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Ultra low dielectric constant polysilsesquioxane films using $T_8(Me_4NO)_8$ as porogen

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ABSTRACT

A class of ultra low dielectric constant polymethylsilsesquioxane (PMSQ) films with $T_8(Me_4NO)_8$ polyhedral oligomeric silsesquioxanes (T_8 POSS) as double-effective porogen was studied. Through the Me_4NO^- groups of T_8 POSS attacking the Si–O–Si chains of PMSQ, the POSS will be connected to the PMSQ crosslink system. POSS has the cage structure, which acted as the closed pores ($\leq$1.5 nm). On the other hand, the Me_4NO^- groups served as the sacrificial template. When they decomposed after annealing, the open pores were then left in the films. The introduction of T_8 POSS can greatly decrease the dielectric constant of PMSQ, and effectively improve its mechanical strength owing to $T_8(Me_4NO)_8$ interconnected with PMSQ. These continuous and smooth films were prepared by spin-coating with thickness in the range of 60–200 nm. The dielectric constant of the films could be controlled by adjusting the proportion of porogen. These films showed good mechanical strength and ultra low dielectric constant. In particular, a POSS/PMSQ film with ultra low dielectric constant of 1.6 and modulus of 7 GPa had been prepared on silicon wafer by spin-coating.

1. Introduction

To overcome signal delays and crosstalk noise between the metal interconnects within integrated circuits, low dielectric constant (low-k) materials are urgently needed to satisfy the rapid development of semiconductor industry [1]. Ultra low dielectric constant ($k \leq 2.0$) materials can in particular achieve the technology nodes below 90 nm. Nowadays dielectric materials used for integrated circuits normally possess permittivity above 3. Nanoporous sol–gel silication materials with k values in the range of 1.5–2.5 have been obtained [2]. To get lower dielectric constant, organic templates are added to silicate-based materials [3]. However, excessive templates tend to reduce mechanical strength sharply at the curing stage which makes the film modulus lower than the usually considered threshold value for industrially viable low-k dielectrics (6 GPa) [4]. In addition, high porosity makes low-k materials suffer low heat conductivity and hydrophilicity [5].

Studies have shown that tiny nanopores ($\leq$1.5 nm) and highly ordered structures are crucial factors in order to achieve ultra low-k dielectric constant and good mechanical strength [6,7]. Pure silica zeolite films as low-k materials (k about 2.0) have been prepared by sol–gel process and these films have elastic modulus of 16–18 GPa [8–10]. Yet at the same time zeolite has or possesses strong moisture sensitivity. Polysilsesquioxane is a class of popular low dielectric constant materials because of its fair mechanical strength, good heat conductivity, fine cohesion to silicon wafers and low moisture sensitivity. PMSQ films with $k = 2.8$ after annealing at 450 °C have been reported [11,12]. However, the mechanical strength of normal nanoporous polysilsesquioxane can't reach the requirement of semiconductor industry because of the open pore structure [13]. It has also been reported that dielectric constant of material can as well be reduced ($k \leq 2$) and mechanical strength is better with the introduction of polyhedral oligomeric silsesquioxanes (POSS) than that of ordinary templates, but the preparation of low-k films with POSS is quite complicated [14–23].

In this paper, T_8 POSS was used as double-effective porogen to prepare PMSQ films with ultra low-k dielectric constant. POSS had a cage structure, which acted as the closed pores ($\leq$1.5 nm). On the other hand, the Me_4NO^- groups served as the sacrificial template. The T_8 POSS could greatly decrease the dielectric constant of PMSQ, and effectively improved its mechanical strength owing to $T_8(Me_4NO)_8$ interconnected with PMSQ. When heated, T_8 POSS was quite stable and the tetramethylammonium cations were decomposed to create ordered nanopores. The films with those dual function pore formation then showed an ultra low-k value and good mechanical strength.

