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The effect of plasma chemistry on the damage induced to porous SiCOH dielectrics.

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ABSTRACT

We have investigated the effects of plasmas of He+H_2, N_2+H_2 and NH_3 on the properties of three porous SiCOH dielectrics (pSiCOH) with ultralow dielectric constants of about 2.4. All plasma treatments have been performed in the same plasma tool under identical RF power and pressure in the plasma. Exposure of the films to the plasmas resulted in structural modifications of the bonding structure of the films, loss of film thickness, and an increase in index of refraction and dielectric constant. The degrees of these modifications varied among the studied films and changed from plasma to plasma.

It was found that Fourier transform infrared spectroscopy (FTIR) analysis can indicate the type of structural modification caused by a certain plasma treatment, but cannot be used to predict the level of damage to the dielectric constant. No correlation was observed between the shrinkage of the film after a plasma treatment and the corresponding increase of the dielectric constant. The increases of the dielectric constant correlated only to increases of the index of refraction caused by the plasma treatments.

The largest damages to the dielectric constants were caused by plasma treatments at room temperature. Among the investigated plasmas, the most damaging one to the porous SiCOH films, at RT or 180 ^oC, was the He+H_2 plasma, while the least damaging one was the NH_3 plasma at 180 ^oC.

I. INTRODUCTION

The successful replacement of silicon dioxide with the low dielectric constant SiCOH material (organosilicate glass) as the interconnect dielectric [1] has required the improvement of the SiCOH films [2] and to overcome a significant number of integration challenges. One of these challenges is the damage caused to the dielectric by the ashing plasma used to strip the photoresist. The oxidative plasmas originally used to strip resist from silicon dioxide dielectrics are generally damaging to SiCOH because they convert the Si-methyl bonds in the SiCOH films into Si-O and Si-OH bonds that in turn lead to water uptake. This results in a degradation of the material and an increase in its dielectric constant (k) and leakage current [3-6]. Ultralow-k dielectrics with $k<2.5$ are more vulnerable to plasma damage due to their increased porosity [7]. Reducing plasmas containing hydrogen have been investigated for resist ashing with the goal to reduce or eliminate the damage to the SiCOH type materials [4-6, 8-10] but with mixed results.

Some studies have shown that hydrogen plasma treatments of SiCOH films can improve their resistance to damage induced by oxygen plasmas used to strip photoresist [4, 11], while other studies have shown that even hydrogen containing reducing plasmas can produce variable degree of damage in the films, depending on the specific plasma conditions [5, 8-10, 12]. The contradictions between the different reported data can stem from the different chemistries of the hydrogen containing plasmas, e.g. dilution in Ar, He, N_2, and the concentration of hydrogen in such plasmas. Furthermore, even for the same plasma chemistry, the modifications produced by a reducing plasma on a low-k film is generally dependent on the type and configuration of the plasma tool used for the resist strip. It is thus difficult to reach a conclusion from the comparison of different studies which plasma chemistry would produce minimal damage to the dielectric during the resist strip.

The present study has compared the effects of several ashing plasma chemistries on the properties of porous SiCOH (pSiCOH) films prepared by PECVD. All plasma treatments were performed on blanket films in one reactor under the same plasma conditions. As it was shown previously that interaction of hydrogen plasmas with pSiCOH films is affected by the process used for the preparation of the film, the current study was performed on three pSiCOH films with different preparation histories.

II. EXPERIMENTAL

Three different plasma chemistries have been investigated in the present study. All plasma treatments have been performed in the same parallel plate reactor, either at room temperature (RT) or at 180 ^{o}C. The conditions of the different plasma treatments are summarized in Table I, which also defines the notations used to describe each set of conditions. All plasmas were sustained by a RF power of 50W, at a pressure of 150 mtorr, and the films were exposed to each plasma for 5 minutes. This time was chosen based on previous experience [10] to enable easier identifications of the modifications induced to the properties of the films. The substrates were mounted on the RF powered electrode and were thus at a negative bias during the exposure to the plasma. The values of the acquired biases are shown in Table I.

