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Template-free sol–gel preparation of nanoporous ORMOSIL films with adjustable refractive index

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ABSTRACT

A nanoporous organically modified silicate (ORMOSIL) film with adjustable refractive index from 1.21 to 1.10 was prepared at room temperature *via* a template-free sol–gel method, using tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as co-precursors and hexamethylisilazane (HMDS) as surface modifier. Heating the ORMOSIL film, the refractive index of the ORMOSIL film can be further decreased to as low as 1.07. This adjustable refractive index thin film can find potential application in optical and microelectronic fields.

1. Introduction

Ultralow refractive index (n) films are increasingly in demand for optical applications such as antireflection coatings, optical resonators, and photonic crystals [1–3]. Since the readily available dense materials with low n are limited to 1.35 (MgF_2), nanoporous materials are appropriately designed to achieve a very low n *via* introducing nanopores into their skeleton. Up to now, many approaches have been explored to create nanoporous films with a low n. Early nanoporous films were achieved by phase separation of polymers [4] and chemical etching [5]. However, the use of some environmentally hazardous solvents or corrosive etchants is a main disadvantage for large-scale applications. Xi and coworkers utilized oblique-angle deposition to create an array of silica nanorods films with n as low as 1.05 [6], whereas the complicated fabrication process results in a high production cost.

Sol–gel method appears attractive in fabrication of nanoporous films because of its ability to independently tailor the microstructure and chemical composition of the deposited films. A now well-developed sol–gel approach to prepare low n silica coatings consists in creating porosity through the use of sacrificial organic templates [7]. However, the post-synthetic removal of the templates can be costly, wasteful, and of environmental concern. Clearly, this problem would be easily overcome if the nanoporous coatings could be prepared in the absence of auxiliary organic templates.

Here, we report a template-free sol–gel method to prepare nanoporous organically modified silicate (ORMOSIL) thin films. Using methyltriethoxysilane (MTES) and tetraethoxysilane (TEOS) as co-precursors and hexamethylisilazane (HMDS) as surface modifier, we obtained an ORMOSIL film with adjustable n from 1.21 to 1.10 at room temperature. The refractive index of the ORMOSIL film can be further decreased to as low as 1.07 by heating the film. The method is very economical and environmental, and allows us to flexibly tailor the n of target films from 1.21 to 1.07.

2. Experimental

The preparation process of the ORMOSIL films is described as follows. First, ORMOSIL sols were prepared following a procedure we reported previously [8]. EtOH, H_2O, $NH_3 \cdot H_2O$, MTES and TEOS were consecutively added into a glass bottle and then stirred at 30 °C for 2 h. The molar ratio of (MTES+TEOS):H_2O:EtOH:NH_3 was 1:3.25:37.6:0.17. After aging at 25 °C for 20 days, the sols were diluted with an equivalent amount of EtOH. HMDS was then added into the above diluted sols, and aged at 25 °C for 7 days. The weight ratio of HMDS to silica was 1.5. All sols were deposited on silicon wafers by dip-coating at a constant withdrawal rate of 0.5 cm/s, and then heat-treated to different temperatures in the range of 25–600 °C in air for 2 h. The sols and their corresponding coatings were named with abbreviations, for instance, M1.0

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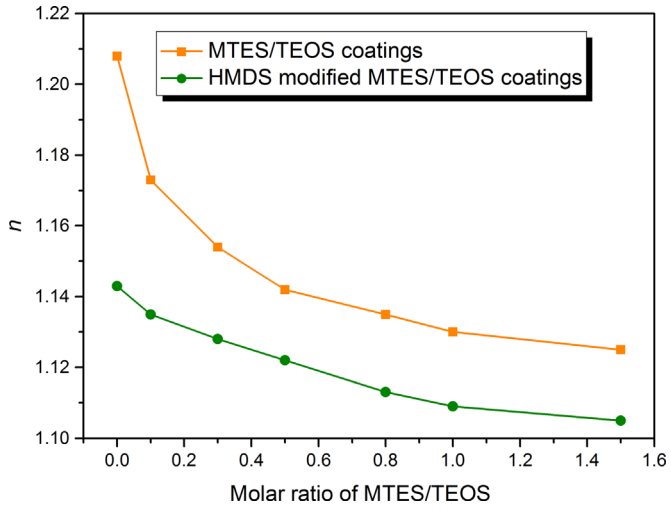

Fig. 1. The refractive indices (n) of the as-deposited MTES/TEOS films before and after the modification of HMDS versus the molar ratio of MTES/TEOS.

indicated sol or coating with MTES/TEOS = 1.0 and HM1.0 for coating derived from the HMDS modified M1.0 sol.

The refractive indices and thicknesses of films were measured using an ellipsometer (HORIBA Scientific UVISEL). The morphology of the silica sols were analyzed using a transmission electron microscope (TEM, FEI Tecnai G2 F20).

3. Result and discussion

Fig. 1 shows the refractive indices of as-deposited ORMOSIL films versus the molar ratio of MTES/TEOS. As the molar ratio of MTES/TEOS increases over the range of 0 – 1.5, the refractive index of MTES/TEOS films decreases rapidly at first, and then approaches a value of 1.12 slowly, while that of HMDS-modified MTES/TEOS films decreases approximately linearly from 1.14 to 1.10.

