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Material Properties and Process Compatibility of Spin-on Nano-foamed Polybenzoxazole for Copper Damascene Process

Takashi Enoki, Kenzo Maejima, Hidenori Saito, and Akifumi Katsumura
Fundamental Research Laboratory, Research Department, Sumitomo Bakelite Co., Ltd., 495, Akiba-cho, Totsuka-ku, Yokohama, 245-0052, JAPAN

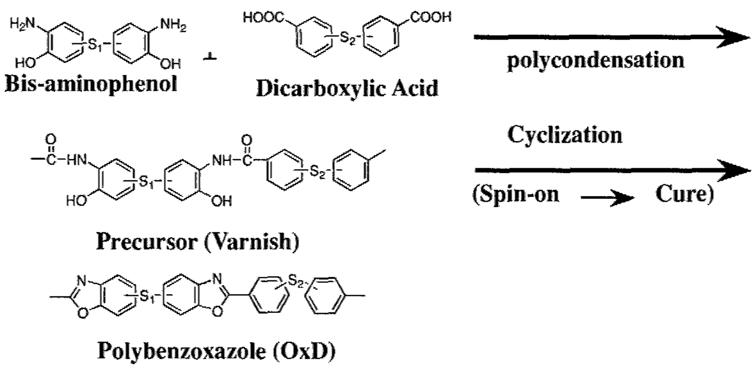
ABSTRACT

We have developed nano-foamed OxD which has good properties such as dielectric constant=2.2, homogeneous distributed nano pores, smooth surface based on polybenzoxazole chemistry and nano-foaming technology. The nano-foamed OxD also has excellent thermal stability, chemical stability and etching property. The developed nano-foamed OxD is one of good candidates for copper damascene structure to achieve shrinking dimensions of future semi-conductor devices.

INTRODUCTION

In shrinking dimensions of future semi-conductor devices, lower dielectric constant (k) material is strongly required in Cu/low k damascene structure. According to the International Technology Roadmap for Semiconductors (ITRS) 2001, ultra low-k interlayer dielectric materials (k < 2.4) will be needed around 2005 [1]. Because the k value of air is one, nano-foaming with air is possible solution to provide lower k material.

Polybenzoxazole [2] is one of excellent heat resistant polymers and is synthesized via cyclization of its precursor (poly(o-hydroxy)amide) by polycondensation between bis-o-amino-phenol and dicarboxylic acid derivative monomers (Scheme 1.).



Scheme 1. Chemistry of Polybenzoxazole. S_1 and S_2 = Spacers

The precursor shows good solubility to several organic solvents, which allows us spin-on application. Once the polybenzoxazole is obtained by cyclization from spun-on precursor by heat, it becomes insoluble and shows high thermal stability. We have designed a spin-on nano-foamed OxD (Oxazole Dielectrics) by taking advantage of polybenzoxazole chemistry considering nano-foaming process [3,4].

In this work, we will report material and process properties of nano-foamed OxD which are important to consider Cu damascene process. We will discuss pore size, surface roughness, thermal stability, chemical stability, process compatibility such as etching property and so on.

EXPERIMENTAL DETAILS

OxD precursor varnishes were spin coated onto silicon wafers to form films from 0.4 um to 1.0 um thick. The films were cured for 1 hour at 250°C and 1 hour at 425°C in N_2 atmosphere. The thickness and refractive index of the films were measured with a spectrometric reflectance tool, n & k analyzer 1500 (n&k Technology, Inc.). All the electrical measurements were done using Hg probe (Automatic Mercury Probe CV System SSM 495, Solid State Measurements Co.,Ltd.). Surface roughness of the film was analyzed by atomic force microscopy (AFM), Nano Scope IIIa (Digital Instruments). Determination of pore size was examined by TEM (transmission electron microscopy and Small Angle X-Ray Scattering (SAXS: Advanced Thin Film X-ray System ATX-G, Rigaku Corporation). Hardness and modulus of the films were determined by nano Indenter XP (MTS Systems Corporation). Thermal stability was examined by Thermal Desorption Spectrometer, EMD-WA1000S (ESCO Ltd.). Chemical stability was examined by Fourier transform-infrared spectrometer, IRus-II (Spectra-tech, Inc.). Etching was done using dry etching system, L-201D-L (Anelva Corporation).

