

OPTICAL PROPERTIES OF HYBRID MATERIALS OF SILICA AND SILSESQUOXANES

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ABSTRACT

Optical properties of materials are very important for many applications. One example is optical computing where photons replace electrons so that the computation speed can be further improved. Optical materials of different refractive index are needed to control the flow of photons. In this paper, the method of creating inorganic-organic hybrid materials was explored to generate materials of different optical properties. Sol gel chemistry was used to synthesize hybrid materials through the copolymerization of inorganic and organic precursors. The study focused on the understanding of the governing principles of the optical properties of the hybrid materials.

Keywords: molecular composite, hybrid material, optical property.

1 INTRODUCTION

In optical computing, electrons in a computer are replaced by photons so that the computation speed can be further improved. Silicon dioxide has been used in optical fibers for digital signal transmission because of its excellent low chromatic dispersion and thus low signal loss. Silicon dioxide is, therefore, an obvious candidate for the optical computing application. However, in order to create optical analogues of electric circuitry and switches, materials of different optical properties are needed to control the photons. In the construction of optical computing devices, polymers are good candidates because of their ease of processing. However, it is known that the optical properties of polymers are limited. One method of expanding the optical properties of polymers and silicon dioxide is through the construction of hybrid materials where materials of better optical functionalities are incorporated to allow the realization of new optical properties that are not achievable using silicon dioxide and polymers alone. The change of optical properties can be realized through the incorporation of organic chromophores into silica or polymers¹ and nanoparticles² of inorganic materials into polymers. In this paper, the increase of refractive index of the base material, silicon dioxide, will be discussed. The control of other optical properties such as the lowering of refractive index, absorption or birefringence, can also use similar approaches. The understanding of the governing principle of refractive index by the composition of hybrid

materials will be valuable in realizing the material by design.

The prediction of optical properties is a longstanding effort. Theoretically, Maxwell's equation can be used for the calculation. The requirement of the precise electromagnetic properties of the material makes the calculation difficult.³ Based on this theory, Lorentz and Lorenz proposed the correlation between molar polarization and molecular polarization. This correlation was used as the basis for the group contribution theory in the prediction of optical properties of polymers.⁴ The group contribution theory applies for single molecule or functional groups that are covalently bonded. When two or more different molecules are mixed together, a composite is formed. The prediction of composite refractive index is generally treated using effective medium models.⁵ The Maxwell-Garnett's theory and improved Bruggeman's theory were used to model the effective electric permittivity of heterogeneous media comprising mono- or poly-dispersed spheres or two intermixing phases.⁶ Volume average theory (VAT) was used to calculate the effective dielectric properties by applying Maxwell's equation.⁷ Parallel and series models were used for structures of two alternating parallel nanophases; but also were believed to set the upper and lower limits on the composite refractive index.^{8,9} Figure 1 shows that volume average model gives the highest composite index while serial model predicts the lowest composite index.

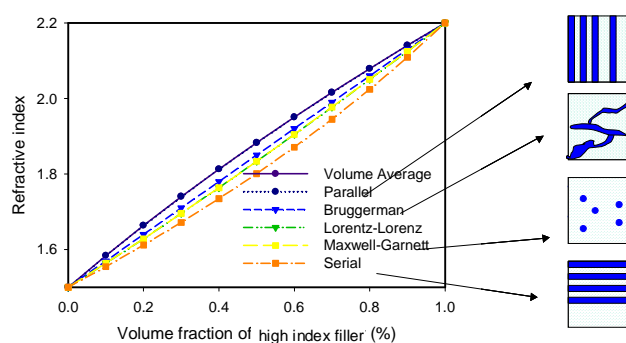


Figure 1. Composite refractive index vs. the volume fraction of high index component assuming that the low index material has a refractive index of 1.5 and the high index material has a refractive index of 2.2.¹ (courtesy of ACS)

In this paper, thin films of hybrid materials were fabricated. The compositions of the hybrid materials were varied systematically. The optical properties of these films were investigated. This study sheds light on new design rules of novel optical materials.