The effects of the plasma treatments have been studied on three different porous pSiCOH dielectrics. The films have been prepared as described elsewhere [13, 14] from mixtures of a SiCOH precursor with an organic porogen precursor. The same SiCOH precursor, but different porogens were used for the preparation of the investigated films. The deposited films were cured by exposing to an energy source to remove the porogen, resulting in the formation of porous pSiCOH films with ultralow dielectric constants (k~2.4). The cured pSiCOH films will be referred to in the following as the *initial* films. The plasma experiments were performed on the cured pSiCOH films.

The bonding structures of the films and their modifications by the plasma treatment were investigated by Fourier transform infrared spectroscopy (FTIR). Because most of the changes induced by the plasma treatments were too small to be seen from the visual comparison of the spectra, the effects of the plasma treatments on the pSiCOH films were analyzed on subtraction spectra, (the spectra of the original films subtracted from the spectra of the plasma treated films) for better revealing the modifications of the films. The index of refraction was measured using a n&k tool and the thickness changes of the films were determined by step height measurements.

The dielectric constants were measured using metal-insulator- semiconductor (MIS) structures with Al dots as described elsewhere [13, 14].

III.RESULTS AND DISCUSSIONS

A. FTIR spectra

Typical FTIR spectra of pSiCOH films and their analysis can be found elsewhere [14, 15]. The effect of the plasma treatments on the pSiCOH films will be presented next through the subtraction FTIR spectra.

1. Treatments at RT

Figure 1 compares the effects of the plasma treatments at room temperature (RT) on the three pSiCOH films. Figure 1.d shows an expanded section of the SiO-SiC region, 1400-600 cm^{-1}, of P1 the spectrum from Figure 1.c with the identification of the locations of the different peaks. While the intensities of these peaks depend on the type of plasma and type of pSiCOH, they are basically the same in all cases. The peak locations and their assignments are listed in Table II and a detailed discussion of their interpretation can be found elsewhere [10].

As shown in Figure 1, all plasma treatments caused increases in the cage fraction of the SiO, indicated by the peak at 1128 cm^{-1} [15] and an increase of $SiMe_3O$ sites (Me =CH_3= methyl), indicated by the peaks at 1246 cm^{-1} and 1307 cm^{-1} [16]. The latter is further confirmed by the increase of the 985 cm^{-1} peak, which is also attributed to the formation of $SiMe_3O$ [10]. In the same time we observe a decrease in the suboxide fraction of the SiO as indicated by the negative peak at 1037 cm^{-1} [15]. The peak observed at 1202 cm^{-1} was tentatively assigned to an increase in of SiOMe bonds [10].

A comparison of the spectra of the SiO-SiC regions in Figures 1.a to 1.c shows that film P3 has the smallest bond modifications in this region as a result of the RT treatment in all three plasmas, while similar, but unequal, bond modifications occur in films P1 and

P2 as a result of the plasma treatments at RT. Film P2 undergoes the smallest modifications in the SiO and SiC bonds in the He+H_2 plasma.

Furthermore, as a result of the exposure to the He+H_2 plasma at RT, all samples got protonated, as indicated by the increase of the absorption band at ~2900 cm^{-1}[15]. The largest protonation occurs in film P3. In the other plasmas there is a loss in the CH band at ~2900 cm^{-1}.

2. Treatments at 180 ^oC

The effects of the plasma treatments at 180 ^oC on the bonding structure of the pSiCOH films are presented in Figure 2. Contrary to the RT plasma treatments, no protonation is observed after the 180 ^oC treatment in the He+H_2 plasma. It can be seen in Figure 2 that the strongest structural changes occur in film P1 after all three plasma treatments at the higher temperature. The other two films (P2 and P3) incur smaller changes and their bonding structures are affected about the same by the He+H_2 and N_2+H_2 plasmas (Figure 2.a and 2.b).

The changes induced in the P2 film by all investigated plasmas at 180 ^oC are substantially lower than those produced by the same plasma treatments at RT (Figure 1). Furthermore, the P3 film is least affected by the NH_3 plasma at 180 ^oC, while P1 film incurs the largest bond modifications in this plasma.

A detailed discussion of the potential chemical reactions in the plasma leading to the bonding modifications described above can be found elsewhere [10]. The results of this study show that structural changes caused by plasma treatment of pSiCOH films are affected by:

- plasma chemistry
- treatment temperature
- history of film preparation.

