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BORAZINE-SILOXANE ORGANIC/INORGANIC HYBRID POLYMER

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Abstract. Borazine-siloxane is an organic/inorganic hybrid polymer that can be synthesized by the hydrosilylation polymerization of a borazine compound containing acetylene groups and siloxane containing hydrosilyl groups. Spin coating a linear-polymer solution produces a thin film that is transformed into a network polymer by annealing. The borazine-siloxane thus obtained has excellent characteristics, such as a low dielectric constant, a high elastic modulus, and good heat resistance. The use of this polymer as an interconnect material should not only improve the performance of ULSIs by reducing the effective dielectric constant of multilayer wiring, but also enable the use of an environmentally friendly dry etching process without PFCs.

1. INTRODUCTION

There is an ever-increasing demand for ULSIs with denser integration and higher performance. The fabrication of denser semiconductor chips requires finer patterning of the wiring material, longer wiring, and multilayer interconnects. However, the increase in the signal delay caused by the greater resistance of the wiring and the larger parasitic capacitance degrades chip performance. It is important to find a solution to this problem. One way of reducing the signal delay that has been proposed is to use wiring material as a copper with a lower resistance and an interlayer dielectric with a lower *k*, rather than the conventional aluminum interconnect structure.

According to the road map (ITRS2001) of interconnect technology, for a microprocessor fabricated on a 65-nm design rule, the effective dielectric constant of all the interconnect layers has to be in the range 2.3 - 2.7, and the *k* value of the dielectric material itself has to be less than 2.4. Various types of spin-coated materials with a low dielectric constant, such organic polymers and porous silica, are now being investigated as replacements for CVD SiO_2 film (dielectric constant, $k > 4.0$); but so far, no suitable materials have been found that provide, for example, both good electrical and good mechanical properties.

We are developing low-*k* organic/inorganic hybrid polymer thin films based on the idea that different components can provide different capabilities. And we have succeeded in developing borazine-siloxane, which can be synthesized by the hydrosilylation polymerization of a borazine compound and a siloxane compound.

Borazine is a very stable molecule, just like benzene, and has been called inorganic benzene because it has a ring structure consisting of 6 elements with alternating boron and nitrogen groups. One report states that borazine is less polarizable than benzene [1], which suggests the possibility that the dielectric constant of a molecule containing borazine units might be low. From simulations on the polarizability and molecular volume of borazine based on the molecular-orbit method, the dielectric constant of a borazine molecule was calculated to

