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# Large scale antireflective glass texturing using grid contacts in anodization methods

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ABSTRACT

Antireflection coatings on glass are highly desirable, since glasses are widely used as a packaging material in the solar industry due to their transparency and durability. In this report, we propose a novel anodizing method using grid line contacts for antireflective nanostructures on a large area glass substrate. The nanoholes on the glass substrate exhibit broadband and omnidirectional antireflective properties, leading to an 11.34% improvement in the short-circuit current and enhanced power conversion efficiency from 7.9% to 8.57%. Moreover, the enhanced optical properties persist for 3 months in an outdoor environment. The proposed anodizing method can be considered as an alternative technique for the fabrication of large area nanostructures.



## 1. Introduction

Light is reflected at a boundary when it travels from one material to another that has a different refractive index. Introducing a gradual change of the refractive index with an antireflective (AR) layer can suppress the reflection and improve the efficiency of optoelectronic systems [1,2]. In particular, nanostructure coatings have attracted much interest as a promising method to improve the performance of solar cells because of their AR property and self-cleaning effect [3–6]. Since most of the reflection loss takes place at the air–glass and glass–silicon interfaces in a commercial Si photovoltaic device, an AR layer at these interfaces is expected to reduce the light loss and improve the energy conversion efficiency of solar cells. AR coatings on glass are highly desirable, since glasses are widely used as a packaging material in the solar industry due to their transparency and durability. For example, an 8% reflection loss across a sheet of glass can be reduced with the aid of AR structures. However, the formation of an AR layer on a typical solar glass panel is challenging because of the large size of the glass panel, which is usually bigger than a few hundred millimeters.

Few mature techniques that can be used to fabricate nanostructures on large substrates such as solar panel glasses have been developed; however, there have been some attempts to make a large area nanostructured layer using novel fabrication methods, such as nanosphere lithography (NSL), nanoimprint lithography (NIL), and laser interference lithography (LIL). Li et al. reported interesting AR properties from a $2 \times 1$ cm$^2$ glass after coating with a layer of 2D colloidal crystal using interface methods followed by RIE etching [7,8]. A roller-based NIL method was used to transfer large area (4 in. wide) nanostructures from a roller mold to a NIL resist [9–11]. The scale-up of an array of photoresist pedestals was successfully demonstrated on a $50 \times 50$ cm$^2$ glass substrate by using LIL methods [12].

Recently, the anodizing method has risen in popularity as an alternative to nano-lithography with the advantage of the dimensional controllability of dense nanoholes [13–17]. The recent achievement of a two-step anodizing technique has demonstrated the formation of periodic arrays of nano-channels [18]. In addition, the direct formation of anodic aluminum oxide (AAO) on top of a substrate leads to a simpler fabrication process by eliminating the tedious AAO film transfer process [19,20]. The directly formed AAO membrane has been utilized as a mask for the etching or deposition on conducting substrates, however the anodization of an Al film on a large area dielectric substrate is still challenging due to the insulating nature of the substrate [21]. Therefore, the anodizing method has not been a preferred choice for large area fabrication on a dielectric substrate compared to other nanolithographic methods such as NSL, NIL, and LIL.

In this report, however, we propose a robust fabrication technique for an AR coating on a large area glass substrate by modifying the anodizing method. The modified fabrication methods facilitate anodization of a $6 \times 6$ in.$^2$ area Al film on a dielectric substrate using grid line contacts. The AR effect from nanostructures has been evaluated by measuring the optical transmission and the photovoltaic performance in indoor and outdoor environments for more

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than 3 months. The short-circuit current of a solar cell with nanostructures is enhanced by 11.34%, leading to an improved power conversion efficiency from 7.9% to 8.57%.

## 2. Experimental details

### 2.1. Preliminary studies for a modified anodizing method

Two types of preliminary samples were prepared to compare the effect of contact types on thin film anodization. A borosilicate glass substrate (BOROFLOAT 33, SCHOTT) is masked with a thermal tape along the edge of the glass in order to define the size of the Al film. 250 nm of Al was deposited by electron beam evaporation (Auto 306, Edwards). An Al film with $3\times3$ cm$^2$ area was prepared with a point-type anode contact. $1\times3$ cm$^2$, $2\times3$ cm$^2$, and $3\times3$ cm$^2$ of Al films were prepared for a line-type anode contact. A copper tape and a conductive silver paste were used to connect the Al films with a voltage source. The copper tape and silver paste were electrically isolated from electrolyte by sealing them with nail polish. Nail polish was also injected on the Al film by an injector along one shorter edge of the Al film, serving as a line-type anode during the subsequent anodization process. The anodization was performed in 0.3 M oxalic acid under 40 V of constant voltage. Subsequently, the anodic membranes were soaked in 5 wt% aqueous phosphoric acid for 90 min to widen the nanoholes and open the pore bottoms.

