Applied Surface Science 292 (2014) 68–73

Contents lists available at ScienceDirect

Applied Surface Science

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

Influence of trimethylethoxysilane on the wetting behavior, humidity resistance and transparency of tetraethylorthosilicate based films

Nan Wang, Dangsheng Xiong*

Department of Material Science & Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form
13 November 2013
Accepted 17 November 2013
Available online 23 November 2013

Keywords:
Superhydrophobic
Humidity resistance
Adhesion
Transmittance

ABSTRACT

Transparent and superhydrophobic films with different adhesion were obtained using trimethylethoxysilane (TMES) as a co-precursor by dip-coating. Silica sol was prepared by keeping the molar ratio of tetraethylorthosilicate (TEOS), ethanol (EtOH), ammonium hydroxide (25%) constant at 1:85.7:8.6, respectively. Along with the increase in molar ratio of TMES/TEOS, the tilt angles of prepared films increased from 2 to 90°. According to the humidity test, the surface roughness is more important in humidity resistance property compared to the chemical compositions; and the films with higher surface roughness showed better humidity resistance. All the films exhibited higher transmittance than the bare substrate in visible light, and better visual transparency was obtained on the films with higher molar ratio of TMES/TEOS.

1. Introduction

The wetting properties of superhydrophobic films have caused tremendous interest in recent years. Lotus leaf surface comprises of micro-nano-hierarchical structures and epicuticular wax crystalloids; such a hierarchically structure and low energy surface provides superhydrophobicity with high water contact angle and low hysteresis, which is called "Lotus-Effect" [1]. It can be explained according to the Cassie–Baxter model in which water droplets rest on a surface composed of air trapped in the microgrooves of a rough surface and tops of these microstructures [2,3]. Inspired by the lotus, many approaches have been developed to prepare superhydrohobic films with self-cleaning properties, such as sol–gel [4,5], lithographic methods [6,7], chemical vapor deposition [8,9],and layer by layer deposition [10,11]. On the other hand, superhydrophobic films with high adhesive forces have also attracted attention in recent years. Surface with a high adhesive force to liquid will have many potential applications such as liquid transportation, biochemical separation, and localized chemical reaction [12]. There are two theories can be used to explain the high-adhesion of the superhydrophobic surfaces [13,14]: one is a droplet in contact with a rough surface, the water can get into the grooves of the rough solid surface that attribute to the capillary effect of the microstructures. This capillary force is so strong that the water droplet can be pinned on surface even when it is turned upside down. The other is the construction of microstructures with appropriate size and topography to control the wetting state in the Wenzel state.

An optically transparent film that exhibits both superhydrophobicity and high visible light transmittance features would be very beneficial for optical devices and photovoltaics. It is not easy to achieve both superhydrophobicity and transparency, because surface roughness and transparency are generally competitive properties. According to Cassie–Baxter model, the roughness could trap air pockets in the surface, which is competitive with high visible light transmittance because the surface structures larger than 400 nm would become a scattering source of light [15,16]. Therefore, to prepare superhydrophobic and transparent films, it is a challenge to balance the high surface roughness requirement of water repellence with the low roughness requirement of optical transparency. On the other hand, the water repellent capability gradually degrades during long-term outdoor exposure, which is the problem that currently hinders the practical applications of superhydrophobic films [17]. Stability of superhydrophobic films in humid atmosphere is relatively recent and has not been sufficiently investigated [18].

In this work, a sol–gel method to fabricate superhydrophobic films with different adhesion was reported. A deep investigation for how surface roughness affects the surface wetting was carried out with special consideration given to the size of the particles . Furthermore, humidity test was performed at different temperatures to study the stability of prepared films and the surface roughness is crucial for humidity resistance. At the same time, the influence of roughness on the optical transmittance is studied.

---

* Corresponding author. Tel.: +86 2584315325.
E-mail address: xiongds@163.com (D. Xiong).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.11.070

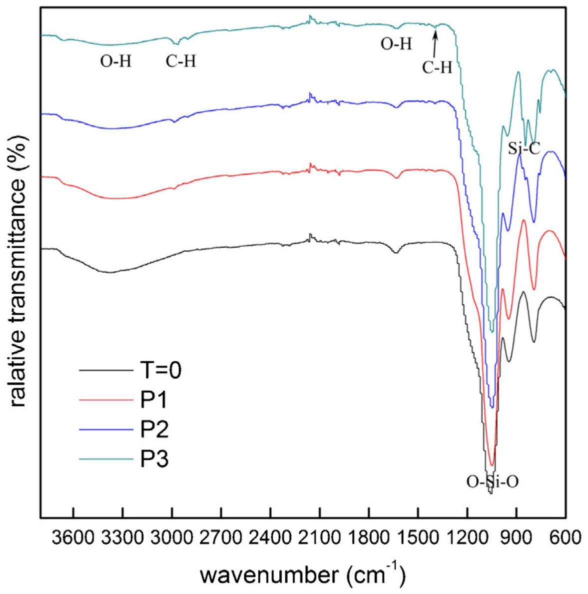

Fig. 1. FT-IR spectra of T = 0, P1, P2, and P3.

