RC22643 (W0211-173) November 18, 2002
Materials Science

IBM Research Report

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CHARACTERIZATION OF LOW-k TO EXTREME LOW-k SiCOH DIELECTRICS

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ABSTRACT

Carbon doped oxide dielectrics comprised of Si, C, O, and H (SiCOH) have been prepared by plasma enhanced chemical vapor deposition from mixtures of tetramethylcyclotetrasiloxane (TMCTS) and an organic precursor. The thermally unstable CH_Y fragments from the organic fraction incorporated in the SiCOH matrix are removed by thermally annealing the deposited films, thereby inducing nanoporosity in the films. SiCOH type of dielectric spanning a range of dielectric constants (k) from 2.8 to 2.05 have been prepared by this approach. The extreme low-k films have a porosity of about 30% with an average pore size below 2.5 nm.

Rutherford backscattering (RBS) combined with forward recoil elastic scattering (FRES) has been used to determine the composition of the SiCOH films and have shown that the reduction of the dielectric constant is caused mainly by an increase in the porosity of the films, with very little changes in the composition of the film skeleton. The films have been characterized by FTIR and the deconvolution of the SiO absorption band has been used to evaluate the structure of the films of different dielectric constants. The results indicate that the organic fraction introduced in the films with ultralow and extreme low-k values is mainly incorporated through substitution at the Si-H bonds in TMCTS and that addition of the organic precursor to TMCTS in a plasma facilitates the enhancement or formation of a porous cage structure.

INTRODUCTION

The replacement of the oxide dielectric in ULSI devices with a real low dielectric constant (k) material has been delayed continuously and has caused outward revisions in time of the International Technology Roadmap for Semiconductors (ITRS) projections since 1997. The 2001 ITRS pushed out again low-k dielectric milestones, decelerating advances to ultralow-k dielectrics (k=1.6-2.2) from 2005 to 2009 [1]. The current "low-k" dielectric is fluorosilicate glass (FSG) which has a k value of about 3.5, only slightly lower than that of the silicon dioxide. The choice of the next best choice for low-k dielectrics, with values of k<3.0 is still ongoing between spin-on and PECVD materials and selections of both types will most probably appear in the first products with low-k dielectrics. The main contenders among the PECVD low-k dielectrics are amorphous materials from the group comprised of Si, C, O, and H which are deposited in conventional PECVD tools [2] and are known by different names, including SiCOH, SiOCH, carbon-doped oxides (CDO), organosilicate glasses (OSG), silicon-oxicarbides, and several trade names given by the various suppliers who provide processes and tooling

for these films. Throughout this paper we will use the term SiCOH to refer to this type of investigated films.

We have reported elsewhere [3-5] that it is possible to reduce the dielectric constants of SiCOH materials to values as low as k = 2.05, indicating the potential extendibility of PECVD dielectrics to several generations of ULSI chips. The dielectric constant is reduced by admixing an organic material to the SiCOH precursor and annealing the deposited films to remove unstable organic fractions from it. The dielectric constant can by adjusted at any value between 2.8 and 2.05 by adjusting the concentration of the organic precursor in the gas feed to the plasma [3, 4]. It was shown [6] that these reduced dielectric constants are achieved by the creation of various amounts of porosity in the films through the annealing.

The present paper reviews several properties of the entire range of SiCOH dielectrics and tries to shed light in the understanding of their structure based on compositional and FTIR analysis.

EXPERIMENTAL

The SiCOH films were deposited on Si (100) wafers using tetramethylcyclotetrasiloxane (TMCTS, $Si_4O_4C_4H_{16}$) as the precursor [2]. Helium was used to carry the TMCTS in a parallel plate PECVD reactor where the plasma was sustained by a 13.56 MHz RF power supply. The films with further reduced k values were prepared by admixing an organic precursor to the TMCTS + He gas feed and annealing the films afterwards in an inert ambience at 400 ^{o}C [3]. The annealing removes the unstable fractions and creates porosity in the material. All results are presented for annealed films unless specified otherwise.

The SiCOH films were characterized by Rutherford backscattering (RBS) in combination with forward recoil elastic scattering (FRES) to determine their atomic composition and by Fourier transform infrared analysis (FTIR) for analyzing their chemical bonding. Deconvolution of the SiO FTIR peak was used to obtain a better understanding of the structure of the porous films and the bonding of the residual organic fragments to the SiCOH matrix. More details on the preparation and characterization of the SiCOH films can be found elsewhere [2-4].