2. Experimental details

The molar ratio of the synthesis solution was 1 methylsilsesquioxane (MSQ)/17 EtOH/0.2 NH_3/2 H_2O. The clear solution was stirred at 60 °C for 4 h. At the same time, a solution of 1 $T_8(Me_4NO)_8$/150 EtOH was obtained at the same way. The above two solutions were then mixed under stirring at room temperature with different proportions. The mixed solution passed through 0.2 μm polytetrafluoroethylene (PTFE) filters before spun on clean electric Si wafers at 4000 rpm for 30 s at room temperature. Afterwards, the films were prebaked in an

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oven at 60 °C overnight in air, and then placed in a tubular furnace purged with N_2. The films were finally heated up to 450 °C at a rate of 5 °C/min and held at the temperature for 4 h before cooling down slowly.

The schematic of the forming procedure of spin-on POSS/PMSQ films is illustrated in Fig. 1. POSS/PMSQ solution was first prepared. Through the Me_4NO^- groups of T_8 POSS attacking the Si–O–Si chains of PMSQ, the POSS would be connected to the PMSQ crosslink system. During the process, T_8 POSS unchained Me_4NO^- groups (TMAO, the black dots) and meanwhile connected to the PMSQ system. Thin films, in which the nanoparticles of POSS were evenly suspended, were then prepared by spin-coating. At last, the films were cured at 450 °C under N_2 atmosphere. POSS has the cage structure, which acted as the closed pores (≤1.5 nm), and is stable at 450 °C, while the Me_4NO^- groups, which served as the sacrificial templates, will decomposed into $N(CH_3)_3$ and CH_3OH after annealing. The open pores were then left in the films. Considering about Si–O–Si bond angle, T_8 nanostructure is more like a sphericity, so small cubes showed in Fig. 1 were just to give a hint.

^{13}C Nuclear Magnetic Resonance (NMR) spectra and ^{29}Si NMR spectra were recorded on a Bruker Avance 300 spectrometer at room temperature operating at 300 MHz.

The film morphology of surface and section was obtained by a Field Emitted Scanning Electron Microscopy (FESEM). The SEM images were obtained using a LEO-1530VP microscope operating at an acceleration voltage of 5 kV.

Atomic force microscopy (AFM) (SPI3800, Seiko Instruments Inc., Japan) was used to study the surface roughness of the films. The AFM observations were performed within 2 μm × 2 μm areas in tapping mode (TAP300AI, resonant frequency: 300 kHz).

The hardness of the film was measured by Micro Hardness Tester HV-1000. The films with thickness of 5–10 μm were prepared to measure film hardness by a Microhardness Tester. Loading force was controlled by loading strength (500 N) and holding time (10 s) at room temperature (about 20 °C) under 50% humidity.

For dielectric constant measurement, a square about 50 × 50 mm of high purity silver paint with thickness of 5 μm was coated on the film as electrode. The backside of the electric silicon wafer was also covered with sliver layer. The capacitance of the aforementioned metal–insulator–metal structure was measured at frequency of 1 MHz on a HP4145B semiconductor parameter analyzer, and the dielectric constant of the film was then calculated. The film was dried at 110 °C overnight to minimize water adsorption, and kept in a desiccator before capacitance measurement. The capacitance was measured in several areas of the sample, and the k value reported here was an average.

Thermal gravimetric analysis (TGA) was carried out with a PE TGA Thermogravimetric Analyzer at a heat rate of 10 °C/min from room temperature to 800 °C under a continuous air flow.

3. Results and discussion

The ^{29}Si NMR spectra of POSS, PMSQ and POSS/PMSQ powders are shown in Fig. 2. In Fig. 2(a), the single peak at −66 ppm shows the PMSQ film is pure and well hydrolyzed. In Fig. 2(b), three divided peaks ranging from −90 to −110 ppm are assignable to the strong electron withdrawing group of –(Me_4NO). The sample of 20 wt.% T_8 POSS/PMSQ exhibits both the peak of PMSQ at −66 ppm and the

