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Low dielectric property of novel mesoporous silica/polymer composites using smart molecular caps: Theoretical calculation of air space encapsulated inside mesopores

Norihiro Suzuki [a], Shosuke Kiba [b], Yusuke Yamauchi [a,c,*]

[a] World Premier International (WPI) Research Center for Materials Nanoarchitechtonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[b] Toyota Tsusho Corporation, 3-8-1 Marunouchi, Chiyoda, Tokyo 100-8320, Japan
[c] Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

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ABSTRACT

Here we demonstrate the fabrication of novel mesoporous silica/polymer composites using smart molecular caps and investigate the low dielectric property. For the preparation of mesoporous silica/polymer composites, the entrance of the mesopores are firstly modified by polysilsesquioxane (POSS) molecules. The large-sized POSS molecules can act as smart caps to prevent a penetration of the polymers into the inside mesopores (to keep the air space in the mesopores). After that, trimethylsilyl (TMS) agents are grafted onto silanol groups at the inner mesopores to reduce the polarity. Then, organically modified mesoporous silicas are mixed with epoxy polymers by mechanical processing. Here, various types organically modified mesoporous silica with different amount of the modified POSS molecules are utilized to prepare the composites. From the specific gravity data, it is proved that 20 wt% POSS modification is the best for effective blocking the penetration of the polymer into the mesopores. In this composite, lots of air space can remain, showing the excellent low dielectric property. On the other hand, when the POSS modification is less, some polymers penetrate the mesopores at the inner parts of the particles, decreasing the air space. In this paper, we propose new parameter “dead pore ratio” and theoretically discuss how much mesopores maintain as air spaces in the composite, which is an important value for understanding for low-*k* property of mesoporous silica/polymer composites.

1. Introduction

For the achievement of the ubiquitous society, high performance devices to realize large-capacity and high speed communication are required. Such devices should have more complicated circuits to realize much functionality. Therefore, the fine circuit fabrication is indispensable. However, the decrement of wiring cross-section and electric wiring spacing increases the resistance (R) and the capacitance (C), resulting in the RC decay. Because the capacitance between interconnect lines is proportional to the dielectric constant (k), the appearance of the low-k material is highly desired in order to prevent the propagation velocity delay of the signal. One of the main strategies for the development of the low-k materials is introducing many pores into the high-k materials. By containing a large amount of low dielectric air ($k \sim 1$), the k-value is decreased. Such porous materials have already been utilized as the interlayer dielectric insulator in ultra-large-scale integrated (ULSI) circuits [1].

Recently, mesoporous silica materials such as KSW-1 [2], MCM-41 [3], FSM-16 [4], and SBA-15 [5], synthesized using a self-assisted surfactant template, have attracted considerable interests due to their highly ordered and uniform mesoporosity. Mesoporous silica films also have been fabricated by the dip-coating [6] or spin-coating method [6–10]. These low-k mesoporous silica films can meet the requirements of the new dielectric films with low-k value ($k < 2.5$) for the applications in the microelectronics and the insulations. However, owing to the poor processability of the mesoporous silica films, it is difficult to endure them with low-k constant, low moisture uptake and high mechanical strength simultaneously.

Incorporation of the mesoporous silica into the low-k polymer (e.g., polyimide) is also the strategy for obtaining the low-k material [11–13]. Such composite has a very important role in the semiconductor industry because almost all LSI parts, including print circuit boards, connectors, and sensors were made up of organic (polymer)–inorganic (silica) hybrid materials. This composite has

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* Corresponding author at: World Premier International (WPI) Research Center for Materials Nanoarchitechtonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.
E-mail address: YAMAUCHI.Yusuke@nims.go.jp (Y. Yamauchi).

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an advantage over the film mentioned above due to its portability and rigidity, which are essential properties for commercial products. However, because the pore size of incorporated mesoporous silica materials is bigger than that of polymer molecules, several blocking materials should be attached to the entrance side of the mesopores to prevent the entry of the polymer.

Since Mal et al. reported on the encapsulation of MCM-41 using coumarin in 2003 [14], several studies about finely controlled release with "complete" cap at mesopore entrances have been published [15–19]. Though the "complete" cap is useful for drag delivery systems, it is not a suitable cap for achieving low-*k* materials. For further lowering the *k*-value, surface of the pores should be changed to hydrophobic to prevent ingress of vapour and liquid species. Usually, porous silicas have surfaces terminated with polar, hydrophilic silanol groups (Si–OH), which allow the easy adsorption of water ($k \sim 80$). This causes the increment of *k*-value dramatically. For that reason, reaction of the silanol groups with organic species containing terminal methyl groups (e.g., trimethylsilylchloride and hexamethyldisilazane) is well known. If the "complete" caps are attached to the mesopores, methylsilation procedure cannot be conducted.