RERULTS & DISCUSSION

Film Properties

Table 1 shows film properties of nano-foamed OxD on 200mm wafers. Dielectric constant is 2.2. A standard deviation of the measurement around 0.7% is found, indicating that the dielectric constant is constant over the wafer. Dielectric constant did not change for 3 months at 25°C for 50 % RH. The leak current value is below $9.1E^{-9}$ A/cm^2 and the films did not show breakdown up to fields of 2.7 MV/cm. Leak current and dielectric breakdown of the nano-foamed OxD are comparable to those of Aromatic organic, hydroxyl silsesquioxane (HSQ), and methyl silsesquioxane (MSQ) [5]. The nano-foamed OxD exhibited good adhesion to various substrate surfaces such as SiC, SiO_2, and Si in a tape pull test.

Standard deviation on film thickness by n&k analyzer was below 0.3% which showed that the nano-foamed OxD was fabricated uniformly. The surface roughness was analyzed by AFM. Roughness was measured over different spots on the sample and the scans were done in 0.5 x 0.5 um^2 areas. Figure 1 shows a 3D image of the film surface. The root means square (RMS) was 1.67 nm, and this value is independent of the area measured.

Table 1. Properties of nano-foamed OxD.

Properties	Unit	Method	Value
Dielectric constant	at 1MHz	Hg probe	2.2
Dielectric breakdown	MV/cm(0.4 um)	Hg probe	2.68
Leak Current at 1MV/cm	A/cm^2 (0.4 um)	Hg probe	$9.1E^{-9}$
Refractive index		n&k analyzer	1.40
Young's modulus	GPa	Nanoindentation	1.5
Hardness	GPa	Nanoindentation	0.12
Thermal Stability	A	TDS	$<1.0E^{-10}$
Adhesion (SiC, SiO_2, Si)		Tape pull test	Pass
Average pore size	nm	SAXS	6.6

Therefore, the nano-foamed OxD has good film qualities (roughness and uniformity) [6] in addition to its good electrical properties.

Pore size was examined by FIB-TEM, and SAXS measurements shown in Figure 2. FIB-TEM picture (Figure 2 (a)) shows that pores whose sizes were below 10nm distributed uniformly. Figure 2 (b) shows pore size distribution by SAXS. The average pore size is 6.6nm with very narrow distributions in which pore sizes are below 12nm.

Thermal stability was demonstrated by TDS measurement. Figure 3 shows thermal desorption spectrum of the nano-foamed OxD. The film shows excellent thermal stability up to 450°C.

Chemical stability is important to consider Cu damascene integration process. The changes in thickness and refractive index of the nano-foamed OxD films were less than 1% after the films were immersed in 10% sulfuric acid, 3% hydrogen peroxide, 2.38%

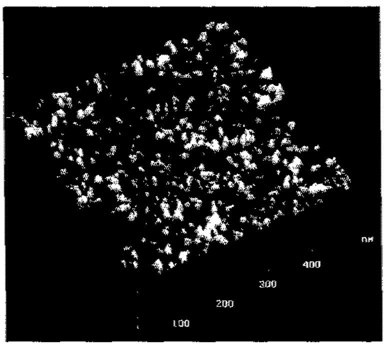


Figure 1. AFM image of the nano-foamed OxD, RMS = 1.67 nm.

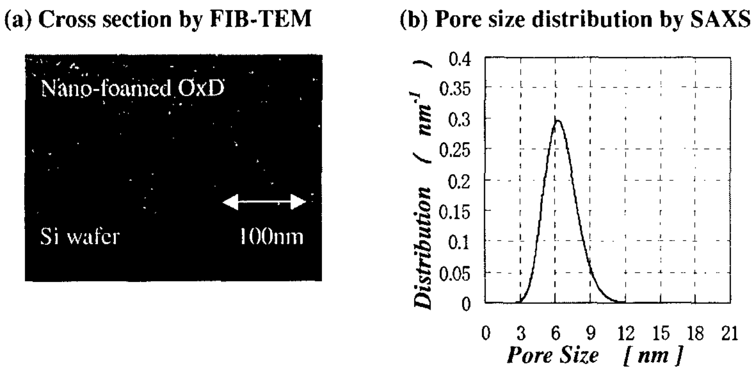


Figure 2. FIB-TEM (a), and SAXS (b) data of the nano-foamed OxD.