RESULTS AND DISCUSSION

It has been shown previously [4] that the dielectric constant of the annealed SiCOH films decreases with increasing fraction of the organic precursor in the gas feed, as shown in Figure 1. For sufficient dilution of the TMCTS precursor the dielectric constant reached a value of 2.05. The entire range of SiCOH films, with k=2.8 – 2.05, is characterized by low leakage currents of about 10^{-9} A/cm^2 at 1MV/cm [4] and relatively low coefficients of thermal expansion of about $12 \times 10^{-6}/^{o}K$ [5]. The hardness and modulus of the SiCOH films decrease with decreasing dielectric constant yet have values similar to bulk polymeric materials of significantly higher dielectric constants [5].

The composition of the different SiCOH films is presented in Figure 2 in terms of the ratios of the concentration of the different elements to the concentration of Si in the films. The addition of the organic precursor to TMCTS in the gas feed to the plasma results mainly in a significant increase in the relative C and H concentration in the films, however the higher concentrations appear to remain constant with increasing dilution of the TMCTS precursor. It has further been shown [6] that the decrease of the dielectric constant is directly related to the decrease of the density of the films caused by the formation of porosity in the structure.
The porosity is created during the annealing of the films by the loss of unstable CH_y fragments from the structure. The results presented in Figure 2 thus show that the annealed films with reduced k values contain residual CH_x fractions in the skeleton of the porous films. The density and porosity values are provided in Table I for several films of different dielectric constants. The results discussed above indicate that the dielectric constant of the SiCOH films is controlled mainly by the porosity induced in the films and it is of interest to understand how this correlates to the structure of the films.

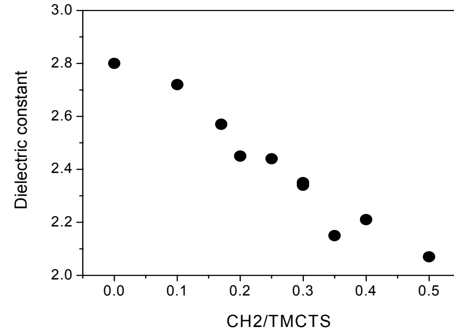

Figure 1: Dielectric constants of SiCOH films vs CH2/TMCTS ratio in the gas feed.

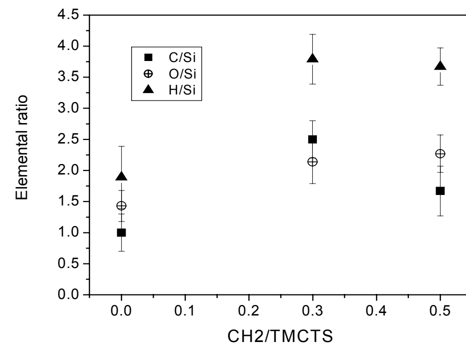

Figure 2: Elemental ratios vs dielectric constant of SiCOH films

Table I. Density and porosity of SiCOH films.

Dielectric constant	Density (g/cm3)	Porosity Fraction	Pore diameter (nm)
2.80	1.32	0	N/A
2.40	1.06	0.20	< 1.5
2.05	0.87	0.29	< 2.5

Structural characterization of amorphous films is extremely difficult and Fourier transform infrared (FTIR) spectroscopy is often used to characterize the different bonds in such films. Figure 3 presents the FTIR spectra of several films with different dielectric constants. SiCOH films with dielectric constants of about 2.8 are characterized by absorptions assigned to a weak $C-H_n$, n = 1-3 stretching at 3000-2800 cm^{-1}, medium Si-H stretching at 2300-2100 cm^{-1}, strong $Si-CH_3$ symmetric bending at 1274 cm^{-1}, strong Si-O-Si stretching at 1250-970 cm^{-1}, strong H-Si-O bending at 887 cm^{-1}, corresponding to larger angle H-Si-O bonds in a cage structure, and strong H-Si-O bending at 801 cm^{-1}, corresponding to smaller angle H-Si-O bonds in ladder structure [7]. As shown in the

insert in Figure 2, the Si-O stretch band appears to have a peak at 1047 cm^{-1} with a shoulder at a larger wavelength. However, the Si-O peak cannot be deconvoluted in two peaks, but instead has to be deconvoluted into three peaks centered at 1035 cm^{-1}, 1065 cm^{-1}, and 1140 cm^{-1} as illustrated in Figure 4. Figure 4.a shows the deconvolution of the Si-O band of a SiCOH film with k=2.8 into three peaks centered at 1023 cm^{-1}, 1063 cm^{-1}, and 1135 cm^{-1}. The peak at 1063 cm^{-1} corresponds to the stretching of smaller angle Si-O-Si bonds in a ladder structure, while the peak at 1135 cm^{-1} corresponds to larger angle Si-O-Si bonds in a cage structure [8]. The peak at 1023 cm^{-1} corresponds to stretching of C-Si-O bonds in a silicon suboxide [9]. Any C-O stretching vibration bands at 1200-1000 cm^{-1} [10] cannot be distinguished here due to overlap with the Si-O stretching band. The approximately equal intensities of the C-Si-O and Si-O-Si peaks suggest that the ring configuration of TMCTS has largely been preserved in the SiCOH film. The similar intensity of the 1135 cm^{-1} peak further indicates the formation of the cage structure in the films, similar to that in spin-on HSQ or MSQ films [8].

