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Thermal Stability of a-C:F,H Films Deposited by Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition

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ABSTRACT

Amorphous carbon films grown with fluorohydrocarbons can be grown to have dielectric constant values around 2.0. The behavior of these films when subjected to thermal excursion is studied. We have investigated material deposited in an ECR plasma, and find that the F:H ratio of the gas mixture is a good guide to material properties. Films deposited at 5°C were placed in a vacuum chamber at 400°C as long as 60 minutes. The film thickness, dielectric constant, and infrared absorption spectrum change with the F:H ratio of the incoming gas and thermal cycling. It was found that the dielectric constant and loss tangent decrease upon heating and that there is an apparent increase in C=C groups. As expected, as the F:H ratio increases, the dielectric constant and thermal stability decrease. Good thermal stability is shown for F:H ratios of 1.5, which result in films with a dielectric constant of ~2.4 after heating.

INTRODUCTION

For interconnect structures used in ULSI applications, one promising class of materials for interlayer dielectric films is organic films deposited by PECVD. These materials are expected to have dielectric constants as low as 2.0, excellent gap fill, and relatively simple implementation. It has been know for many years that fluorohydrocarbons in rf plasmas can form polymeric films. This polymer has been a factor in the etching of silicon oxide and silicon, either by promoting anisotropic etching by sidewall passivation or inhibiting etching altogether [1-3]. Recently, attention has shifted towards the development of similar films deposited with similar precursors for low dielectric constant (low-k) materials [4-7]. Such fluorinated organic films are being considered as candidates for the next generation of inter-layer dielectric films in the interconnect structure of integrated circuits. Glow discharge work has shown that organic thin films for interlayer dielectric applications made using simple fluorohydrocarbon gas mixtures can have dielectric constants as low as 2.0 [4,5].

Most of the work to date on these materials has concentrated on electrical and optical properties. One major issue for such organic films is thermal stability during subsequent processing steps, which typically reach 400°C. It has been shown that the materials with the lowest dielectric constants tend to be thermally unstable, in that they lose a significant amount of their volume [4,6,8]. Post-deposition thermal behavior of the films is important in understanding how they will change during subsequent processing steps that involve thermal cycling.

In order to determine the suitability of the material as an intermetal dielectric, it is necessary to measure the impedance of the material. Infrared spectroscopy can be used to develop an understanding of the functional molecular groups within the material as well as monitor how these change upon thermal cycling. In addition, ellipsometric measurements can be used as a monitor of changes in film properties. In this study, the dielectric constant of the films is evaluated as a function of the plasma gas composition, and as a function of thermal soaking time at 400°C. The effect of thermal cycling on optical properties will also be discussed.

EXPERIMENTAL

The films were deposited in an electron cyclotron resonance, (ECR), PECVD reactor under the following constant conditions: substrate electrode temperature of 5°C with

open loop control, pressure of 2 mTorr, total gas flow of 20 sccm, and 600W source power at 2.45 GHz. The varied parameters were the applied bias, between 0 and -120V, and the fluorine to hydrogen ratio of the incoming fluorohydrocarbon gas mixture, between 1.5 to 3. Typically, for high-density plasmas, the atomic composition of the incoming gases rather than the actual compound flow rates is what governs the subsequent process [9]. Samples were deposited on wafers with either conductive surfaces or bare p-type Si (ρ ~ 10 Ω-cm).

The simplest device on which to perform impedance measurements is a parallel plate capacitor consisting of two conductive plates and the material of interest as the dielectric. To make the capacitor structure, a 500Å TiN/ 7500Å W/ 500Å TiN stack was grown on p-type Si as the bottom electrode. The W-based conductive layer was used because of its resistance to grain growth in the time-temperature regime covered in the experiments. The surface roughness of the stack was reduced to less than 20nm by use of chemical mechanical polishing of the W surface. The stack had a 15 mm x 15 mm square etched from it to act as a window for FTIR measurements. After the films were grown and thermally cycled, Ti/Au dots ranging from 0.8 to 2.1 mm in diameter were evaporated onto the film to complete the capacitors. The advantage of this type of

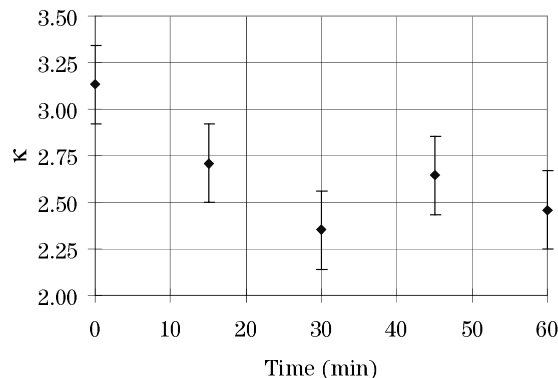

Figure 3: Dielectric constant at 10^5 Hz as a function of a thermal soak at 400°C in 4 Torr Ar. The growth conditions were -50V bias, and a 1.5 F:H gas mixture.

