Thin Solid Films 622 (2017) 11–16

Contents lists available at ScienceDirect

Thin Solid Films

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

Optical functionality of micro- and nanostructured silica surfaces prepared by a sol-gel phase separation method

Triin Kangur [a,b], Valter Kiisk [a], Ardi Loot [a], Martin Timusk [a,b], Martin Järvekülg [a,b,*]

[a] Institute of Physics, University of Tartu, W. Ostwaldi Str 1, 50411 Tartu, Estonia
[b] Estonian Materials Technologies Competence Center, Riia 181B, 51014 Tartu, Estonia

ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form 15 September 2016
Accepted 12 December 2016
Available online 14 December 2016

Keywords:
Sol-gel
Phase separation
Silica
Moth-eye
Microlens
Optical coating

ABSTRACT

We report a wet chemical method for spray-coating of large areas with microscopic transparent hemispherical silica structures using sol-gel phase separation in tetraethyl orthosilicate sols. Suitable adjustment of preparation conditions (amount of sprayed solution, its concentration, water content, amount of catalyst) led to the formation of sufficiently small, high aspect ratio and densely packed structures, which impose notable antireflective, light scattering and hydrophobic surface properties.

1. Introduction

In recent years, biomimetic approaches have become increasingly popular in designing novel functional materials [1,2]. For example, suitably refined surface texturing (e.g. pyramidal texturing [3], black silicon [4], microlens [5], moth-eye structures [6]) can provide antireflective and light trapping properties over a reasonably wide range of wavelengths and incidence angles. These are important qualities for applications like solar cells, photodetectors, optical surfaces, etc. [7–9]. In particular, a number of increasingly complex solar cell structures are being studied to improve the absorption of incident light for enhanced photoconversion efficiency [10–12]. However, the top-down lithography methods that have been applied in these cases are not easily scalable. For this consideration, bottom-up roll-to-roll or self-formation approaches have more potential [13,14]. Moreover, certain variation in the moth-eye structures (placement, size or shape of the pillars or domes) may even lead to a better overall performance compared to a perfectly regular array [6,15]. Although most solar cells require texturing of semiconductor surfaces (usually silicon), silica structures can be useful as templates for surface etching [16]. In addition, silica textured surfaces are appropriate to reduce reflections from glass surfaces of optical elements and windows [17,18], where specular transmittance may or may not be needed, depending on the application.

Metal alkoxide-based sol-gel methods can be used for the preparation of a vast range of different materials, including various oxide coatings. Several applying methods, including spraying, can also be used to cover large contiguous areas [14,19]. Methods based on induced phase separation in sol-gel systems are a development in the field that have been applied mainly for producing porous oxides with different morphologies and pore sizes [20]. One of the most studied paths of phase separation is the spinodal decomposition, which generally results in a co-continuous structure. Phase separation can also proceed through the nucleation and growth mechanism, where dispersed separated domains of one phase are formed in the other [21,22]. We have previously demonstrated that the latter process can also yield single layers of round surface features with diameter from below 200 nm to tens of microns [23] with possible applications as biomimetic self-cleaning hydrophobic coatings [24]. The hemispherical geometry and surface density of obtained structural elements suggests that this method can also produce microlens and functionally graded moth-eye-like optical interfaces [6,16].

In this work, we used an easily scalable spray coating method to produce structured silica surfaces by phase separation in tetraethyl orthosilicate (TEOS) sols. Diffuse reflectance and angularly resolved measurement of scattered light were applied to study the optical functionality of samples coated with round surface features with 300 nm to 3 μm diameters. The hydrophobicity of various obtained surfaces was also determined to explore the possibility of achieving simultaneous optical (anti-glare) and self-cleaning (hydrophobic) functionalities [25].

* Corresponding author at: Institute of Physics, University of Tartu, W. Ostwaldi Str 1, 50411 Tartu, Estonia.
E-mail address: martin.jarvekylg@ut.ee (M. Järvekülg).

http://dx.doi.org/10.1016/j.tsf.2016.12.017
0040-6090/

2. Experimental

2.1. Sample preparation

Structured coatings were prepared by spraying a sol of TEOS in alcohol (1-propanol, ethanol) using nitric acid as catalyst. All chemicals were purchased from Sigma-Aldrich. The mixing of chemicals was carried out on a magnetic stirrer at room temperature. The first step was dilution of TEOS in alcohol, whereas the alcohol-TEOS volume ratio (T) was varied for different concentrations. Secondly, for hydrolysis and condensation reactions, the acid in water was added dropwise to alkoxide solution. For varying water-alkoxide molar ratio (R) and acid-alkoxide molar ratio (K), different amounts of water (deionized water) and nitric acid were added. Finally, the solution was left to stir for 3 h before spraying. The substrates, 25 × 25 mm pieces of soda-lime glass slides, were cleaned with methanol and hydrochloric acid solution (1:1) for 30 min followed by methanol rinse in ultrasonic bath and drying in nitrogen flow. In case of all the samples except S6, the sols were sprayed on the substrate by using a vertically positioned spray gun combined with a home-built trigger system, the distance between the nozzle and substrate was fixed at 15 cm. The amount of sprayed solution (A) was varied, coatings formed as a result of one passing of spray. In addition, in order to demonstrate the scalability of the method, sample S6 was prepared using an industrial spray coater (customized Ceetec Duo FlexSpray) with minimal optimization of spraying parameters such as the speeds of substrate, movement of the guns, spraying pressure, etc. In the latter case the coating also formed from several overlapping lines of spray. All the coating procedures were carried out in ambient lab environment of 23 ± 1 °C and 20–49% relative humidity. However, the preparation of each series in which T, R, K or A was varied, was carried out in immediate sequence to minimize the influence of possible changes in ambient conditions. After coating, the samples were air-dried and heated at 200 °C for 1 h.