B. Thickness modifications

The thicknesses of the films are changed by the plasma treatments. These changes are summarized in Figure 3. The plasma treatments at RT (Figure 3.a) caused very small changes, in the range of experimental errors, in the thickness of the P2 films. The largest shrinkage occurred in P1 films, where the smallest shrinkage was caused by the He+H_2 plasma and the largest shrinkage of ~ 4.5% was caused by the NH_3 plasma (Figure 3.a). Film P3 incurred a significant thickness reduction only in the N_2+H_2 plasma.

A different behavior is observed in Figure 3.b, for the treatments performed at 180 ^oC. The decreases in the thickness of all films after all plasma treatments are in most cases larger than after the same treatments at RT. The smallest shrinkage for the films treated at 180 ^oC is observed in the P3 film (as compared to film P2 at RT) and is almost independent on the type of plasma used. The largest thickness reduction occurred again, as in the RT treatments, in P1 films but this time the dependency on the plasma chemistry is opposite to that observed for RT treatments, namely the largest shrinkage occurs in He+H_2 plasma and the smallest on in the NH_3 plasma.

No correlation was observed between the structural modifications reflected in the FTIR spectra in Figures 1 and 2 and the thickness reduction in the corresponding films.

C. Index of refraction

The changes in the index of refraction (n) caused by the plasma treatments of the different films are presented in Figure 4. The figure shows that, at both temperatures, the treatment in He+H_2 plasma caused the largest increases in the index of refraction, while the smallest changes were induced by the NH_3 plasma. The changes in n resulting from plasma treatments at RT are about double the changes occurring at 180 ^oC. The larger changes at RT may be related to the formation of SiOH bonds and water uptake at the lower temperatures. The amount of these bonds and to the adsorbed water may be enough for affecting the index of refraction but too small to be detected in the FTIR spectra. The largest changes in n after treatment at RT occur in P1 films, but after the 180 ^oC treatments they occur in P3 films. The smallest changes in the index of refraction were observed for the P2 films at 180 ^oC.

With regard to the plasma chemistry, the smallest changes in the index of refraction were caused in all films by exposure to the NH_3 plasma treatment.

The investigated pSiCOH dielectrics are porous materials and it is expected that their index of refraction will correlate with the density of the films. If the changes in film thickness discussed above were correlated with changes in film density, the changes in index of refraction should correlate with the changes in film thickness. However a comparison of Figures 3 and 4 shows that this is not the case. For example, the RT treatment in He+H_2 plasmas caused the smallest change in film thickness, but resulted in the largest increase in the refractive index. In another case, the thicknesses of P2 films were almost not affected by the RT plasma treatment, but large increases in the index of refraction were observed for same films after He+H_2 and N_2+H_2 plasma treatments. And, while the thickness changes were generally larger after the 180 ^oC treatment, the changes in the refractive index were larger after the RT treatments.

The apparent discrepancy between the effects of the plasma treatments on shrinkage and indices of refraction of the films can be explained if one assumes that the thickness reduction is not always a result of film densification. It is possible that the larger thickness reduction obtained for some films, or after the 180 ^oC treatments vs. RT treatments, is at least partially due to removal of film by plasma etching. This part of the shrinkage is not reflected in the modification of the measured index of refraction of the remaining films. The changes in the index of refraction are caused by modifications of the bonding structure of the films, however no correlation could be established between the FTIR spectra and the indices of refraction.

D. Dielectric constants

The modifications induced in the pSiCOH films by the exposure to the different plasmas described above are reflected in the damage induced in the dielectric constants of the films. The bonding modifications caused by the plasma treatments, illustrated in Figures 1 and 2, and the associated molecular rearrangements of the film structures [10] result in increases in the values of the dielectric constant. The changes in k are illustrated in Figure 5, which presents the dielectric constants of the different films before and after the plasma treatments.

The k values of the films increased after all plasma treatments and, similar to other film properties, the amounts of increase are dependent on the specific film and the plasma

treatment conditions. The dielectric constants are generally higher after the treatments at RT (Figure 5.a) than after the treatments at 180 ^{o}C (Figure 5.b) and this may be explained again by formation of SiOH bonds during the RT treatments and water uptake afterwards. Small amounts of water can have a significant impact in increasing the values of the dielectric constants.