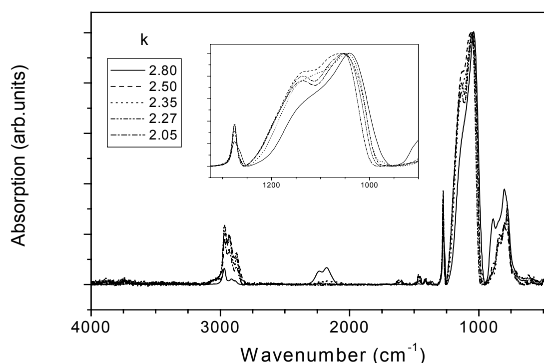

Figure 3: FTIR Spectra of SiCOH films of different dielectric constants. The spectra are displayed at identical Si-O peak height.

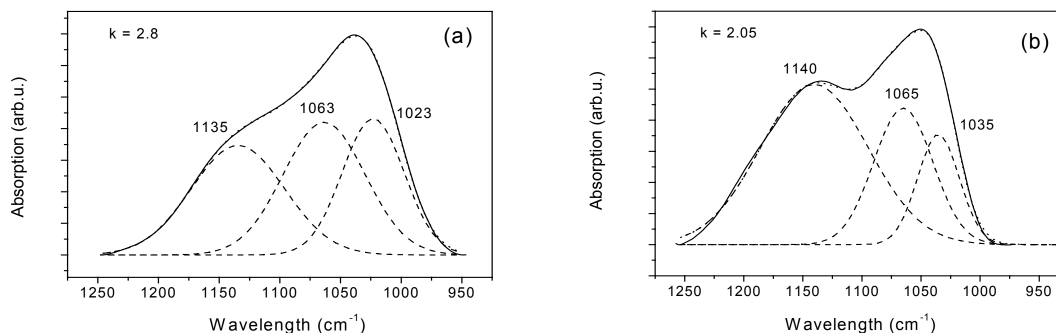

Figure 4: Deconvolution of the SiO absorption band of SiCOH films. a) k=2.8; b) k=2.05.

As shown in Figure 3, the spectra of the films with lower k values, prepared with the addition of the organic precursor, are characterized by an absence of Si-H peaks, strongly increased $C-H_n$ stretching vibration at 3000-2800 cm^{-1}, and an apparently increased relative $Si-CH_3$ absorption peak (the insert in Figure 3 shows that the height of the $Si-CH_3$ peak increases with decreasing k value). The increased $C-H_n$ stretching vibration is consistent with an increase in C/Si elemental ratio in these films (see Figure 2). The loss of the Si-H peaks with the increased $C-H_n$ peaks suggests that the organic precursor is reacting with the Si-H bonds in TMCTS during the formation of the film. A reduction in the peak intensity of the H-Si-O bending absorptions at 950-650 cm^{-1} is consistent with substitution of the organic precursor at Si-H sites. Furthermore, the Si-O band of the films with reduced k has broadened and shifted to higher wavenumbers. The

deconvolution of the Si-O peak shown in Figure 4.b shows that the positions of the cage Si-O-Si and suboxide C-Si-O peaks of the film with k=2.05 shifted to slightly higher wavenumbers, i.e. 1140 cm^{-1} and 1035 cm^{-1}, respectively.

The observations discussed above are summarized for the entire range of investigated films in Figures 5 and 6. The scatter of the values shown in these figures can be attributed to experimental errors and errors in the deconvolution calculations. While the figures present the parameters for annealed films, similar values were obtained, within the experimental errors, for the as-deposited films. As shown in Figure 5, the relative area ratio of Si-O cage/Si-O ladder increases with decreasing dielectric constant, indicating that the addition of the organic precursor has contributed to the enhancement of the cage structure. The formation of the cage structure is consistent with increasing porosity as shown in Table 1. Interestingly, the relative area ratio of C-Si-O/ Si-O ladder decreases with addition of organic precursor (corresponding to decreasing dielectric constant in Figure 5). This might be attributable to a decrease in the relative area of the C-Si-O peak due to an enhanced fragmentation of the TMCTS ring and formation of Si-O-CH_m bonds to be discussed later.