### 2.2. Fabrication of large scale AR glasses

$6\times6$ in.$^2$ borosilicate glasses were cleaned with deionized (DI) water to remove dust and particles on the glasses. 250 nm of Al film was deposited on the cleaned glasses. Before the anodizing process, cross-checked grid lines with a 1 in. gap were applied on an Al film using nail polish to protect the underlying Al lines from oxidization. After forming an AAO membrane under the same anodizing and pore widening conditions as mentioned above, ICP-RIE etching (SLR-770, Plasma-Therm) was conducted using the AAO layer as an etch mask. The plasma etching (5 mTorr, 100 W RIE, 500 W ICP, $CF_4$ 20 sccm, Ar 5 sccm, and 4 min) transferred the array of nanoholes onto the glass surface. Finally the remained AAO and Al lines were removed by soaking into 5 wt% phosphoric acid. The nail polish grid lines were simultaneously peeled off during the removal of underlying Al lines.

### 2.3. Solar cell packaging

$5\times5$ in.$^2$ crystalline Si solar cells were cut into two pieces and the $I_{sc}$ was measured by a transducer (CASR 6-NP, LEM). The $5\times5$ in.$^2$ solar cell was laminated between a polymer back sheet and a front AR and planar glasses as shown in Fig. S3. A set of solar cells packaged with planar glass was prepared as a control sample. Ethylene vinyl acetate (EVA), an adhesive encapsulant that minimizes reflection, was used at the glass and solar cell interfaces to protect solar cells from humidity and dust.

### 2.4. Indoor and outdoor characterization

We measured the spectral transmission of textured glasses using a spectrophotometer (UV-3700, Shimadzu) in the wavelength range 400–1000 nm. The surface morphology was investigated by using a SEM (NanoSEM 230, FEI). The photovoltaic performance of the packaged cells was evaluated using a Newport class-A solar simulator under AM 1.5 illumination. The outdoor solar cell characterization was performed on the roof of a ~30 m tall building at the National University of Singapore for 4 months. Packaged solar cells were facing in southern direction and mounted with a tilt angle of 20°. A transducer was connected to both electrodes of a packaged solar cell; therefore $I_{sc}$ flowing through the transducer was converted to a voltage. $V_{oc}$ was directly measured from two electrodes of a packaged solar cell. The values of converted $I_{sc}$ and $V_{oc}$ were stored by a data acquisition tool (NI USB-6009, National Instrument) every 1 s.

## 3. Results and discussion

Recently we have reported that a random array of nanoporous structures formed by anodizing an Al thin film provides an effective template for sub-wavelength structures on a glass surface [22,23] in which a thin Al film on the small substrate of $1\times1$ cm$^2$ was completely anodized. With a large area Al film on an insulating substrate, however, an electric discontinuity can occur during the anodizing process and the formation of AAO can be localized near the anode contact point. In order to solve this problem, we investigate various contact designs as follows.

### 3.1. Effects of contact type on anodization of a thin Al film

Fig. 1 shows two types of AAO samples to examine the effect of the contact schemes. Anodization of a 250 nm thick Al film was carried out with a point contact (~3 mm in diameter) and a line contact (~0.5 mm width and 1 cm long) as shown in Fig. 1(a)–(d). Three different sizes of Al films in Fig. 1(b)–(d) were prepared to determine how large an area can be fully anodized by the line contact. After the anodizing step, as can be seen in Fig. 1(a), color gradation is observed on the $3\times3$ cm$^2$ point contact sample. This results from the localized anodization near the electrode contact. According to the scanning electron microscope (SEM) images of the point contact sample in Fig. S1, the AAO membrane in the darker area away from the contact has defective holes. Another

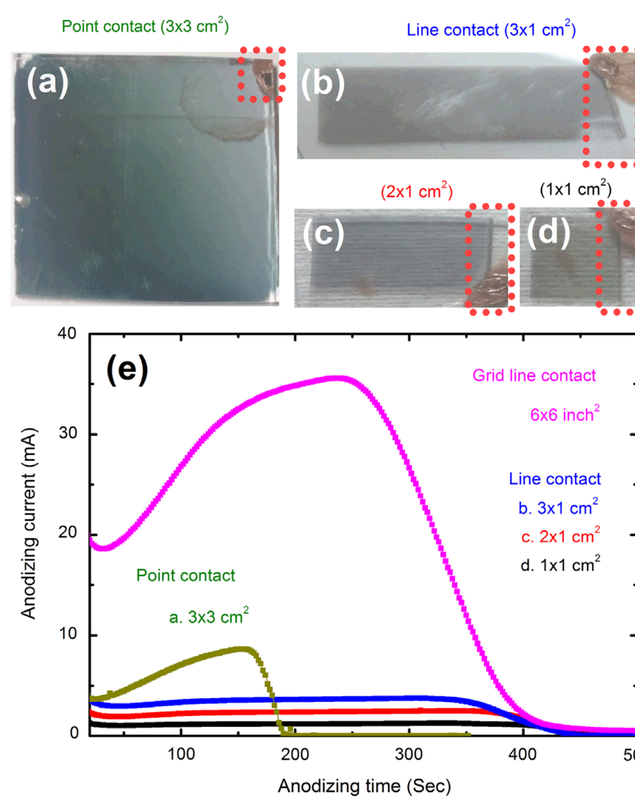


**Fig. 1.** Anodized AAO thin films. (a) Point-type anode contact and (b)–(d) line-type anode contact. The dotted boxes in (a)–(d) indicate the anode contact on each sample. (e) Anodizing current versus time curves.