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Novel Porous Films Having Low Dielectric Constants Synthesized by a Liquid Phase Silylation of Spin-On Glass Sol for Intermetal Dielectrics

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A novel synthesis of highly porous inorganic SOG films like aerogels using a conventional spin-on processing have been developed. The porous films exhibit low dielectric constants as low as 2.3 and size of pores was about 80 nm. The dielectric constants of the films can be compared with organic polymers, and the films exhibited relatively low hygroscopic characteristics. The novel synthesis of the porous film is a first step to develop nanofoam materials for future low k dielectrics.

1. Introduction

With the shrinkage of feature size of devices into the deep submicron region, interconnect delay caused by a wiring capacitance degrades circuit performances of LSIs(1,2). Integration of low k materials into devices is a key issue for a reduction of wiring capacitance(3). For future LSIs, intermetal dielectrics with low k less than 2 should be needed. Porous materials such as nanofoams have possibilities to realize such low k characteristics. Low density materials such as aerogels show extremely low k characteristics ($\varepsilon<2$)(4). However, these materials have a difficulty for processing due to inevitableness of a drying procedure at supercritical conditions(4). In this paper, we report the novel synthesis of highly porous inorganic SOG films like aerogels using conventional spin-on processing. The porous films formed by a liquid phase silylation of an SOG sol exhibit low dielectric constants as low as 2.2. We proposed a new approach to develop nanofoam materials for intermetal dielectrics for future devices.

2. Experiments

The SOG used in this study was commercially available Tokyo Ohka T10. Silylation of T10 was carried out by the reaction with triphenylsilanol which was added to the SOG solution. The resulting solution was stirred for 1 hour at room temperature. Then the chemically modified SOG solution was applied to a 150 mm diameter Si wafer by a spin coater at the spin speed of 4000 rpm. The coated films were prebaked on a hotplate for 3 min. at 160 ℃. Cure baking was carried out at 400 ℃ for 30 min. in a nitrogen atmosphere. Silylation of SOG sol was confirmed by IR spectral measurements for the coated films. Dielectric constants of the films were calculated from the capacitance at 1 MHz and the film thickness. Thickness of the films was evaluated using a scanning ellipsometry.

3. Results and Discussion

Formation of porous films by a liquid phase silylation of a SOG sol

Triphenylsilanol(TPS) was used for the silylation of a SOG sol. Fig. 1 shows IR spectra of coated films of SOG with no treatments(Fig. 1(a)), and chemically modified SOG before (Fig. 1(b)) and after (Fig. 1(c)) a hotplate baking procedure. As shown in Fig. 1(b), IR spectra of coated films of chemically modified SOG on a Si wafer exhibits absorption peaks due to the triphenlysilyl moieties. The relative intensities of the absorption peak at 1120 cm^{-1} increased in proportion to added amounts of TPS and the absorption peak at 950 cm^{-1} due to silanol groups decreased as shown in Fig. 2. This result indicates that silanol groups of SOG sol were silylated by TPS. These peaks due to triphenylsilyl moieties completely disappears after 160 ℃ 3 min. baking procedure(Fig. 1(c)). SEM photographs of the films silylated with different amounts of TPS after 400 ℃ 30 min. cure baking show highly porous morphologies(Fig. 3). From the FTIR and optical microscopic observations, formation of pores occurs during a hotplate baking procedure at 160 ℃. The results indicate that this low temperature and rapid formation of pores is caused by a desilylation reaction of TPS moieties. And pores did not vanish

after a 400 ℃ cure baking procedure. As shown in Fig. 3(b), at 7.2 $x10^{-4}$ mol of TPS added, pore sizes were about 80 nm and dielectric constant was 2.3.

Dielectric constant reduction by pore formation

Fig. 4 shows a dependence of dielectric constants of porous SOG films upon added amounts of TPS. By increasing added amounts of TPS, the values of dielectric constants were reduced abruptly from 4.5 to 2.2 at $1.1x10^{-3}$ mol TPS (TPS/SiO2 molar ratio 3:20). To investigate the dependence of dielectric constants upon pore sizes, the variations of pore sizes with added amounts of TPS was estimated by SEM observations. As shown in Fig. 3, the films having larger pores shows smaller dielectric constants. This fact clearly indicates that pore formations are essential for the reduction of dielectric constants of the films. This was also supported by the reduction of refractive indices of the porous films caused by TPS addition as shown in Fig. 5. Deterioration of dielectric constants of the porous films by moisture uptake was estimated by exposing porous films to atmosphere. As shown in Fig. 6, during first 90 hours, dielectric constants increased from 2.3 to 2.6(about 13% increase). However, after the period, no changes in dielectric constants were observed for more than 500 hours. From the observation, the porous films have relatively small hygroscopic characteristics. Fig. 7 shows a cross-sectional SEM view of the porous films. Pores shows a discrete structure. So relatively small hygroscopic characteristics of the films can be attributed to the discrete pore structure.

