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The dispersion of polymethylsilsesquinoxane into polyimide

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Summary

Through the pretreatment of 4, 4'-oxydianiline(ODA) with polyhydrogenmethylsiloxane (PHMS) using sodium hydroxide as a catalyst and subsequent reaction of this pretreated PHMS-ODA with 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride(BTDA), polysiloxane can be attached to the polyamic acid by the silyl ester bond. By the thermal treatment of this polysiloxane—polyamic acid compound, well dispersed polymethylsilsesquinoxane(PMSQ) into polyimide can be obtained.

Introduction

Owing to the unique properties of polyimide, especially, high temperature resistance and dielectric property, polyimides are useful in the microelectronics industry from fabrication aid to inter level insulator.(1-3) But to use polyimide in electrical application, especially dielectric layer in the multilayer of semiconductor, besides its unique properties, polyimides require some other properties, i. e., no water uptake and good adhesion to the surface of SiO_2 layer, metal, and wafer. These properties reasonably satisfied by the incorporation of silicone block in polyimide main chain.(4 -14) Other method to improve the properties of polyimide is to disperse the silicone compounds in polyimide matrix by the sol-gel process.(15 -19) To disperse the silicone compounds in polyimide matrix by the sol-gel process, tetraethoxysilane should be hydrolyzed in polyamic acid solution, so water and acid must be added during this hydrolysis step.

In this article, we described the method of dispersing polymethylsilsesquinoxane(PMSQ) into polyimide matrix by using polyhydrogenmethylsiloxane(PHMS) as a precursor. By this method, without hydrolysis step we can disperse the PMSQ into polyimide and this material was characterized by Fourier transform-infrared spectroscopy(FT-IR), scanning electron microscopy(SEM), differential scanning calorimetry(DSC) and thermogravimetric analysis(TGA).

Experimental

Materials

The chemicals used were all of commercial-grade quality and purified before use as described in the following: 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride (BTDA), 98%(Aldrich Chemical Co.), was purified by vacuum sublimation. 4, 4'-oxydianiline(ODA), (Wakayama Seika Kogyo Co. Ltd.), was recrystallized from an ethanol-water mixture and dried in a vacuum oven until constant weight. PHMS, Merck, was used without further purification.

Sodium hydroxide, pearl 99%(Hayashi Pure Chemical Industries Ltd.), was used. The solvents, tetrahydrofuran(THF), (Aldrich Chemical Co.), was dried with sodium and N,N-dimethylacetamide(DMAc), anhydrous, 99%(Aldrich Chemical Co.), was used without further purification.

The preparation of BTDA-ODA polyimide

0.02 mole of ODA was placed in an oven-dried round bottom flask equipped with a magnetic stirring bar and 100ml of DMAc and 100ml of THF was added. To this solution, 0.02 mole of BTDA was added as a solid. Subsequently, the flask was flushed with dry nitrogen and sealed. After stirred overnight, this polyamic acid solution was cast onto the glass plates and dried in vacuum oven. The conversion of the polyamic acid film to polyimide was achieved by the heat treatment for 2 hours at 100 °C, 2 hours at 200 °C, 2 hours at 250 °C, and 2 hours at 300 °C.

The conversion of PHMS to PMSQ

The oily PHMS was cast onto the glass plates. The conversion of the PHMS film to PMSQ was achieved by the heat treatment for 2 hours at 100 °C, 200 °C, 250 °C, and 300 °C respectively.

The dispersion of PMSQ into polyimide matrix

0.04 unit mole of PHMS and 0.02 mole of ODA was placed in an oven-dried round bottom flask equipped with a magnetic stirring bar and 100ml of THF was added. To this solution, catalytic amount of NaOH was added as a form of pearl(30 mg, ca. 4 ~ 5 grains). Subsequently, the flask was flushed with dry nitrogen and sealed with septum. As the reaction proceeded, H_2 gas was evolved. To reduce the pressure that was resulted from the hydrogen gas, the gas outlet syringe with a toy balloon was inserted through the septum. After stirred overnight, 100ml DMAc was added and 0.02 mole of BTDA was added as a solid to this solution and the flask was flushed with dry nitrogen. After stirred for 1 day, this solution became very viscous and NaOH grains were discarded by decanting the product polymer solution to other round bottom flask. This polymer solution was cast onto the glass plate and dried in vacuum oven. The heat treatment was same as the case, the preparation of BTDA-ODA polyimide.

