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The Effect of Hydrogen Addition on the Fluorine Doping Level of SiOF Films Prepared by Remote Plasma-Enhanced Chemical Vapor Deposition Using SiF_4-Based Plasmas

Vladimir PANKOV, Juan Carlos ALONSO and Armando ORTIZ
Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico, AP 70-360, 04510 Mexico D.F., Mexico

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Fluorinated silicon dioxide films (SiOF) have been prepared by high-density remote plasma-enhanced chemical vapor deposition from silicon tetrafluoride (SiF_4), oxygen and helium feedstock gas mixture at substrate temperature as low as 175°C. Addition of hydrogen has been found to control the fluorine doping level of the SiOF films over a wide range of fluorine concentrations while the SiF_4-to-O_2 flow rate ratio is kept constant. It has been confirmed that hydrogen addition does not lead to the incorporation of hydrogen in detectable quantities into the grown film with Si–F_x bond concentrations in the range of 0.5–4.9 at.% because of effective mutual scavenging behavior of fluorine and hydrogen in the entire range of hydrogen flow rates used. The decrease in the refractive index of the SiOF films from 1.463 to 1.410 and the increase in Si–O–Si bonding angles from about 137° to about 148° were found to be approximately linear with the increase in fluorine concentration. The hydrogen added to the process gas mixture has been found to play an active role in the film formation process affecting both the surface reactions and properties of the obtained SiOF films.

KEYWORDS: remote plasma-enhanced chemical vapor deposition, RPECVD, silicon tetrafluoride, SiF_4, SiOF, fluorinated silicon dioxide film, interlayer dielectric

1. Introduction

In the last few years, fluorinated SiO_2 films (hereafter referred to as "SiOF") have been considered as one of the most promising interlevel dielectric materials due to their low dielectric constant and high gap-filling properties.[1–6] Low temperature deposition of these films using plasma-enhanced chemical vapor deposition (PECVD) process has attracted great interest among the manufacturers of ultra-large-scale integrated circuits because of the opportunity to reduce the total thermal budget of the fabricated devices when multiple deposition procedures are used.

The feedstock gas mixtures currently used for SiOF film PECVD process can be divided into two groups based on the principle of SiOF film formation. The first one makes use of different, i.e., separated, silicon and fluorine gas sources. For example SiH_4, tetra-ethoxy-silane (TEOS) and 1,2bis-difluoromethylsilyl-ethane (FASi-4) as silicon source gases are used along with CF_4 and C_2F_6 as fluorine source gases.[3,7–9] The fluorine doping level in this case can be easily controlled by the ratio of the silicon source gas-to-fluorine gas flow rates that allows the Si/O atomic ratio in the SiOF film to be kept approximately constant. However, it has been found that moisture stability, the main problem of SiOF films, can be considerably improved when Si–F bond containing feedstock gases are used.[1,10] The second group of reactive gases includes SiF_4,[6,11–14] tri-ethoxy-fluoro-silane (TEFS)[2,10] among others. In this case the native Si–F bonding units transfer directly into the growing film during deposition and build immediately into the SiOF network.

The application of silicon halides as a silicon source for PECVD process of silicon-based materials has been reported by numerous authors. SiF_2, SiF_4, Si_2F_6 gases have been used to produce Si, SiO_2, Si_3N_4 films by conventional PECVD.[11,15–17] The main problem related to use of these gases is the difficulty to dissociate SiF_4 using conventional parallel plate PECVD equipment because Si–F bond energy is rather high (128.4 kcal/mol compared with 70.4 kcal/mol for Si–H bond).[18] For this reason, the additional plasma predecomposition of SiF_4 has been used by Alonso *et al.* to prepare SiO_2 films.[19] A more promising method was recently proposed for the preparation of SiOF films from silicon halides based on the use of high-density remote PECVD (RPECVD) techniques. Along with minimization of radiation damage to substrate surface, these techniques produce plasmas with ion densities up to $10^{12}\,cm^{-3}$ compared with $10^{10}\,cm^{-3}$ for conventional capacitively coupled plasmas.[20] As a result, SiF_4 can be completely dissociated even if only oxygen is added.[6,12] The main problem that seems to appear in this case is the control of fluorine doping level. For example, Shapiro *et al.*[1] and Kim *et al.*[12] varied the SiF_4/O_2 gas flow rate ratio in the range of 0.1–10 to change the fluorine concentration in the prepared SiOF films. However, at high values of SiF_4/O_2 gas flow rate ratio, the films were found to be not only fluorine rich but also silicon rich with an extremely high density of microvoids. Moreover, it is known that the moisture stability of SiOF film is highly sensitive to the Si/O atomic ratio of the film.[4] Therefore, another process parameter should be determined instead of SiF_4-to-O_2 flow rate ratio to control the fluorine doping level of SiOF films while keeping the Si/O atomic ratio constant.