4. Conclusion

A novel synthesis of highly porous inorganic SOG films like aerogels using a conventional spin-on processing have been developed. The porous films exhibit low dielectric constants as low as 2.3 and size of pores was about 80 nm. The novel synthesis of the porous film is a first step to develop nanofoam materials for future low k dielectrics.

5. References

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6. Acknowledgment

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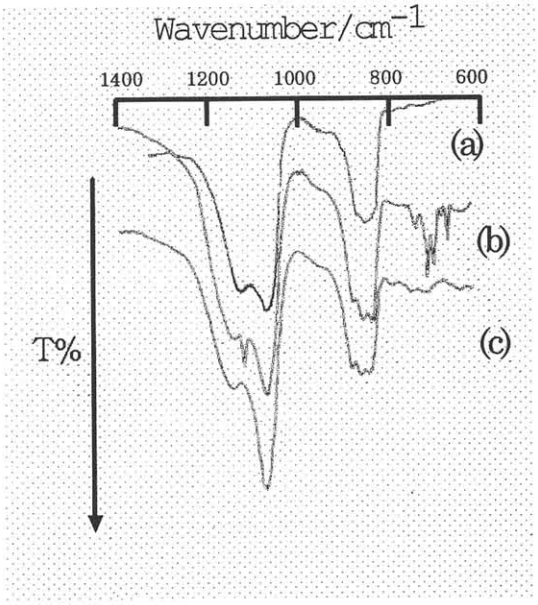

Fig. 1 . IR spectra of coated films.

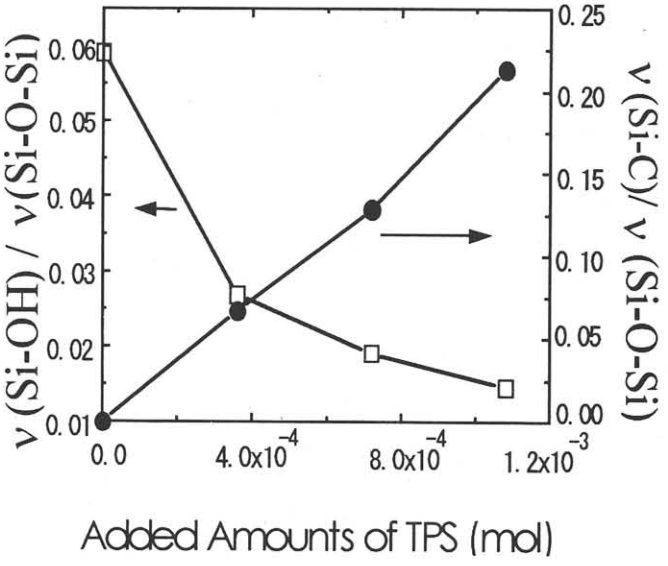

Fig. 2. Dependencies of relative intensities of IR absorption peaks on added amounts of TPS.

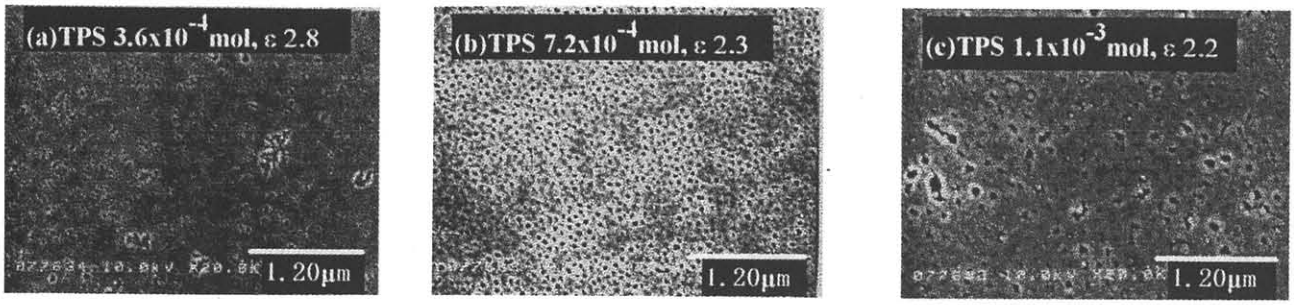

Fig. 3. SEM photographs of the films silylated with different amounts of TPS after 400 ℃ 30 min. cure baking.