Measurements

Fourier transform-infrared (FT-IR) spectroscopy

Infrared spectra were obtained using a Bomem Michelson Series MB 100. PHMS was cast onto the potassium bromide(KBr) pellet. The solution of PHMS-ODA in THF was cast onto the KBr pellet and the solvent was dried in air oven at 80 °C for 5 minutes.

Differential scanning calorimetry(DSC)

DSC measurements were conducted with a Perkin-Elmer DSC 7 under air atmosphere. In order to determine the glass transition, the sample(about 15mg) was heated up to 400 °C with 40 °C/min, then cooled to the starting temperature with 200 °C/min. The second heating curve with 40 °C/min from 100 °C to 400 °C was used for the data determination.

Thermogravimetric analysis(TGA)

TGA of the polymer samples was carried out on a Mettler TG-50 instrument in air. The measurement was performed at a heating rate of 40.0 °C/min. The weight of samples tested was about 15mg.

Scanning electron microscopy(SEM)

All samples were gold coated and examined by a JEOL JSM-6400 scanning electron microscope.

Result and discussion

In a cosolvent, DMAc : THF = 1 : 1, the BTDA-ODA polyamic acid and PHMS gave homogeneous solution. But the solvent was evaporated in forced air oven by the heat treatment, two phase, solid polyamic acid and oily PHMS, was formed. As the curing temperature was higher than 200°C, the oily PHMS converted into the brittle PMSQ by the formation of Si-O-Si bonds in place of the Si-H bonds.(20)

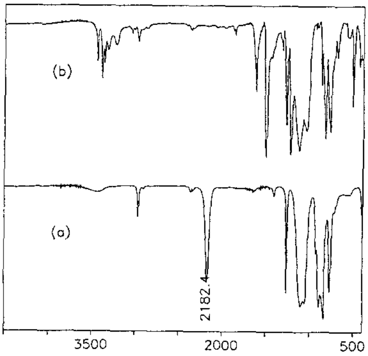
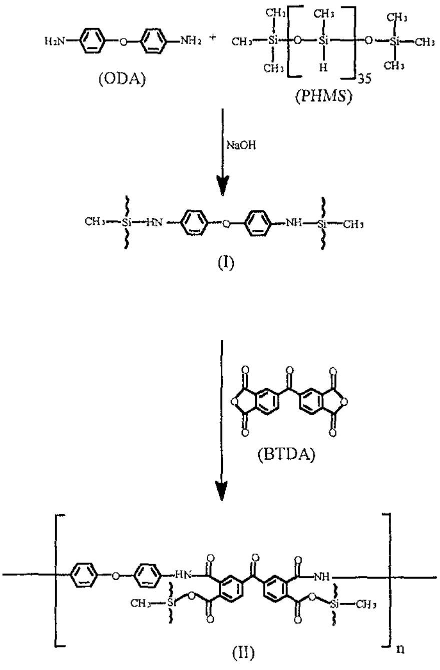


Figure 1. FT-IR spectra of (a) PHMS only (b) reaction product of PHMS-ODA after 5 minutes drying in forced air oven.

As the curing was completed, PMSQ domains were formed under the polyimide matrix, i.e., the dispersion of PMSQ in polyimide matrix could not be achieved. But by the method described in experimental section, the dispersion of PMSQ could be achieved. When ODA was reacted with PHMS in the presence of catalytic amount of NaOH, Si-N bond was formed with the evolution of hydrogen gas by the reaction between silyl hydride and amine proton.(21-22) Figure 1 shows the FT-IR spectra of PHMS(a) and the reaction product of PHMS and ODA(b).

In PHMS spectrum, the strong band at 2182 cm^{-1} represents the Si-H stretching vibration. (20) But in the reaction product of PHMS and ODA, this strong band at 2182 cm^{-1} disappeared by the formation of Si-N bond (see (I) of scheme 1). The ring-opening polyaddition of N-silylated diamine ((I) of scheme 1) to BTDA afforded polyamic acid silyl esters (see (II) of scheme 1).(23-24) When the compound(II) was cured, imidization occurred without forming a oily phase that was formed in the simple mixing of PHMS and polyamic acid in THF/DMAc cosolvent. We think that these phenomena were caused from two reason. One is that as the silicone group attached to the polyamic acid by the silyl ester bond, the phase separation to the solid polyamic acid and oily siloxane phase could not occur at the drying step in the vacuum oven. The other is that the Si-O-Si bond formation, i.e., the conversion of polysiloxane group to PMSQ was triggered by the imidization when the compound(II) was cured. In other words, as the Si-O-Si bond formation and imidization occurred



Scheme 1

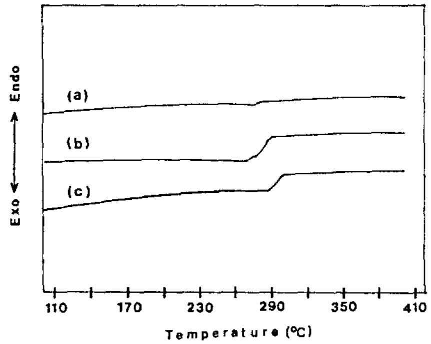


Figure 2. DSC thermograms of (a)PMSQ (b)polyimide (c)PMSQ-polyimide film.

almost simultaneously, there was no chance of the aggregation of the polysiloxane.