2.2. Characterization

The structural features of the obtained silica coatings (the diameter of the formed dome-shaped elements and geometry) were investigated by scanning electron microscope (SEM) analysis (FEI Helios Nanolab 600). The samples were tilted to 45° angle for more precise view of the domes' shape. For conductivity, the samples were previously sputter coated with a 2 nm layer of gold using a SC7640 Auto/Manual High Resolution Sputter Coater.

For investigating the roughness and morphology of structured surfaces atomic force microscope (AFM) images were obtained with Dimension Edge™ AFM System (Veeco Instruments Inc.) in tapping mode at room temperature. Mean roughness (R_a) of the surface, height of the domes and number of domes per area were estimated by using the Gwyddion 2.43 software.

Water contact angles (WCAs) were measured from optical micrographs taken with a digital photo camera. Samples were stored at closed box for clean storage, and rinsed with methanol and dried in compressed air before WCA measurements. WCAs were acquired from 4 μl water droplet at three different locations on each sample and the obtained values were averaged.

Diffuse reflectance spectra of the coated glass slides were measured with Cary 5000 UV–Vis-NIR spectrophotometer. Some artefacts present in the spectra were further reduced by normalizing against the known reflectance of uncoated glass slide measured for reference.

Complementary light scattering measurements were conducted on a home-built automated goniometric system in the reversed Kretschmann [26]. A laser beam was perpendicularly incident on the coated glass slide which was attached to a semicylindrical prism (using an index-matching oil). The angular dependence of the forward scattered light emerging from the prism was measured with a photodiode. Such configuration allowed a more direct assessment of the coated front surface by eliminating the reflections from the back surface. The results for *s*- and *p*-polarized light were averaged to obtain effectively the response for unpolarized light.

3. Results and discussion

3.1. Formation of SiO_2 structures

Depending on synthesis conditions, it was possible to obtain structured silica surfaces with vastly different dome sizes (diameters 50 nm–3 μm), shapes and surface densities seen in Figs. 1 and 2. Representative characteristics of samples are presented in Tables 1 and 2.

The processes that lead to the formation of the round coating elements have been discussed in our earlier studies [23,24]. In general, the thermodynamical balance in the sol is interrupted by solvent evaporation and condensation of partially hydrolyzed TEOS. This activates nucleation and growth of dispersed TEOS-rich domains, which deposit on the glass substrate. It is necessary to point out that the studied case is significantly different from phase separation in thicker layers that produces porous films [20,27] as the deposited sol is in all of its volume affected by the vicinity of either substrate-sol or sol-air interface [28]. In addition, as the precursor was applied by spraying in the present work then the results were also different compared to earlier studies where structured surfaces were obtained by spin-coating [23,24]. The total surface area of the precursor is maximized in aerosol phase, leading to significant increase in solvent evaporation and exposure to air humidity. While the solvent concentration can be adjusted so that the sol is liquid (i.e. not gelled) when it reaches the substrate, the hydrolysis and condensation of TEOS is inevitably faster and more sensitive to ambient environment than in the case of spin-coating. Also, as the substrate is not rotated with spraying, imperfect spreading of the sol can in some cases

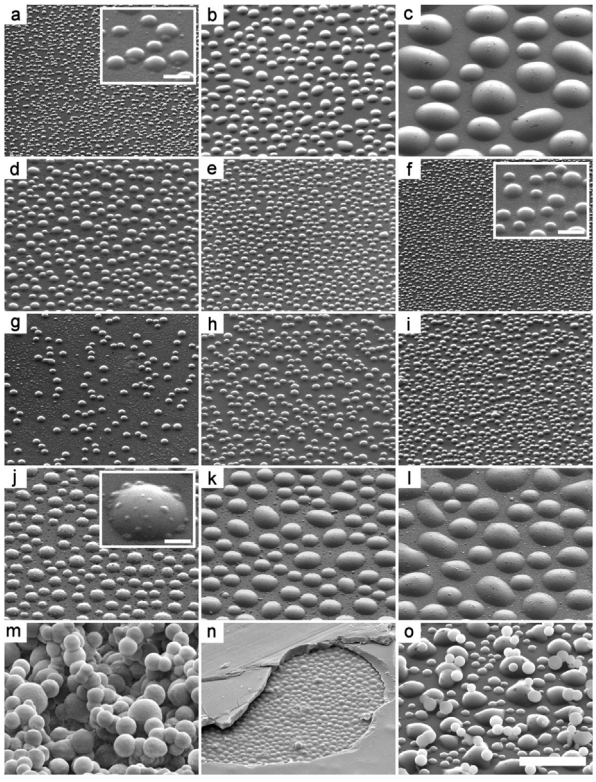

Fig. 1. SEM micrographs of representative structured silica surfaces on glass substrate obtained upon the following choice of sol and spray parameters: A = 35 μl, 55 μl, 75 μl (a–c); T = 10, 15, 20 (d–f); R = 0.5, 1, 1.5 (g–i); K = 0.05, 0.1, 0.2 (j–l). Silica surfaces formed at borderline conditions: macroporous film with T = 1 (m); two-layered structure with R = 2 (n); domes with K = 0.2 at concentration T = 10 (o). The length of the scale bar is 5 μm (for inset 400 nm).