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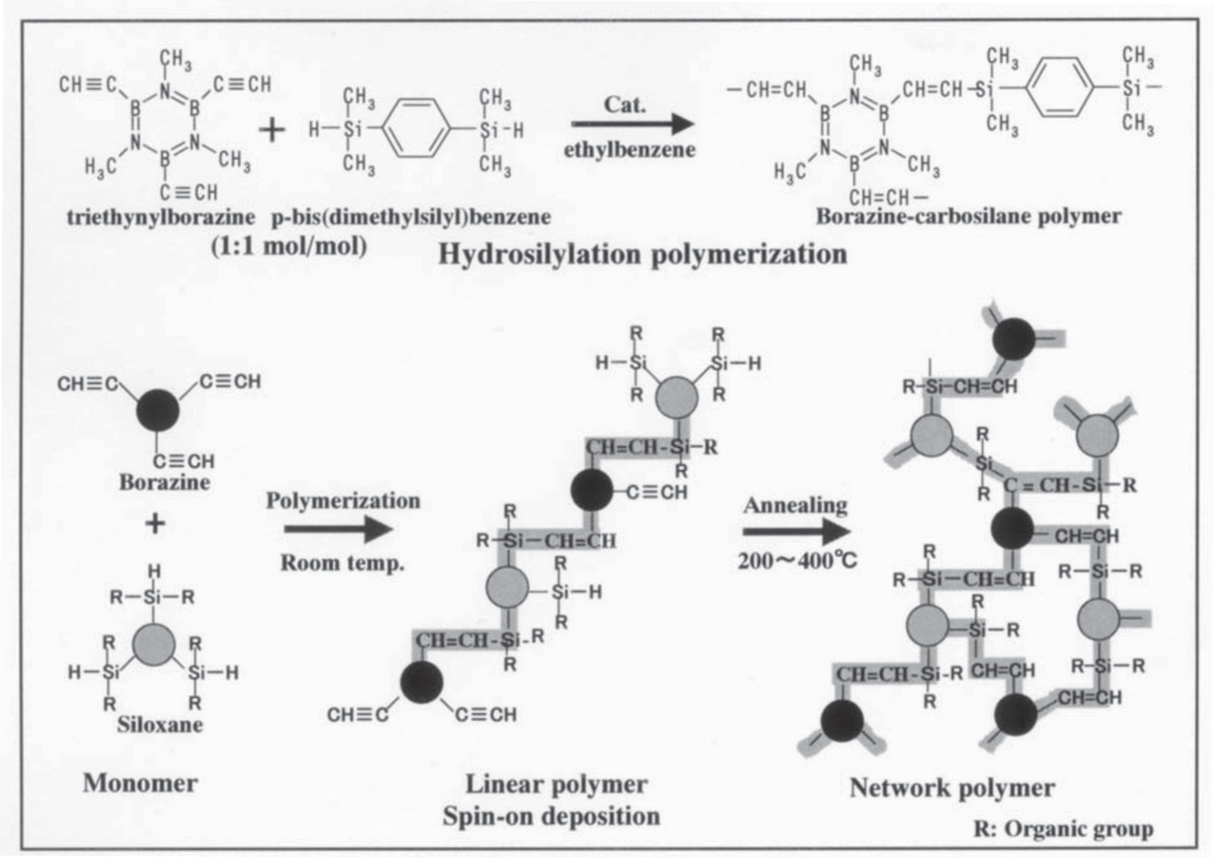


Fig. 1. Borazine-siloxane organic/inorganic hybrid polymer.

be a very low 1.9. This is the same as the value for cyclohexane and perfluorobenzene, and is smaller than the value for benzene, which is 2.2. It has been reported that the dielectric constants of poly(borazylene) and poly(borazinylamine) are 1.94 and 2.04, respectively, which were calculated using the Clausius-Mossotti equation [2]. Furthermore, the dielectric constants of borazine oligomers, such as poly(borazylene), are 30% smaller than those of benzene oligomers. However, poly(borazylene), which is produced by the dehydration coupling of borazine, decomposes easily in a moist environment. Little is known about polymers containing borazine, but they are being investigated as a precursor for boron-nitrite fiber [3,4]. Polymers containing borazine are a new and very promising type of low-*k* material.

2. EXPERIMENTS

2.1. Synthesis and thin firm formation

Borazine-siloxane can be synthesized by the hydrosilylation polymerization of a borazine compound with two or more unsaturated groups (e.g. acetylene) and a silicon compound that has two or more hydrogen atoms bonded to a Si atom. The reaction is triggered by a catalyst. In this study, borazine-siloxane was synthesized by the hydrosilylation polymerization of B,B',B''-triethynyl-N,N',N''-trimethyl-borazine and 1,3,5,7-tetramethylcyclosiloxane using platinum-divinyltetramethyldisiloxane complex as a catalyst. When polymerization takes place in a dilute solution of an aromatic solvent, such as ethylbenzene, at room temperature or 40 °C, the result is a homogeneous solution of linear polymer. The polymerization readily produces gelation because both the borazine and siloxane compounds have 3 or more functional groups. In order to obtain a uniform thin film by spin-coating, the polymer solution must not contain any gel that is insoluble in the solvent or any residual unreacted monomers. The end point of the polymerization is determined by monitoring the amount of unreacted borazine compound with a gas chromatograph. Spin-coating the polymer solution on a silicon wafer produces a thin film of linear polymer. Subsequent annealing at a temperature in the range 200-400 °C transforms the film into a network structure due to intermolecular crosslinking. The structure is illustrated in Fig. 1.