It is known that reactive hydrogen atoms are able to extract fluorine from the Si–F bonds when introduced to the SiF_4-based PECVD reaction chamber.[16,17] We have earlier reported on the use of hydrogen in the SiF_4-based plasmas to scavenge the free fluorine produced as a by-product of SiF_4 dissociation.[11,13,14] So, it can be assumed that controlled addition of hydrogen to the SiF_4/O_2 feedstock gas mixture is able to govern the fluorine doping level of SiOF films prepared by RPECVD keeping the SiF_4-to-O_2 flow rate ratio constant. Some changes in the deposition rate and properties of the obtained SiOF films are also expected because of the creation of additional silicon precursors as a result of hydrogen controlled chemical decomposition of SiF_4 gas.

In this study we show the effect of hydrogen addition on both the SiOF film deposition process and fluorine incorporation into the SiOF films prepared by high-density RPECVD from SiF_4/O_2/He feedstock gas mixture at substrate temperature as low as 175°C.

2. Experimental

SiOF films were deposited in the reaction chamber equipped by an inductively coupled plasma source mounted on the top flange (see Fig. 1); the detailed geometry is described elsewhere.[21] Some changes in plasma source and matching network design were made to achieve a high-density plasma regime. To obtain a base residual pressure as low as 10^{-6} Torr the chamber was preliminarily pumped with a 100 l/s Alcatel CFV/100 turbomolecular pump. A mechanically rooted blower/rotary pump arrangement was used to maintain the required pressure and gas flow rate values during deposition.

The films were deposited on n-type (100) silicon substrates of 200 Ω·cm. Before loading, all the substrates were etched in "P"-etch solution [15 parts of HF (49%), 10 parts of HNO_3 (70%), and 300 parts of H_2O] for 5 min to remove the native oxide, followed by rinsing in deionized water, and final blowing with dry filtered nitrogen.

SiF_4 was used as both silicon and fluorine source gas at flow rates varying from 5 to 20 sccm. SiF_4 and H_2 were introduced into the reaction chamber through the individual gas distribution rings placed in the vicinity of the substrate holder outside the plasma glow discharge region (see Fig. 1).

The feedstock gases O_2 and He were supplied into the plasma region through the different feed inlets placed on the top of the plasma source. The O_2 flow rate was varied in the range of 40–100 sccm. Since the distance between the SiF_4 injecting ring and the plasma zone is rather small (of about 5 cm), the sum of flow rate of O_2–He gas mixture was kept constant at a value as high as 250 sccm which is sufficient to prevent the diffusion of SiF_4 gas into the plasma region. The total pressure during all deposition cycles was held constant at 500 mTorr using a throttle valve. It was impossible to initiate a high-density plasma regime in the absence hydrogen addition using radio frequency (rf) power up to 700 W at 13.56 MHz frequency. Therefore hydrogen flow rate was varied in the range of 5–80 sccm and plasma was maintained by 320 W of rf power for all depositions. The substrate temperature was held constant at 175°C during all deposition cycles. Film thicknesses were targeted for 1000 Å to assure an accurate determination of both the thickness and refractive index using laser ellipsometry.

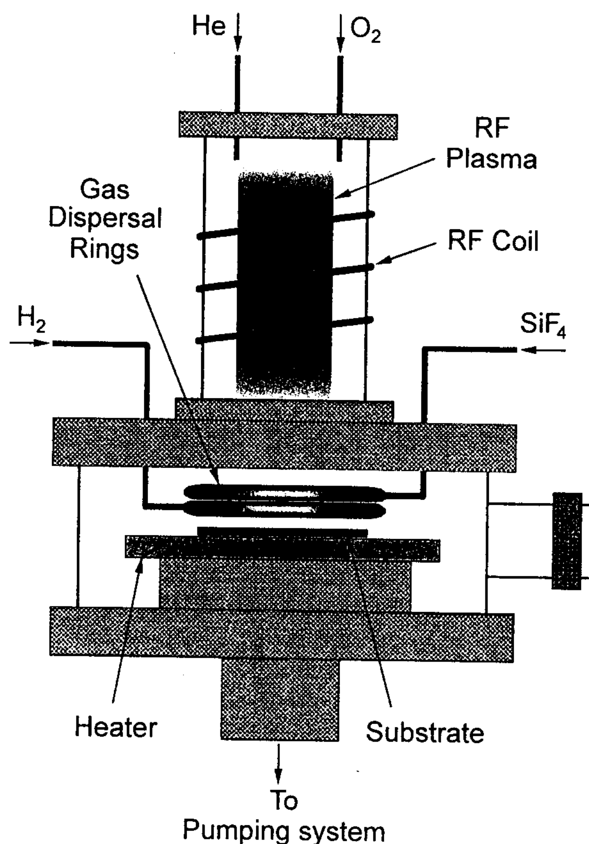

Fig. 1. Schematic of the RPECVD reaction chamber equipped with an inductively coupled high density plasma source.