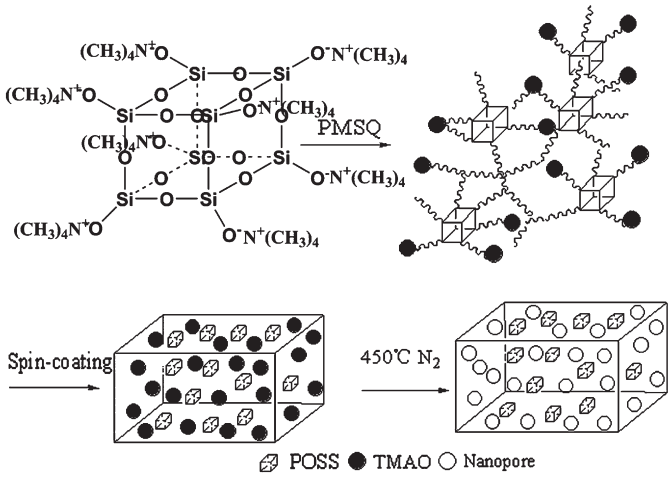

Fig. 1. Schematic of the formation procedure of spin-on POSS/PMSQ films with T_8 nanoparticle suspensions.

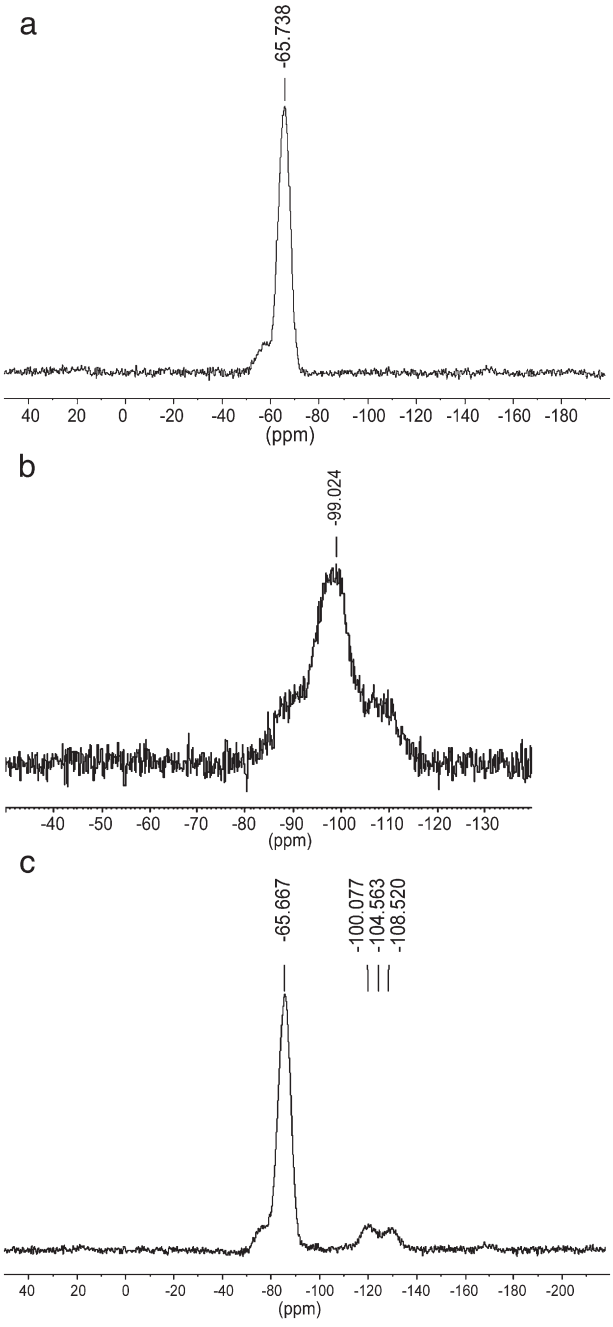

Fig. 2. ^{29}Si NMR spectra of POSS, PMSQ and POSS/PMSQ powders: (a) pure PMSQ without T_8; (b) pure POSS of $T_8(Me_4NO)_8$; (c) T_8 20 wt.% POSS/PMSQ.