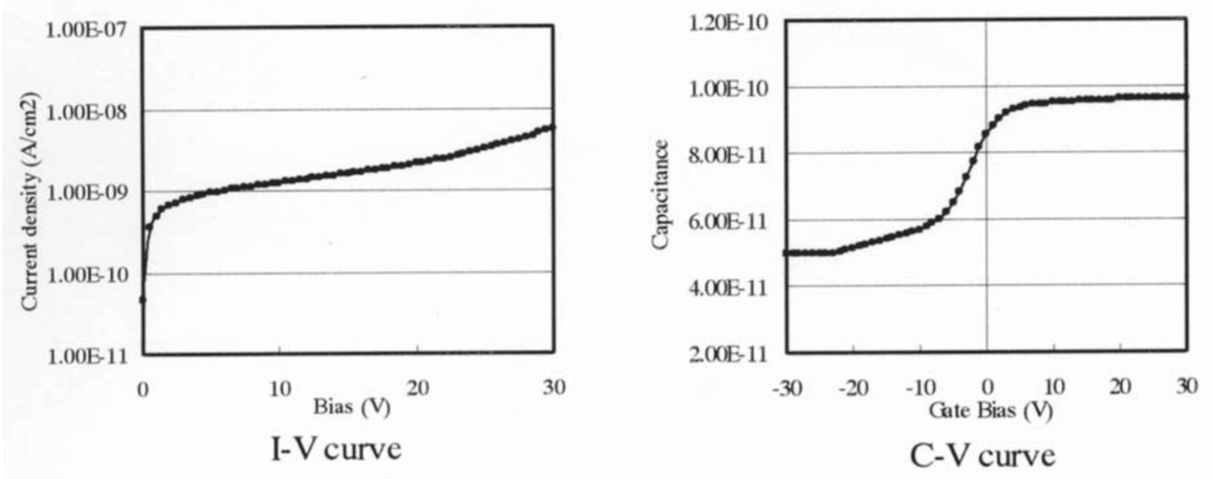


Fig. 2. I-V curve and C-V curve of borazine-siloxane polymer thin film (1MHz).

2.2. Evaluation of borazine-siloxane thin film

The possibility of using borazine-siloxane as an interlayer dielectric was evaluated through measurement of the electrical, mechanical, thermal and optical properties. Regarding the electrical properties, the dielectric constant and leakage current density were measured using electrical analysis equipment (Agilent Technology: HP4071) and a manual probe. Regarding the mechanical properties, the elastic modulus and hardness were measured using nanoindentation equipment (Hysitron Inc.: Triboscope System). Regarding the thermal properties, the weight loss due to heating was estimated using thermal analysis equipment (Seiko Instruments, Inc.: EXSTRA 6600) and the thermal conductivity was measured using 3Ω thermal-conductivity analysis equipment (Toray Research Center, Inc.). In addition, the optical properties and film thickness were examined by measuring the refractive index with an ellipsometer (Jobin Yvon: UVISEL2483M).

3. RESULTS AND DISCUSSION

3.1. Physical properties of borazine-siloxane

3.1.1. Electrical properties.

In order to measure the electrical properties, an MIS structure was formed by depositing aluminum electrodes on a thin film of polymer coated on an n-type low-resistivity Si wafer (Resistivity: 9 – 12 Ωcm). The dielectric constant was calculated from the following formula using data taken from C-V curves measured at a frequency of 1 MHz.

$$\Sigma = \frac{C_{max} d}{\varepsilon_0 S},$$

where C_{max} is capacitance (F), d is film thickness (m), ε_0 is the permittivity in a vacuum (F/m), and S is electrode area (m^2). The leakage current density was calculated from measured I-V curves.

The dielectric constant was found to range from 2.3 to 2.8, depending on the chemical structures of the borazine and siloxane, and also on the temperature and atmosphere used for annealing. Fig. 2 shows C-V and I-V curves for films annealed at 200 °C for 1 hour, 300 °C for 30 minutes, and 400 °C for 30 minutes in argon gas. The C-V curves yield a dielectric constant of 2.4. The leakage current density in a 1-MV/cm electric field was at most 10^{-9} A/cm^2. However, when the polymer film was annealed at a temperature of over 500 °C or in air, the dielectric constant was greater than 3, and the leakage current density was over 10^{-7} A/cm^2. Judging from these electrical properties, borazine-siloxane is quite suitable for use as an interlayer dielectric.

