RC22009 (98878) 30 March 2001 **Materials Science**

IBM Research Report

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Ultralow-k dielectrics prepared by plasma enhanced chemical vapor deposition

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ABSTRACT

Carbon doped oxide materials (SiCOH films) with ultralow dielectric constants have been prepared by PECVD from mixtures of SiCOH precursors with organic materials. The films have been characterized by Rutherford backscattering and forward recoil elastic scattering analysis, FTIR and index of refraction measurements, and measurement of step heights in the films. The electrical properties of the films have been measured on metal insulator silicon structures. By proper choice of the precursor and deposition conditions, the dielectric constants of the SiCOH films can be reduced to values below 2.1, demonstrating the extendibility of PECVD prepared carbon doped oxides as the interconnect dielectrics for future generation of VLSI chips.

The advances in the performance of the ULSI chips have been hindered in recent years by the difficulties of introduction of new materials in the interconnect part of the Si chip technology. While a large effort is invested for many years to replace the SiO_2 dielectric with materials having a significantly lower dielectric constant and about 150 different dielectric materials have been identified by SEMATECH in the mid-1990s [1], the progress has been much less successful and the SIA roadmap for the interconnect dielectric has been revised continuously from 1997 [2]. In spite of that, there is still an ongoing discussion on the best choice of the low-k dielectric: spin-on or PECVD material. One of the principal criteria for the choice of a new interconnect dielectric is its extendibility to later chip generations, requiring further reduced k values. The advocates of the spin-on polymers base their arguments on the fact that spin-on polymers might offer extendibility to ultralow-k values [3,4] and the belief that the PECVD films are unable to provide this extendibility [1]. The main contenders among the PECVD low-k dielectrics are materials from the group comprised mainly of Si, C, O, and H (SiCOH) [5], also called carbon doped oxides, or silicon oxicarbides. A comparison of some of these materials, which are characterized by dielectric constant values in the range of 2.8 to 2.65, can be found elsewhere [6]. We have shown previously [7] that is possible to reduce the dielectric constants of the SiCOH materials to values below k=2.4 and claimed that it might be possible to further reduce the k value by optimizing the preparation conditions and choice of precursor. In the present paper we report SiCOH based dielectrics having ultralow-k values down to 2.1, demonstrating the extendibility potential of the PECVD dielectrics to future generations of VLSI chips.

The ultralow-k films were prepared as dual phase materials [7] by the PECVD technique described elsewhere [5] for the preparation of the regular SiCOH films. For the preparation of the ultralow-k films an organic precursor (CH) was admixed to the precursor used for the deposition of the SiCOH films. The RF power was kept at levels sufficiently small to produce pure SiCOH films having low-k values of about 2.8, yet sufficiently high to dissociate the organic precursor and incorporate its fragments in the deposited films. The films were characterized by Rutherford backscattering (RBS) and forward recoil elastic scattering (FRES), Fourrier transform infrared analysis (FTIR) and n&k Analyzer 1280. Thickness changes were measured in steps formed in the films. The dielectric constants (k) were measured on silicon-insulator-metal structures using highly doped, electrically conductive Si substrates and Al dots structures. The breakdown fields and leakage currents were determined from I-V curves measured on the same structures.

Figure 1 presents a comparison of FTIR spectra obtained from a SiCOH films with k=2.8 and from a modified ultralow-k film from the present study with k=2.2. The spectra were obtained after annealing the films at 400 ^{o}C. The spectrum of the SiCOH film in Figure 1.a, typical for most carbon doped oxide films, is characterized by the strong SiO peak at 1042 cm^{-1}, the $Si\text{-}CH_3$ peak at 1275 cm^{-1}, a doublet SiHx peak at 2235 and 2176 cm^{-1} and a very small CH_x peak [5] at 2966 cm^{-1}. The shoulder at higher wavelength is indicative of some degree of caged SiO bond structure. The spectrum of the ultralow-k film in Figure 1,b displays an enhanced CH peak at around 2930 cm^{-1} and has a clearly separated SiO peak at 1135 cm^{-1}. This peak is an indicator of the existence of caged SiO bonds in the ultralow-k film and a reflection of enhanced porosity in the film. The spectrum of the as-deposited ultralow-k film is similar to that in Figure 1.b, but has a higher CH peak at 2930 cm^{-1}. The reduction of the CH peak during annealing is an indication of the loss of CH fragments from the film during annealing.

The RBS and FRES analysis showed that the C concentration increased and the O concentration decreased in the as deposited films with increasing fraction of the CH precursor in the gas feed, however the H concentration remained essentially constant. The annealing caused a strong loss of C and H from the films, but little changes in the O/Si ratio. These results indicate that the annealing causes the removal of significant amounts of CH_x species from the films, which can cause in turn the formation of nanopores in their structure. The annealed ultralow-k films had significantly higher C and H concentrations than the pure SiCOH film, indicating the incorporation of significant amounts of CH_y fragments in the structure of the annealed films. These fragments can also contribute to the formation of a less denser structure in the films.

The loss of CH_x species during annealing is associated with significant reduction in film thickness. The fraction of thickness reduction during annealing increases continuously with increasing fraction of the CH precursor in the gas feed to the reactor, but levels out at about 28%. The thickness changes in the ultralow-k films during annealing are significantly lower than those observed previously for the dual-phase films deposited with a different organic precursor. The latter reached a thickness reduction of 50% for small fractions of the organic precursor in the gas feed [7].

