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Research Report

Novel Low-k Dual-Phase Materials Prepared by PECVD

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ABSTRACT

Dielectric materials based on Si, C, O, H (SiCOH) have been demonstrated previously with dielectric constants of about 2.8. This value could be potentially further reduced by increasing/introducing porosity in the SiCOH films. Depositing multiphase films containing at least one thermally unstable phase and annealing the films to remove this labile phase from the material could create the enhanced porosity. Dual-phase materials, SiCOH-CH, have been prepared in the present study by PECVD from mixtures of a SiCOH precursor with a hydrocarbon. The films have been characterized as-deposited and after thermal anneals of up to 4 hours at 400 ^{0}C. The atomic composition of the films has been determined by RBS and FRES analysis and their optical properties have been determined by FTIR and n&k measurements. Metal-insulator-silicon structures have been used to measure the electrical properties of the dual-phase films. After an initial anneal at 400 °C, accompanied by a significant loss of CH and some SiH species and a thickness loss of up to 50%, the films stabilized. Depending on the deposition conditions and concentration of the CH precursor in the feed gas, the dielectric constant decreased by 10-15% during the stabilization anneal and reached values as low as 2.4. These initial results indicate the possibility to further reduce the dielectric constant of PECVD produced SiCOH films and the potential to incorporate such films in the interconnect structures of future ULSI chips.

INTRODUCTION

The electrical properties of the interconnect dielectric (ILD) become as critical as the those of the metal wiring for achieving high performance in the shrinking, high speed ULSI devices. Low dielectric constant materials are required for the ILD to reduce propagation delays, cross-talk noise between metal wires, and power dissipation from RC coupling. The research done on low-dielectric constant (low-k) materials is well reflected in the proceedings of this symposium of the last 5 years.[1] However, the search for an integratable low-k dielectric material is still a work-in progress which appears to elude the original roadmap for low-k interconnect dielectrics.[2] Some promising low-k materials can be deposited by spin-on techniques while other can be prepared by plasma enhanced chemical vapor deposition (PECVD) processes. The latter can produce films that are more crosslinked than spin-on polymeric films and be therefore mechanically tougher.

Low-k materials comprised of Si, C, O and H, (SiCOH films) and prepared by plasma enhanced chemical vapor deposition (PECVD) have been reported previously by the present authors [3] and are being offered by equipment vendors under different trade names.[2] The materials, often referred to as carbon-doped oxides, are characterized by dielectric constants of about 2.8, almost independent of the source.

Further lowering of the dielectric constant could potentially be achieved by increasing or introducing porosity in the SiCOH films. Depositing multiphase films containing at least one thermally unstable CH phase in addition to the SiCOH phase and annealing the films to remove the labile phase from the material could produce such enhanced porosity. (*The CH and SiCOH notations in this paper reflect the atomic compositions of the phases but not their stoichiometry*)

In the present work, we report a dual phase dielectric prepared by incorporating a CH phase in the SiCOH films and annealing the films to remove a significant fraction of the thermally less stable CH phase.

EXPERIMENT

The dual-phase SiCOH-CH films were prepared by the same PECVD method as described elsewhere [3] but adding a hydrocarbon (CH precursor) to the SiCOH precursor feed to the reactor. The substrates were placed on the powered electrode, thus acquiring a negative bias relative to the plasma. The RF power was kept at levels small enough to produce pure SiCOH films having low-k values of about 2.8, yet sufficiently high to dissociate the hydrocarbon and incorporate its CH fragments in the deposited films. After deposition, the films were annealed in helium for 4 hours at 400 °C to remove the less stable fraction of the films.

The dual-phase films were characterized by Rutherford backscattering (RBS) to determine the atomic composition with the exception of hydrogen and forward recoil elastic scattering (FRES) for the hydrogen content. Fourrier transform infrared analysis (FTIR) was used to characterize the different bonds in the films. The index of refraction, and optical gap were measured with a spectrometric reflectance tool, n&k Analyzer 1280 from n&k Technology, Inc. Dielectric constant (κ) measurements were performed on metal-insulator-silicon (MIS) structures using highly doped, electrically conductive Si substrates and Al dots structures. The backside of the Si wafer was coated with a blanket Al film to obtain good electrical contact. Breakdown and leakage currents were determined from I-V curves measured on the same structures.

RESULTS AND DISCUSSIONS

Composition and optical properties

Figure 1 presents the composition of as-deposited SiCOH-CH films as a function of the ratio of the precursors in the gas feed to the reactor. It can be seen that the C and H concentrations increase and the Si and O concentrations decrease continuously with increasing CH precursor fraction in the gas feed. The RBS/FRES analysis showed significant material loss during annealing, the loss increasing with increase concentration of the hydrocarbon in the gas feed. In addition, the annealing caused a decrease in the concentration of C and H and corresponding increase in the concentration of Si and O, indicating a preferential loss of CH specimens from the SiCOH-CH films.

