Solar Energy Materials and Solar Cells 170 (2017) 95–101

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Mechanically robust, humidity-resistant, thermally stable high performance antireflective thin films with reinforcing silicon phosphate centers

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ARTICLE INFO

Keywords:
Antireflection
Robustness
Durability
Hierarchical nanopores
Silicon phosphate

ABSTRACT

High performance, function durability, thermal stability and mechanical robustness have long been pursued for advanced antireflective thin films. In the current work, we developed a novel and effective approach to fabricate mechanically robust, humidity-resistant, thermally stable high-performance antireflective thin films with reinforcing silicon phosphate centers from an acid-catalyzed hybrid silica sol. The thin film has a hierarchically nanoporous structure, resulting in favorable antireflective properties. After being coated with the antireflective thin film, the maximum and average transmittances of K9 glass increase from 92.1% and 92.0% (400–800 nm) to 99.7% and 98.8% (400–800 nm), respectively. In addition, the thin film shows favorable humidity-resistance and heat-resistance, and these extraordinary performances are attributed to its rich heat-resistant and hydrophobic groups. Moreover, mechanical strength measurements indicate the thin film has extraordinary 5H pencil hardness and 5A adhesion to substrate because of the formation of silicon phosphate centers in the thin film, which significantly reinforce the thin film. These high-performance antireflective thin films are promising in solar energy utilization, especially in solar cells.

1. Introduction

Light reflections from optical materials surfaces are undesirable in consequence of a loss of transmitted light. Antireflective (AR) thin films can reduce light reflections and have significant application prospects in solar cells, solar collectors, smart windows, display panels and lenses [1–8]. The principle of antireflection is the light interference between air and substrate. Theoretically, a homogeneous single-layer AR thin film with zero-reflection need a reflective index of $(n_a n_s)^{1/2}$ and a thin film thickness of a quarter wavelength of incident light, where n_a, n_c and n_s are the refractive indices of air, thin film and substrate, respectively [9]. As the refractive indices of air and commercial glass are 1 and 1.52, respectively, the optimal refractive index of AR thin film should be ca. 1.23 [9–11]. However, the refractive indices of available substances are generally higher than 1.35 [9,12,13]. Thus, nanoporous and nanoarray structures are mainly used to obtain low refractive index thin films.

To date, various approaches have been developed to obtain nanoporous [14–17] and nanoarray [9,11,18] materials with low refractive index, such as reactive ion etching (RIE) [5,19,20], acid or base chemical etching [21,22], nanoparticles deposition [23–26] and template methods [27,28]. Although the RIE method generically provides a nanoarray structure surface, resulting in excellent broadband AR properties, it is restricted by its expensive and complex equipment as well as small-area productions and low outputs [5,19,29]. The acid or base chemical etching approaches represent top-down routes to preparation of AR thin films, but the thin film via the base etching is mechanically weak and the acid etching method is time-consuming [21,22]. The assembly of nanoparticles on substrates has been widely investigated because of its design flexibility of film structure, but the obtained films usually show weak robustness and need further enhancing their mechanical strength [30]. The template methods are one of the general approaches to nanoporous structures. Specially, the acid-catalyzed silica system with micelles as template is a potential facile and low cost route to practical AR thin films with good mechanical strength [27,31]. As a result, various robust silica-based AR thin films have been prepared by this method [10,27,28]. Nevertheless, adsorption of water from air could seriously reduce the transmittance of those mesoporous AR thin films [32]. Therefore, it is still a big issue to obtain AR thin films simultaneously with favorable durability and mechanical robustness.

Recently, an antireflective film was prepared with outstanding 6 H

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http://dx.doi.org/10.1016/j.solmat.2017.05.068
Received 4 April 2017; Received in revised form 27 May 2017; Accepted 29 May 2017
Available online 02 June 2017
0927-0248/

