

IBM Research Report

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ABSTRACT

We have shown previously that the dielectric constants of PECVD prepared SiCOH dielectrics can be extended to ultralow-k values of $k=2.0$. The reduction in the dielectric constants has been achieved by adding an organic precursor to the tetramethylcyclotetrasiloxane (TMCTS) used for the preparation of the SiCOH dielectric and annealing the films to remove the thermally less-stable organic CH_x fractions from the films, thereby adding porosity and reducing the density of the films. To assess the effects of the reduction of the dielectric constant on other physical properties of the material, the density and composition of the films have been determined by RBS and FRES and the porosity has been measured by PAS/PALS, SAXS and ellipsometric porosimetry. In addition the films have been characterized structurally and topologically by TEM and AFM.

It has been found that addition of the organic precursor reduces the Si fraction in the films, however, there is no direct correlation between dielectric constant and film composition. The dielectric constant and density decrease with increasing porosity in the films, which reaches values of 30-39% for k values of 2.05. The pore size increases with decreasing k, however the diameter remains below 5 nm for $k=2.05$. This is significantly smaller than the pore size typically found in porous spin-on films and may provide an integration advantage compared to spin-on films having similar k values.

INTRODUCTION

The advancement in performance of ultra-large scale integrated (ULSI) circuits is still being hindered by the difficulties encountered in introducing new dielectrics into Si chip interconnection technology. The delay in the introduction of insulators of reduced dielectric constants is marked by continuous revisions outwards in time of the International Technology Roadmap for Semiconductors (ITRS) projections since 1997. The 2001 ITRS pushed out again low-k dielectric milestones, e.g. decelerating advances to ultralow-k dielectrics ($k=1.6-2.2$) from 2005 to 2009. [1] The determination of the best choice for low-k dielectrics is still ongoing, with primary choices being spin-on polymers and PECVD glasses. The main contenders among the PECVD low-k dielectrics are amorphous materials from a group comprised of Si, C, O, and H which are deposited in conventional PECVD tools [2] and known by different names, including SiCOH, SiOCH, carbon-doped oxides (CDO), silicon-oxycarbides, organosilicate glasses (OSG) and several trade names given by the various suppliers who provide processes and tooling for these films. The generic term SiCOH will be used throughout this paper to refer to the films that we have developed.

We have demonstrated elsewhere [3, 4] that it is possible to reduce the dielectric constants of SiCOH materials to values as low as $k = 2.05$ by creating porosity in the films through the admixing of an organic material to the SiCOH precursor, thus demonstrating the potential extendibility of PECVD dielectrics to future generations of ULSI chips. In this paper we present the porosity in SiCOH materials of different dielectric constants and discuss their properties as

rosity in SiCOH materials of different dielectric constants and discuss their properties as related to this porosity.

EXPERIMENTAL

The SiCOH films were deposited from tetramethylcyclotetrasiloxane ($\text{Si}_4\text{O}_4\text{C}_4\text{H}_{16}$, TMCTS) with the addition of an organic precursor. As discussed elsewhere [4], we have found that superior films are obtained from TMCTS [2], and that the choice of the proper organic precursor is critical in achieving ultralow-k values. It was assumed that the ring structure of TMCTS might be preserved in the film to produce nanoporous materials with low dielectric constants. The films were deposited on Si (100) substrates under conditions described in details elsewhere. [3-5] After deposition the films were annealed at 400°C in an inert ambient to remove the unstable organic fractions and induce porosity in the material. The results presented here are for annealed films.