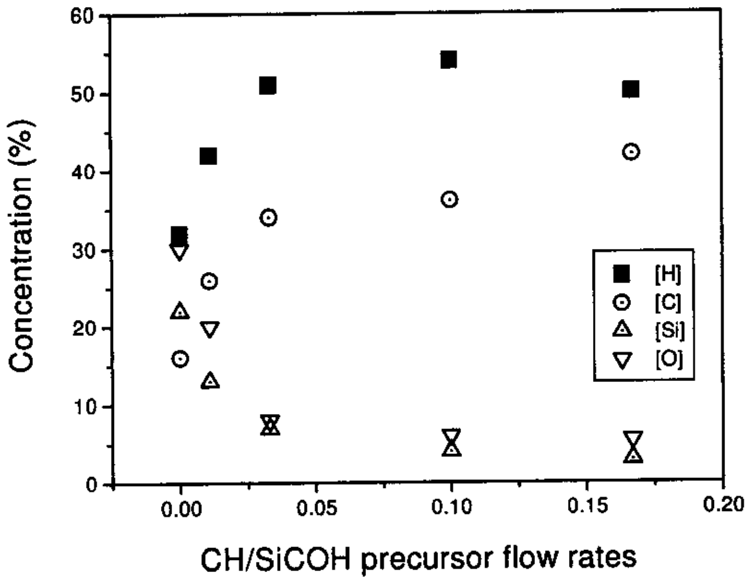


Figure 1. Composition of dual phase films vs precursor flow ratio

Figure 2 presents a comparison of FTIR spectra obtained from an as-deposited SiCOH film (a), a CH film deposited from the pure hydrocarbon (c), and a film obtained from a mixture of the SiCOH and CH precursors (b). The spectrum of the SiCOH film is characterized by the strong SiO peak at 1045 cm^{-1}, the Si-CH_3 peak at 1274 cm^{-1}, a doublet SiH_x peak at 2233 and 2177 cm^{-1} and a relatively very small CH_x peak at 2966 cm^{-1}. [3] In contrast to this spectrum, the spectrum of the CH film is characterized by a strong CHx band with several peaks around 2900 cm^{-1}.[4] The film deposited from a mixture of the SiCOH and CH precursors displays the peaks characteristic of both the SiCOH and the CH films, indicating at least the existence of a significant amount of CH bonds incorporated in the SiCOH structure (Figure 2, b). A closer look at the 1270 cm^{-1} peak indicates that it is in fact a doublet (See Figure 3, c), the secondary peak most probably corresponding to an epoxide type (COC) bond. The FTIR spectrum in Figure 2, b thus indicates the formation of a dual phase SiCOH-CH film, to the extent that the amorphous SiCOH and CH structures could be considered phases.

The effect of annealing on the FTIR spectrum of the dual phase film is illustrated in Figure 3. The comparison of the spectra in Figure 3, a and b, shows the strong decrease of the CH peak relative to the SiO peak as a result of the annealing, while the comparison of the expanded parts of the spectra in Figure 3, c and d, shows an associated decrease in the COC peak of the doublet at 1270 cm^{-1}. The results thus indicate a significant loss of the CH and probably also CO specimens from the dual phase films during annealing. The changes result in a decrease of the C concentration and an increase in the Si concentration in the annealed films as indicated by RBS/FRES.