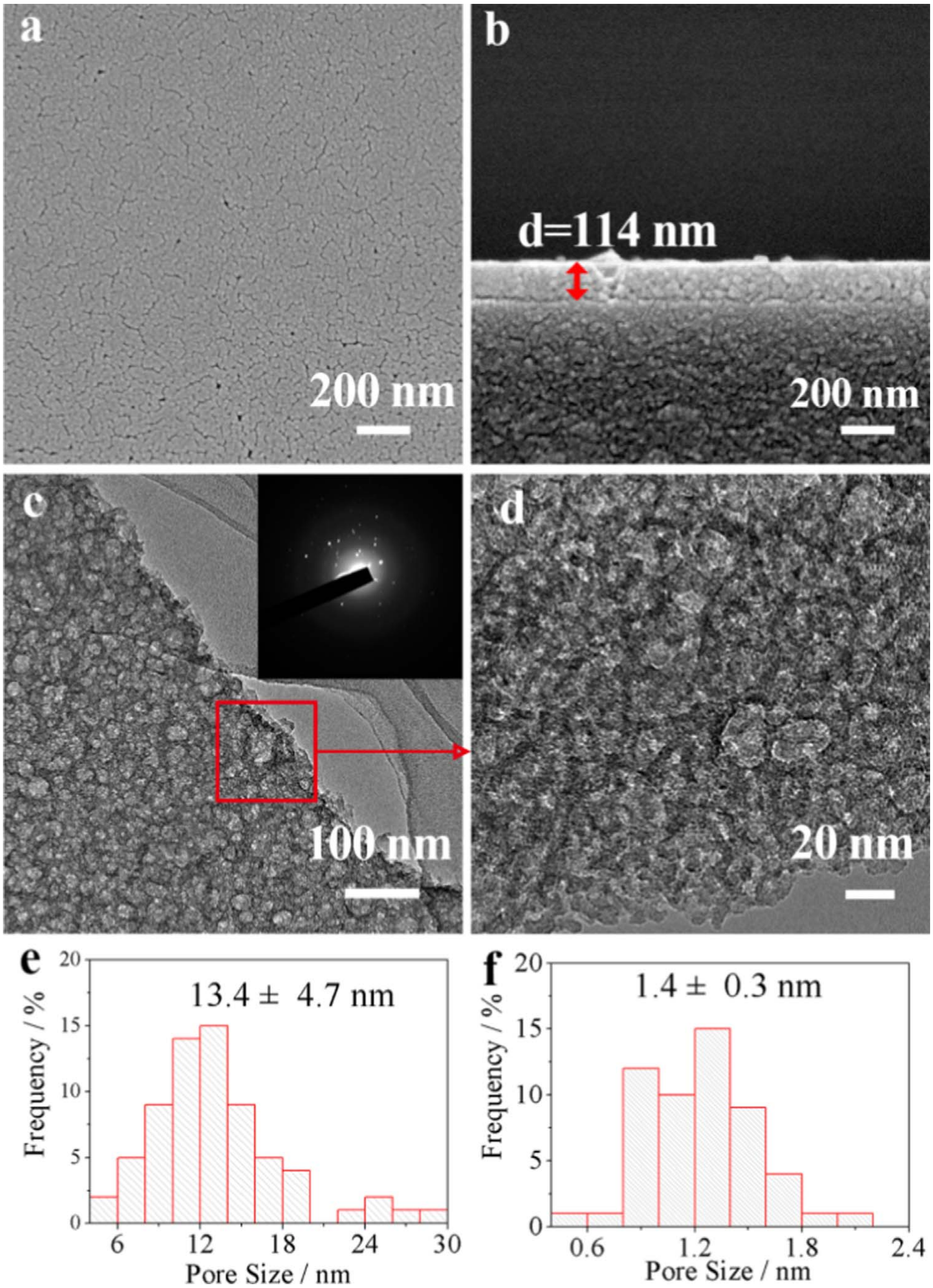

Fig. 1. Top-view (a) and cross-section (b) SEM and TEM (c and d) images of thin film. Inset in (c) is a selected area diffraction pattern. Histograms of pore size distributions (e and f) obtained from (c and d), respectively.

pencil hardness via crosslinking silica nanoparticles in the film by Si-O-P as linkage, though its long-term humidity-resistance needs to be further investigated [33]. Very recently, we introduced methyl into AR thin films, resulting in favorable humidity-resistance and mechanical robustness [10]. This system is a compromise between humidity-resistance and mechanical robustness, and the mechanical robustness still need improvement for practical applications. Thus, it is still a significant issue to fabricate both robust and durable AR thin films.

In this paper, we demonstrate an approach to fabrication of high-performance humidity-resistant AR thin films with reinforcing silicon phosphate centers from an acid-catalyzed hybrid silica sol. The thin films possess hierarchical nanopores, which are remarkably different from conventional single nanoporous thin films via acid-catalyzed silica sol with CTAB as template [10]. The hierarchically porous structure of thin films result in excellent broadband AR properties. The hydrophobic methyl groups present in the thin films effectively prevent water from entering their mesopores. Moreover, the silicon phosphate centers forming in the film structure endow the thin films with extraordinary mechanical robustness.

2. Experimental

Chemicals. Tetraethyl orthosilicate (TEOS, 98%) and methytrimethoxysilane (MTMS, 97%) were purchased from Alfa Aesar. Phosphoric acid (85%), Cetyltrimethyl ammonium bromide (CTAB), hydrochloric acid (38%), and absolute ethanol (99.5%) were obtained from Beihua Fine Chemicals. Ultrapure water with a resistivity higher than 18.2 MΩ•cm was used in all experiments, and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

Preparation of sol and thin film. Hybrid sols were synthesized as follows: MTMS/TEOS/HCl/H_2O/EtOH with a molar ratio of 0.5:0.5:0.004-0.007:3-6:41 were mixed, and then 1.5–2.5 wt% CTAB