These variations in refractive indices were determined by both the morphology and the chemical compositions of the silica particles in the sols and the corresponding films. Fig. 2a shows that the pure silica sol is composed of independent silica particles, whereas along with the increase of molar ratio of MTES/TEOS, the discrete silica particles gradually transform into particle chains or rings (Fig. 2b and c). Moreover, during the film deposition with this pure silica sol, the capillary force resulting from the evaporation of pore fluid during drying promotes volume shrinkage of the film and continued condensation between –OH species on adjacent silica particles. A large amount of Si–O–Si bonds formed between particles results in an irreversible drying shrinkage of the film [9].

Incorporating methyl groups on the silica particles by MTES leads to a further aggregation among silica particles with the ultimate formation of a three-dimensional network (Fig. 2b and c). During the corresponding ORMOSIL films deposition, the flexible particle chains or rings could resist, to some extent, the capillary force and thus the network collapse, just like a cushion. In addition, the introduction of non-hydrolyzable $-CH_3$ species would significantly reduce the formation of Si–O–Si bonds between the residual –OH species, hence the shrinkage induced by capillary tension is somewhat reversible and potential to “spring-back” due to the repulsive interactions among hydrophobic $-CH_3$ moieties as the tension is released upon drying [10]. Since the quantity of the introduced $-CH_3$ species is limited by the maximum ratio of MTES/TEOS used, surface modification to the sol particles with HMDS

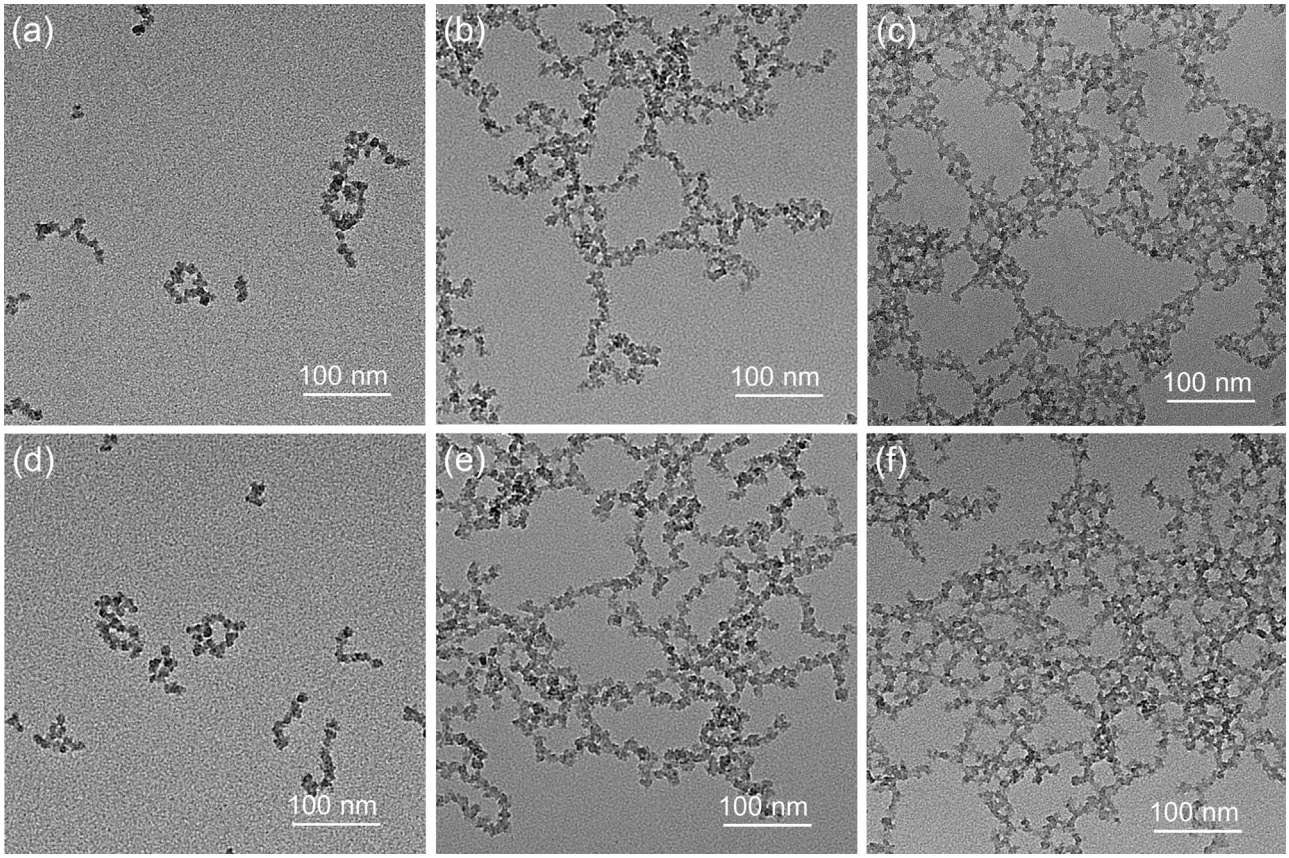

Fig. 2. TEM images of different silica composite sols. (a) M0, (b) M0.8, (c) M1.5 and (d) HM0, (e) HM0.8, (f) HM1.5.