2 EXPERIMENTAL

2.1 Synthesis of molecular composites of copolymers of silica and silsesquioxane

Phenyltrimethoxysilane (Ph TMS), (3-glycidoxypropyl)trimethoxysilane (Glycidoxypropyl TMS), p-methoxyphenyltrimethoxysilane (MethoxyPh TMS), cyclohexene ethyltrimethoxysilane (Cyclohexene ethyl TMS), methyltrimethoxysilane (Methyl TMS), allyl trimethoxysilane (Allyl TMS), and tetraethyl orthosilicate (TEOS) were obtained from Gelest and Aldrich, and unless otherwise indicated, they were used as received. Denatured 95% ethanol was obtained from Fisher. Concentrated nitric acid, obtained from Aldrich, was diluted to 0.01N with deionized water.

A 20-mL glass vial was charged with ethanol and TEOS, and 0.01N HNO₃ was added. This mixture was stirred with a magnetic stir bar for approximately 1 hour at room temperature. The trimethoxy silane monomer of different organic functional group was added at a predetermined ratio. The mixture was stirred at least overnight at room temperature. During the reaction, the alkoxy silane groups are first hydrolyzed and then condensed to form Si-O-Si bond. The siloxane that is formed from trimethoxy silane with organic functional group is called silsesquioxane. For example, the reaction of Methyl TMS yields methyl silsesquioxane (Methyl SSQ). The sol was diluted to ~4% solids (0.85mL diluted to 10mL) with ethanol before coating.

2.2 Thin film Fabrication

The above solutions were coated on bare Si wafers at a predetermined spin rate using a spin coater from Headway Research Inc. The coating was subsequently cured on a hotplate at 240 °C for 1 min. The typical thickness of the film is about 50 nm.

2.3 Characterization Methods

Refractive index and film thickness were measured by an ellipsometer. (VUV-VASE Model VU-302 with WVASE 32JA Woollam Corp. Nebraska). The refractive index measurement has a standard deviation of 0.004. All these materials have excellent transparency and no absorption.

The morphology was studied by AFM. Topography and phase images were captured at ambient temperature by

using a Digital Instruments (now Veeco) Multi-Mode AFM equipped with a NanoScope IV controller.

3 RESULTS AND DISCUSSION

Morphology of Molecular Composites of Copolymers of Silica and Silsesquioxane

All the molecular composites were shown to be homogeneous by both AFM and TEM. (Figure 2) There is no separate domain larger than 1 nm.

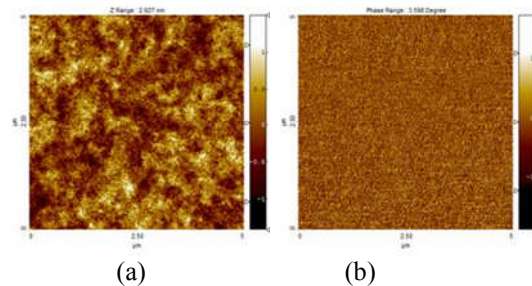


Figure 2. AFM image of a copolymer of silica and silsesquioxane; (a) topological image (the highest depth is 1nm); (b) phase image

3.1 Optical Properties of Molecular Composites of Copolymers of Silica and Silsesquioxane

Table 1 shows the refractive index of a series of copolymers of Glycidoxypropyl TMS and TEOS. The mole percent was calculated assuming all the alkoxy groups were hydrolyzed and condensed. The volume percent was calculated assuming the density of silsesquioxane polymer was 1.5 g/cm³ and that of silica was 2.0 g/cm³. The changes in the assumption of crosslinking degree and densities can affect the output value but does not change the correlation between the mol% vs refractive index, and vol% vs. the refractive index. All the other calculations are made under the same assumption.

Table 1. Refractive index of copolymers of Glycidoxypropyl TMS and TEOS (mol% and vol% in the table are the mole percent and volume percent of glycidoxypropyl silsesquioxane in the final film; same definition was used for the rest of the paper)

Glycidoxypropyl Silsesquioxane		Refractive index at 632nm
mol%	vol%	
0	0	1.405
12	34	1.435
30	61	1.452
46	76	1.469

Table 2 shows the refractive index of a series of copolymers of Cyclohexene ethyl TMS and TEOS. Similarly, Table 3, Table 4, and Table 5 show the changes

of refractive indices with the amount of allyl silsesquioxane, phenyl silsesquioxane and methoxyphenyl silsesquioxane respectively.