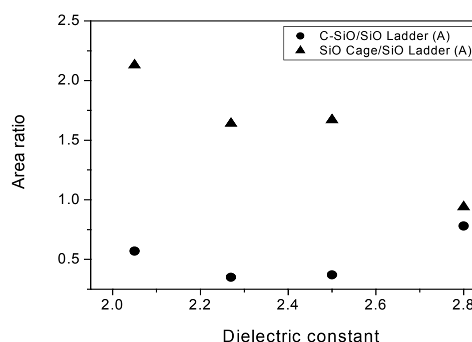

Figure 5: Area ratios of the deconvoluted oxide peaks vs the dielectric constant of the SiCOH films.

The FWHM values of the deconvoluted SiO peaks are presented in Figure 6 which shows that the FWHM of the ladder SiO and of the C-Si-O peaks decrease with decreasing dielectric constant and that the FWHM of the cage SiO peak increases with decreasing dielectric constant. The increase in the cage SiO peak's FWHM might be attributable to an increasing variety of bonding environments in the cage structure. The decrease in the ladder SiO and C-Si-O peak's FWHM is possibly attributable to a less variable ladder Si-O-Si and C-Si-O bond angle in the cage structure.

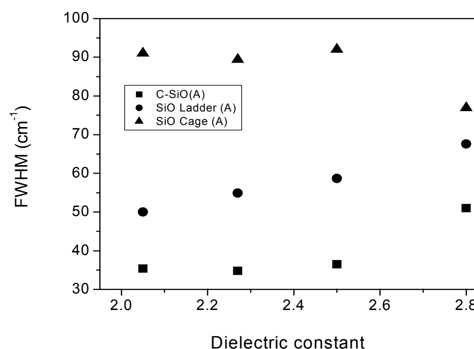

Figure 6: FWHM of the deconvoluted oxide peaks vs the dielectric constant of the SiCOH films.

The intensity ratio of the Si-CH_3/SiO (total absorption from 1200-1000 cm^{-1}) peaks is often used to qualify SiCOH films. Figure 3 showed that the height of the Si-CH_3 peak at 1274 cm^{-1} increased with decreasing dielectric constant, corresponding to increasing dilution of TMCTS with the organic precursor and increased incorporation of CH_x fragments in the film. However, the real parameter to be compared is the ratio between the integrated peak areas of the Si-CH_3 and SiO peaks. This ratio is shown as a function of the dielectric constant of the annealed films in Figure 7. One surprising observation (not shown in the figure) is that the Si-CH_3/SiO intensity ratios are the same, within experimental error, for the as-deposited and the annealed films, in spite of the fact that a large amount of CH_x fragments are lost from the films during annealing.

Another interesting observation reflected in Figure 7 is the fact that the $Si-CH_3/SiO$ area ratio increases only slightly with increasing dilution of TMCTS and reaches a maximum. The value of this maximum is only 12.5% higher than for the films deposited from pure TMCTS. Figure 2 showed that the films deposited from the mixtures of TMCTS with the organic precursor contain significantly higher amounts of C and H than the films deposited from pure TMCTS, therefore one might expect this to be reflected in significantly higher $Si-CH_3/SiO$ area ratios. As this is not the case, it has to be assumed that the CH_x fractions added to the films are not connected in $Si-CH_3$ bonds. We have shown above that the organic precursor is most probably incorporated by substitution at the Si-H sites. It is therefore possible that the connection of the CH_x fragments occurs through $Si-O-CH_m$ bonds. The infrared absorption of these bonds is contained in the 1200-1000 cm^{-1} peak and is not separable from the Si-O absorption peak and therefore not detectable by FTIR.

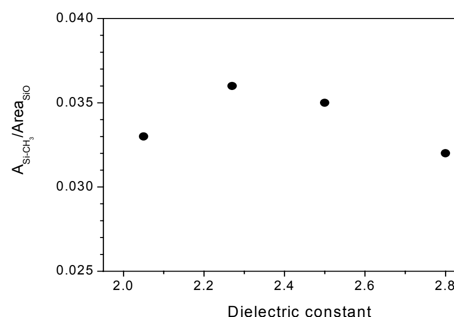

Figure 7: Relative intensity of Si-CH3 peak vs the dielectric constant of the SiCOH films
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CONCLUSIONS

Deposition of the SiCOH films from mixtures of TMCTS with an organic precursor results in the incorporation of CH_z fragments in the structure and the partial loss of these fragments through annealing causes the formation of nanopores and reduction of the dielectric constants of the films to extreme low-k values.

FTIR analysis showed that the SiCOH films with dielectric constants of 2.8 to 2.05 comprise three types of Si-O bonds, namely Si-O-Si ladder, Si-O-Si cage, and C-Si-O, and that the organic fraction added in the films with ultralow and extreme low-k values is mainly incorporated through substitution at the Si-H bonds in TMCTS, probably through $Si-O-CH_m$ bonds.

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