At RT, the NH_3 and N_2+H_2 plasmas have a similar effect and increase less the dielectric constant than the He+H_2 plasma (Figure 5.a). At 180 ^{o}C, the smallest increase in the dielectric constant has been obtained for all studied films after the treatments in NH_3 plasma. This plasma treatment has caused the smallest modifications of the dielectric constants among all investigated conditions.

The relation between the modification of dielectric constants and those of other films characteristics is illustrated in Figures 6 and 7, which present the data for all films and all plasma treatments. Figure 6 shows that there is no correlation between the increases in dielectric constants and film shrinkage. Contrary to that, Figure 7 shows a direct correlation between the increase in the indices of refraction and increases in dielectric constant. The scatter of the data points can be associated with errors in the measurements of the refractive index.

IV. CONCLUSIONS

We have investigated the effect of three plasma chemistries, He+H_2, N_2+H_2, and NH_3, on the properties of several pSiCOH dielectrics. All plasmas were sustained in the same reactor under identical RF power and pressure in reactor. Exposure of the films to the plasmas resulted in structural modifications of the bonding structure, loss of film thickness, and an increase in index of refraction and dielectric constant.

For all plasma chemistries, the effect of plasma treatment on the properties of a pSiCOH film is affected by the history of its preparation. This underscores the complexity of predicting the behavior of a pSiCOH film in specific plasma chemistry. Observations reported for a certain porous pSiCOH film can not be assumed to be identical for different films with a different preparation history.

FTIR analysis can indicate the type of structural modification caused by a certain plasma treatment, but cannot be used to predict the level of damage (increase in value) to the dielectric constant. There is also no correlation between the shrinkage of the film after a plasma treatment and the corresponding increases of the dielectric constant. The increases of the dielectric constant correlate only to increases of the index of refraction caused by the plasma treatments.

The largest damage of the dielectric constant of blanket films is caused by plasma treatments at room temperature. Among the investigated plasmas, the most damaging one to the pSiCOH films, at RT or 180 ^{o}C, is the He+H_2 plasma, while the least damaging one is the NH_3 plasma at 180 ^{o}C.

The above observations cannot be straightly extrapolated to damage that can occur on the sidewalls of patterned dielectrics. In the patterned structures the combined influence of the dimension of the pattern profile on the transport of reactive gases, plasma sheath and transport of positive ions through the sheath can result in different relative damage in the studied plasmas, than reported for the blanket films [5, 8].

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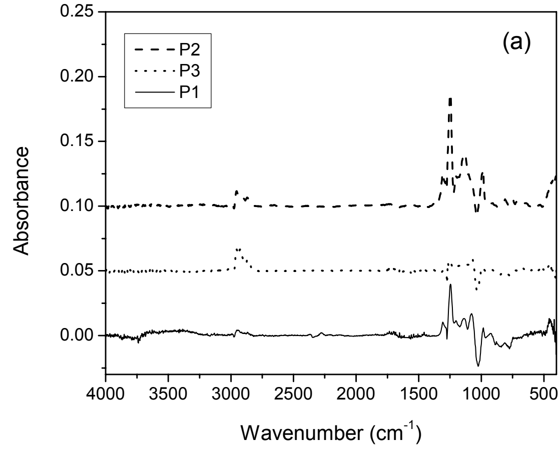
Table I: Plasma treatment conditions

Treatment	Flow (sccm)	Temperature (^oC)	DC Bias (-V)
$He+H_2$	95+5	RT	155
$He+H_2$	95+5	180	120
N_2+H_2	50+10	RT	110
N_2+H_2	50+10	180	115
NH_3	50	RT	130
NH_3	50	180	160

Table II. FTIR peak assignments in the SiO-SiC region.