Ellipsometric measurements were made using a Gaertner L117 ellipsometer incorporating a He–Ne laser source with a wavelength of 630 nm. Fourier transform infrared (FTIR) absorption spectra was measured using a Nicolet 210 double-beam spectrometer ranging from 400 to 4000 cm^{-1}. Each spectrum was averaged over 90 spectra with a nominal resolution of 4 cm^{-1}. The spectra of the corresponding silicon substrates were subtracted from those of the films deposited on the substrates. The maximal sensitivity of FTIR spectrometer was about 0.1% of transmittance. The area of 940 cm^{-1} Si–F_x absorption band after baseline correction was employed for determining the atomic concentration of Si–F_x units. Si–O–Si bonding angles were calculated from the position of the Si–O stretching vibration peak. Both techniques are described in detail in ref. 6 and the maximal error in Si–F_x content determination was reportedly estimated as 20%. Etch rate measurements were carried out using standard "P"-etch solution described above.

3. Results and Discussions

3.1 *The effect of hydrogen on the deposition process*

Figure 2 shows the variation in SiOF film deposition rate with the hydrogen flow rate for different SiF_4/O_2 flow rate ratios. At low values of SiF_4/O_2 flow rate ratio (0.14 and less), an increase in the hydrogen flow rate leads to a slow decrease in the deposition rate with the subsequent saturation at hydrogen flow rate values of about 40–60 sccm. However, at higher values of SiF_4/O_2 flow rate ratio (0.29 and more) the relationship changes significantly. In this case the deposition rate initially increases as a small amount of hydrogen is added to the reaction chamber, reaches a maximum value and then decreases slowly with further increase in hydrogen flow rate. The position of the maximum strongly depends on the value of SiF_4/O_2 flow rate ratio shifting from the hydrogen flow rate of 20 sccm to 40 sccm with increasing of SiF_4/O_2 flow rate ratio from 0.29 0.50.

To explain the above relationship, the main species taking part in the SiOF film formation process should be considered in detail. The main precursors responsible for the film growth are assumed to be SiF_x fragments and even Si atoms accompanied by various fluorine species including free fluorine radicals in the ground and excited state, F_2, and fluorine ions, F^-, as a result of impact dissociation of SiF_4 gas by hot electrons coming from the extended plasma region.[12,15,19] SiF_x moieties can then undergo gas phase or surface reactions with

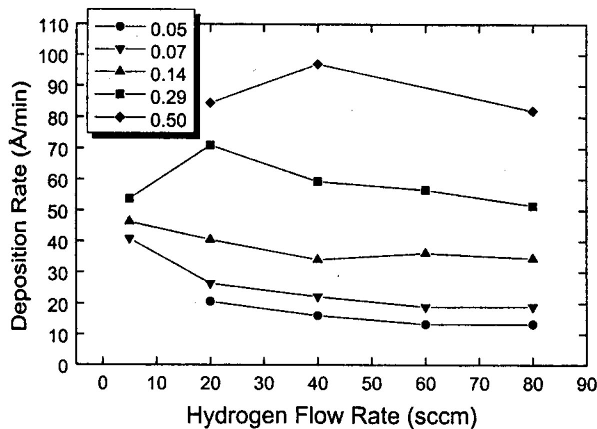

Fig. 2. Deposition rate of SiOF films versus hydrogen flow rate under various SiF_4/O_2 flow rate ratios.

excited and/or ionized oxygen species resulting in the production of $Si(O-)_xF_{4-x}$ network structural units. Helium ions and metastables are not assumed to play a considerable role in SiF_4 dissociation because of their effective quenching by oxygen in the plasma zone through Penning reactions.[22-24]

In our study it was observed that the plasma generation process was very sensitive to H_2 gas addition. For example, the value of plasma power necessary to initiate RF discharge decreased considerably if even negligible amount of H_2 was added, especially when low values of SiF_4/O_2 flow rate ratio were used. Hence, it may be assumed that H_2 introduced into the reaction chamber absorbs a certain part of electron energy that facilitates initiation and following sustaining of high-density plasma discharge. It was also reported elsewhere that even for conventional low-density PECVD, reactive hydrogen atoms are able to remove the fluorine atoms passivating free silicon bonds at the surface of the depositing layer and thus favoring considerably the deposition process.[16,17] This is due to the high chemical affinity between fluorine and hydrogen. It is also surmised that in the conditions of high-density plasmas the ability of reactive hydrogen atoms to detach fluorine from the SiF_x species can result in the formation of additional film precursors. However, HF which is a product of these reactions, is known to be able to etch SiO_2 through direct attack on the Si–O–Si network even in the absence of water.[25]

