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Title	Effect of sputtering with hydrogen dilution on fluorine concentration of low hydrogen content fluorinated amorphous carbon thin films with low dielectric constant
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Citation	Journal of Applied Physics, 86(5): 2468-2472
Issue Date	1999-09-01
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/4537
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Description	

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Effect of sputtering with hydrogen dilution on fluorine concentration of low hydrogen content fluorinated amorphous carbon thin films with low dielectric constant

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(Received 21 December 1998; accepted for publication 4 June 1999)

The fluorine concentration of fluorinated amorphous carbon (a-C:F) thin films with a low dielectric constant was controlled using magnetron sputtering with hydrogen gas dilution into CF_4 gas. The structural, optical and defect properties of these films were investigated by infrared (IR) absorption, x-ray photoelectron spectroscopy, ultraviolet visual spectroscopy and electron spin resonance as well as dielectric constant measurements. IR absorption spectra of the films with various fluorine concentrations prepared by hydrogen gas dilution showed no vibration modes between hydrogen and carbon atoms in CH, CH_2, and CH_3 configurations, suggesting that the hydrogen concentration of these films is less than a few at. %. Furthermore, the structural properties change at a fluorine concentration of approximately 50 at. %. However, the dielectric constant of 2.5 that is required for the interlayer materials for the next generation of ultralarge scale integrated devices remains unchanged at this fluorine concentration. Based on these results, the thermal stability of these a-C:F films is discussed briefly. © *1999 American Institute of Physics.* [S0021-8979(99)08417-0]

I. INTRODUCTION

The demand for improvements in the switching performance of ultralarge scale integrated (ULSI) devices has led to an increased need for materials with a low dielectric constant because the parasitic capacitance of the interconnections causes a delay in switching performance. For example, since the dielectric constant of fluorine-doped silicon oxide (SiOF) films is lower than that of SiO_2 films,[1,2] e.g., around 3.5 for a SiOF film in which the fluorine concentration is approximately 15 at. %,[2] these films are candidates for interlayer dielectrics. However, the dielectric constant of the interlayer materials for the next generation of ULSI devices must be less than approximately 2.5.[3] In addition, SiOF films have poor reliability in humid conditions. Recent reports indicate that fluorinated amorphous carbon (a-C:F) films have a relatively low dielectric constant,[4,5] e.g., 2.1 for a-C:F films deposited by conventional rf plasma chemical vapor deposition (CVD)[4] and 2.3 for those deposited by helicon-wave plasma CVD.[5] Since then, many investigations on a-C:F films have been carried out.[6–12] We prepared a-C:F films with a fluorine concentration of approximately 67 at. % (Ref. 9) and a dielectric constant of 2.2 (Ref. 10) by plasma CVD using carbon tetrafluoride (CF_4) and methane (CH_4) gases at $R=0.97$, where R is the ratio of the CF_4 flow rate to the total flow rate. However, these films have relatively poor thermal stability, e.g., the dielectric constant increases and the film thickness decreases after annealing at around 300–350 °C.[10] One of the origins of the poor thermal stability is reportedly a reduction in the average coordination number, i.e., the reduction of a cross-linked structure.[4–6,10–12] In addition, it has been reported that the bond strength of the CF_3 and CF_2 bonding configurations against thermal annealing is weaker than that of the CF bonding configuration.[10] This result is consistent with the proposed model that the poor thermal stability is due to a reduction in the average coordination number, since an increase in the CF_3 and CF_2 bonding configurations causes a reduction in the average coordination number. Therefore, a-C:F films with a fluorine concentration of approximately of 67 at. % have poor thermal stability, despite the fact that these films have a low hydrogen concentration.

