

IBM Research Report

Hydrogen Plasma Effects on Ultralow-k Porous SiCOH Dielectrics

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ABSTRACT

This study investigated the interactions of hydrogen plasmas with ultralow-k porous SiCOH (pSiCOH) films and their dependency on the values of the original dielectric constant, porogen used for the preparation of films, and substrate temperature during the plasma treatment. pSiCOH films of similar dielectric constants have been prepared by plasma-enhanced chemical vapor deposition (PECVD) using an identical SiCOH skeleton precursor, but two different organic porogens. The films exposed to the hydrogen plasmas have been characterized by optical techniques, shrinkage characterization, and electrical measurements. It was found that the hydrogen plasma modifies the structure of pSiCOH's oxide skeleton and reduces the concentration of the Si-(CH₃)₁ bonds, resulting in an increase of the dielectric constant. The degree of modification, for films prepared from same precursors, is larger for films with lower dielectric constants (k) and is affected by the porogen used to prepare films with similar k values.

I. INTRODUCTION

Hydrogen plasmas have been investigated for various treatments of SiCOH type films. Such films are either spin-on prepared hybrid organo-silicon polymers (HOSP, MSQ), or plasma-enhanced chemical vapor deposition (PECVD) prepared SiCOH films^{1, 2}. It was claimed by some authors that hydrogen plasma treatments of these films can improve their resistance to damage induced by oxygen plasmas used to strip photoresist^{3, 4}. But other authors have shown that even plasmas of hydrogen diluted in helium or nitrogen can produce variable degree of damage in the films, depending on the specific plasma conditions⁵.

Hydrogen plasmas have also been used to cure porous SiCOH films. A hydrogen plasma treatment at 400 °C was used for introducing porosity in a SiCOH type film prepared by PECVD⁶, while it was shown elsewhere that hydrogen plasma can cure porous MSQ at temperatures as low as 250 °C⁷. We found that long exposure of as deposited SiCOH films to hydrogen plasmas at temperatures below 200 C did not remove the porogen⁸. In the latter case, the hydrogen plasma densified the annealed porous film and increased its dielectric constant⁸.

It is further evident from a comparison of the results mentioned above that the interaction of hydrogen plasmas with SiCOH type films is affected by the processing of the specific film and by the conditions used to maintain the hydrogen plasma. Furthermore, unless the plasma conditions are adjusted properly, a hydrogen-dominated chemistry can breakdown carbonaceous species, increase the crosslinking in the films and increase their dielectric constant^{8,9}.

The goal of this work was to study in more details the effects of hydrogen plasma on the properties of porous SiCOH (pSiCOH) films prepared by PECVD and the dependency of these effects on the substrate temperature and bias during the plasma treatment and on the precursors used for preparing the films.

II. EXPERIMENTAL

The investigated porous pSiCOH films have been prepared by PECVD, as described elsewhere^{1, 2}, using the same SiCOH skeleton precursor but two different organic precursors (porogens). The PECVD conditions have been adjusted to obtain films with different values of the dielectric constants (k), therefore expecting to have different degrees of porosity¹⁰. The investigated films are described in Table I, which shows also the original dielectric constants of the films and the k values after the plasma treatments.

The hydrogen plasma treatments have been performed in a parallel plate reactor, either at room temperature or at 180 °C. The room temperature treatment was performed either on the grounded or biased electrode while the 180 °C treatment was performed only on the biased electrode (the grounded electrode could not be heated in the current plasma tool). The pressure in the plasma was maintained at 100 mtorr. The notations of the different treatments are defined in Table II.

The original and treated films were characterized by Fourier transform infrared spectroscopy (FTIR), n & k measurements for the determination of the index of refraction, and step height measurements for the determination of thickness changes. The dielectric constant was measured using metal-insulator-semiconductor (MIS) structures with Al dots.