It is assumed that the above processes are not able to explain the complexity of the relationships presented in Fig. 2. On the other hand, a reasonable explanation can be given in terms of the difference in etching activity to SiOF films of various species interacting with a substrate surface during film growth. It is quite obvious that the etching ability of various fluorine species in SiF_4-plasma differs considerably. For example, it is known that F^- ions etch SiO_2 rapidly whereas the etch rate of SiO_2 by fluorine radicals is relatively low.[26] HF is assumed to act as a moderate etchant compared with the most reactive part of fluorine species. When low SiF_4 flow rates are used, (0.14 or less) a correspondingly small amount of highly reactive fluorine species is produced in the plasma region. Consequently, a low value of H_2 flow rate (less than 5 sccm) is necessary to completely scavenge this kind of fluorine species. As the H_2 flow rate increases to more than 5 sccm, the concentration of HF, a product of this reaction, increases proportionally and saturates when all free fluorine species (including slightly reactive particles) are consumed leading to the corresponding changes in deposition rate (see Fig. 2).

For high values of SiF_4/O_2 flow rate ratio (0.29 and more) the initial concentration of highly reactive fluorine species is much higher, resulting in intensive etching of the growing film by these species even at H_2 flow rates of 5 sccm and more. The mechanism of SiOF film etching by fluorine atoms consists of two steps. First, free fluorine atoms passivate Si dangling bonds on the SiOF film surface, forming a stable chemisorbed layer as it was described in refs. 15 and 27, that can partially impede the deposition of SiOF film. Second, near-neighbor fluorine atoms can detach a Si atom from the most strained and reactive Si–O bonds of the SiOF network leading to etching of the growing SiOF film. As a result, total film growth can completely cease as observed by Han *et al.*[6] for high values of SiF_4/O_2 flow rate ratio. When hydrogen is added to the feedstock gas mixture, it starts to scavenge the most reactive part of free fluorine species. The subsequent increase in H_2 flow rate leads to an increase in SiOF deposition rate of up to the maximum which probably corresponds to the complete elimination of the highly reactive fluorine component. However, further increase of H_2 flow rate leads to the partial suppression of film growth because of the increasing of HF concentration. Saturation is expected when all free fluorine species are bound to hydrogen. Thus, optimal hydrogen addition considerably increases the SiOF film deposition rate compared with hydrogen-free RPECVD process, in particular, when high values of SiF_4-to-O_2 flow rate ratio are used, due to the effective scavenge of the most reactive part of free fluorine species produced by SiF_4 electron impact dissociation.

In conclusion, the deposition of SiOF film using $SiF_4/O_2/H_2$-based plasmas should be considered as a continuous competition between both deposition and etching processes in the presence of fluorine species and HF, and the obtained deposition rate is determined by the position of the equilibrium point. Optimal hydrogen addition is able to considerably increase the deposition rate compared with hydrogen free RPECVD process when high values of SiF_4-to-O_2 flow rate ratio are used.

3.2 The presence of hydrogen in the films

The main reason why some researchers have used hydrogen-free RPECVD process is to avoid the incorporation of hydrogen or hydrogen-related groups into the SiOF film which is considered to result in instability of film properties. To study the presence of H in our films produced using $SiF_4/O_2/H_2$-based plasmas, FTIR measurements were performed. Figure 3(a) shows the typical FTIR absorption spectrum of as-deposited SiOF film with maximal concentration of fluorine (of about 4.9 at.%). This spectrum shows absorption bands at 1075, 810 and 445 cm^{-1}, corresponding to the fundamental Si–O stretching, bending and rocking vibrational modes, respectively.[3,5,6,9] Fluorine incorporated in silicate glass generates silicon fluoride sites, and the additional absorption band at about 940 cm^{-1} is associated with the vibrations of fluorine-related structural groups.[5,6,8,9,28] The area of this band is a direct indication of fluorine concen-

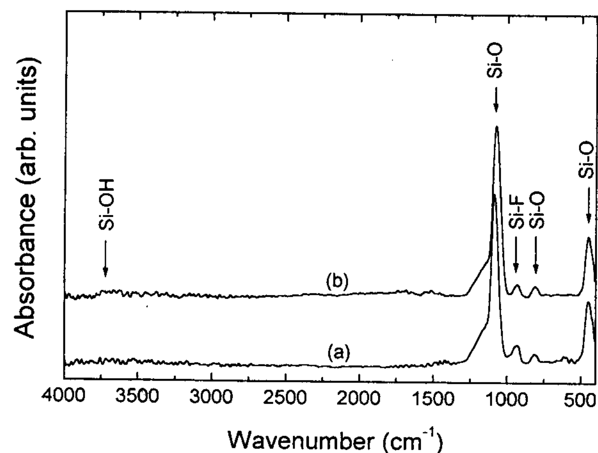

Fig. 3. FTIR spectra of (a) as-deposited SiOF film prepared with Si–F_x bond concentration of 4.9 at.%, and (b) SiOF film prepared with Si–F_x bond concentration of 3.9 at.% after etching in "P"-solution and following exposure to atmosphere for two months.

