Materials Research Bulletin 109 (2019) 183–189

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Antireflective and self-cleaning glass with robust moth-eye surface nanostructures for photovoltaic utilization

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ARTICLE INFO

Keywords:
Antireflection glass
Nanostructured surface
Self-cleaning
Omnidirectional and broadband antireflection

ABSTRACT

Omnidirectional and broadband antireflection (AR) self-cleaning coatings are crucial for the performance enhancement of photovoltaic (PV) modules. Herein, we demonstrate biomimetic moth-eye structures on glass through inductively coupled plasma (ICP) etching process using thermal dewetted copper nanoparticles as the masks. Moreover, the etched glasses are chemically treated to strengthen the nanostructures. The moth-eye glass exhibits excellent AR effects with a reflectance below 3% over the wavelength range from 570 to 950 nm. As the incident angles of the light increasing from 0o to 60o, the relative improvement of the power conversion efficiency (PCE) of PV module with moth-eye glass produces a dramatically increases from 4.6% to 9.9%, compared with that of PV modules with flat glass. Additionally, the moth-eye glass also possesses superhydrophilic self-cleaning and antifogging abilities, which are attractive for outdoor applications.

1. Introduction

Photovoltaic (PV) is considered as a potential alternative strategy for traditional fossil fuels because of its environmental friendly and sustainable advantages. At the end of 2017, the global PV module production capability is evaluated to be above 130 GW [1], in which the rigid PV modules are dominant in both solar power plants and distributed systems. The broadband anti-reflection is vital important for solar cells and their corresponding modules. An intensive study has been performed on the wafer level, such as fine tuning pyramids [2], black silicon [3] AR coating [4]. In the rigid PV modules, glass sheets are normally chosen as the outmost protective layers for PV cells against the harsh environment, because of their excellent properties such as high transparency, chemical inertness and low cost. Light need transmit the glass to be absorbed in the silicon material. However, due to the refractive index mismatch between the air and the glass, the undesirable reflection can cause 8–9% light loss in visible spectrum [5], which hinders the power conversion efficiency (PCE) of modules. Therefore, reducing this light reflection loss is crucial for the efficiency enhancement of rigid PV modules.

To suppress the reflection, quarter-wavelength ($\lambda/4$) thin-films made of nanoporous materials with lower effective refractive index [6], such as SiO_2 [7–9], ZnO [10], CaF_2 [11], have been widely fabricated onto the glasses of modules serving as antireflection (AR) coatings. Whereas, these AR films based on $\lambda/4$ design can only achieve low reflection in a relatively narrow range of wavelengths and incidence angles [12]. The potential thermal and stress mismatches may possibly cause the spalling of AR films as well [13]. Inspired by excellent broadband AR ability of insect compound eyes in nature, continuous efforts have been focusing on mimicking the sub-wavelength scale structures with gradient refractive index for optical surfaces to suppress reflection [14–16]. Through nanoimprint lithography, biomimetic three dimensional (3D) nanostructures have been successfully constructed using transparent polymers [17] such as polydimethylsiloxane (PDMS) [18–20], polymethyl-methacrylate (PMMA) [21], and ethylene-tetrafluoroethylene (ETFE) [22], which demonstrated excellent broadband and omnidirectional AR performance as the window layer of PV modules. Unfortunately, because of the nanoscales of the structures as well as the poor mechanical durability of polymers [23] (lower Young's modulus, such as 1.7–1.9 MPa of PDMS [24], 2–4 GPa of PMMA [25], and ~1.1 GPa of ETFE [26] compared with 70-100 GPa of glass [27]), these AR nanostructures are vulnerable to dust particles in the dirty outdoor surroundings [28]. We recently demonstrated micro-sized 3D pillars [29] and triangular prisms [30] on ETFE films through hot

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https://doi.org/10.1016/j.materresbull.2018.09.029
Received 6 June 2018; Received in revised form 8 September 2018; Accepted 17 September 2018

embossing process to suppress the reflection of PV modules. Although the AR ability of these micro-sized structures is slightly poorer than those nano-sized structures, the mechanical durability is significantly enhanced, which is valuable for the practical outdoor applications. These attempts have widely boosted the performance of flexible modules with polymer window layers. However, they are still not proper for the rigid modules because of the higher requirements of mechanical durability.

Another strategy is to directly construct AR structures on mechanical robust cover glass of PV modules [31]. Duell and coworkers [32] combined four commercially available structured glass (grooves, pyramids, inverted pyramids and lightly textured) into PV modules to investigate the AR properties. All these structured galsses increase the short-circuit current density (J_{SC}) of the PV modules at normal incidence angles. And the PV module encapsulated in glass with pyramids structure exhibit the highest J_{SC} improvement of 3.2% compared with PV modules encapsulated in flat glass. Moreover, the improvement of J_{SC} became more significant when incidence angles increased. However, it is risky for the concaves of hundreds of micrometers in these structures to trap and accumulate the dust particles, which are difficult to be cleaned. By considering the dusts on the surface of PV modules can reduce its generated electricity and the added cost for cleaning the dusts, the actual cost of the electricity generating for these PV modules in the outdoor is likely to be increased significantly.