The SiCOH films were characterized by Rutherford backscattering (RBS) and forward recoil elastic scattering (FRES) to determine their atomic composition. The same data were used together with the thickness values of the films to calculate film densities. The surface roughness of the films was measured by atomic force microscopy in the tapping mode. The porosity of the A. Grill et.al. p1 of 6

films was measured by several techniques. The degree of porosity was determined by positron annihilation spectroscopy (PAS) [6] and ellipsometric porosimetry (EP). [7] The pore size was evaluated by positron annihilation lifetime spectroscopy (PALS) [6], small angle X-ray scattering (SAXS) [8], EP, and transmission electron microscopy (TEM). The mechanical properties were determined by nanoindentation measurements. The dielectric characteristics were measured on silicon-insulator-metal structures using highly doped Si substrates and Al dot top electrodes. The dielectric constants (k) were determined from capacitance measurements combined with thickness profilometry. The breakdown fields and leakage currents were determined from I-V curves measured on these same structures.

RESULTS AND DISCUSSION

It was shown elsewhere [3] that with increasing addition of the organic precursor to TMCTS in the gas feed to the plasma, the dielectric constant of the SiCOH film decreases from 2.8 to about 2.0. It was also shown that the leakage current in films having ultralow-k values is very similar to that for films deposited from TMCTS only and having $k=2.8$ [3], indicating that the leakage current is not affected by the decrease in the dielectric constant. The breakdown field of the ultralow-k film is about 5.5 MV/cm [3], again similar to that of regular SiCOH films. [2]

The RBS/FRES analysis showed that the addition of the organic precursor to the gas feed to the deposition reactor causes a decrease in the relative concentration of Si in the films. However, the analysis also showed no significant changes in the composition, within the experimental errors, between films deposited with different fractions of organic precursor in the gas feed. This indicates that the dielectric constants do not correlate directly with the elemental composition of the films.

Table I presents the density, hardness (H) and Young's modulus (E) of several SiCOH films of different dielectric constants. All three properties decrease with decreasing k and there appears to be a direct correlation between film density, mechanical properties and dielectric constant. This is illustrated in Figure 1, which shows that there is a linear dependence between the dielectric constants and the densities of the films. The ultralow-k films also have the lowest mechanical properties. As the variation in properties cannot be correlated to the composition of the films, it

may be expected that they are related to the film porosity. No pores could be detected by scanning electron microscopy (SEM) in either of the films. However, AFM of the top surface of the films showed an average roughness of 2.69 nm and a Z range (maximal peak to valley value) of 2.96 nm for the k=2.8 films as compared to an average roughness of 3.48 nm and a Z range of 5.792 nm for k=2.05 films. The increased roughness in the lower k films may be a reflection of the porosity in these films.

Table I. Properties of SiCOH films.

Dielectric constant	Density (g/cm³)	Modulus (GPa)	Hardness (GPa)
2.8	1.32	16.2	1.69
2.4	1.06	4.2	0.28
2.05	0.87	3.3	0.21

Table II presents the porosity fractions and pore sizes in the different films as determined by PAS/PALS, SAXS and EP. Quantitative values for porosity were not extracted from the SAXS data, however, increasing scattering intensity was observed with the samples having lower dielectric constants and is qualitatively consistent with an increase in porosity. The porosity obtained by the different techniques are dependent upon the different means in which the pores are probed and by the assumptions made to interpret the results. PAS/PALS, EP and SAXS probe the pore volume, surface area, and cross section, respectively. The results presented in Table II are therefore within reasonable agreement.

Table II. Porosity in SiCOH films.

CHx/ TMCTS	Dielectric constant	Porosity fraction		Pore size		
		PAS (%)	EP (%)	PALS (nm)	SAXS (nm)	EP (nm)
0	2.8	0	0	N/A	N/A	N/A
0.2	2.4	20	20	1-4	<1.5	1.2
0.2	2.4		8			>2
0.5	2.05	29	39	1-7	<2.5	4-5

The data in Table II show that the SiCOH films deposited from TMCTS without addition of the organic precursor had no measurable porosity. The dielectric constant of these films (k=2.8) is therefore determined by the amount of Si-CH₃ bonds incorporated in the films and probably by their orientation in the amorphous material. The addition of the organic precursor to TMCTS results in the formation of porosity in the films, the porosity increasing with increasing concentration of the organic precursor to the gas feed. A porosity of 20% to 28% (according to the measurement technique) was determined in the films prepared at a CHx/TMCTS ratio = 0.2, increasing

to 29% to 39% for the films prepared at a CH_x/TMCTS ratio = 0.5. The formation of porosity and its increasing fraction with increasing amount of organic precursor in the deposition gas mixture can explain the decreasing dielectric constant, decreasing density and decreasing mechanical properties in these films. Figure 2 shows the porosities obtained by the two methods, PAL and EP, vs the dielectric constants and it illustrates the decrease of the dielectric constant with increasing porosity.