Optical measurements included infrared transmission using a Nicolet ECO-8 transmission FTIR system and ellipsometry at 632 nm using a Rudolph FE-IIID variable angle ellipsometer. Infrared measurements were converted into absorbance using the thin film approximation and the Si signal was subtracted by using a reference wafer associated with the wafer lot. The ellipsometer was used to determine real, (Re(**N**)), and complex, (Im(**N**)), components of the refractive index.

Electrical measurements were made with an HP4284A LCR meter and a manual probe test stand. The majority of measurements were made at 100 kHz to facilitate loss tangent, (tan d or tan δ), measurements. However, spot comparisons of measurements at 1 MHz indicate no significant change in the dielectric

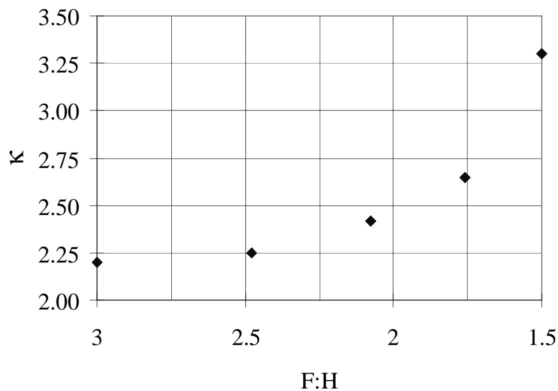

Figure 1: Dielectric constant as a function of F:H ratio in the gas mixture.

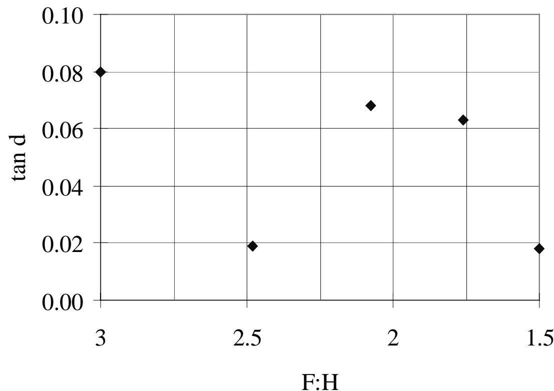

Figure 2: Loss tangent as a function of F:H ratio in the gas mixture.

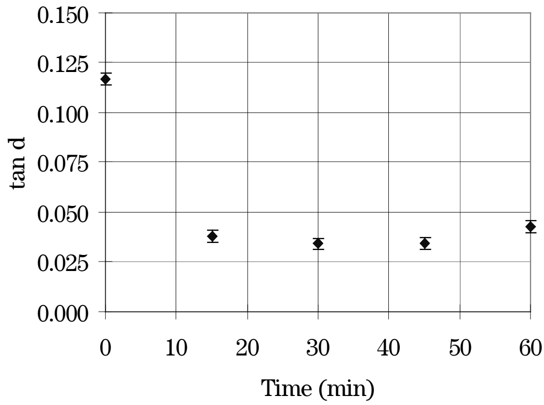

Figure 4: Loss tangent at 10^5 Hz as a function of a thermal soak at 400°C in 4 Torr Ar. The growth conditions were -50V bias, and a 1.5 F:H gas mixture.

constant.

RESULTS

Figures 1 and 2 show the effect of the gas mixture on the dielectric constant and the tan δ. As the amount of fluorine injected declines, the dielectric constant rises, while tan δ appears scattered. The mean of the tan δ values for these films is about 0.050. This compares with a tan δ for polyimide of about 0.010. Substrate bias was not shown to have an effect on dielectric constant up to -80V, and some indicatic

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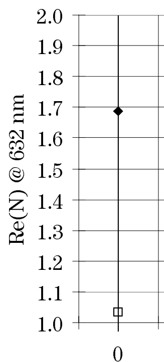

Figure 5: Re(**N**) soak at 400°C in -40V bias, and a 1.5 F:H gas mixture.

