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Extraordinary high broadband specular transmittance of sodalime glass substrate by vapor phase etching

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Abstract

In this paper, we present a simple method to fabricate the antireflective porous surface on sodalime glass using a single step HF-vapor phase etching method. Under optimal conditions, both-sides etched glass substrate exhibited a broadband enhancement in the transmittance with maximum transmittance as high as 99.2% at ~500 nm with extremely low diffusive scattering. The measured transmittance exceeds by ~7.6% as compared to plain glass (91.6%). X-ray photoelectron spectroscopy results confirmed the formation of a fluoride layer comprising of NaF and CaF_2 on sodalime glass substrate after etching. Field emission scanning electron microscopy results showed the formation of porous structure with randomly distributed pores of size <150 nm. The refractive index of the porous fluoride layer was found to be 1.28 and lowest reflectance of 0.6% has been achieved. Moreover, reflection (measured at 500 nm) remains below 1.5% over a range of incident angles (8–48°), which is ascribed to the fact that refractive index follows a gradual change in the nanoporous surface. The theoretical transmittance of the optimized etched glass determined by finite difference time domain simulation shows a good agreement with the experimental results. The silicon solar cell covered with both-sides optimized etched glass showed a relative increase of ~4% in power conversion efficiency as compared to a solar cell covered with a plain glass.

Keywords: Vapor phase etching; Antireflection; Specular transmittance; Nanoporous surface

1. Introduction

Glass substrate has been extensively used in numerous optical and electronic devices such as optical lenses, eye glasses, display devices, mobile phone screen, light emitting diodes (LED), and photovoltaic (PV) modules, because of its advantageous properties such as low cost, high transmittance, excellent stability against water and UV radiation (Xiong et al., 2010; Yeo et al., 2014; Leem et al., 2015). However, ~8% of incident light is lost due to Fresnel reflection at air/glass interface (Mahadik et al., 2015; Yoldas, 1980), which causes a performance deterioration of many optical and electronic devices. Therefore, this reflection loss cannot be ignored and should be minimized. Antireflection (AR) coatings are a solution to eliminate the reflection loss, and have been successfully used in numerous applications such as: (i) PV and solar thermal applications to enhance the device efficiency (Groep et al., 2015; Kalogirou, 2004), (ii) display applications for elimination of the undesirable ghost image or veil glares to achieve high brightness and contrast (Hiller et al., 2002; Groep et al., 2015) and (iii) laser and sensor applications (Yoldas and Partlow, 1985). For single layer coating, two conditions should be satisfied to achieve the minimum reflection from glass surface (Xiong et al., 2010; Raut et al., 2011) (1) First, the optical thickness

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of the coating should be one fourth of the incident wavelength ($t \sim \lambda/4$). (2) Second, the refractive index (RI) of the coating should be equal to $\sqrt{n_{glass}}$, where n_{glass} is RI of glass and its value is 1.52. Therefore, the ideal RI value of coating material should be ∼1.23. No dense coating material is available in nature which has the RI close to the ideal value (1.23). However, some fluoride materials such as LiF ($n = 1.39$), MgF_2 ($n = 1.38$) and CaF_2 ($n = 1.42$) have low value of RI as compared to n_{glass}, but these values are still large to achieve the minimum reflection from glass surface (Xiong et al., 2010; Groep et al., 2015). The ideal value of RI can be achieved by creating a nanoporous microstructure of dense materials or by depositing a layer of nanoparticles having controlled fraction of empty space (porosity/voids). But, size of pores/particles may enhance the diffuse scattering that decreases the specular transmittance, thus, lowering the quality of AR coatings (Park et al., 2005; Yancey et al., 2006; Kim et al., 2007).