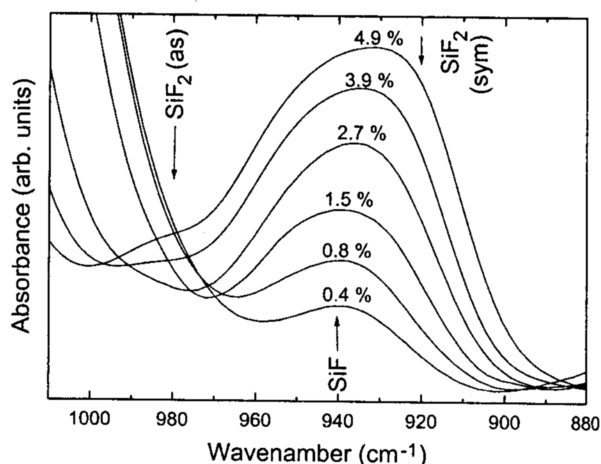

Fig. 4. FTIR spectra of SiOF films prepared with various Si–F_x bond concentrations in the region of 880–1100 cm^{-1}.

tration in the film and has been used in this study for determining atomic percentage of Si–F_x units in SiOF film through the procedure described elsewhere.[6] As seen in Fig. 3(a), there is no evidence for the presence of the absorption bands at 2260 cm^{-1} or at 875 cm^{-1} associated with bond-stretching and bond-bending vibrations, respectively, of Si–H groups in SiOF host network.[29] The absence of a definite feature in the range of 3400–3600 cm^{-1} assigned to SiO–H and HO–H absorption bands in as-deposited films even at the maximal fluorine concentrations shows that fluorine and hydrogen effectively scavenge each other during the deposition process leaving the film free of hydrogen. However, it has been reported that at about 920 cm^{-1}, the band assigned to the Si–OH bending vibration with non bridging oxygen can be present in FTIR spectrum of the hydrogen-containing oxide films.[28,30] Thus, detailed studies of the absorption band in the range of 800–1100 cm^{-1} should be performed.

Figure 4 shows FTIR absorption spectra of SiOF films with various Si–F_x bond concentrations in the range of 880–1110 cm^{-1}. Over the range of fluorine concentrations, a definite absorption band with a shape close to Gaussian and with its maximum located at about 940 cm^{-1} can be observed. It is usual to attribute the peak at about 940 cm^{-1} to the stretching vibration mode of the fluorine atom which is built into the $(O-)_3Si-F$ structural group assigned to the silicon monofluoride, SiF.[5,6,8,9,28] Consequently, this peak area increases gradually with increasing Si–F_x bond concentration, as seen in figure. However, at the Si–F_x bond concentration of about 4.9 at.%, a definite shoulder is observed at the higher wave number side that may be due to the appearance of an additional absorption peak at about 980 cm^{-1}. Many authors attribute this peak to the asymmetric stretching vibration mode of silicon difluoride in the $(O-)_2Si(-F)_2$ structural group confirming speculations by corresponding calculations.[2,5,6,9] However, the presence of the related $Si(O-)_2F_2$ bond-bending and bond-rocking vibrational modes expected in the region below 400 cm^{-1} has not been revealed until now. Other authors have assigned this absorption peak to the near-neighbor Si–F stretching vibration corresponding to the co-operative vibration mode for the pair of Si–F bonds *via* the oxygen structure.[4,15,16] Hence, the assignment of the peak at about 980 cm^{-1} is rather disputable and should be the subject of subsequent studies.

Another feature of the absorption band in the range of 900–1000 cm^{-1} is the gradual shift of the main peak maximum from 940 cm^{-1} to about 930 cm^{-1} with the increase in fluorine content that can be caused by appearance of an additional absorption peak located at about 920 cm^{-1}. This peak can be assigned to the symmetric stretching vibration mode of silicon difluoride in $(O-)_2Si(-F)_2$ structural group usually accompanied by the corresponding asymmetric mode mentioned above.[2,5,6,9]

It has been reported that the peak at 920 cm^{-1} can also be attributed to the Si–OH bending vibration with non bridging oxygen.[26,28] This peak is usually accompanied by more intense Si–OH stretching absorption band at 3600 cm^{-1}.[2,29] However, in our case there is no reliable evidence for the presence of the latter band in any of our as-deposited samples even in those made with the highest fluorine concentration. Hence, it is unlikely that SiOH groups are present in our films in a quantity exceeding the detection limit of the FTIR spectrometer.

In conclusion, a low content of $(O-)_2SiF_2$ sites or/and near-neighbor interaction of fluorine atoms along with the absence of Si-H, Si-OH and H-OH groups in detectable quantities even at the maximal fluorine concentrations indicates that in high-density plasma, the electron impact dissociation of SiF_4 gas is very effective in the formation of homogenous SiOF films, i.e., those composed predominantly of monofluoride. On the other hand, hydrogen addition does not lead to the incorporation of hydrogen in detectable quantities into the grown film because of the effective mutual scavenging behavior of fluorine and hydrogen over the entire range of hydrogen additions being used.