Table 2. Refractive index of copolymers of Cyclohexene ethyl TMS and TEOS

Cyclohexene ethyl Silsesquioxane		Refractive index at 632nm
mol%	vol%	
0	0	1.405
12	32	1.436
29	59	1.468
45	74	1.477
57	83	1.488

Table 3. Refractive index of copolymers of Allyl TMS and TEOS

Allyl Silsesquioxane		Refractive index at 632nm
mol%	vol%	
0	0	1.405
7	14	1.420
19	33	1.466
32	49	1.473
43	61	1.504
100	100	1.461

Table 4. Refractive index of copolymers of Phenyl TMS and TEOS

Phenyl Silsesquioxane		Refractive index at 632nm
mol%	vol%	
0	0	1.405
10	24	1.445
25	48	1.479
39	65	1.498
51	75	1.512
100	100	1.548

Table 5. Refractive index of copolymers of Methoxyphenyl TMS and TEOS

Methoxyphenyl Silsesquioxane		Refractive index at 632nm
mol%	vol%	
0	0	1.405
12	32	1.453
29	59	1.474
44	74	1.503

3.2 Governing Principle of the Optical Properties of Different Hybrid Materials

The silsesquioxanes used to form the copolymers with silica were selected based on the potential of refractive index increase. According to the group contribution theory⁴, the functional groups of high electric and magnetic permeability can increase the refractive index. In this study, polar bonds of C-O in glycidoxy and C=C-C in allyl, cyclohexene, phenyl and methoxyphenyl were studied. It is observed from Table 1 to 5 that the refractive

index of the formed molecular composite increases with the amount of added silsesquioxane polymer.

Figure 3 and Figure 4 are plots between the refractive index and the composition dictated by mole percent and volume percent of the phenyl silsesquioxane respectively. These two figures clearly indicate that there is a linear correlation between the refractive index and the volume fraction of the phenyl silsesquioxane in the molecular composite. The linear correlation between refractive index and the volume fraction of the component agrees with Maxwell-Garnett's theory shown in Figure 1 (yellow line). This is consistent with the fact that no phase separation was observed in the molecular composite.

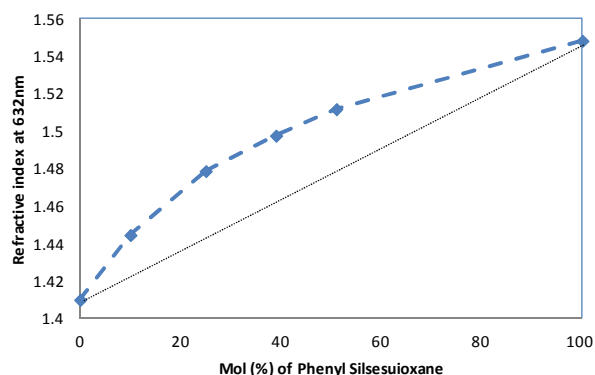


Figure 3. Plot of refractive index vs. mol% of phenyl silsesquioxane in a copolymer of phenyl silsesquioxane and silica.

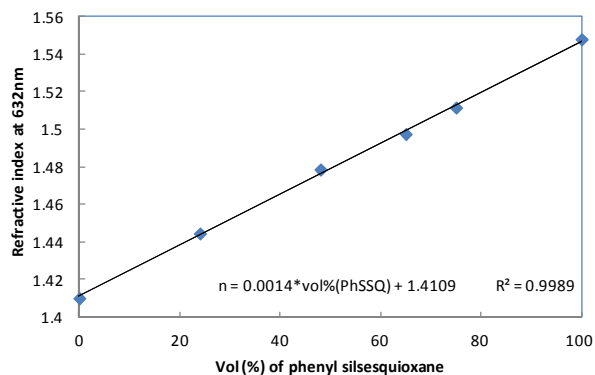


Figure 4. Plot of refractive index vs. vol% of phenyl silsesquioxane in a copolymer of phenyl silsesquioxane and silica.

Indeed, an excellent linear correlation is present between the volume fraction of the component and refractive index in the molecular composites between Glycidoxypropyl SSQ, Cyclohexene ethyl SSQ, Phenyl SSQ, Methoxyphenyl SSQ and silica. They can be normalized and fit into one curve as shown in Figure 5.

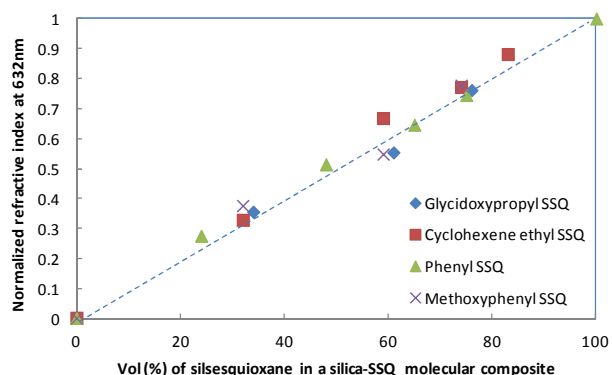


Figure 5. Linear correlation between the refractive index of the molecular composite and the volume fraction of the components for different organic functional groups.