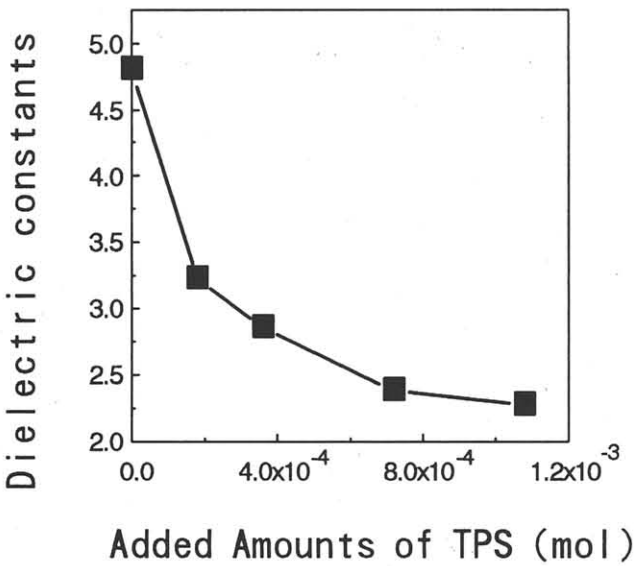

Fig. 4. Dependence of dielectric constants of porous films upon added amounts of TPS.

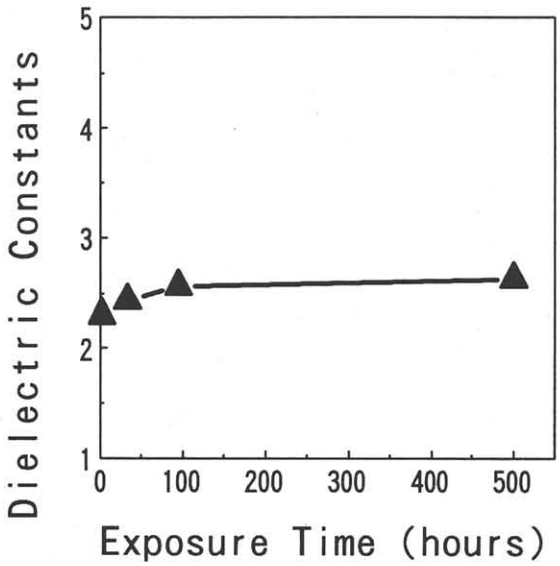

Fig. 5. Time variations of dielectric constants by exposing porous films to atmosphere.

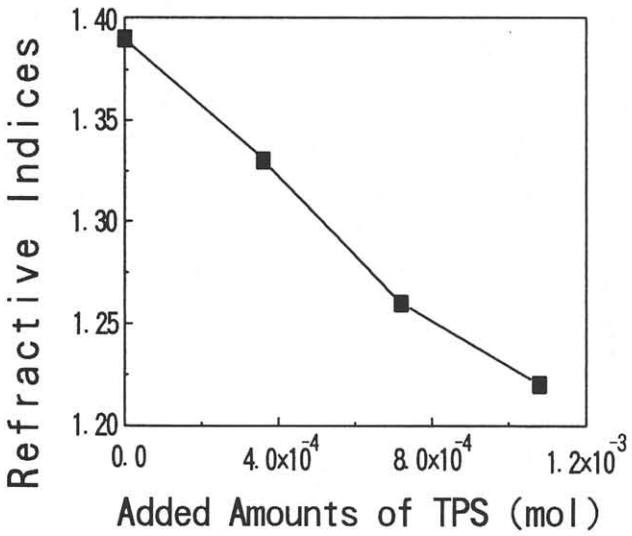

Fig. 6. Dependencies of refractive indices upon added amounts of TPS.

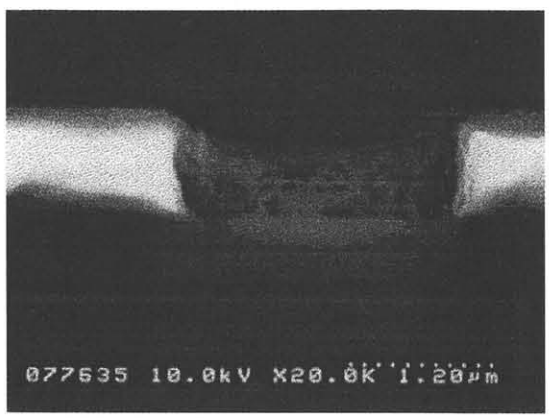

Fig. 7. A cross sectional SEM view of the porous films.