3.3 *Control of fluorine doping level by hydrogen addition*

The main goal of hydrogen addition is to offer a new parameter that enables control of the fluorine doping level in SiOF film while keeping the SiF_4/O_2 flow rate ratio constant. The atomic percentage of Si–F_x units in SiOF film, calcu-

lated on the base of the technique described above, was used as a quantitative measure of the fluorine doping level. Figure 5 shows the concentration of Si–F_x units in SiOF film as a function of hydrogen flow rate under various SiF_4-to-O_2 flow rate ratios. As seen in this figure, the main effect of hydrogen addition is to decrease the fluorine concentration in SiOF films as the hydrogen flow rate increases over the range of SiF_4-to-O_2 flow rate ratios. There are three reasons for this behavior. The first is due to the fact that a-Si:H:F and SiOF films can contain defect centers, such as oxygen vacancies, denoted as Si dangling bonds.[7] It was also reported that both hydrogen and fluorine are able to passivate and neutralize these bonds, thus forming Si–H or Si–F termination. As an increased amount of hydrogen is introduced to the gas mixture, competition between the passivation of Si dangling bonds by H and F can shift toward lower fluorine concentration, decreasing the ability of SiOF to admit fluorine. However, this mechanism seems to be improbable because there was no evidence that H-related groups were present in the FTIR absorption spectra of our samples in detectable quantities.

Another cause of the fluorine content reduction may be the result of the scavenging ability of hydrogen. Since the dissociation energy of SiF_4 is quite high, SiF_4 must be dissociated incompletely by hot electrons. As a result a fraction of fluorine can be incorporated into the growing film in the form of silicon di- or/and trifluoride. Moreover, it was reported that some amount of SiF_4 molecules can be trapped inside microvoids when SiF_4 is used as a source gas.[31,32] The presence of F_3Si–F stretching mode in the FTIR spectrum is very difficult to detect due to the overlapping of the corresponding absorption peak at 1015 cm^{-1} onto the most intense Si–O stretching bond at 1070 cm^{-1}.[6] However, highly reactive hydrogen atoms are known to be able to scavenge not only free fluorine from the downstream region, but also to extract the excessive fluorine from the Si–F bonds including SiF_x moieties and $(O–)_xSi(F–)_{4-x}$ precursors[1,33] resulting in the decrease of the total fluorine content. In other words, hydrogen addition can suppress the formation of the F–Si–F bonds or near-neighbor Si–F bonds known to be undesirable due to their effect on SiOF film moisture stability. The homogeneity

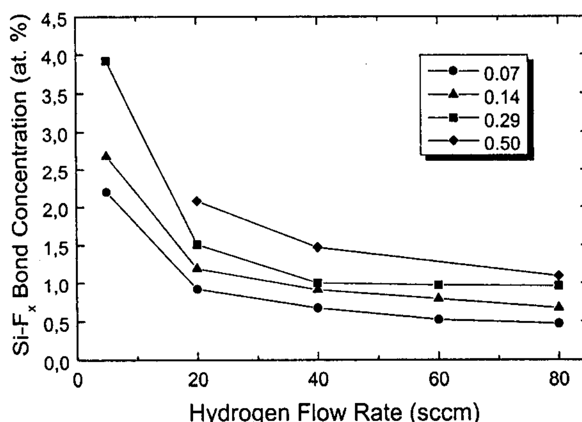

Fig. 5. Si–F_x bond concentration in SiOF film versus hydrogen flow rate under various SiF_4/O_2 flow rate ratios.

of the obtained SiOF films in this case should be better. The presence of hydrogen in the downstream region in the form of individual atoms should be expected because only 8.8 eV electron energy is necessary to dissociate hydrogen gas that can easily back-diffuse into the plasma region.[34]

As seen in Fig. 5, the concentration of Si–F_x bonds in SiOF film increases steadily with the increased value of SiF_4/O_2 flow rate ratio similarly to those observed in ref. 6 presumably due to the increased concentration of $(O–)_3SiF$ precursors. The use of very high SiF_4/O_2 flow rate ratios (probably more than 1) to obtain high fluorine doping levels seems to be unreasonable because the unfavorable change in the Si/O atomic ratio of the film results in Si-rich oxide formation along with the incorporation of undesirable SiF_2, SiF_3 and SiF_4 species. However, it is known that only a small fraction of SiF_4 gas undergoes electron impact dissociation because the energy necessary to dissociate SiF_4 is rather high.[18] So, the major fraction of SiF_4 molecules is usually removed by the pumping system without decomposition. A more promising method to increase the level of fluorine doping is to determine additional factors for improving efficiency of SiF_4 decomposition along with limiting its degree of decomposition up to monofluoride moieties. Complete decomposition of SiF_4 up to Si and F atoms has been observed in a regime of high-density plasma,[12] but seems to be unfavorable; first, it reduces the maximal level of fluorine doping because of the volatile character of fluorine, and second, it changes the mechanism of film formation resulting in SiOF film growth from separate Si and F precursors instead of the direct transfer of Si–F bonding units into the SiOF network. As a result, the moisture stability of obtained SiOF films is expected to be low. Alternative factors are assumed to be rf power, hydrogen addition and the position of feedstock gases inlet with respect to the substrate and plasma region.