Further, copolymers of two silsesquioxanes, Methyl SSQ and Allyl SSQ, were synthesized. When the refractive indices of the composites are plotted against the volume fraction of Ally SSQ, it is observed that the composite refractive index is no longer linearly correlated with the volume fraction of the component. Rather, as shown in **Figure 6**, the composite refractive index is lower than that is predicted. The cause of this behavior is still under investigation.

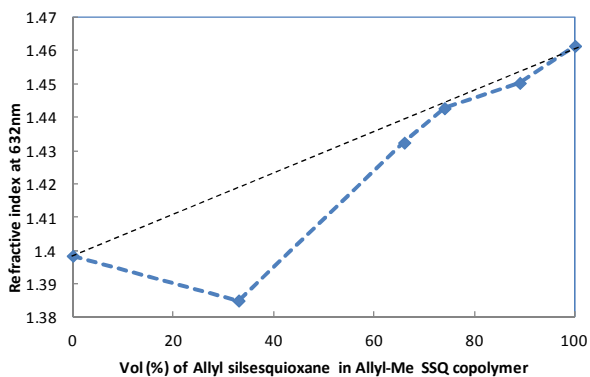


Figure 6. Plot of refractive index vs. vol% of Allyl silsesquioxane in a copolymer of Me silsesquioxane and Allyl silsesquioxane

4 CONCLUSION

The optical properties of a class of organic-inorganic hybrid materials were studied. The hybrid materials are synthesized through the copolymerization of tetraalkoxy silane and trialkoxy silanes of different organic substitute groups. The composition of the hybrid materials were varied from inorganic component rich to organic component rich. It was found that no phase separation of larger than 1 nm could be detected by AFM and TEM. This led to the belief that molecular composites were formed. Five different trimethoxysilanes, glycidoxypropyl trimethoxysilane, ally trimethoxysilane, cyclohexene ethyl trimethoxysilane, phenyl trimethoxysilane and

methoxyphenyl trimethoxy silane, were studied as the organic component of the hybrid materials. It was found that there is a linear correlation between the refractive indices of the molecular composites and the volume fraction of the components. This agrees with the prediction of Maxwell-Garnett's theory, which considered the material comprises monodispersed, nanosized spheres arranged in a cubic lattice structure. However, in a molecular composite made of allyl silsesquioxane and methyl silsesquioxane, the composite refractive indices were observed to be lower than that predicted by Maxwell-Garnett's theory. Further investigation to explain this behavior is undergoing.

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REFERENCES

1. Rao, Y.; Chen, S., Molecular Composites Comprising TiO₂ and Their Optical Properties. *Macromolecules* **2008**, *41* (13), 4838-4844.
2. Rao, Y.; Antalek, B.; Minter, J.; Mourey, T.; Blanton, T.; Slater, G.; Slater, L.; Fornalik, J., Organic Solvent-Dispersed TiO₂ Nanoparticle Characterization. *Langmuir* **2009**, *25* (21), 12713-12720.
3. Born, W., *Principles of Optics*. Cambridge University Press: Cambridge, 2001.
4. Krevelen, D. W. v., *Properties of Polymers*. Elsevier: New York, 1997.
5. Gehr, R. J.; Boyd, R. W., Optical Properties of Nanostructured Optical Materials. *Chemistry of Materials* **1996**, *8* (8), 1807-1819.
6. (a) M. Garnett, J. C., *Philos. Trans. R. Soc. London* **1904**, *203*, 385; (b) Boyd, R. W., *Nonlinear Optics*, Elsevier: 2003; (c) Bruggeman, D. A. G., *Ann. Phys. (Leipzig)* **1935**, *24*, 636.
7. Rio, J. A. d.; Zimmerman, R. W.; Dawe, R. A., *Solid State Commun.* **1998**, *106*, 183.
8. Garahan, A.; Pilon, L.; Yin, J.; Saxena, I., *Journal of Applied Physics* **2007**, *101*, 014320.
9. Bottcher, C. J. F., *Theory of Electric Polarisation*, Elsevier: New York 1952.