3.1.2. Mechanical properties.

In order to ensure that a new low-*k* material can be used as an interlayer dielectric, it is necessary to understand the mechanical properties of the thin film. Unlike conventional silica-type materials, which have an excellent elastic modulus and hardness, new low-*k* materials developed as interlayer dielectrics, such as porous silica and organic polymer, tend to have poor mechanical properties, that is, a rather low elastic modulus and hardness. However, in this study, the nanoindentation method yielded values as high

Table 1. The hardness and elastic modulus of low-*k* materials.

Low-k material	*Dielectric constant*	*Hardness*, GPa	*Elastic modulus*, GPa
Silica	3	2.3	9.9
Porous Silica	2.2	0.6	3.8
Organic Polymer	2.7	0.4	5
Borazine-siloxane	2.5	1	15

as 15 GPa for the elastic modulus and 1 GPa for the hardness of a thin film of borazine-siloxane. As can be seen in Table 1, the mechanical properties of borazine-siloxane are superior to those of porous silica and organic polymer, and are good enough for practical use.

3.1.3. Thermal properties. The thermal stability and thermal conductivity of borazine-siloxane were also investigated. The thermal resistance was assessed from the measured weight loss during heating from room temperature to 1000 °C in air. For polymer annealed either at 200 °C for 1 hour or 300 °C for 30 minutes, the 1%, 5% and 10% weight-loss temperatures are 404 °C, 563 °C and 725 °C, respectively. These values are much better than those for polymers with a typical thermal resistance, such as polyimide, for which the 5% and 10% weight-loss temperatures are 400 °C and 500 °C, respectively. Regarding organic polymers, the weight-loss temperatures tend to decrease as the dielectric constant becomes lower. In contrast, borazine-siloxane has high weight-loss temperatures in spite of its low dielectric constant because it is an organic/inorganic hybrid polymer.

Since boron nitrite ceramics have a high thermal conductivity, it was expected that borazine-siloxane would also. However, the value obtained was only 0.168 W/mK, which is at the level of the smallest value for low-*k* organic polymers. Measurement of the thermal conductivity of various low-*k* materials by the 3W method has revealed a relationship between dielectric constant and thermal conductivity; more specifically, the thermal conductivity tends to become lower as the dielectric constant becomes smaller [5].

3.1.4. Optical properties. The refractive index of borazine-siloxane polymer was determined by ellipsometry measurements on a thin film on a wafer. The value was found to be 1.46 at a wavelength of 633 nm. This is quite small, even compared to the value of 1.55 for low-*k* organic polymer thin film. The fact that the refractive index (which, when squared, yields the electrical polarization component of the dielectric constant) is smaller than the dielectric constant obtained from electrical measurements demonstrates that borazine-siloxane is indeed a low-*k* material.

3.2. Application of borazine-siloxane thin film

3.2.1. Etching characteristics. Since boron reacts with chlorine to produce BCl_3, it was speculated that polymers containing a borazine ring could be etched with chlorine gas. Since borazine-siloxane contains three borazine rings and siloxane, and also organic components that link them, it should be possible to etch it with a variety of gases. That is, it should be possible to etch the organic components with oxygen or a mixture of hydrogen and nitrogen, the borazine with chlorine; and the siloxane with a perfluorocarbon (PFC). As shown in Table 2, etching tests revealed that borazine-siloxane can be etched with chlorine at a rate of 460 nm/min, with a $C_4F_8/O_2/Ar$ mixture at a rate of 220 nm/min, and also with a nitrogen/hydrogen mixture at a low etching rate of 11 nm/min. Although silica, which has a siloxane structure, must generally be etched with PFC gas, borazine-siloxane can be etched with

Table 2. Etching characteristics of borazine-siloxane polymer.