In conclusion, hydrogen addition was found to reliably control the fluorine doping level in SiOF films over a wide range of fluorine concentrations while the SiF_4-to-O_2 flow rate ratio was kept constant.

3.4 *The effect of fluorine incorporation on the film properties*

It is well known that the change of fluorine concentration in SiOF films changes the properties of the obtained films, including film polarizability, density, and chemical reactivity because of the strong effect of the highly electronegative fluorine atoms incorporated into the SiOF network on its neighborhood. To compare the properties of the SiOF films obtained using $SiF_4/O_2/H_2/He$ high-density remote plasma with those reported elsewhere, refractive index and etch rate of the obtained films versus fluorine concentration have been studied.

Figure 6 shows that the value of the refractive index decreases gradually with an increase in Si–F_x bond concentration similar to the results reported elsewhere.[6,8,10] At minimal fluorine concentrations, the value of the refractive index is similar to that of thermally grown oxides, i.e., in the range of 1.460–1.463 and reaches the value of 1.410 at the maximal Si–F_x bond concentration of about 4 at.%. The refractive index is known to be dependent on different film properties, including the amount of polarizable species, the Si/O ratio, and film density.[10] Low dispersion of the obtained refractive

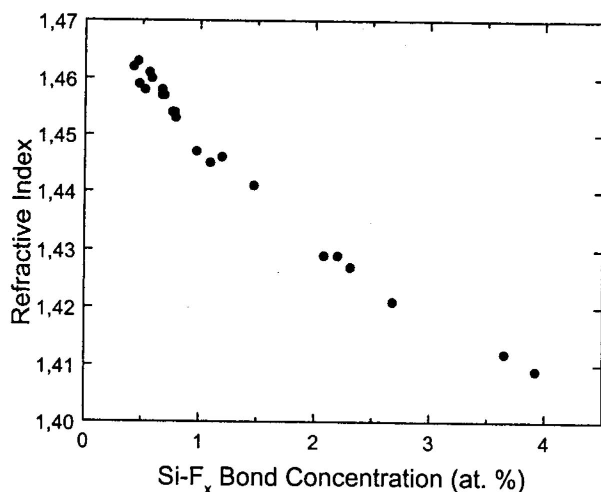

Fig. 6. Refractive index of SiOF films versus Si–F_x bond concentration.

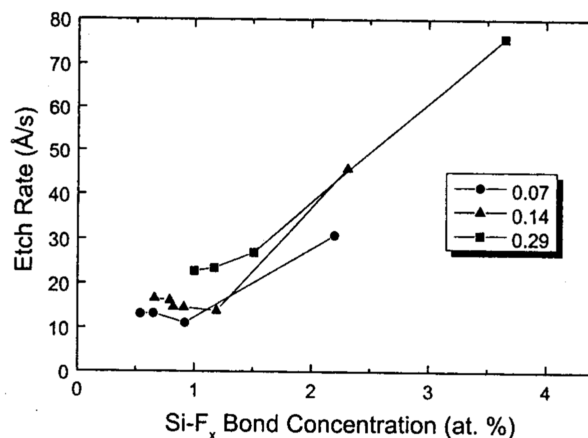

Fig. 7. Etch rate of SiOF films in "P"-solution versus Si–F_x bond concentration under various SiF_4/O_2 flow rate ratios.

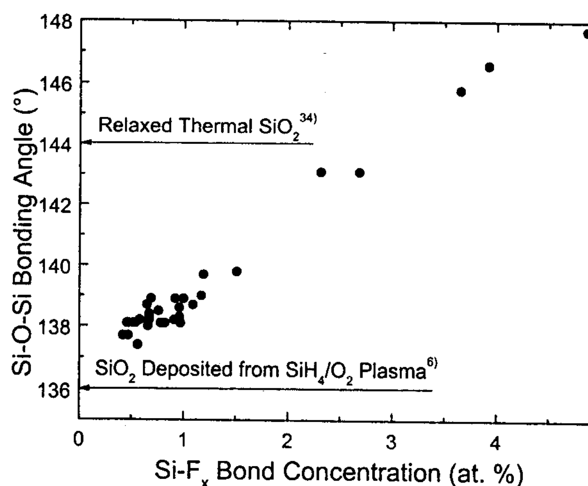

Fig. 8. Si–O–Si bonding angle versus Si–F_x bond concentration.

index value over the range of SiF_4-to-O_2 flow rate ratios allows us to assume that the Si/O ratio in the films is approximately the same and that the refractive index depends only on the fluorine doping level. The incremental decrease in the refractive index of SiOF films with the increase of fluorine concentration may be assigned to the decrease in film density along with decreasing film electronic polarization. The density of the SiOF films, in turn, can depend on two factors; first is the value of macrovoid fraction in the film, and second is the value of Si–O–Si bridged bonding angle of Si–O–Si structural units affecting the formation of microvoids within three- or four-folded ring structures typical for SiOF films.[4,9,33] The contribution of this geometrical factor to the total film porosity seems to be insignificant because of the relatively small range of the Si–O–Si angle change. So, the change in film electronic polarization along with the macrovoids presence are assumed to be the main factors determining the refractive index value.