The reduction in the average coordination number seems to be caused by the incorporation of fluorine and hydrogen because hydrogen as well as fluorine atoms incorporated in the film network terminate the carbon bonds. This indicates that an increase in the average coordination number, i.e., an increase in the dimension of the film network, is required in order to improve the thermal stability of these films without increasing the dielectric constant. In other words, it is necessary to reduce the fluorine concentration in a-C:F films without increasing the dielectric constant and without increasing the hydrogen concentration. However, since plasma CVD using only CF_4 results in no film deposition, CH_4 gas is mixed with the CF_4 gas. This implies that hydrogen atoms are incorporated into a-C:F films deposited by plasma CVD. For example, a-C:F films with high fluorine concentrations prepared by plasma CVD have low hydrogen concentrations, whereas films with relatively low fluorine concentrations

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have high hydrogen concentrations.[9,10] Furthermore, infrared (IR) spectra obtained for *a*-C:F films prepared using plasma CVD with hydrogen gas dilution into CF_4 gas showed larger vibration modes due to carbon and hydrogen bonded as CH, CH_2, and CH_3. In addition, the deposition rate for *a*-C:F films prepared using plasma CVD with hydrogen gas dilution into CF_4 is smaller than that for *a*-C:F films prepared using plasma CVD with CF_4 and CH_4 gases. Therefore, in this study, we examined the preparation of *a*-C:F films with low fluorine concentration, low hydrogen concentration and low dielectric constant using magnetron sputtering with hydrogen gas dilution into CF_4 gas.

II. EXPERIMENT

Samples were prepared by magnetron sputtering with a 90 mm diameter graphite target in H_2 gas dilution into CF_4 gas, in which the ratio of the CF_4 gas flow rate to total gas flow rate, r, $r=[CF_4]/\{[CF_4]+[H_2]\}$ was varied while the total gas flow rate was kept constant at 2 sccm. Single-crystalline Si, Corning 7059 glass and SiO_2 substrates were fixed on the 80 mm diameter water cooled substrate holder. CF_4 and H_2 gases were introduced into the chamber through separate gas lines and sputtering was performed at an rf power of 100 W (power density of 0.14 W/cm^2) and with a gas pressure of 2 mTorr. Electron spin resonance (ESR) measurements were carried out at room temperature at a frequency of 9.2 GHz using a standard microwave power of 1 mW and a standard magnetic field modulation of 3.2 G. X-ray photoelectron spectroscopy (XPS) spectra were observed using an Al $K\alpha$ x-ray anode operating at 10 kV and 12 mA. The dielectric constant and optical band gap were determined by the capacitance–voltage (C–V) characteristics at 1 MHz and by a Tauc plot, respectively. Thermal annealing was performed in a vacuum of approximately 10^{-5} Torr for 1 h at each temperature (200 and 300 °C).

III. RESULTS AND DISCUSSION

The fluorine concentration of *a*-C:F films prepared by magnetron sputtering was estimated by XPS and is shown in Fig. 1 as a function of r, where r is the ratio of CF_4 flow rate to the total flow rate. The fluorine concentration decreases with decreasing r, i.e., with an increase in H_2 gas flow rate. This can be attributed to the fact that the fluorine-related species generated by decomposition of CF_4 molecules decreases as a result of the combination of atomic hydrogen species and fluorine-related species. IR spectra obtained for *a*-C:F films prepared at various values of r are shown in Fig. 2(a) and are compared with those obtained for *a*-C:F films prepared by plasma CVD with a CH_4 and CF_4 gas mixture. The intensity of each spectrum in Fig. 2(a) is normalized by the film thickness. Fluorine-related vibration modes decrease with decreasing r. Here, note that all the IR spectra obtained for films prepared by sputtering showed no vibration modes for carbon and hydrogen atoms in CH, CH_2, and CH_3 configurations, despite the fact that H_2 gas was used. This result suggests that the fluorine concentration in *a*-C:F films with low hydrogen content can be controlled using sputtering with H_2 dilution. In addition, all the IR spectra obtained for *a*-C:F

