Thermally Stable Antireflective Coatings Based on Nanoporous Organosilicate

Suhan Kim[1], Jinhan Cho[2], Kookheon Char[1,*]

[1]School of Chemical and Biological Engineering & NANO Systems Institute - National Core Research Center (NCRC), Seoul National University, Seoul 151-744, Korea
[2]School of Advanced Materials, Kookmin University, Chungneung-dong, Songbuk-gu, Seoul 136-702, Korea
kdhong@silla.ac.kr

Introduction

Nanoporous materials have recently been studied for the application to antireflective coatings (ARC), since nanoporous films can achieve the refractive index as low as 1.230, which is theoretically required to achieve the zero reflectance on a glass. To realize antireflection, porous layers prepared by nanoporous multilayer[1,2], polymer blends[3] and silica particle coating[4,5] were applied. However, these approaches have limitations in mechanical and thermal stability as ARC. In present study, nanoporous organosilicate thin films were fabricated for the antireflective coating, since nanoporous organosilicate films have good adhesion on glasses and good thermal stability over 400 °C. Nanoporous organosilicate thin films were realized by the microphase separation of pore generating components mixed with an organosilicate matrix. The refractive index of such nanoporous organosilicate films was controlled in the range of 1.390 ~ 1.225. Optical properties of prepared nanoporous organosilicate films were also tested toward the application to antireflective coating. With a nanoporous single layer with n ~ 1.225, 99.85% transmittance in the visible range was achieved. In order to overcome the limitation on the narrow wavelength for high transmittance imposed by the single nanoporous films, bilayer films with different refractive indices in each layer were prepared. Optical properties of nanoporous bilayer films thus prepared were compared with nanoporous single layer films and it is demonstrated that the novel broadband antireflective coatings with improved transmittance can be easily achieved by the nanoporous bilayer films.

Experimental

Materials A poly(methyl silsesquioxane) (PMSSQ) copolymer used as a matrix material to realize nanoporous thin films was synthesized by the sol-gel reaction with methyltrimethoxysilane (MTMS, Aldrich) and 1,2-bis(trimethoxysilyl)ethane (BTMSE, Aldrich).[6,7] The feed ratio of MTMS and BTMSE was 90/10 by mol%. A tetra-functional block copolymer (Tetronic 150R1, BASF) was used as a pore generating material (porogen). For the broadband antireflective bilayer films, tetraorthosilicate (TEOS, Aldrich) 90 mol% and MTMS 10 mol% were copolymerized.

Film preparation The PMSSQ copolymer was mixed with 0, 20 and 40 wt% of porogens in methyl isobutyl ketone (MIBK). Concentrations of prepared solutions of the matrix/porogen were varied from 4.5 to 9.0 wt% to change film thicknesses. Solutions were spin-coated on glasses at 3000 rpm for 30 seconds. For the development of nanopores, spin-coated films were calcined at 420 °C for 1 hour. In order to prepare bilayer films, an organosilicate copolymer for high refractive index was first spin-coated on a glass and cured at 200 °C. Then, a solution of the matrix/porogen was spin-coated on the cured high refractive index layer and calcined at 420 °C for 1 hour.

Results and discussion

UV-vis transmittance for glasses spin-coated by nanoporous films was investigated, as shown in Figure 1. UV-vis transmittance gradually increases with the decrease in the refractive index of nanoporous films when compared with the glass. At 40 wt% porogen loading, which leads to a refractive index of 1.225, the maximum transmittance of 99.85 % is achieved.

However, single layered ARC films have the limitation that high transmittance can be obtained only in the narrow wavelength range. In order to overcome the limitation imposed by the single nanoporous films, bilayer films with different refractive indices were prepared by placing a high refractive index layer at the bottom, which has a refractive index of 1.447 and a film thickness of 86 nm.

UV-vis transmittance of a bilayer ARC film was measured and compared with the single layer ARC film, as shown in Figure 2. Although the bilayer ARC film shows the maximum transmittance of 99.38, which is slightly lower than that of the single layer ARC film, the bilayer ARC film yields novel broadband antireflection with 98% or higher in transmittance at wavelengths ranging from 400 to 900 nm.

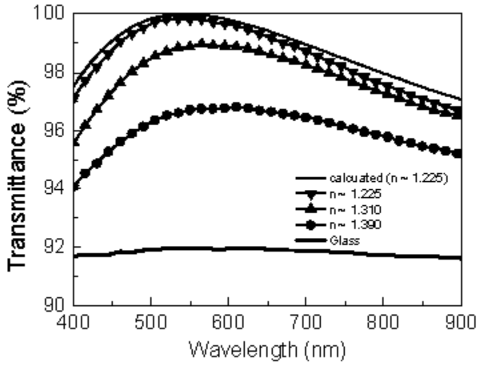

Figure 1. UV-vis transmittance of glasses coated by nanoporous films with different refractive index.

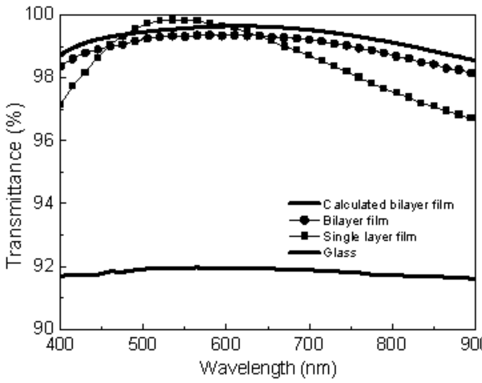

Figure 2. UV-vis transmittances of single layer and bilayer ARC films.

Conclusion

Nanoporous organosilicate films were prepared by the microphase separation between an organosilicate matrix and a pore generating material. The refractive index of the prepared nanoporous films can be lowered to 1.225 by incorporating nanopores within the matrix. Glasses coated by nanoporous organosilicate films show the maximum transmittance of 99.85%. The wavelength of maximum transmittance can be varied with different film thickness by changing the solution concentration. Broadband antireflective coatings were achieved by organosilicate bilayer films with a different combination of refractive indices and film thicknesses.

References

[1] Hiller, J.; Mendelsohn, J. D.; Rubner, M. F. *Nat. Mater.* **2002**, 1, (1), 59.
[2] Nolte, A. J.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2004**, 20, (8), 3304.
[3] Walheim, S.; Schaffer, E.; Mlynek, J.; Steiner, U. *Science* **1999**, 283, (5401), 520-522.
[4] Hattori, H. *Adv. Mater.* **2001**, 13, (1), 51.
[5] Zhang, X. T.; Sato, O.; Taguchi, M.; Einaga, Y.; Murakami, T.; Fujishima, A. *Chem. Mater.* **2005**, 17, (3), 696.
[6] Kim, S.; Toivola, Y.; Cook, R. F.; Char, K.; Chu, S. H.; Lee, J. K.; Yoon, D. Y.; Rhee, H. W. *J. Electrochem. Soc.* **2004**, 151, (3), F37-F44.
[7] Toivola, Y.; Kim, S.; Cook, R. F.; Char, K.; Lee, J. K.; Yoon, D. Y.; Rhee, H. W.; Kim, S. Y.; Jin, M. Y. *J. Electrochem. Soc.* **2004**, 151, (3), F45-F53.