Etching gas	*Etching rate*	*Selectivity*
Cl_2	460 nm/min	vs. Photoresist = 1.6
$C_4F_8/O_2/Ar$	220 nm/min	vs. SiO_2 = 1.4
O_2	11 nm/min	vs. Photoresist = 1/33
N_2/H_2	50 nm/min	vs. Organic polymer = 1/7

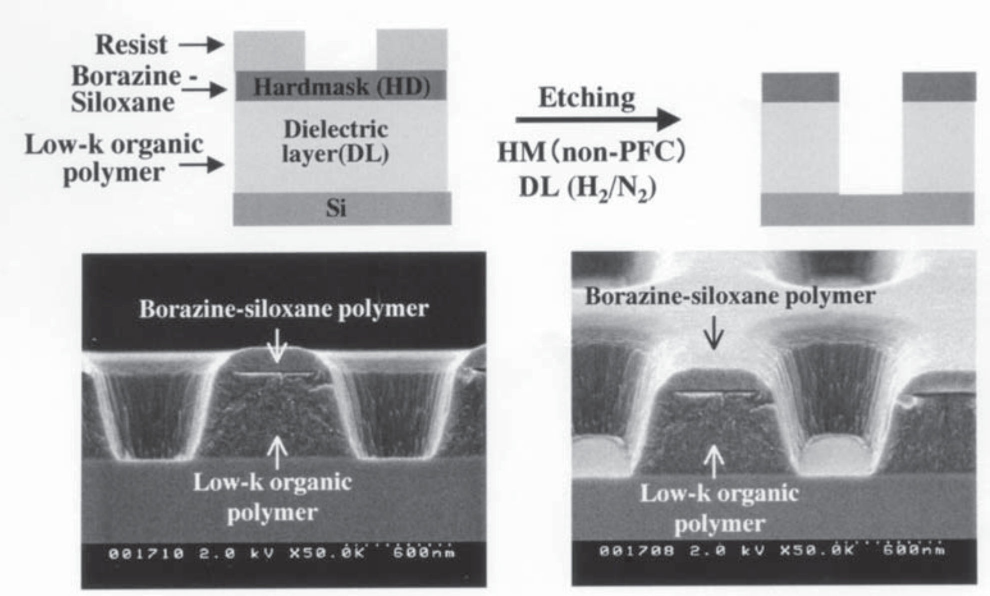


Fig. 3. Cross section SEM photographs of etched profiles.

chlorine, even though it contains siloxane, thus obviating the need to etch with a PFC. Since PFCs have a global-warming coefficient 10,000 times larger than that of carbon dioxide, it is essential to reduce their use. In this regard, borazine-siloxane, which can be etched without PFCs, provides an environmentally friendly alternative.

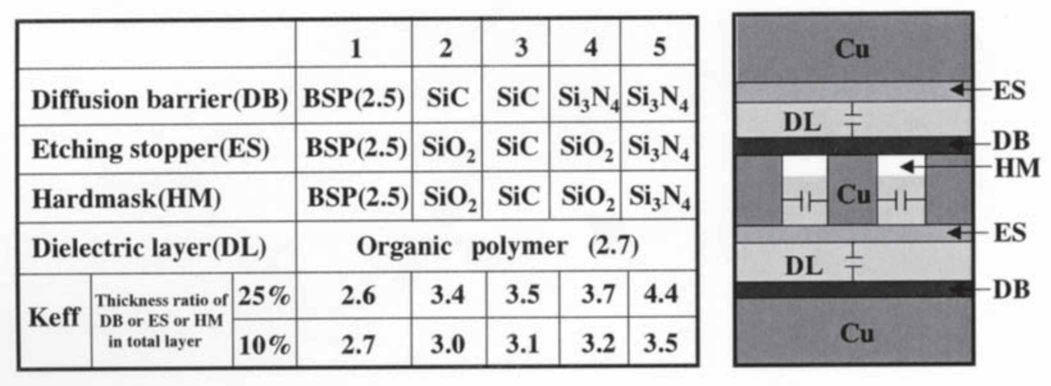
3.2.2. Effectiveness as Cu diffusion barrier. In order to test the effectiveness of borazine-siloxane as a Cu diffusion barrier, two structures were fabricated: one consisted of a thin Cu film deposited on an organic-polymer thin film, and the other consisted of a borazine-siloxane thin film sandwiched between Cu and organic-polymer thin films. They were heated at a temperature of 400 °C for 6 hours. Then, the polymer/Cu interface was observed by SEM, and the Cu concentration of the organic polymer was measured by SIMS.

