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Broadband quasi-omnidirectional sub-wavelength nanoporous antireflecting surfaces on glass substrate for solar energy harvesting applications

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ABSTRACT

A cost effective, facile and scalable method to fabricate the stable broadband antireflective (AR) surface on glass substrates for solar energy applications is still a challenge. In this paper, we have demonstrated a simple and non-lithographic method to fabricate the broadband quasi-omnidirectional AR nanoporous surface on glass substrates by hydrofluoric (HF) acid based vapor phase etching method. Both-sides etched sodalime glass substrate under optimized conditions showed broadband enhanced transmittance with maximum total transmittance of ~97% at 598 nm. The measured transmittance exceeds by ~5.4% as compared to plain glass (91.6%). Field emission scanning electron microscopy results showed that an AR nanoporous surface with graded porosity was formed on sodalime glass substrate after etching. Due to the graded porosity, the fabricated nanoporous surface on sodalime glass substrate showed excellent broadband enhanced transmittance, and exhibited low reflectance < 2.8% over a wide range of incidence angles (8–48°). The mechanism of nanostructured surface formation and the effect of etching parameters on transmittance have been discussed in detail. To get more insight, the theoretical transmittance of the optimized sample has been determined by finite difference time domain simulation, which confirms a good agreement of AR property with the experimental results. Furthermore, these AR nanoporous surface showed good adhesion property, excellent thermal and chemical stability, and exhibited outstanding stability against outdoor exposure. These properties signify its strong potential in various solar energy devices.

1. Introduction

Anti-reflecting (AR) surfaces on various substrates, e.g., glass, silicon, germanium, etc. are extremely important to enhance the efficiency of solar energy harvesting devices [1–3]. Glass substrate is commonly used in the solar industry due its low cost, high transmittance and excellent stability against water. It is well known that for normal incidence, 8–9% of incident light is reflected back from air/glass interfaces and because of this reflection loss, glass substrate shows transmission < 92% [4,5]. This unwanted reflection loss causes a performance deterioration of energy harvesting devices, therefore, AR surface on glass substrate is highly desired. In addition, AR surface is very important in numerous optical and electronics applications such as: optical lenses, automotive glasses, cathode ray tubes, display panels, lasers, telecommunications and sensors [6–10]. Reflection can be reduced either by deposition of an AR coatings or by creating an AR structure on the glass. To achieve the AR property, two conditions should be satisfied for zero reflection [6,11]: (i) The optical thickness of the coating/structure should be λ/4, where λ denotes the wavelength of the incident light and (ii) the refractive index of the coating/structure (n_c) should be $\sqrt{n_{air} \times n_{glass}}$, where n_{air} and n_{glass} are refractive indices of air and glass substrates, respectively. Refractive index of glass is ~1.53, therefore, the ideal value of n_c would be 1.23 to achieve minimum reflection at glass/air interface. However, homogeneous coatings/structures, which satisfy these two conditions, cannot minimize the reflection over a broad range of wavelength [6]. To achieve the broadband AR properties the refractive index should change gradually rather than a uniform refractive index in the coatings/structures [6,12,13].

The effective broadband AR coatings/structures are extremely important for solar energy harvesting devices as these devices receive radiation from the sun in the whole range of solar spectrum (350–2500 nm). Over the last decades, various methods have been used to enhance the transmittance over a broad range of wavelength, which include vacuum and non-vacuum based

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processes, e.g., evaporation, chemical vapor deposition, sputtering, reactive ion etching, sol–gel, layer-by-layer dip-coating, polymer coating, chemical etching and self-assembled process [6,12–19]. Vacuum based methods are very expensive and not easy to apply over large surfaces, particularly for the photovoltaic modules. However, silica coatings by sol-gel techniques (a non-vacuum process) have the potential for large area applications with economically feasible solution. But the performance of these coatings degrades with time, exhibit poor adhesion and lack reproducibility in the fabrication process [20,21]. Polymer based AR coatings show an excellent transmittance in both visible and NIR regions [13,16]. However, these coatings are not suitable for solar energy applications on account of their poor thermal and mechanical stability and also suffer from photo-degradation [22,23]. Furthermore, broadband omni-directional AR moth-eye nanostructures have been fabricated using other alternative emerging lithography techniques [6,16], but these nanostructures are not easy to fabricate and these techniques are expensive as well.