Over the last decades a variety of methods have been demonstrated to fabricate the AR surface on glass substrate such as electron beam evaporation, chemical vapor deposition (CVD), reactive ion etching, sputtering, spin coatings, layer by layer deposition, sol–gel process, nanophase separation of polymer and nano-imprint lithography, (Walheim et al., 1999; Raut et al., 2011; da Silva et al., 2011; Askar et al., 2013; Shin et al., 2013). Apart from all above mentioned techniques, chemical etching has also been widely used as it is the most convenient and scalable approach to produce the excellent broadband AR surface on glass (Chinyama et al., 1993; Du and He, 2012; Yao and He, 2013). Moreover, etched glass surface showed good durability and outstanding antifogging properties as well. Although, chemical etching was started around seven decades before, its usage to improve the transmittance is still being reported because of its simplicity and scalable approach (Du and He, 2012; Liu et al., 2012; Wang and Zhao, 2014). Chemical etching can be classified into two categories: dip or liquid phase etching and dry or vapor phase etching. Vapor phase etching is more controlled process than dip etching but it requires either very long etching time (Cathro et al., 1984; Yao and He, 2013) or lithographic methods to create the AR nanostructured surface on glass (Wang and Zhao, 2014). Based on dry etching, numerous lithography-free methods have also been used for realizing the nanostructured AR surface on glass substrate. Lee et al., fabricated the tapered subwavelength antireflection structure on Si substrate using capacitively coupled plasma reactive ion etching (CCP-RIE) with Cl_2 and N_2 gases (Lee et al., 2009). Prior to etching thin film of thermally dewetted Pt/Pd nanodots was used an etching mask. Hien et al. fabricated the nanostructured surface on glass substrates by two steps lithography free Ar/CF_4-based plasma etching process (Hien et al., 2011). In first step, a metal film of 10 nm was deposited on glass substrate as a sacrificial layer. An AR grassy surface was fabricated using a single step lithography free CF_4/O_2 based reactive ion etching process (Song et al., 2013). After etching, an enhancement of the 4.15% in the transmittance (with T_{max} ∼97%) has been achieved. Yu et al. demonstrated a two steps lithography-free method to create the nanostructured surface on sodalime glass substrates by CF_4 plasma etching a sacrificial layer of SiO_2 (Yu et al., 2015). But all these methods require vacuum based techniques, generation of plasma and use of sacrificial layer, therefore, these methods are costly, time consuming and inappropriate for large area applications. To the best of our knowledge, a non-vacuum base single step, fast and lithography/mask free dry etching method to produce the AR surface with reflectance as low as <1% (T_{max} >99%) has not been reported so far.

In this paper, we report a simple, non-lithographic and single step method to fabricate broadband AR nanoporous surface on sodalime glass substrate using hydrofluoric (HF)-vapor phase etching. Compared to other AR fabrication methods, it requires a very less fabrication time and does not use any costly apparatus. Both-sides treated glass substrate exhibits a broadband enhancement in the transmittance with a maximum transmittance as high as 99.2% ∼500 nm with remarkable stability in the transmittance spectra against 30 days of outdoor exposure. We also demonstrate the effect of broadband high transmittance on solar cell power conversion efficiency.

2. Experimental details

Sodalime glass slides (Blue Star) were used for the present study. Before etching process, they were rinsed with DI water followed by sonicating them in acetone and propanol solutions for 15 min. The etching experiment was performed in a Teflon beaker and the schematic diagram of the etching setup is shown in Fig. 1(a). Cleaned sodalime glass substrates were etched using HF (40%) vapor at different substrate temperatures (room temperature to 100 °C). Transmittance (specular and total) and reflectance spectra were recorded with a UV–Vis–NIR spectrophotometer (PerkinElmer, Lambda 950) over a spectral range of 300–800 nm using 150 mm integrating sphere detector. To study the angle dependent AR property, reflectance was measured at different incident angles (8–68°) using universal reflectance accessary. The surface morphology and the roughness of the etched sodalime glass were investigated by field emission scanning electron microscopy (FESEM, Carl Zeiss, SUPRA 40VP) and atomic force microscopy (AFM, Bruker, Nano). X-ray photoelectron spectroscopy (XPS, SPECS) was used to examine the composition of the glass surface before and after etching. For the theoretical analysis, finite difference time domain (FDTD, Lumerical Solutions, Inc.) trial license was used to verify the AR properties of etched surface. For photovoltaic characterization, current–voltage (I–V) measurements were performed on mono-crystalline silicon solar cell of area is 4 cm^2 under incident power (P_i) of 100 mW/cm^2.