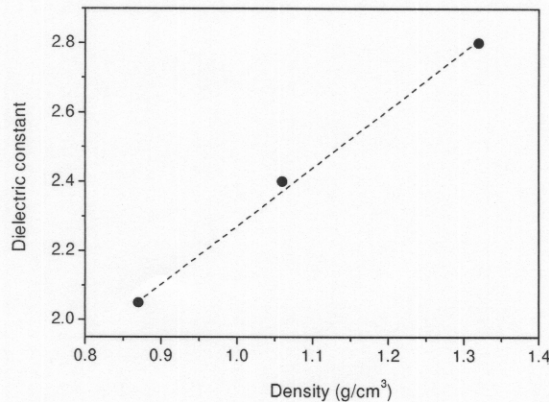


Figure 1. Dielectric constant as a function of density in SiCOH films.

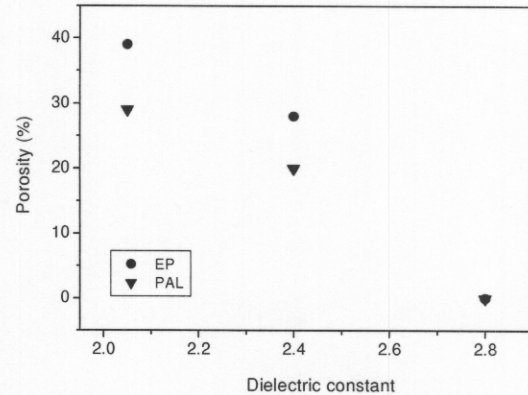


Figure 2. Porosity vs dielectric constant in SiCOH films.

Figure 3 presents a comparison between the experimental values of density and dielectric constant and values calculated assuming that the films are simple mixtures of the nonporous SiCOH ($k=2.8$) and pores containing air ($k=1$). The calculations were performed for different samples using porosity values obtained by PAS and EP. The results in Figures 3 show that the experimental values of the density and dielectric constant could be calculated with porosity values averaging between those obtained by the two techniques, indicating that the measured porosity fractions are quite reasonable.

As can be seen in Table II, the average pore size in the SiCOH films increases with the porosity fraction. The porosity in the ultralow- k film is further illustrated in Figure 4 which shows a TEM micrograph of the film with $k = 2.05$. The porous, amorphous material was investigated in out of focus conditions. In these conditions, depressions are visible due to the pores in the film. In the $k=2.8$ sample with no porosity such depressions are not observed (picture not shown). From the size of the depressions an average pore size of the order of 1.5-2.2 nm we deduced. Using an image processing software we deduced a pore volume fraction of 24-28% from the TEM micrographs of the films with $k=2.05$.

In any case, the pore size in the ultralow- k PECVD prepared SiCOH films is significantly smaller than that observed in porous spin-on films of similar dielectric constants, where they can reach values of 15-20 nm. [9] The small pore size in the PECVD films can provide advantages during the integration of these ultralow- k films in the interconnect structure, preventing/reducing penetration of metals, gases, liquids or other dielectric materials into the SiCOH films.

The potential robustness of the ultralow-k SiCOH was demonstrated by chemical-mechanical polishing (CMP) of a stack Si/SiO₂/ultralow-k SiCOH/liner/Cu. The stack was CMPed under typical conditions without the occurrence of any delamination in the stack.