Among all these AR coating/structure methods, the chemical etching is very simple, inexpensive and also has the capability to produce an effective broadband AR surface on glass with excellent durability without any additional coatings [11,24,25]. The chemical etching process has been performed in two ways: dip or liquid phase etching and vapor phase etching. So far, dip etching technique has been extensively used to enhance the transmittance of the glass using a variety of etchants such as KOH, NaOH, fluorosilicic acid (H_2SiF_6), HF and HF-based solutions [24,26–30]. But, there are many drawbacks of dip etching methods such as long etching time, require need for phase separation, and use of multiple etching agents [31–33]. In case of dip etching, both sides of the glass are etched simultaneously, which may not be desired in photovoltaic modules. On the other hand, the vapor phase etching method has the ability to etch one side of glass independently and it can be effectively controlled as compared to dip etching method [33]. Notably, this method has the potential to reduce the amount of hazardous acid with extra environmental benefits. This method has been used extensively for the past several decades for removing the oxide layer from silicon wafer for semiconductor and MEMS applications [34,35], but very much less work has been devoted to fabricate the AR nanostructured surfaces on glass since its discovery [25]. Recently, Wang and Zhao used HF-vapor phase etching method to create nanostructures on sodalime glass using nanosphere lithography, which enhances the transmittance in the visible wavelength [36]. Yao and He also demonstrated a vapor phase etching method using H_2SiF_6 to make the AR nanoporous surfaces on glass substrate, but it requires a very long etching time (24–48 h) [11].

In this paper, we have reported a very simple vapor phase etching method to fabricate the durable and high performance broadband quasi-omnidirectional AR nanoporous surface on sodalime glass substrates. This method does not require any kind of nanolithography technique as well as long etching time and can also be applicable to various types of glasses used in the solar energy applications.

2. Experimental details

Sodalime glass slides (Borosil) of dimension 35 mm × 25 mm × 1.25 mm have been used as substrates for the present study. The etchant solution was prepared by adding the silica gel (LobaChemie, 6–20 mesh, Blue) and DI water in HF (40%) acid and the as-etched glass substrate was air annealed at 250 °C for 30 min. The details about the experiments can be found in the supplementary information. The schematic diagram of the etching setup is shown in Fig. S1 of the supplementary information. To perform the stability tests, all samples were prepared under optimized conditions. Further details can be found elsewhere [37].

Transmittance and reflectance spectra were recorded with an UV–vis–NIR spectrophotometer (PerkinElmer, Lambda 950) over a spectral range of 300–2200 nm using 150 mm integrating sphere detector. To study the omni-directional AR property, reflectance was measured at different incident angles (8–68°) using universal reflectance accessary. The surface morphology of the etched sodalime glass substrates was investigated by field emission scanning electron microscopy (FESEM, Carl Zeiss, SUPRA 40VP) and energy dispersive spectrum (EDS, Oxford Instruments) was used to measure the chemical composition of the plain and etched glass. The surface roughness was determined by using atomic force microscopy (AFM, Bruker). For the theoretical analysis, finite difference time domain (FDTD, Lumerical Solutions, Inc.) trial licence was used to verify the effect of AR nanoporous surface on transmittance of glass substrate. Further details about FDTD simulation can be found in the supplementary information.

3. Results and discussion

3.1. Transmittance of the optimized sample

The total transmittance (T_{tot}) spectra of plain glass, etched glass and annealed etched glass (optimized sample) along with the solar spectrum are shown in Fig. 1(a). The root mean square roughness (σ_{rms}) values are 3, 6, and 21 nm, respectively for these samples. It can be seen that etched glass shows an enhancement in T_{tot} as compared to plain glass over the whole spectral range. Moreover, annealed etched glass (250 °C, 30 min) showed a further improvement in T_{tot} spectrum over a broad range of wavelength with a maximum T_{tot} of ~97% at 598 nm. Although, the maximum T_{tot} value is less than that of reported values for AR glass surfaces

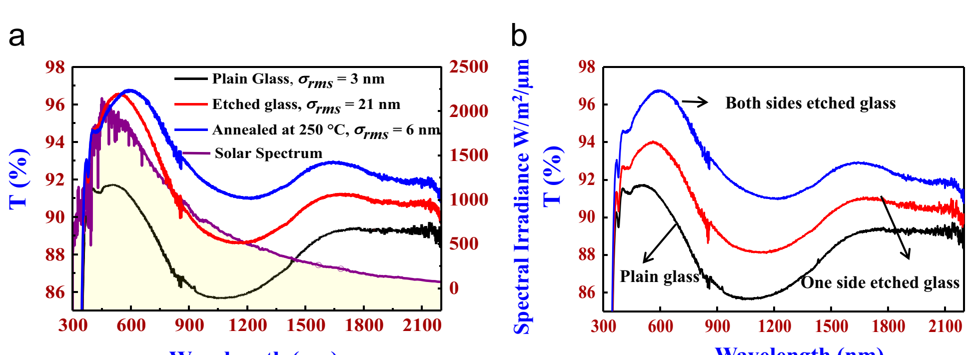

Fig. 1. Transmittance spectra of: (a) plain glass, etched glass and annealed etched glass along with the solar spectrum, and (b) plain glass, one side and both sides annealed etched glass.