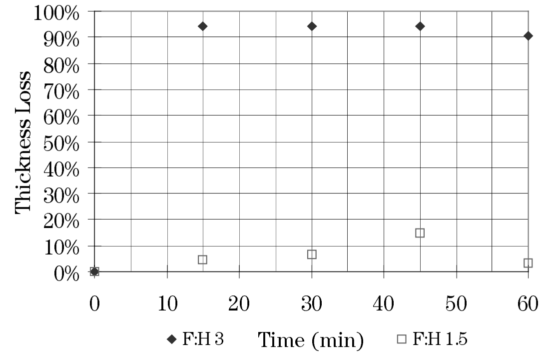

Figure 6: Film thickness loss, measured by profilometry, as a function of a thermal soak at 400°C in 4 Torr Ar. The bias condition was -40V.

with a continually decreasing slope magnitude with respect to time from nearly 0 to about 0.019.

Figure 6 displays the effect of thermal treatments, where successive cycles were performed on the same film. Generally, the films lost thickness upon heating. It was observed for a few samples that the film thickness increased a few percent [4]. The thickness loss for the 1.5 F:H film is about 7%, while for the F:H 3.0 film it is about 95%. It appears that the majority of film loss occurs within the first few minutes of the heat cycle,

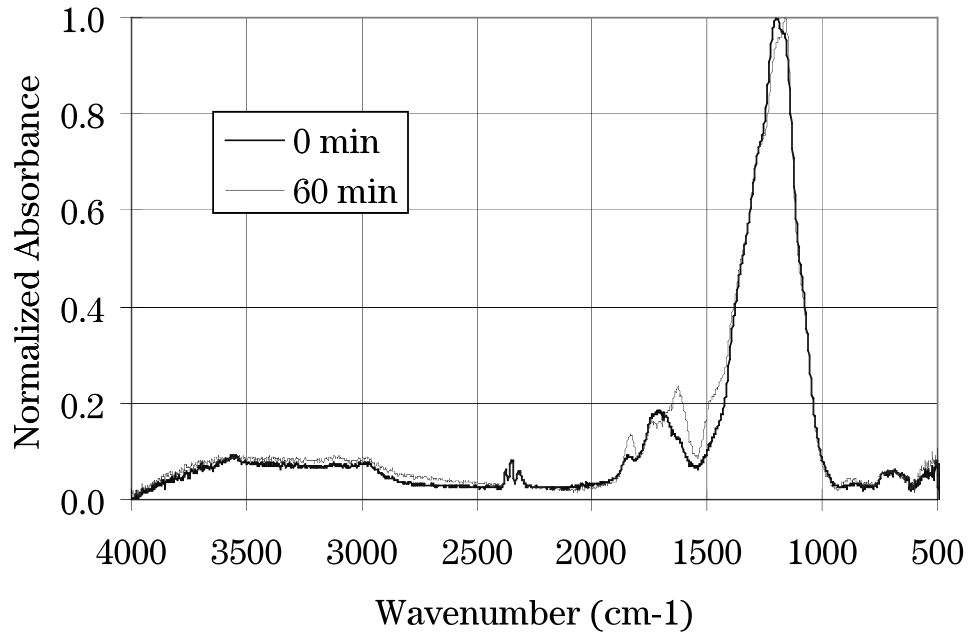

Figure 7: FTIR spectra of -40V bias F:H 1.5 film before any annealing and after a cumulative 60 minute therı cycle at 400°C. The spectra at 30 and 45 minutes were identical to the one at 60 minutes.

1200 cm^{-1} band, in the shape of the 1650 cm^{-1} band and in the height of the 1800 cm^{-1} band. The major differences in the two spectra include the increase in the 1200 cm^{-1} band relative to the 1150 cm^{-1} band, an increase in the bands around 1470, 1635, and 1835 cm^{-1}, and a decrease in the band around 1700 cm^{-1}.

DISCUSSION

The data shows that films with dielectric constants as low as 2.2 can be deposited, but that even films with as-deposited dielectric constants over 3.0 will decrease to 2.4 upon heating. The traditional explanation for the effect of fluorine on the dielectric constant is that it lowers the dielectric constant by virtue of its strongly localized bonds. For example, in the presence of aromatic groups with fluorine termination, the localization comes at the expense of the aromatic π-bond delocalization. This helps to explain the time-zero dielectric constant value.

Another apparent role is the ability of fluorine to affect the microstructure of the film. Its presence may decrease the degree of cross-linking in the film, which can increase the ring statistics (leading to larger microvoids), and increase the volume of material given over to unconnected, low-molecular weight compounds that evaporate upon heating. Finally, its presence as a network end-group can alter the decomposition kinetics of the film.

