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The Effect of Thermal Cycling on a-C:F,H Low Dielectric Constant Films Deposited by ECR Plasma Enhanced Chemical Vapor Deposition

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Abstract

Thin films of a-C:F,H have been investigated to understand the effect of post-deposition annealing on density, dielectric constant, and composition. Although the initial dielectric constant value for the films was 3.2, the value decreased to about 2.4, and the loss tangent decreased from 0.12 to 0.03 after heating to 400ºC. Correspondingly, the film density decreased on the order of 10%, and an increase in the C=C content of the infrared spectra was observed. Most of these measured properties reached at least 75% of their final value within 5 minutes annealing. These results suggest that a more open film network is the basis of the lower dielectric constant.

Introduction

Amorphous organic films deposited by PECVD are being evaluated as an interlayer dielectric film for integrated circuits. These materials are expected to have dielectric constants as low as 2.0, excellent gap fill, and relatively simple implementation. It has been known 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-κ) materials (4-8). 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 can be deposited using simple fluorohydrocarbon gas mixtures can be deposited with dielectric constants as low as 2.0 (4,5).

In our previous work on this material system, it was shown that those organic films with as-deposited κ from more than 3 down to 2 can be produced by high-density plasma CVD (8). However, the dielectric constant was inversely related to thermal stability. Since the volume has been seen to expand upon heating, it was speculated that the film microstructure transforms into a more open network, and the presence of fluorine plays a key role in the film formation or stabilization process (4,8). Most of the work to date on these materials has concentrated on electrical and optical characterization of as-deposited films. One major issue for such organic films is thermal stability during subsequent processing steps, where the temperature typically reaches 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 fraction of their volume (4,6,9). However, changes in film density that can be observed may help describe some of the factors that determine the dielectric constant. Post-deposition thermal behavior of the films is important in understanding how they will change during subsequent processing steps. In the present work, we investigate changes in thickness, density, dielectric constant, loss tangent (tan δ), and infrared spectra of a-C:F,H films after thermal cycling.

Experimental

The films were deposited in an Oxford electron cyclotron resonance (ECR) reactor described previously (8). This system has a close-coupled ASTeX source and He backside cooling for the substrate. The parameter varied was presence or absence of a –40V applied bias. The thermal treatment of the wafers was performed in the CVD chamber of a cluster tool at 4 Torr with 1200 sccm Ar flowing and a lamp-heated susceptor held at 400°C. The nominal wafer temperature was about 360°C. Two annealing series were performed for infrared spectroscopy (ir) and density measurements. The first series consisted of two 30 minute intervals, and the second series consisted of three 5 minute, one 15 minute, and finally one 30 minute interval. Films deposited on p-type Si wafers were used to measure the ir spectrum before and after each thermal cycle. For each ir series, a single sample was used. 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. For density measurements, the wafer mass was measured prior to deposition using a Chan microbalance. Film thickness and thickness uniformity were determined using a 632 nm Rudolph variable angle ellipsometer. Then the film was subjected to a thermal cycle, and the measurements repeated. Films deposited on metal-coated substrates were used to examine the electrical properties after thermal soaks of 15, 30, 45 and 60 minutes. For the electrical measurements, each film was used once.

Results

Both film thickness and mass decrease as a function of thermal cycling. Fig. 1 shows the thickness loss of the film expressed as a percentage of the as-deposited thickness, as a function of cumulative heating time. Most films demonstrate a thickness loss of almost 5% by 30 minutes, and about 7% by 60 minutes. Only the biased film with short thermal cycles shows a greater thickness loss, achieving 17% by 30 minutes. The wafers are expected to

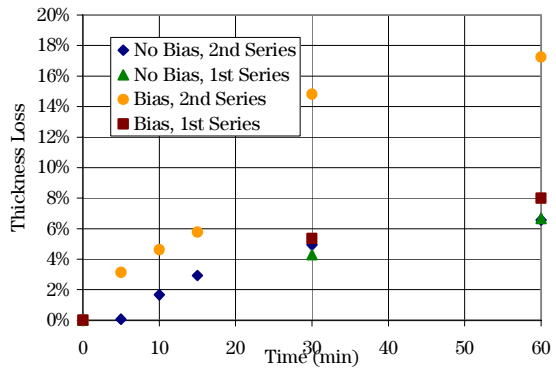

Fig. 1: Thickness loss as a function of cumulative heating time.

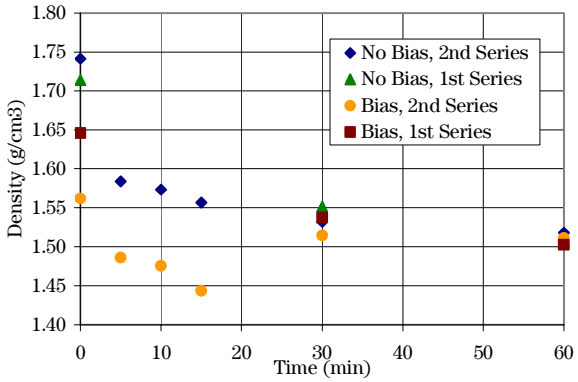

Fig. 2: Film density as a function of cumulative heating time.

reach the susceptor temperature within 30 seconds, so the cumulative time difference at temperature between the short and long-term heating is no more than 5% at 30 minutes.

Fig. 2 is a plot of the film density as a function of heating time, and clearly shows that it drops upon heating. The densities ranged from about 1.74 g/cm^3, to a low of 1.44 g/cm^3, with a single film exhibiting a 10% density decrease. All samples show a continuous decrease in density and converge at about 1.52 g/cm^3, except for the biased from the 2nd series. The last two data points for that film indicate a density increase relative to the previous three points. This behavior has been repeated with other films grown and heated under the same conditions. After 30 minutes of heating, all of the film densities converge regardless of applied bias or thermal history.