Wavenumber (cm^{-1})	Bond assignment
1307	$SiMe_3O$
1274	$SiMe_1$
1246	$SiMe_3O$
1202	$SiOMe_1$
1128	Cage Si-O-Si , angle ~150°
1063	Network Si-O-Si, angle ~144°
1037	Silicon suboxide, angle <144°
985	$SiMe_3O$
780	$SiMe_1$



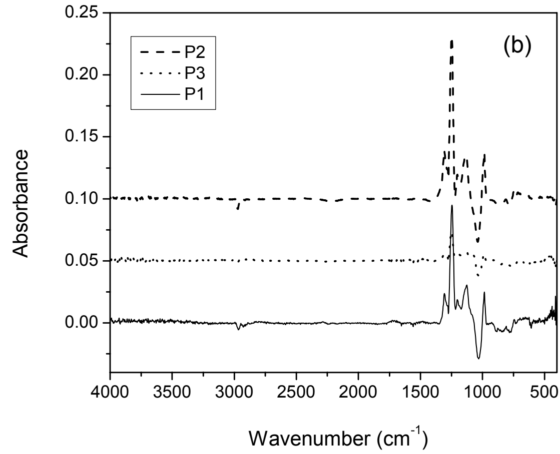
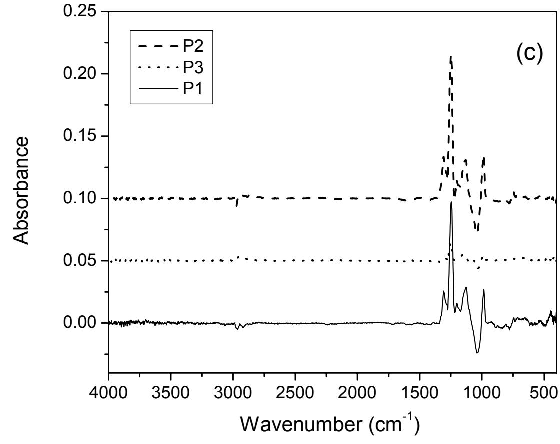


Figure 1 a&b: Subtraction FTIR spectra of pSiCOH films plasma treated at RT. a) $He+H_2$ plasma, b) $N2+H_2$ plasma



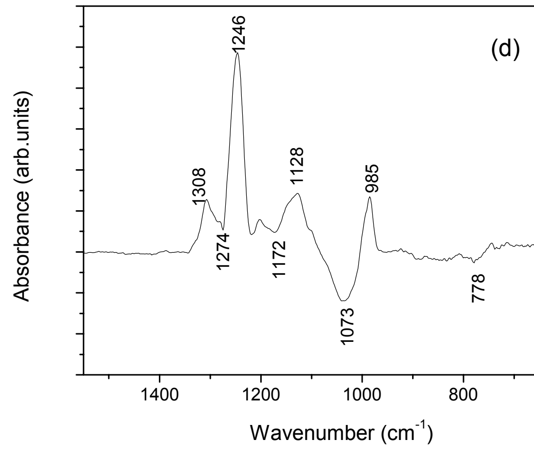
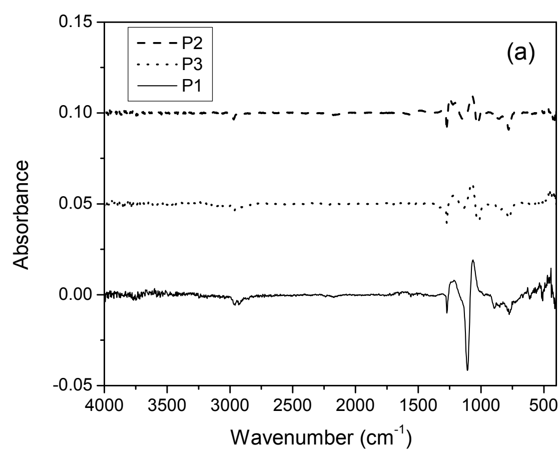


Figure 1c&d: c) NH_3 plasma; d) expanded spectrum of film P1 from c).



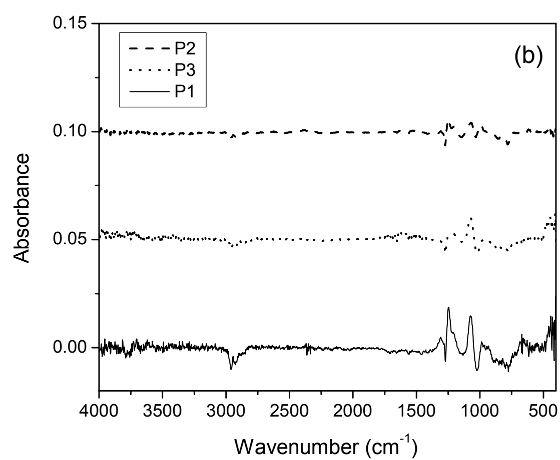


Figure 2a&b: Subtraction FTIR spectra of pSiCOH films plasma treated at 180 °C. a) He+H_2 plasma, b)N2+H_2 plasma