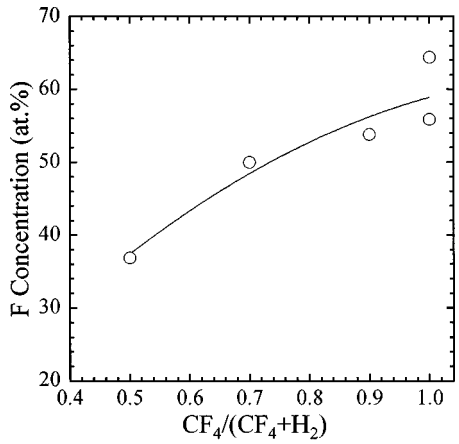

FIG. 1. Fluorine concentration of *a*-C:F films prepared by magnetron sputtering as a function of the ratio of CF_4 gas flow rate to total gas flow rate. The line is a guide for the eye.

films prepared by magnetron sputtering showed vibration modes due to C═C having a $F_2C{=}C<$ bonding configuration located at around 1720 cm^{-1} and a $F_2C{=}CF$ bonding configuration located at around 1860 cm^{-1}.[13] Furthermore, the IR bands located at around 1720 cm^{-1} tend to show a doublet structure in which an additional peak appear at

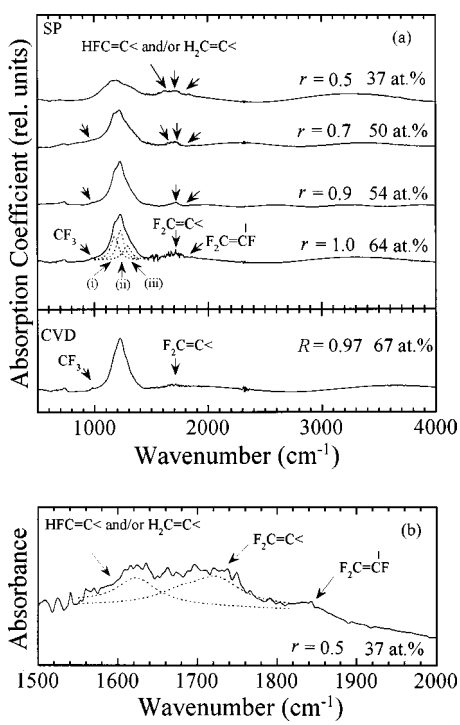

FIG. 2. (a) IR spectra of *a*-C:F films prepared by magnetron sputtering in comparison with that of a film prepared by plasma CVD with CF_4 and CH_4 gases at $R=0.97$, where R is the ratio of CF_4 flow rate to the total flow rate. The deconvoluted lines are shown with dotted curves on the spectrum for the $r=1.0$ film. Arrows (i), (ii), and (iii) indicate the CF_2 (sym.), CF_2 (asym.) and CF modes, respectively. $F_2C{=}C<$, $F_2C{=}CF$, and $HFC{=}C<$ and/or $H_2C{=}C<$ modes are also indicated by arrows. Fluorine concentrations estimated by XPS are shown on the right hand side. (b) A typical deconvolution pattern for $F_2C{=}C<$ and $HFC{=}C<$ and/or $H_2C{=}C<$ modes. The deconvoluted lines are shown with dotted curves on the spectrum for the $r=0.5$ film.

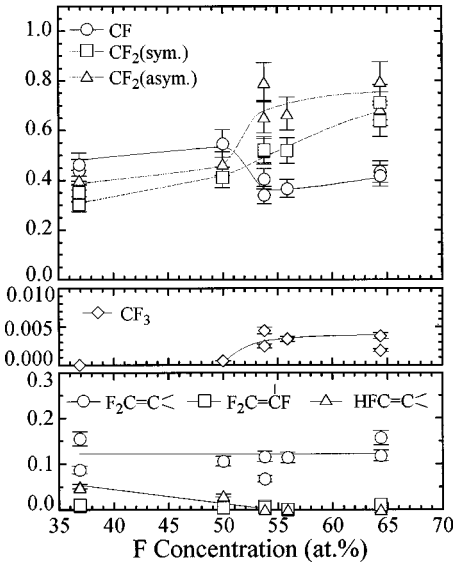

FIG. 3. Intensity of the CF_3, CF_2 (sym.), CF_2 (asym.), CF, $F_2C{=}C<$, $H_2C{=}C<$, and $F_2C{=}CF$ modes observed in IR spectra of *a*-C:F films prepared by magnetron sputtering as a function of fluorine concentration estimated by XPS. The intensity of the $H_2C{=}C<$ and/or $HFC{=}C<$ modes are also plotted. The intensity of each mode is normalized by film thickness without taking into account the oscillator strength. The lines are guides for the eye.