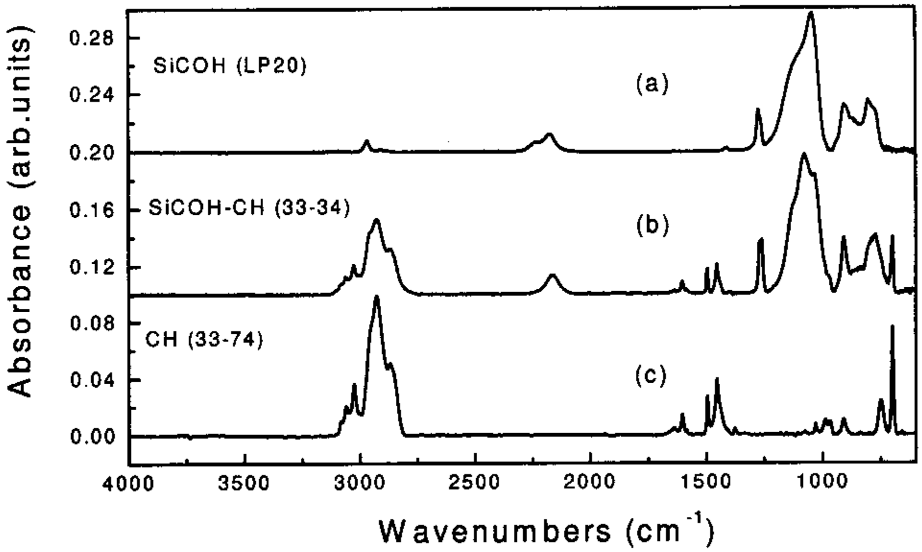


Figure 2. FTIR spectra of SiCOH, CH, and dual phase films

Two optical properties of the dual-phase films, namely the index of refraction at 633 nm and the optical gap are shown in Figure 4 as a function of the ratio of the precursors in the gas feed. The index of refraction increases and the optical gap decreases with increasing concentration of the CH precursor in the gas mixture. These changes are associated with corresponding increases in C concentration in films as indicated in Figure 1. Increasing the C concentration in the films causes an increase in the index of refraction, starting from values close to that of SiO_2, and corresponding decreases in the values of the optical gap. Removal of CH fractions by annealing caused only small changes in the optical gap and no significant changes in the index of refraction.

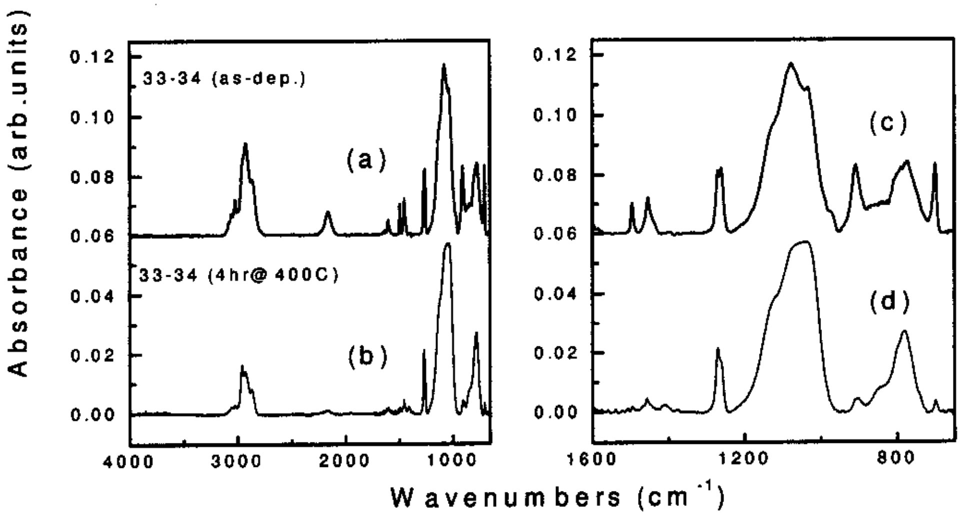


Figure 3. FTIR spectra of a SiCOH-CH film. (a), (c) – as deposited; (b) and (d) after annealing

Electrical properties

The electrical characteristics of the dual-phase films are presented in Figures 5 and 6. Figure 5 shows the dielectric constant of the annealed films as a function of the ratio of the precursors in the gas feed. The dielectric constant of a single phase SiCOH film prepared in similar conditions is 2.85 as reported previously.[3] With incorporation of the secondary CH phase in the films the dielectric constant of the annealed films decreases and reaches a minimum of 2.4 at a precursor ratio of about 0.06. The existence of a minimum in the dielectric values can be correlated to the thermal stability of the dual-phase films that were prepared with the intention to change during annealing. While FTIR indicated that the annealing causes a relatively larger loss of the CH specimens, RBS showed that the annealing is associated with loss of both CH and SiCOH fractions. These losses occurring during annealing could result in formation of nanoporosity in the films and lower density if the film would maintain its geometrical dimensions. The formation of porosity in the film will in turn reduce its the dielectric constant. The loss of material during annealing increases with increasing fraction of the CH phase, therefore the corresponding decrease of the dielectric constant observed in Figure 5. However, measurement of steps generated in the films showed that the film thickness also decreases during annealing. The thickness reduction increased with increasing fraction of CH precursor in the gas feed and reached values up to -50% for the investigated conditions. Thus, the potential porosity formation during annealing is competing with the reduction (collapsing) of the film thickness and for large fractions of CH phase this competition can result in a reversal in the changes of the film density during annealing. While this is to a certain extent a speculative assumption at this stage, it can nevertheless explain the minimum observed in the dielectric constant.