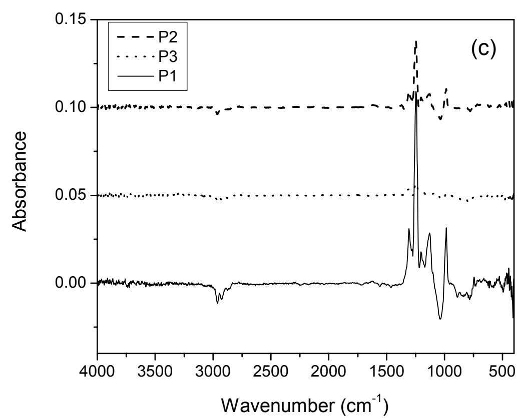
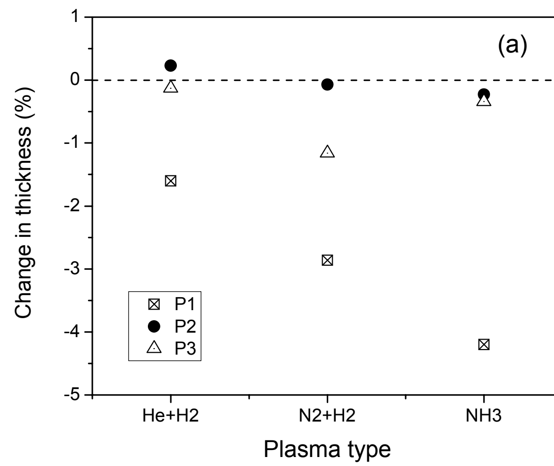


Figure 2c: Subtraction FTIR spectra of pSiCOH films plasma treated at 180 ^{o}C. (c) NH_3 plasma.



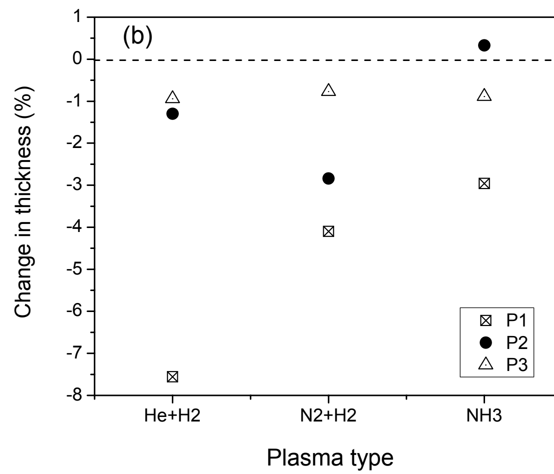
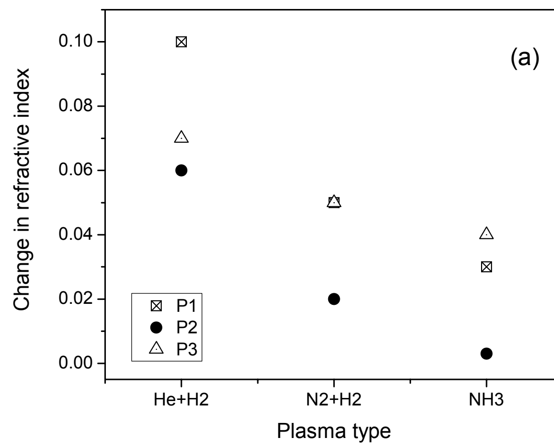


Figure 3a&b: Thickness modification by plasma treatments. a) at RT ; b) at 180 ^{o}C.