Figure 2 is the DSC thermograms of PMSQ(a), polyimide(b), and PMSQ-polyimide system(c). PMSQ shows weak endotherm at 278 °C and polyimide shows T_g at 284 °C. The PMSQ-polyimide system shows T_g at 295 °C and no weak endotherm at 278 °C that is shown in PMSQ. The disappearance of weak endotherm of PMSQ and the displacement of the T_g by 11 °C of the polyimide in PMSQ-polyimide system indicate good dispersion of PMSQ into polyimide matrix.

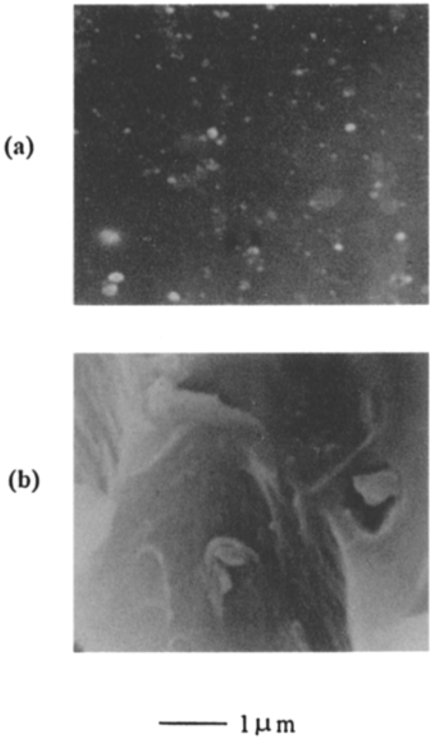


Figure 3. Scanning electron micrographs of the PMSQ-polyimide film. (a) surface (b) fractured cross-sectional area.

Figure 3 is the SEM photographs of the PMSQ-polyimide film of surface(a) and fractured cross-sectional area(b). In the fractured cross-sectional area(b), conspicuous phase boundary between PMSQ and polyimide is not shown. In the surface (a), small particles within 0.2 μm diameter are well dispersed in the polyimide matrix.

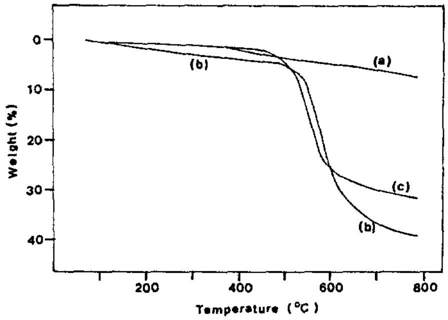


Figure 4. TGA thermograms of (a)PMSQ (b)polyimide (c)PMSQ-polyimide film.

Though we assume that this particles are PMSQ, to consider the weight percentage of PMSQ(21.1%) in PMSQ-polyimide system, the amount of PMSQ particles are less than the expectation. So, we can conclude that the rest of the PMSQ's are very well dispersed in the polyimide matrix like a miscible blending. This good dispersion of PMSQ supports the DSC data explained above.

Figure 4 is the TGA thermograms of PMSQ(a), polyimide(b), PMSQ-polyimide system(c). The TGA trace shows that PMSQ's initial weight does not diminish seriously up to 800 °C and the ten weight percent decomposition temperature of polyimide and PMSQ-polyimide film are 552 °C and 539 °C respectively. But when the temperature is higher than 600 °C, PMSQ-polyimide film shows good thermal property than the polyimide film only.

Conclusion

Though the PHMS and PMSQ were immiscible with polyimide, through the pretreatment of aromatic diamine(ODA) with PHMS and the subsequent reaction of this pretreated PHMS-ODA with aromatic dianhydride(BTDA), PHMS could be attached to the polyamic acid. When this PHMS-polyamic acid solution was heated in the forced air oven, the imidization and Si-O-Si bond formation occurred simultaneously. As a result, the dispersion of PMSQ into polyimide could be achieved.

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