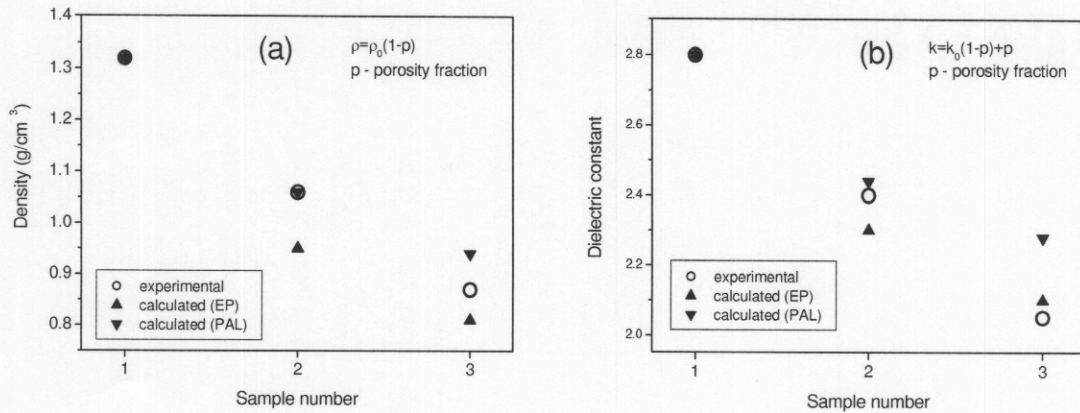


Figure 3. Comparison between experimental and calculated densities (a) and dielectric constants (b) of SiCOH films.

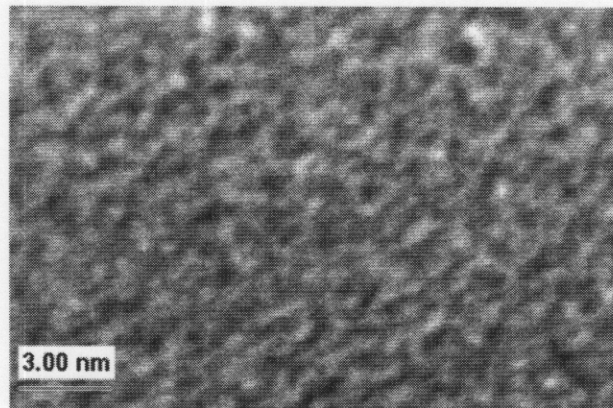


Figure 4. Out-of-focus TEM micrograph of SiCOH film with $k=2.05$

CONCLUSIONS

The results described above show that it is possible to produce porous films by the PECVD technique. While SiCOH films deposited from TMCTS are non-porous, porosity can be induced in the films by preparing them from mixtures of TMCTS with an organic precursor. Increasing the concentration of this organic precursor in the gas feed to the deposition reactor increases the porosity fraction in the films and the size of the pores. The film density, dielectric constants and mechanical properties correlate directly with the porosity fraction in the film. The SiCOH films of $k=2.05$ have a porosity of about 35% and an average pore diameter of only about 5 nm.

The pore size in the ultralow-k film is significantly smaller than that observed in organic or inorganic spin-on dielectric films of similar dielectric constant, providing a potential benefit in the integration of this ultralow-k material in an interconnect structure.

A metallization stack built on the ultralow-k SiCOH performed well under Cu CMP conditions providing a good indicator for the potential extendibility of SiCOH integration using ultralow-k PECVD films.

ACKNOWLEDGEMENTS

The authors are thankful to S. Cohen and D. Klaus for electrical characterization, E. Simonyi for nanoindentation, A. Kellock from Almaden Research Center (ARC) for RBS/FRES measurements, M. Weber and K.G. Lynn from Washington State University for positron annihilation measurements, L. Lurio from Argonne National Labs and M. Toney and H.-C. Kim from ARC for SAXS measurements, and K.P. Mogilnikov from XPEQT for help in EP analysis.

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