around 1650 cm^{-1}, with a decrease in *r*. This result suggests that the $HFC{=}C<$ and/or $H_2C{=}C<$ bonding configurations appear with increasing H_2 gas flow rate (decreasing *r*), since the IR bands due to $HFC{=}C<$ and $H_2C{=}C<$ reportedly appear at around 1650 and 1600 cm^{-1}, respectively.[14] Deconvolution of the IR spectra was carried out in order to investigate the structural properties of the network. The CF_n group ($n=1$, 2, and 3), $F_2C{=}CF$ and $HFC{=}C<$ and/or $H_2C{=}C<$ were deconvoluted by Lorentzian line and a typical deconvolution pattern for the CF_n group is indicated by the dotted lines, (i), (ii), and (iii), in Fig. 2(a). On the other hand, an asymmetric line was used for the deconvolution of $F_2C{=}C<$ as shown in Fig. 2(b), since the line shape due to $F_2C{=}C<$ seems to be asymmetric.[13] The asymmetric line was created by a combination of two Lorentzian lines.

The results of the deconvolution are shown in Fig. 3 as a function of the fluorine concentration, where each intensity is normalized by the film thickness without considering the oscillator strength. The error bars in this figure are primarily due to uncertain film thicknesses, since the film thicknesses varied depending on the position of the substrate holder. The film thickness was at its maximum value at the center of the substrate holder and decreased with increasing the distance from the center. In fact, the film thickness had its maximum value within a radius of approximately 20 mm from the center and 60%–30% of the maximum at a distance of approximately 30 mm from the center. The CF bonding configuration was dominant, and no CF_3 bonding configuration was observed below a fluorine concentration of approximately 50 at.%. However, the CF_2 bonding configuration became dominant and the CF_3 bonding configuration appeared when the fluorine concentration exceeded approximately 50 at.%. These results suggest that the film structure of the network changes at a fluorine concentration of approximately 50 at.%. In other words, the dimension of the film network decreases when the fluorine concentration exceeds approximately 50 at.%. Therefore, this fluorine concentration may correspond to the percolation threshold. In addition, the IR signal intensity due to the $F_2C{=}C<$ bonding configuration obtained for *a*-C:F films prepared by sputtering remained unchanged with respect to the fluorine concentration and those due to the $HFC{=}C<$ and/or $H_2C{=}C<$ bonding configurations obtained for these films increased as the fluorine concentration was decreased. In particular, it may be important that the IR spectra due to the $HFC{=}C<$ and/or $H_2C{=}C<$ bonding configurations are observed for *a*-C:F films prepared by sputtering in order to investigate the hydrogen concentration in the films and the role of hydrogen for thermal stability. Nevertheless, we believe that the hydrogen concentrations of these *a*-C:F films are lower than those of films prepared by plasma CVD with CF_4 and CH_4 gases because the vibration modes between carbon and hydrogen atoms in CH, CH_2, and CH_3 configurations are not observed in the films prepared by sputtering. The fact that the oscillator strength for CH is much larger than that for $HFC{=}C<$ and $H_2C{=}C<$,[14] and the fact that the oscillator strength for CH_2 and CH_3 is expected to be larger than or nearly equal to that for $HFC{=}C<$ and $H_2C{=}C<$, support this interpretation. Furthermore, the results showing that an increase in $HFC{=}C<$ and/or $H_2C{=}C<$ concentration with decreasing fluorine concentration as well as the approximately constant concentration in the $F_2C{=}C<$ bonding configuration with respect to fluorine concentration suggest that the C=C bonding configuration for *a*-C:F films prepared by sputtering increases with decreasing fluorine concentration. Since the IR signal intensity due to $F_2C{=}C<$ obtained for films prepared by sputtering was larger than that obtained for films prepared by plasma CVD, *a*-C:F films prepared by sputtering contain many C=C bonds, i.e., a large graphite region, compared to those prepared by plasma CVD.