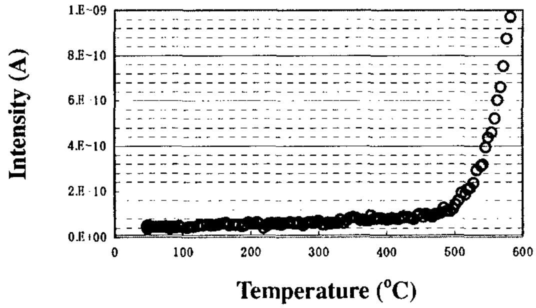


Figure 3. Thermal behavior of the nano-foamed OxD by TDS measurement.

tetra-methyl ammonium hydroxide, 1,1,1,3,3,3-hexamethyldisilazane, organic solvents such as N-methyl-2-pyrrolidone, isopropyl alcohol, 1-methoxy-2-propanol acetate, ethanolamine, respectively at 25°C for 10 minutes and rinsed with diionized water and dried at 200°C for 10 minutes. The nano-foamed OxD shows good chemical stabilities because of its chemical structure.

Compatibility to integration process

Nano-foamed OxD can be dry-etched by N_2 / H_2 chemistry [7] with sufficient etching selectivity against plasma-deposited tetra-ethoxy silane (TEOS) which indicates that SiO_2 can be used as etch stopper for OxD in damascene process. The combination of nano-foamed OxD and SiO_2 also leads to lower effective dielectric constant. The nano-foamed OxD is attractive as dielectrics due to sufficient etching selectivity [8] and possible lower effective dielectric constant.

Figure 5 shows behaviors of dielectric constant and refractive index during N_2 / H_2 reactive ion etching (RIE) and resist stripper treatment (cleaning). The film thickness decreased during etching, but it did not change after resist stripper treatment. The dielectric constant and the refractive index did not change during both RIE etching and resist stripper treatment. The chemical composition did not change supported by the IR spectra of the films which were the same through the processes (Figure 6). Figure 7 shows the etched profile on nano-foamed OxD after N_2:H_2 etching. The nano-foamed OxD was etched perpendicularly. Etched residues were cleaned with ACT-NE-14. Therefore, it is suggested that the nano-foamed OxD has compatibility to N_2 / H_2 etching process and cleaning.

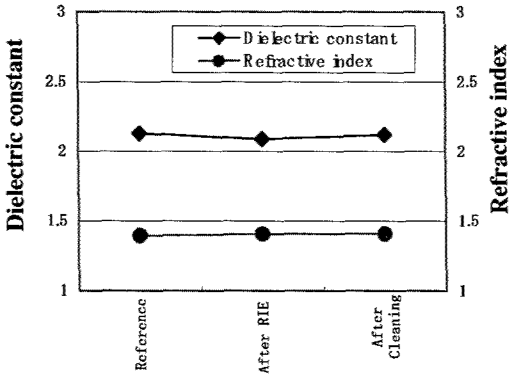


Figure 5. Behaviors of refractive index and film thickness on the nano-foamed OxD film during RIE and cleaning: etching gas: N_2 : H_2 = 2.5 sccm : 7.5 sccm, RF output = 10W, etching time = 30 sec.; cleaning: the film was immersed in resist stripper, ACT-NE-14 (Ashland Specially Chemical Company) at 25°C for 30 minutes, rinsed with deionized water, dried at 130°C for 10 minutes.

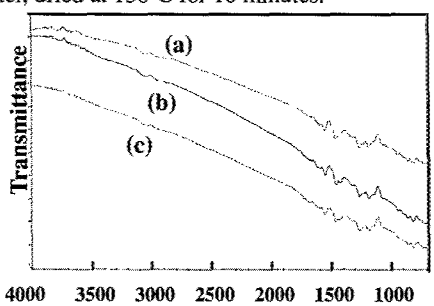


Figure 6. FT-IR spectra of nano-foamed OxD film: (a) reference, (b) after RIE, and (c) after cleaning.

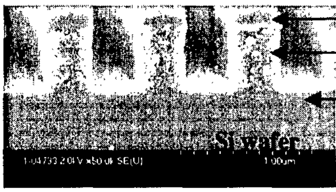


Figure 7. SEM micrograph of etched profile on nano-foamed OxD after N_2:H_2 etching.

CONCLUSIONS

It is demonstrated that the nano-foamed OxD shows excellent film properties such as film uniformity, thermal stability, adhesion, chemical stability with k=2.2 and homogeneous nano-order pores. In addition, the nano-foamed OxD shows chemical stability during N_2:H_2 etching and cleaning and is etched perpendicularly, suggesting compatibility to copper damascene process.

ACKNOWLEGEMENTS

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