination of heat and pressure, spending tens of minutes. A conical micro-grating structured polymer film prepared by UV imprint lithography was used for efficient light harvesting and protection in silicon photovoltage modules [23]. The UV imprint process comprises spin-coating and UV exposure steps and so is time-consuming and difficult to separate the film from the mold. Kang et al. [25] fabricated a polydimethylsiloxane (PDMS) film with micro-scale pyramids on its surface by sol-gel process. The result demonstrated that power conversion efficiency is increased by 6.8% when using the PDMS film as a protective layer of solar cell, indicating that the pyramid structure exhibits an anti-reflection property. However, it takes even hours before the PDMS film is completely cured in sol-gel process and a cautious separation for the PDMS film and mold is needed. UV imprint and sol-gel processes are capable of fabricating nanostructures on the polymer substrate surface. However, when vacuum is not used during both processes, air may be trapped in the cavity, resulting in bubble defects [35,36]. Therefore, sufficient time must be provided for the air to escape. Injection molding can provide a faster and cheaper alternative. Injection molding is an industrially established technique and capable of replicating micro/nanostructures on polymer surfaces [37–42]. Nevertheless, to the best knowledge of authors, only few researches were reported on using injection molding to prepare antireflective micro/nanostructured surfaces [43–45], especially micropyramid structured surfaces.

Based on the aforementioned background, a strategy by combining electroless plating, electroplating, and microinjection compression molding (μ-ICM) is proposed to fabricate antireflective microstructured surface in this work. μ-ICM, which combines microinjection molding (μ-IM) with imprinting lithography, is typically used in high-efficient, high-precise, low-cost, and large-scale production and quite qualified for rapid fabrication [38,39,46]. Using the proposed strategy, PS replica with randomly arranged micropyramids on its surface is prepared, which exhibits an antireflective property and enhanced light transmittance.

2. Experimental

The overall process for fabricating the PS replicas with pyramids from etched silicon wafer consisted of three steps, that is, silicon wafer etching (Fig. 1(1)), nickel mold insert fabrication (Fig. 1(2)), and PS replica preparation (Fig. 1(3)).

2.1. Silicon wafer etching

Boron-doped (1–3 Ω cm) n-type, (100)-oriented silicon (Si) wafers with a thickness of 200 ± 20 μm were used. The wafers were cut into square plates with a dimension of 30×30 mm^2 (Fig. 1(a)). The plates were ultrasonically cleaned in acetone and then in deionized water for 15 min for each step, to entirely remove organics and other impurities on the wafers. Then the plates were anisotropically etched in aqueous alkaline solution (3 wt% NaOH, 10 wt% isopropyl alcohol) [10] at 80 °C for 20 min to form the pyramids on their surfaces (Fig. 1(b)). Finally, the etched silicon wafers were thoroughly rinsed with ethanol and deionized water, and dried in nitrogen gas stream.

2.2. Nickel mold insert fabrication

The steps for fabricating the nickel mold insert with negative pyramid structures comprised electroless nickel plating [47], electroplating [48], and etching (Fig. 1(2)) in this work. Electroless nickel plating can be used to deposit electrical conductivity nickel layer on microscale structures [47]. Electroplating is an inexpensive way to replicate micro/nanoscale structures, and replicated nickel shim can be used as a template in injection molding [45].

The electroless nickel plating on the aforementioned etched silicon wafer included pretreatment and nickel deposition, and the compositions and concentrations in the corresponding solutions and the process parameters are listed in Table 1. The etched silicon wafer was pretreated via sensitization and activation to provide catalytic nuclei for the release of nickel iron in the reduction reaction of following electroless plating. Specifically, the silicon wafer was first immersed in the sensitizing solution for 10 min and then in the activating solution for 5 min at room temperature. Subsequently, the wafer was dried in ambient atmosphere, ensuring that palladium catalytic nuclei were adhered to the surface of the pyramid structure. After that, the pretreated silicon wafer was immersed into the electroless nickel plating solution at 50 °C with magnetic stirring. In the plating solution, $NiSO_4{\cdot}6H_2O$ and $NaH_2PO_2{\cdot}H_2O$ acted as main salt and reductant, respectively. The solution was adjusted to pH = 9.1 with ammonia water. After 5 min of the electroless plating, the pyramid structured silicon wafer covered with conductive nickel layer (Fig. 1(c)) was taken out of the solution, rinsed thoroughly with deionized water.

The electroplating was performed with the aforementioned electroless nickel plated silicon wafer acting as a cathode and a Ni-S plate as an anode in the electroplating solution, in which the compositions, concentrations, and process parameters are listed in Table 2. A power supply (IT7000 DC Power Supply, ITECH Electronic Co., Ltd. USA) was used to provide a constant current density of 4 A/dm^2. To guarantee the uniformity of the electroplating solution, a magnetic stirring at 150 rpm was applied. After electroplating for 2 h, an approximately 400 μm thick nickel layer was deposited on the conductive nickel layer on the silicon wafer (Fig. 1(d)). Finally, the silicon wafer was corroded away by wet etching with NaOH at 80 °C, yielding the nickel mold insert after cleaning and drying (Fig. 1(e)).

2.3. PS replica preparation

The PS replicas were molded via the μ-ICM technology in this work, as shown in Fig. 1(3). PS (grade N1841H, Hong Kong Petrochemical Co. Ltd) with a refractive index of 1.6 was used as the material for molding the replica. The equipment used for fabricating the replicas comprises an 80 t injection-molding machine (KM80SP180CX, Krauss-Maffei, Germany) and a microinjection compression mold equipped with a temperature control apparatus. As a template, the previously fabricated nickel mold insert was mounted on the mold cavity surface, as shown in Fig. 1(f). In the μ-ICM process, the mold cavity was first partially filled with molten PS when the mold was partially closed (Fig. 1(g)). Then the mold was compressed in the thickness direction to finish the melt filling (Fig. 1(h)). Finally, the PS melt was packed under the compression force and simultaneously cooled down [49]. The molding parameters, including injection rate (154 cm^3/s), melt temperature (235 °C), mold temperature (100 °C), compression force (280 kN), and cooling time (14 s), were kept constant. It should be noted that the cycle time for