The dielectric constant obtained for films prepared by sputtering as a function of the fluorine concentration is shown in Fig. 4. The dielectric constant of films after annealing at 300 °C is shown by triangles and the fluorine concentration after annealing is shown in parentheses. The dielectric constant obtained for *a*-C:F films, including those prepared by plasma CVD with CF_4 and CH_4 gases at $R=0.97$, where *R* is the ratio of the CF_4 flow rate to the total flow rate,[9,10] seems to change in a similar manner with respect to the fluorine concentration. Here, it is worth noting that no change in the dielectric constant was observed for variations in the fluorine concentration at around 50 at.%, e.g., the dielectric constant was approximately 2.5. It is important to investigate this behavior of the dielectric constant to improve thermal stability since the dimensions of the film structure increase below a fluorine concentration of approximately 50 at.%, indicating an increase in the cross-linked structure below this concentration. In fact, the thermal stability of the film with a fluorine concentration of approximately 50 at.% was improved compared with that of the film with a fluorine concentration of approximately 67 at.%, as shown in Fig. 4, i.e., small changes in the dielectric constant and the fluorine

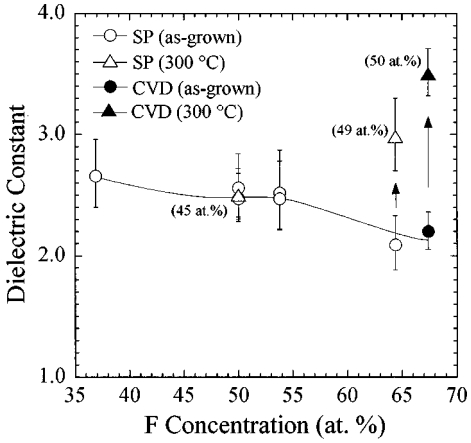

FIG. 4. Dielectric constant of a-C:F films prepared by magnetron sputtering compared with those prepared by plasma CVD with CF_4 and CH_4 gases as a function of fluorine concentration estimated by XPS. The dielectric constant and the fluorine concentration of films after annealing at 300 °C are shown by triangles and in parentheses, respectively. The line is a guide for the eye.

concentration after annealing at 300 °C are observed for the film with a fluorine concentration of approximately 50 at. %. However, the changes in the dielectric constant of the film with a fluorine concentration of 65 at. % prepared by sputtering is comparable to that of the film with a fluorine concentration of 67 at. % prepared by plasma CVD, suggesting that the thermal stability of the a-C:F film prepared by sputtering is similar to that of the film prepared by plasma CVD. Since the graphite structure is weaker than the diamond structure with respect to thermal annealing, further investigation into the effects of the $F_2C{=}C<$, $HFC{=}C<$, $H_2C{=}C<$, and $F_2C{=}CF$ bonding configurations on thermal stability is needed in order to prepare more stable a-C:F films with a low dielectric constant.

Figure 5 shows the dangling bond density, g value, and peak-to-peak linewidth obtained by ESR measurements as a function of the fluorine concentration. The dangling bond density and the linewidth increased with increasing fluorine concentration. These results are similar to those obtained for a-C:F films prepared by plasma CVD and can be explained in the same way.[9,10] That is, the increase in the dangling bond density is due to the larger atomic diameter of fluorine, and the increase in the line width is due to the hyperfine interaction between fluorine nuclei and the dangling bond. An increase in the dangling bond density with an increase in the fluorine concentration indicates that it is necessary to reduce the fluorine concentration without increasing the dielectric constant. Furthermore, the optical band gap obtained for films by sputtering increases with an increase in the fluorine concentration as shown in Fig. 6, suggesting that this increase is due to bonding of carbon and fluorine. This is quite natural since the strength of the bond between carbon and fluorine is larger than that of the bond between two carbon atoms. Furthermore, an increase in the optical band gap results in an increase in the g value with increasing fluorine concentration, as shown in Fig. 5, since band states related to the optical band gap influence the g value.[9,10]