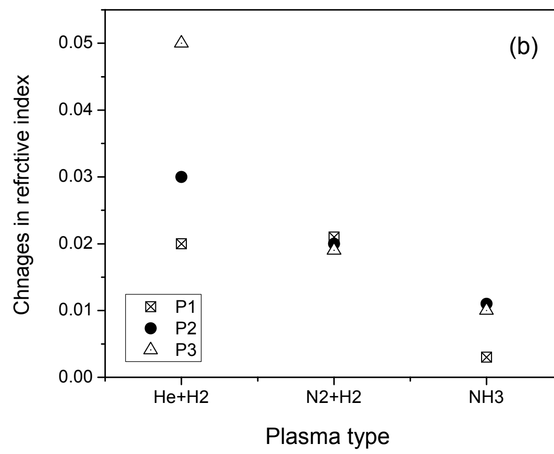
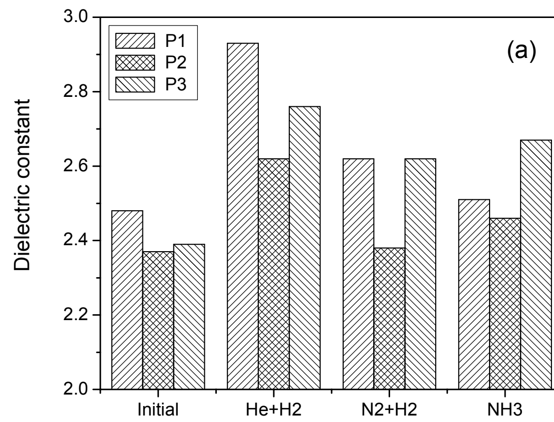


Figure 4a & b : Changes in refractive index as a result of plasma treatments. a) treatments at RT ; b) treatments at 180 ^{o}C.



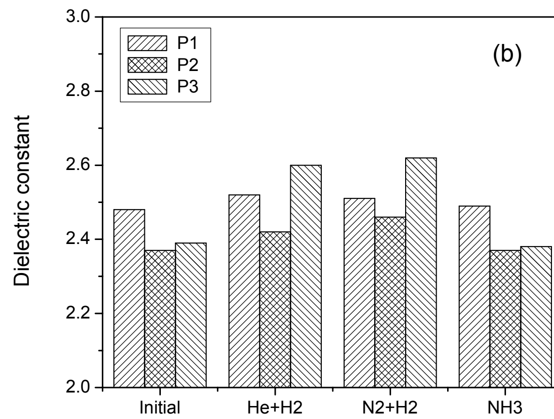


Figure 5 a & b : The effect of the plasma treatments on the dielectric constant of pSiCOH films. a) treatments at RT ; b) treatments at 180 ^{o}C.

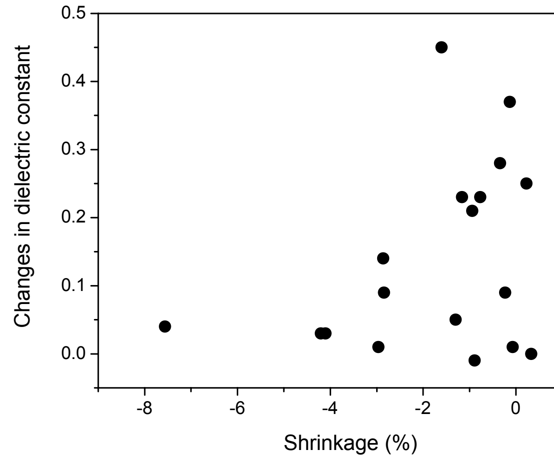


Figure 6: Changes in dielectric constants vs. film shrinkage caused by the plasma treatments.

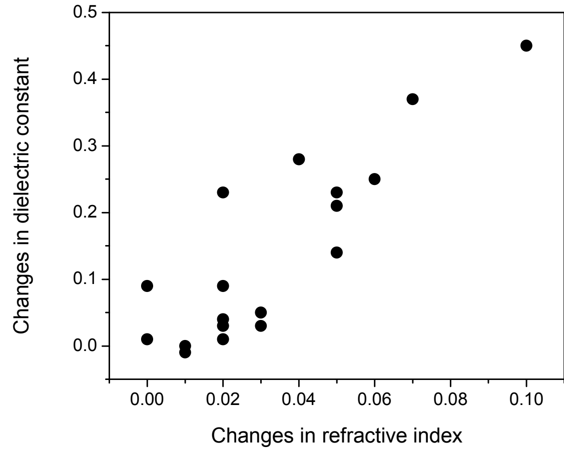


Figure 7: Changes in dielectric constants vs. changes in indices of refraction caused by the plasma treatments.