Fig. 3 is a plot of κ and tan δ as a function of heating time and shows that both decrease with time. Each sample was heated only once before the measurement. From an initial value of 3.1, κ drops down to around 2.4 after the initial heating cycle, and tan δ decreases by 4x to 0.03 after the first heating cycle.

Fig. 4 shows the time evolution of the ir spectrum of a sample after each heating cycle. The spectral bands in the range from 1400 to 1900 cm^{-1}, associated with C=C groups, show the greatest changes in shape during heating. (There is no noticeable change in the 2900 cm^{-1} C-H(s) band, though the signal is low.) The main C-F (1200 cm^{-1}) band shows only a slight intensity change. No noticeable difference in ir spectra was seen between the biased and unbiased films. Most of the changes occur between the as-deposited state and the first heating cycle, and indicate an increase in C=C content.

Discussion

The density data from the biased sample from the 2nd series with short thermal cycles in Fig. 2 shows that the behavior of biased films upon heating is different from unbiased films. One possible explanation is that the film undergoes a net densification between the 15 and 30 minute anneal. The larger percentage thickness loss for this film, compared to the other samples, implies that the film may be microstructurally different from the other films.

It is clear that the films undergo both a volumetric and density drop as a function of thermal cycling. The data show that film density reach their final value very quickly. The fact that these two parameters vary at different rates implies that two separate mechanisms are occurring. The one associated with density change is probably an outgassing phenomenon where trapped gases or low molecular-weight polymers evolve from the film. The other might be the densification of the film through either a chemical conversion, material loss from the film surface, or both.

The microstructural role of fluorine is not entirely clear in partially fluorinated organic polymeric networks. There are several mechanisms by which fluorine may influence microstructural behavior. It may be possible that fluorine decreases the degree of cross-linking in the film, which may increase the microvoid size. This would increase the volume of material given over to unconnected, low-molecular weight compounds that evaporate upon heating. Finally, its presence as a network terminating end-group can alter the decomposition kinetics of the film.

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 in the film during heating, leading to an increase in the mean microvoid size, 2) evolution of gases from the film through decomposition, and 3) evolution of trapped, unreacted gases. A large-scale increase in the microvoid size can manifest itself by volumetric expansion of the film. Expansion upon heating has been noted for some films in our experience, as well as in other work (4,8). The films cannot increase in mass by absorbing material from external sources, (since they are annealed in a pure Ar atmosphere), so their density decreases.

Evolution of trapped gases can also decrease the density of the film. It is possible that gases are trapped during

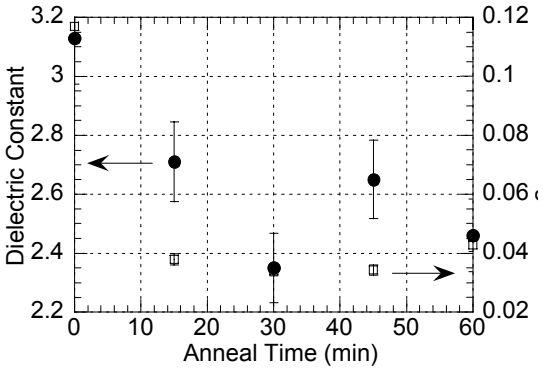

Fig. 3: Dielectric constant (**κ**) and loss tangent (tan **δ**) at 10^5 Hz as a function of a thermal anneal at 400°C in 4 Torr Ar for biased films.

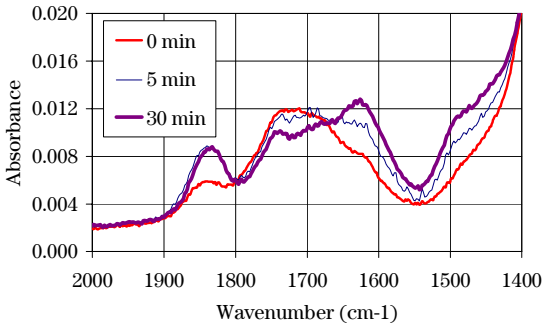

Fig. 4: FTIR between 1400 and 2000 cm^{-1} of time evolution of a biased sample.

deposition due to low substrate temperatures. In this work, the films were deposited at 5°C to maximize deposition rates. Arai *et al.* have shown that the deposition rate goes to zero at temperatures above 140°C for similar processing conditions (10). Because the deposition rate is controlled by the surface adsorption lifetime, there is a reasonable probability of gas entrapment in the film. Upon heating of the film in subsequent steps, this material may evaporate leaving voids. 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. The reaction 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 expansion for some films.

Changes in infrared spectra support the idea that the material undergoes substantial microstructural changes upon heating as well. Most of the bands in the range between 1400 to 1900 cm^{-1} increase and these are associated with sp^2 C=C groups in various configurations, including olefinic, and aromatic groups (7,11-12). One hypothesis 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.

Conclusions

Thin films of a-C:F,H films with dielectric constants of about 3.2 were deposited in and ECR PECVD system with and without bias. What has been shown here is that, upon annealing at 400ºC, the dielectric constant decreases to around 2.4, and the density drops by around 10%. The films lose density, most of it within the first 5 minutes of heating, presumably by the loss of evolved gases. Measurements of density, infrared spectra, **κ**, and tan **δ** show that the films undergo the majority of their change after the first heating cycle. This indicates that the films can reach a relatively stable state in a few minutes. The data also show that applied bias can influence density evolution, in that biased films underwent densification after an initial density decrease, whereas unbiased films did not. Collectively the results suggest that annealing these a-C:F,H films promotes a larger microvoid size leading to a lower dielectric constant.

Acknowledgements

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