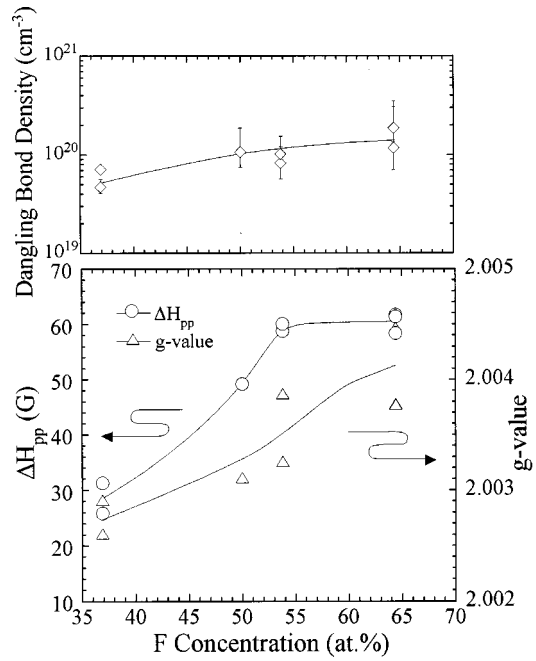

FIG. 5. Dangling bond density, g value, and peak-to-peak linewidth, ΔH_{pp}, of a-C:F films prepared by magnetron sputtering as a function of fluorine concentration estimated by XPS. The lines are guides for the eye.

IV. CONCLUSIONS

In summary, low hydrogen content fluorinated amorphous carbon (a-C:F) thin films with various fluorine concentrations and with a low dielectric constant were prepared using magnetron sputtering with hydrogen gas dilution into CF_4 gas. In particular, the dielectric constant of an as-grown a-C:F film with a fluorine concentration of approximately 50 at. % and that of the film after annealing at 300 °C were approximately 2.5. This is the value required for the interlayer materials for the next generation of ULSI devices. The structure of the film network changed when the fluorine concentration fell below approximately 50 at. %; that is, the di

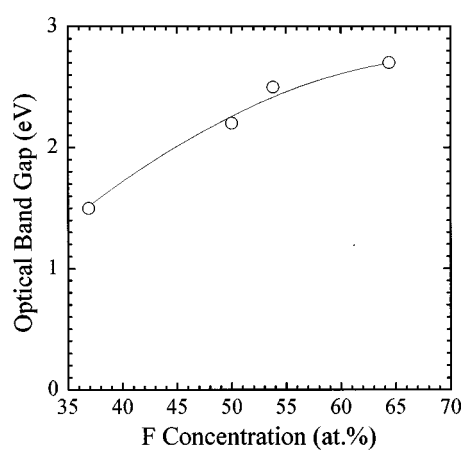

FIG. 6. Optical band gap estimated by Tauc plot of a-C:F films prepared by magnetron sputtering as a function of fluorine concentration estimated by XPS. The line is a guide for the eye.

mension of the network increased when the fluorine concentration fell below approximately 50 at. %. Furthermore, this result is consistent with the result that no change in the dielectric constant after annealing at 300 °C was observed for the *a*-C:F film with a fluorine concentration of approximately 50 at. %. In addition, the dangling bond density increased with an increase in the fluorine concentration, suggesting that the fluorine concentration of the films must be less than approximately 50 at. %. Further investigations are required to clarify the effects of the incorporation of hydrogen and fluorine atoms, the existence of C═C bonding due to the $F_2C{=}C<$, $F_2C{=}CF$, $HFC{=}C<$, and/or $H_2C{=}C<$ bonding configurations, and the effect of dangling bond density on thermal stability.

ACKNOWLEDGMENTS

The authors would like to thank T. Hayashi of Toyama Prefectural University (present: Hitachi Ltd.) and T. Amano of Toyama Prefectural University for experimental assistance. They also would like to thank H. Sakima and H. Terasaki of Toyama Prefectural University for technical assistance. This work was supported in part by a grant from the Hokuriku Industrial Advancement Center.

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