The changes in the concentration of the CH_x species incorporated in the SiCOH structure affect the optical properties of the films. The index of refraction at 633 nm and the optical gap of the as deposited films were found to be almost independent of the CH

fraction in the gas feed. Both the index of refraction and the optical gap decreased after the annealing of the films and became dependent on the organic fraction in the feed gas. The index of refraction decreased down to 1.37 and the optical gap increased to 3.4 with increasing CH fractions in the gas feed. The behavior is different from that observed for the dual-phase films, where only small changes in the optical gap and no significant changes in the index of refraction were observed after annealing [7].

The dielectric constants of the discussed films are presented in Figure 2 as a function of the concentration of the organic CH precursor in the gas feed. After the first anneal, the dielectric constants decrease continuously with increasing fraction of CH, reaching ultra-low values down to 2.1 at a CH fraction of 0.5 . This ultralow-k value is significantly lower then the minimum value of 2.4 obtained previously for the dual-phase films [7]. The dielectric constant of a pure SiCOH deposited under similar plasma conditions, without the addition of the organic precursor, is 2.85 [5]. A subsequent anneal of the ultralow-k films for 4 hours at 400 ^{o}C reduced further the dielectric constants to values as low as k=1.95, indicating that the annealing conditions of the deposited films are not yet fully optimized. The values of the dielectric constants of the PECVD deposited ultralow-k films are similar to the values of 2.19-2.2 reported for porous spin-on films [3,4] and can be related to the nanoporosity induced in the SiCOH films by the removal of volatile CH_x species during the annealing and by the residual CH_y species incorporated in the films. Furthermore, the ultralow-k values may be related to an apparent cage structure of the SiO bonds, induced by the addition the CH organic to the precursor of the films, as indicated by the FTIR spectrum in Figure 1.b. Figure 3 shows the dependence of the leakage currents on the electric field for an ultralow-k film with k=2.18. The leakage current increases with increasing electric field, but has a low value of only 1.10^{-9} A/cm^2 at 1 MV/cm, similar to a pure SiCOH film [5]. The breakdown fields of the investigated ultralow-k films are in the range of 5 - 6 MV/cm, indicating that the films are suitable candidates for the back-end dielectric of VLSI interconnects.

The results described above show that it is possible to decrease the dielectric constants of the PECVD prepared carbon doped oxide films to values < 2.1, proving the extendibility of the PECVD films for future generations of VLSI chips. As it is expected that the PECVD deposited films will have superior mechanical properties to spin-on films of similar dielectric constants, the PECVD ultralow-k films have the potential to become a strong competitor to the spin-on ultralow-k films as the interconnect dielectric. It may be possible to reduce even more the k values of the PECVD films by further optimization of the deposition parameters or by better choice of the organic precursor which is added to the SiCOH precursor.

The authors are thankful to D.Klaus for electrical characterizations, R.Carruthers for the preparation of the SIM structures, and A.Kellock from Almaden Research Center for RBS/FRES analysis.

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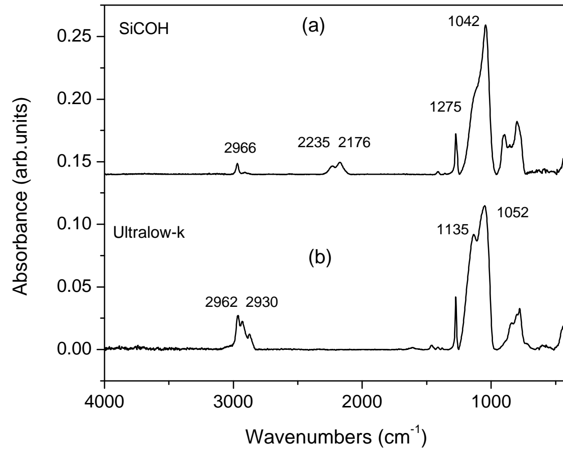

Figure 1. FTIR spectra of SiCOH and ultralow-k PECVD dielectric films.

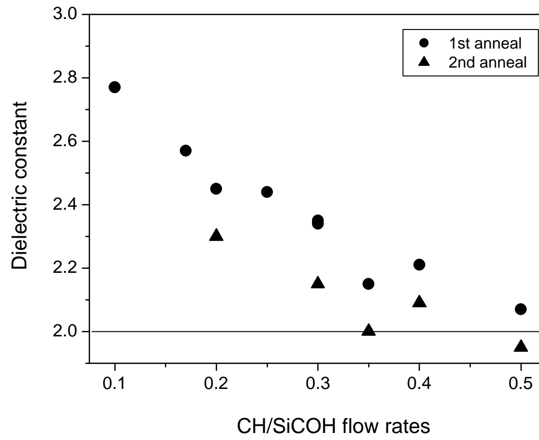

Figure 2. The dielectric constants as a function of the ratio of precursor flow.

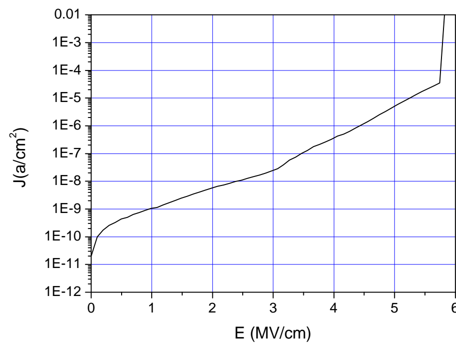

Figure 3. Leakage current in annealed ultralow-k film.