SEM images revealed marked damage to the organic-polymer/Cu interface due to heating, while the borazine-siloxane/Cu interface remained unchanged. Thus, the insertion of a borazine-siloxane thin film suppresses the degradation of an organic polymer due to Cu diffusion. The SIMS measurements showed that heating caused Cu to diffuse throughout the organic polymer in the double-layer structure, while the insertion of a borazine-siloxane layer dramatically suppressed the diffusion. These results demonstrate that borazine-siloxane should act as a very effective diffusion barrier in multilayer interconnects.

3.2.3. Use of borazine-siloxane as a hard mask for an interconnect structure. As mentioned above, the large global-warming coefficient of PFCs makes PFC-free processing technology very attractive. Thus, it would seem that the use of an organic polymer that can be etched without PFCs as an interlayer dielectric would be very beneficial to the environment. This is in contrast to conventional SiO_2, which requires PFC gas for etching. However, even if an organic polymer is used, PFC gas must still be used for dry etching. That is, since a resist is organic, just like the polymer, it cannot be used as a hard mask for etching the polymer. That means that an inorganic thin film, such as SiO_2, SiC, or Si_3N_4, deposited by CVD must be used; and these materials must be etched with PFC gas. So, the use of an organic polymer does not necessarily result in a significant reduction in the amount of PFCs required.

Furthermore, when an organic polymer with a low dielectric constant is used, since the inorganic film used as a hard mask has high dielectric constant, the effective dielectric constant of the two together is not small. The dielectric constants of SiO_2, SiC, and Si_3N_4 are 4.3, 4.5, and 7.0, respectively. Our solution is to use borazine-siloxane for the hard mask. That is, the combination of an organic polymer for the interlayer dielectric and borazine-siloxane for the hard mask should result not only in the complete elimination of PFCs from the processing, but also in a reduction of the effective dielectric constant.

Table 3. The effective dielectric constants of multilayer interconnect, which was calculated based on a simulation model.



			1	2	3	4	5
Diffusion barrier(DB)			BSP(2.5)	SiC	SiC	Si_3N_4	Si_3N_4
Etching stopper(ES)			BSP(2.5)	SiO_2	SiC	SiO_2	Si_3N_4
Hardmask(HM)			BSP(2.5)	SiO_2	SiC	SiO_2	Si_3N_4
Dielectric layer(DL)			Organic polymer (2.7)				
Keff	Thickness ratio of DB or ES or HM in total layer	25%	2.6	3.4	3.5	3.7	4.4
		10%	2.7	3.0	3.1	3.2	3.5

This effect was confirmed experimentally. A Si wafer was coated with an organic-polymer thin to a thickness of 500 nm, and that was coated with a 175-nm-thick layer of borazine-siloxane. The borazine-siloxane was etched with chlorine gas through a photoresist mask patterned by lithography to form a hard mask, and the hard mask was then used to etch the organic polymer with a mixture of nitrogen and hydrogen, as shown in Fig. 3. This experiment demonstrated that the use of borazine-siloxane could be instrumental in developing an environmentally friendly interconnect technology.

Next, based on a simulation model, the wiring capacitance was calculated by the finite element method. Table 3 shows the effective dielectric constant of an interconnect structure that employs a low-*k* organic polymer as an interlayer dielectric, and borazine-siloxane as a hard mask, an etching stopper, and a Cu diffusion barrier. The effective dielectric constant is a small 2.6, which is within the 2.3 - 2.7 range required for the 65-nm technology node. Table 3 also shows that the use of a conventional inorganic thin film, such as SiO_2, SiC or Si_3N_4, results in a dielectric constant of 3 or more, which is too large.

4. CONCLUSION

As predicted by simulations, the dielectric constant of polymer containing borazine rings was found to be small. Borazine-siloxane, an organic/inorganic hybrid polymer, is a very suitable low-*k* interlayer dielectric for interconnects, because it can be coated to a uniform thickness and because of its excellent physical properties. Not only will the use of borazine-siloxane improve the performance of ULSIs, but it will also contribute to making semiconductor manufacturing more environmentally friendly by reducing the need for PFCs. The next stage of this research calls for the actual fabrication of multilayer wiring structures that employ borazine-siloxane.

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