In this paper, we proposed antireflective and self-cleaning glass with robust moth-eye nanostructures. Thermal dewetting method was used to transfer the pre-deposited copper (Cu) thin-film on glass into nanoparticles. Then the inductively coupled plasma (ICP) etching process was performed to directly build moth-eye structures on the glass surface while the Cu nanoparticles served as etching masks. A variety of metals, such as Ag, possess the similar dewetting as Cu [33]. The Cu was chosen because of its properties of low temperature of dewetting, good resistance under dry etching and low cost. The etched glasses were subsequently chemically strengthened to ensure mechanical durability. Mono-crystalline silicon (*c*-Si) PV cells were encapsulated by the moth-eye glass sheets as the optical window. The moth-eye glasses exhibit superior superhydrophilicity with a water contact angle (CA) of ~0o, providing with excellent self-cleaning and anti-fogging properties, which are attractive for PV modules in the outdoor environment to handle the dust accumulation and fog condensation problems.

2. Materials and methods

2.1. Fabrication of AR glass

As illustrated in Fig. 1a, the fabrication process of AR glass involved four key steps, named deposition, dewetting, ICP etching and lift-off, respectively. Cu ultra-thin films with the thicknesses of 3, 5 and 8 nm were primarily deposited on flat strengthened glasses (Corning Inc.) by a direct current (DC) magnetron sputtering system. The deposition process was proceeding in Ar atmosphere at a working pressure of 0.4 Pa, applying a DC-power of 100 W on the Cu target. Then the as-deposited metal films were thermally dewetted in a tube furnace to generate nanoparticles upon the substrate through self-organized process. The dewetting process proceeded at temperature of 400–600 °C for 10–60 min, using mixed H_2 (20% vol in Ar) gas to avoid oxidation of the nanoparticles. Subsequently, the obtained metal nanoparticles were used as etching mask during an ICP (ICP-5100 system, Beijing Chuangshi Weina Technology Co., Ltd.) process to achieve moth-eye structures on the glass surface. The etching parameters were kept at 700 W radio frequencies power with 400 W accelerating voltages, and a mixture of 40 sccm Ar/5 sccm SF_6 was adopted as etching gas at a pressure of 0.4 Pa. Besides, the distance between substrate and electrode was fixed at 6 cm to achieve a stronger ion bombarding power. After the dry etching, the glasses were cleaned in Piranha solution (70% (w/w) sulfuric acid and 30% (w/w) hydrogen peroxide) at 150 °C for 5 min to entirely remove the remaining metal and sulfide residue. Then the glass sheets were subjected to molten potassium nitrate at 450 °C for 3 h to chemically strengthen the moth-eye structures via the replacement of K^+ for Na^+ creating a robust compressive stress layer. Finally, the glasses were ultrasonically cleaned in isopropanol and deionized (DI) water for 5 min, respectively, and dried with blowing N_2.

2.2. Encapsulation of the PV modules

The as-prepared moth-eye glass was then attached onto a *p*-type mono-crystalline silicon passivated emitter and rear cell (PERC, $2 \times 2\ \text{cm}^2$, provided by Jinneng Clean Energy CO., Ltd.) as the cover glass (Fig. 1b and c). Concretely, the premixed PDMS (Sylgard 184, Dow Corning, 10:1 ratio with the curing agent) was firstly poured into a petri dish. Then the solar cell together with a flat backboard glass underneath it was immersed into the liquid PDMS leaving the electrode leads outside, successively followed by a vacuum degas and solidifying process at 60 °C for 3 h. Afterwards, the moth-eye glass was firmly attached onto the PDMS surface without air gap by means of electrostatic force. Finally, the integrated PV module was taken out of the dish through resecting the redundant PDMS with a blade.

2.3. Characterizations

All the Scanning electron microscope (SEM) images were collected on a Hitachi S-4800 SEM at 3.0 kV. Tapping mode atomic force microscope (AFM, NT-MDT AFM-Raman-SNOM Integration Systems) with 12 nm diameter tips were used to scan the surface of moth-eye glasses. A fiber-optics spectrometer (Maya 2000 Pro, Ocean Optics) equipped with an integrating sphere (15 cm in diameter) is employed to obtain the reflectance spectra on the PV modules over the wavelength range of 300–1100 nm. A Kruss kontaktwinkle DSA100 setup was used to measure the CA while a 5 μL water drop was loaded on the surface of samples. The current density-voltage *(J-V)* characteristic of PV modules was conducted on a solar simulator (94,063 A, Newport Corporation) equipped with a 450W Xe lamp whose output power was calibrated to the standard AM 1.5 global illumination. The external quantum efficiency (EQE) measurement of PV modules was performed by a PV

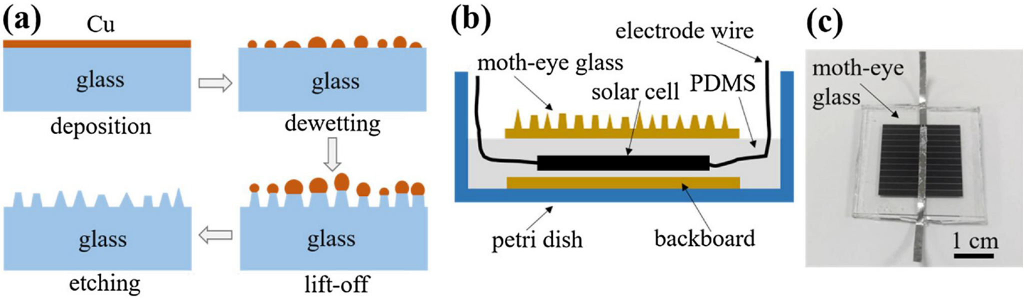

Fig. 1. (a) Schematics of AR glass fabrication process. (b) Schematics structure of the encapsulated PV module. (c) Photograph of the encapsulated PV module.