The etch rate of PECVD silicon oxides in "P"-solution is known to be very sensitive to film porosity and to the presence of non relaxed small angles.[35] In the case of SiOF films the additional factor appears due to the presence of a highly electronegative fluorine atom in the Si(2)–O–Si(1)–F bonding unit leading to the electron shift toward the F atom with the resulting weakening of the Si(2)–O bonding.[36]

As seen in Fig. 7, the "P"-etch rate of SiOF films generally increases with the increase of fluorine concentration, although the relationship is rather complicated and initially etch rate slowly changes in the range of Si–F_x bond concentrations less than 1.5 at.%. A similar relationship was observed by Bazylenko *et al.*[8] The weakening of the Si–O bond mentioned above seems to increase with increased fluorine concentration resulting in the corresponding incremental fraction of etch rate. The presence of nonrelaxed small angles can be estimated from the FTIR spectroscopy data.

The values of Si–O–Si bond angles versus fluorine concentration calculated from the position of Si–O stretching vibrational peak on the base of an elementary central force model[37,38] are presented in Fig. 8. It is known that the Si–O–Si bonding angle in relaxed thermal oxides is approximately 144° and is generally about 7–10° smaller in the as-deposited RPECVD oxides, which leads to increased reactivity of Si–O–Si groups.[29] For our films, the increase of bonding angle from about 137° to about 148° is approximately linear with the increase in fluorine concentration and is assumed to be due to a change in Si–O bonding configuration from the tetrahedral sp^3 to the planar sp^2 state as speculated elsewhere.[5] A similar increase in Si–O–Si bonding angles is usually accompanied by considerable reduction in film chemical reactivity.[9,29] So, the competition between Si–O bond weakening and relaxation of strained Si–O–Si bonding angles is assumed to be responsible for the complexity of the observed relationship of SiOF film etch rate versus fluorine concentration.

As seen in Fig. 8, for samples with Si–F_x bond concentration of more than 3 at.%, the value of the Si–O–Si bonding angle exceeds 144°, corresponding to the completely relaxed annealed thermal oxide. One explanation might be that the compressive stresses in the film are changed by the tensile stresses similar to the changes observed by Yoo *et al.* at the Si–F content greater than 5%.[39]

Compared with the reported results the obtained SiOF films can be characterized as dense, rather stable with relatively

low content of non relaxed Si–O–Si bonding angles. This is also confirmed by low water content in the SiOF films prepared with Si–F_x bond concentration of 4 at.% after etching in "*P*"-solution and following exposure to atmosphere for two months [see Fig. 3(b)].

4. Conclusions

Based on the obtained results several conclusions concerning the effect of hydrogen addition on the SiOF film RPECVD process using $SiF_4/O_2/H_2$/He plasma and SiOF film propertiescan be obtained.

The deposition of SiOF films using $SiF_4/O_2/H_2$-based plasmas should be considered as a continuous competition between both deposition and etching processes in the presence of both free fluorine atoms and volatile HF. Hydrogen addition in the SiF_4/O_2 reaction gas mixture at the optimal values enables considerable increase in the deposition rate when high values of SiF_4-to-O_2 flow rate ratio are used compared with hydrogen-free RPECVD process.

The absence of reliable evidence for the presence of $(O-)_2SiF_2$ sites or/and near-neighbor interaction of fluorine atoms even at the maximal fluorine concentrations allows us to assume that in high-density plasma, an electron impact dissociation of SiF_4 gas is very effective in the formation of homogenous SiOF films. The absence of Si–H, Si–OH and H–OH groups in detectable quantities even at the maximal fluorine concentrations provides evidence that hydrogen addition does not lead to the detectable incorporation of hydrogen into the growing film because of the effective mutual scavenging behavior of fluorine and hydrogen over the entire range of hydrogen flow rates being used.

Hydrogen addition was found to be able to reliably control the fluorine doping level in SiOF films over a wide range of fluorine concentrations while the SiF_4-to-O_2 flow rate ratio was kept constant.

The hydrogen added in the reaction gas mixture plays an active role in the film formation process, strongly affecting both the surface reactions and properties of the obtained SiOF films. Compared with the reported results, the obtained SiOF films can be characterized as dense, rather stable and with relatively low content of non relaxed Si–O–Si bonding angles.

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