Therefore, we have focused appropriately-sized smart caps which enable to prevent the penetration of the polymer during the mechanical composite processing and also provide enough space for organic species to access the inner mesopore surface. In our recent work, we have succeeded in preparation of mesoporous silica/polymer composites with low dielectric constant, by utilizing polysilsesquioxane (POSS) as a smart cap at mesopore entrances [20]. The smart caps were preferably grafted nearby the mesopore entrance (Fig. 1). Since the POSS molecule is slightly smaller then the mesopores, they cannot be encapsulated and thereby give rise to small voids. These voids were too small for polymers to penetrate into the mesopores, but were enough size for trimethylsilyl (TMS) agents to go through. Thus, methylsilation was conducted even after attaching POSS molecules.

However, the effect of the grafted POSS amounts on the dielectric constants is still ambiguous. In this paper, we prepared several types of mesoporous silica/polymer composites with different amounts of the POSS molecules and investigated their dielectric constants. In particular, we proposed new parameter "dead pore ratio" to understand how much the mesopores maintain as air spaces in the composite. Through the quantitative estimation of the dead pore ratios, we carefully investigated the proper amount of the modified POSS molecules. Furthermore, by using NMR measurements, we theoretically calculated how much the silanol groups in the original mesoporous silica were grafted by the POSS molecules and TMS agents.

2. Experimental section

2.1. Materials

Mesoporous silica (TMPS) with a 4.0 nm pore diameter was purchased from Taiyo Kagaku Co. Ltd. Tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries Ltd. Polysilsesquioxane (POSS) used as smart caps onto the mesopore entrance was 1,3,5,7,9,11,14-heptaisobutyltricyclo [7.3.3.1(5,11)] heptasiloxane-*endo*-3,7,14-triol, which was obtained from Hybrid Plastics Inc. 1,1,1,3,3,3-Hexametyldisilazane (HMDS) and 2-phenyl 4,

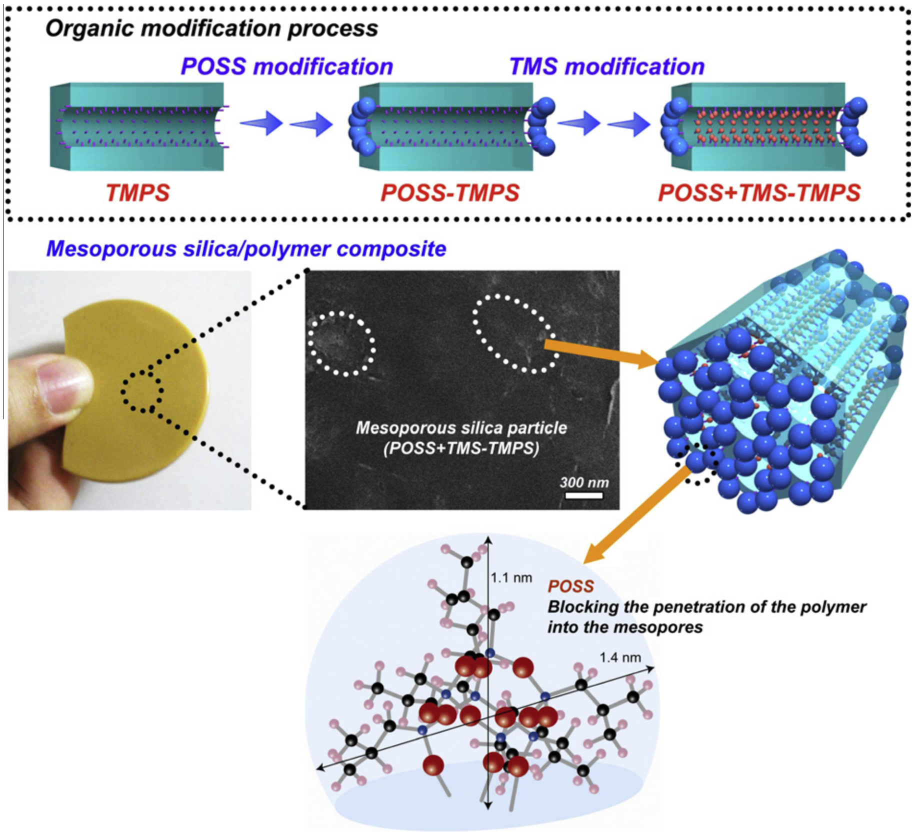

Fig. 1. Schematic presentation of preparation of mesoporous silica/polymer composites. In the chemical structure of the POSS molecule attaching to the TMPS surface, the red, blue, black and purple spheres indicate oxygen, silicon, carbon, and hydrogen atoms, respectively. An estimated size is also noticed. A light blue dome near the POSS molecule is the supposed area where epoxy polymer cannot enter due to the steric hindrance of isobutyl groups. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)