Thermal stability data supports the idea that the presence of fluorine during film deposition lowers the degree of cross-linking, in that films with as-deposited $\kappa \sim 2$ (F:H ~ 3) are not thermally stable, when compared to films with $\kappa \sim 3$ (F:H ~ 1.5). It is thought that thermal stability is directly related to the degree of cross-linking formed by carbon [4,8]. The presence of fluorine as a network-terminating end-group may inhibit cross-linking by its lower dissociation probability relative to hydrogen. A lower degree of cross-linking in the film increases the likelihood that a given collection of atoms is a trapped, volatile molecule. One method by which voids may be created is to drive out these gases by heating.

The effect of voids on the film is to lower the dielectric constant by density reduction, since a void will have a dielectric constant close to that of vacuum. There are three mechanisms by which density reduction may occur: 1) changes in the character and number of network bonds the film during heating leading to an increase in the mean ring statistics, 2) evolution of gases from the film through decomposition, and 3) evolution of trapped, unreacted gases. A large-scale increase in the ring statistics can manifest itself by volumetric expansion of the film. Thickness expansion upon heating has been noted for some films in this work, as well as others [4]. The film cannot increase in mass by absorbing material from external sources, (they are annealed in a pure Ar atmosphere), so its density decreases.

There is evidence of mass loss in these films upon heating. The fact that thickness normalized 1200 cm^{-1} band decreases upon heating indicates that the molecular groups that make up this band are decreasing. Since this band is the only portion of the spectrum in which fluorine-containing stretching motion absorb, it is likely that fluorine-containing groups are leaving the film.

Changes in infrared spectra supports the idea that the material undergoes substantial microstructural changes upon heating as well. The bands at 1470, 1600, and 1850 cm^{-1}, which change most noticeably, are associated with sp^2 C=C groups in various configurations, including olefinic, and aromatic groups [7,10-12]. D'Agostino *et al.* show measurable quantities of sp^2 bound carbon groups in similar films [13]. The increase in these bands implies creation of sp^2 groups. One hypothesis that could be drawn from the data is that thermal cycling of the film promotes generation of C=C (sp^2) groups formed at the expense of C–C (sp^3) groups. The 1200 cm^{-1} band is mostly attributed to fluorinated carbon groups [14]. In this band, the most noticeable change is around 1150 and 1200 cm^{-1}. The

1200 cm^{-1} band could be associated with $=CF_2$(as) asymmetric stretch motion, (carbon has a *sp*^{2}-bond to the network), and the 1150 cm^{-1} could be associated with the $–CF_2$(as) (the carbon has two *sp*^{3}-bonds with the network), or the $=CF_2$ symmetric, (s), motions. Since the 1200 cm^{-1} band appears to grow at the expense of the 1150 cm^{-1} band, it is more likely that the 1150 cm^{-1} band is dominated by $–CF_2$ groups. If it were associated with the $=CF_2$(s) motion, it would be more likely to track with the 1200 cm^{-1} band. It may not be possible to see changes in the $=CF_2$(s) band, if it has a lower absorbance than the $=CF_2$(as).

When a C–C to C=C reaction occurs, it is at the expense of carbon bound to other atoms. This may result in the loss of atoms from the network such as network terminating F or H atoms, (possibly in the form of gases.) It may also result in the loss of network bonds between carbon atoms with the effect of creating a more open network. A more open network may explain the thickness increase for some films.

Evolution of trapped gases can also decrease the density of the film. It is possible that gases are trapped during deposition. In this work, the films were deposited at 5°C to maximize deposition rates. Arai *et al.* have shown for similar processing arrangements, that the deposition rate can go to zero at temperatures above 140°C [15]. Low temperature deposition of films can also promote entrapment of gases. Because the deposition rate is being controlled by the surface adsorption lifetime, there is a reasonable probability of entrapment in the film. Upon heating of the film in subsequent steps, this material may evaporate from the film leaving voids.

SUMMARY AND CONCLUSIONS

This work has shown that organic films with dielectric constants less than 2.2 can be deposited by high density plasma PECVD at 5°C. Films deposited with F:H of 1.5 gas mixture sustain a 7% thickness loss after 400°C for 60 min. and have a dielectric constant around 2.4. Post-deposition heating causes several changes in the film, including a decrease in the tan δ, increases in the infrared absorbtion band around 1600 cm^{-1}, and an increase in Im(**N**).

The data presented suggests that the film density decreases upon heating. Density reduction could play a major role in the change of κ and tan δ. Changes in the infrared spectrum show that there is post-heating creation of C=C groups in the material.

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