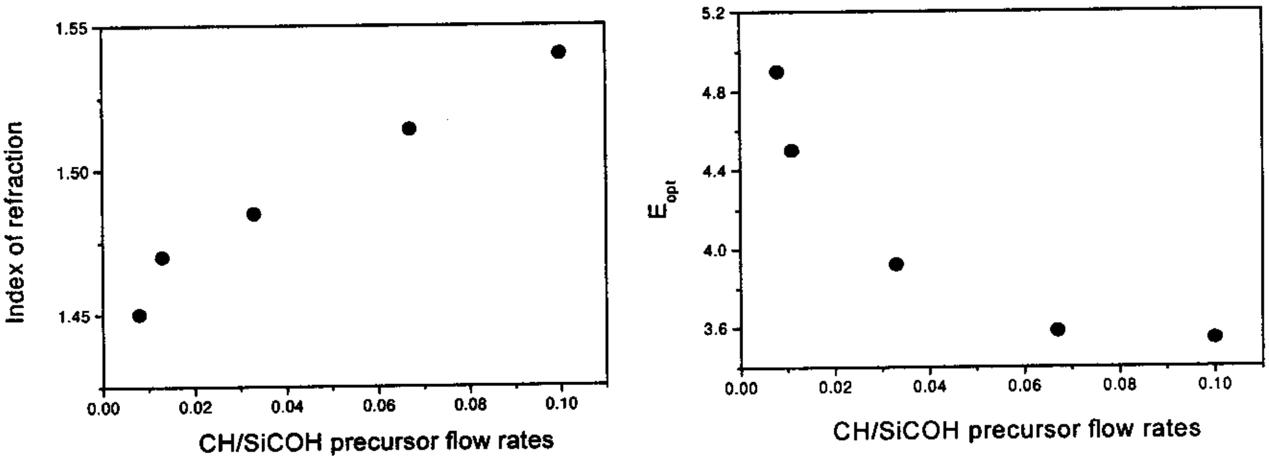
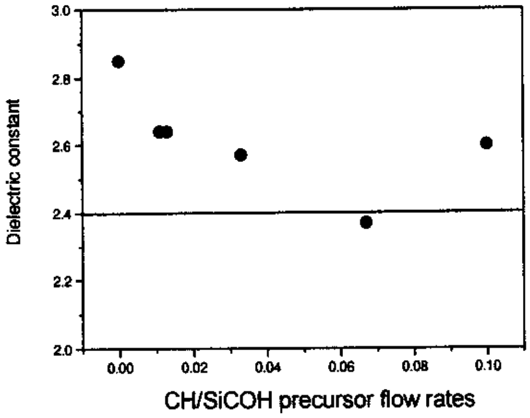


Figure 4. Index of refraction at 633 nm and optical gap of as deposited SiCOH-CH films.

A typical dependence of the leakage currents on the electric field is illustrated in Figure 6 for an as-deposited and annealed dual-phase film. The leakage current is essentially unaffected by the annealing and has a low value of 2.10^{-9} A/cm^2 at 1 MV/cm, typical for SiCOH films. The breakdown fields of the investigated dual phase SiCOH-CH films are in the range of 4.5 to 6 MV/cm. These values make the films suitable candidates for the back-end dielectric of ULSI interconnects.

The behavior observed in the investigated films is most probably related to the precursor used for the CH phase and the dissociation of both the CH and SiCOH precursors in the plasma. It may therefore be possible to further reduce the dielectric constant by optimizing the deposition conditions and the choice of precursors.



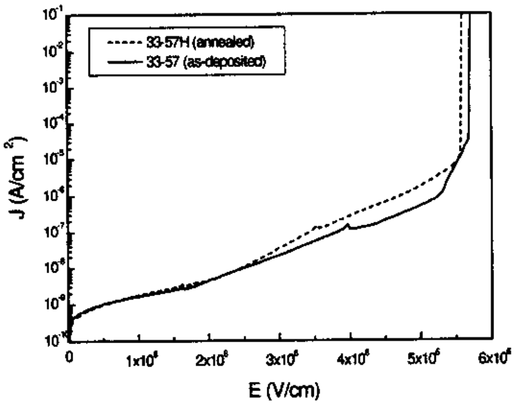


Figure 5. (left) Dielectric constant of annealed SiCOH-CH films.
Figure 6. (right) Leakage currents in as-deposited and annealed SiCOH-CH films.

SUMMARY

Dual-phase SiCOH-CH films were prepared by PECVD from mixtures of the SiCOH precursor with a hydrocarbon. Annealing of the films resulted in preferential loss of CH fractions from the films. By increasing the ratio of the CH precursor to SiCOH precursor in the gas feed the dielectric constant of the annealed dual phase films decreased from 2.85 to a minimum of 2.4. This value could be potentially further reduced by optimization of the deposition conditions and choice of precursors.

The dual-phase films have low leakage currents, of about 10^{-9} A/cm^2 at 1MV/cm, and breakdown fields of about 5 MV/cm.

The PECVD dual-phase SiCOH-CH films have, therefore, a strong potential to extend the carbon doped oxide dielectrics (SiCOH) to lower dielectric constants and their potential as candidates for the BEOL interconnect dielectric.

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