2. Experimental

2.1. Pre-treatment of substrates

To obtain uniform coating, the pre-treatment is required. The glass substrates were carried out by cleaning with deionized water and then ultrasonically cleaned with ethanol for 20 min, followed by soaking the substrates in the piranha solution (1:3 w/w H_2O_2/H_2SO_4) at 80 °C for 3 h. Then the substrates were cleaned with deionized water to remove the surface contamination and dust. All glass substrates were kept at 80 °C for 1 h before dip-coating.

2.2. Fabrication of superhydrophobic films

The coating solution was prepared of TEOS, CH_3CH_2OH, and H_2O in molar ratio of 1:85.7:8.6 with 13.8 M NH_4OH as a catalyst and trimethylethoxysilane (TMES) as a co-precursor. The molar ratio of TMES/TEOS (T) was 0, 0.3, and 0.6. Firstly, the mixture of NH_4OH, CH_3CH_2OH, and H_2O was stirred at 60 °C for 40 min. Then the mixture of TEOS with different molar ratio of TMES was added dropwise. The reaction mixture was further stirred for 2.5 h. Then the reaction mixture of T = 0, T = 0.3 and T = 0.6 were left for aging at room conditions for 1, 10, and 15 days, respectively. Finally, the pre-treated substrates were soaked into the different colloids and then withdrawn with a speed of 3 mm/s. All the substrates were coated three times and then kept at 40 °C for 10 min before next coating, which is necessary to produce chemical bonds between the deposited films and the substrates. All the films were desiccated in an oven at 200 °C for 3 h to remove the residual solvent after dip-coating. In addition, the prepared films of T = 0 were soaked in 9 wt.% chlorotrimethylsilane (TMCS) in hexane at 50 °C for 3 h. After the modification of TMCS, the film of T = 0 is denoted as P1. The films of T = 0.3 and T = 0.6 are denoted as P2 and P3.

2.3. Characterization

The morphology of the prepared films was characterized by Field-emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4800). Atomic Force Microscopy (AFM, Bruker Multi Mode 8) was used in ScanAsyst mode for roughness measurements. Fourier transform infrared (FT-IR, Nicolet IS-10) spectroscopic studies of the films were carried out using spectroscopy in 400–4500 cm^{-1} range. Optical transmission measurements were performed using a UV–vis spectrophotometer (Shimadzu, UV-2400) in the wavelength range of 350–750 nm with a step size of 1 nm. The contact angles (CAs) and tilt angles (TAs) were carried out with a contact angle measurement instrument (JC2000D2, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd.). The effect of humidity resistance properties of the prepared films were studied in a humidity chamber (RGDS-500, Surui Instruments Co., Ltd.).

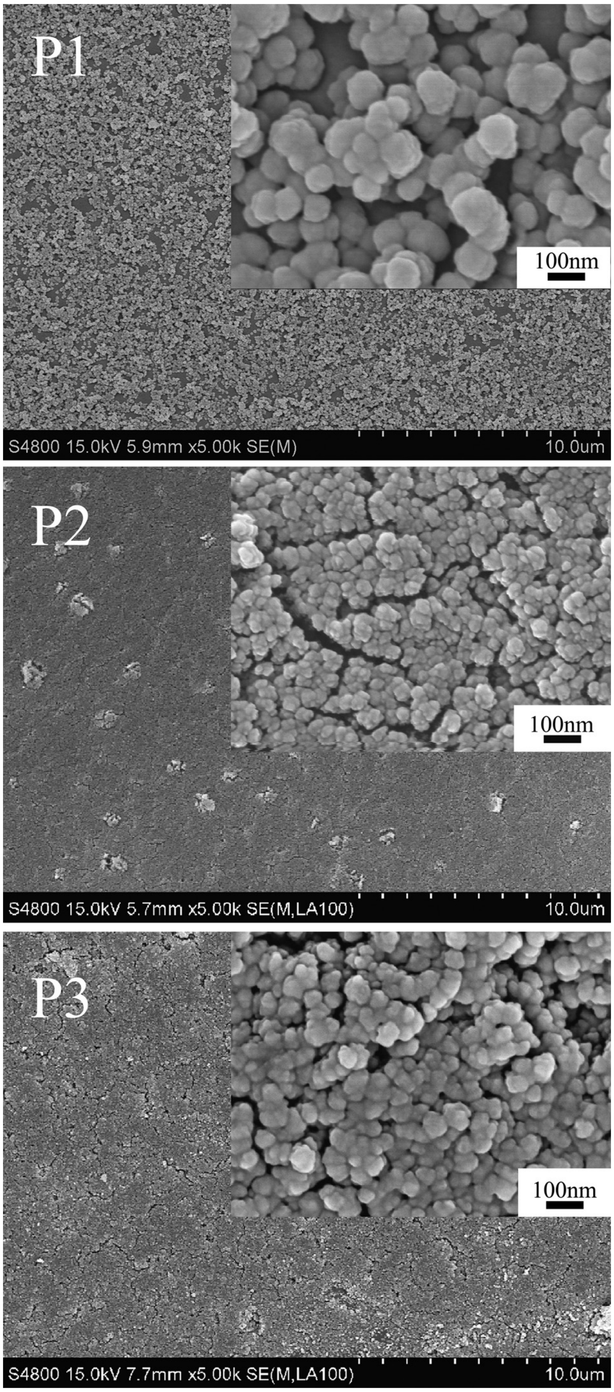

Fig. 2. FE-SEM images of P1, P2, and P3.