III. RESULTS AND DISCUSSIONS

A. Effect of treatment time

Sample P1-1 was treated in the hydrogen plasma for different times, between 1 and 10 min., to study the effect of the exposure time on the properties of the films. The dependence of the refractive index and of the changes in film thickness on the treatment time is illustrated in Figures 1 and 2 respectively. The figures show that there is essentially a linear dependence of the respective properties on the exposure time to the hydrogen plasma, both at room temperature (CB) or at high temperature (HB). The data also show that the changes in the refractive index are larger, while the shrinkage is smaller after the CG, CB treatments than after the HB treatment. The differences between the values obtained after CG and CD treatments are very small, probably within the experimental errors.

The rest of the samples were therefore treated for a constant time of 5 minutes, because some of the changes occurring after 1 minute of plasma treatment may be too small to be measured with sufficient accuracy (e.g. see FTIR Results).

B. FTIR Results

No significant changes were observed in the FTIR spectra after 1 minute treatment of the samples in the hydrogen plasma, therefore only spectra of samples treated for longer times will be discussed next. Figure 1 shows the baseline-corrected spectra of the as-received P1-1 film and after its exposure to a CB treatment for 5 min. The spectra are shown at full scale. The most visible differences between the two spectra is observed at wavenumbers below 1500 cm^{-1} , therefore this region is shown expanded in Figure 1.b with the identification of the observed peaks. It can be seen that the CB plasma treatment caused a relative increase in the cage fraction of the SiO, indicated by the peak at 1132 cm^{-1} ¹¹, and an increase of SiMe₃O sites (Me = methyl), indicated by the peaks at 1248 cm^{-1} and 1306 cm^{-1} ¹². SiMe₃O compounds are known to split the 1250 cm^{-1} band with the weaker component appearing as a shoulder on the high frequency side of the band¹³. Although weaker than SiMe, the SiEt (Et=CH₂CH₃) band also absorbs at 1250 cm^{-1} and is another probable contributor¹³. A weak absorption observed at 1380 cm^{-1} is additional evidence of SiEt. The formation of some SiOH bonds by the CB treatment is also indicated by the broad absorption band at $3400\text{-}3700\text{ cm}^{-1}$ visible in Figure 1.a.

The spectrum of the P1-1 sample after 5 minutes HB treatment, at $180\text{ }^\circ\text{C}$, appeared to be very similar to that of the untreated samples. The subtraction of the two as-collected spectra (spectrum after HB treatment minus the spectrum of the pretreated sample) was therefore obtained to follow the changes that occurred during the hydrogen plasma treatment. Similar subtraction spectra will be discussed for the other samples and treatments too. Figure 4 presents the subtraction spectra of the P1-1 samples treated under the different conditions. It can be seen that there is almost no difference between the

subtraction spectra of the films treated at room temperature on the biased and grounded electrodes. This indicates that the substrate bias has no significant effect on the changes introduced in the bond structure of the films by the hydrogen plasma treatment. However we observe a strong effect of the substrate temperature on these changes.

Thus, the room temperature treatments, CG and CB, resulted in decreased suboxide fraction, increased SiMe_3O and/or SiEt and increased cage fraction, as indicated by the decrease of the peak at 1044 cm^{-1} and increase in the peaks at 1248 cm^{-1} , and 1133 cm^{-1} , respectively. An increased peak at 1200 cm^{-1} is also observed and tentatively assigned to SiOMe , but a strong corresponding methoxy absorption at 2820 cm^{-1} ¹³ is not observed, increasing the probability that the 1200 cm^{-1} peak likely has some contribution from the longitudinal optic (LO) component of the asymmetric stretch of the SiO_4 unit at 1180 cm^{-1} and/or from an Si alkyl such as ethyl, propyl or butyl which have which have absorbances at $1250\text{-}1220\text{ cm}^{-1}$, $1220\text{-}1200\text{ cm}^{-1}$, $1200\text{-}1190\text{ cm}^{-1}$, respectively¹³. Additional evidence of Si ethyl in the film is found by the weak absorbance at 1380 cm^{-1} . The increase of the 990 cm^{-1} peak is attributed to the formation of SiMe_3O and/or Si alkyl¹³, which contribute to the suboxide fraction of deconvoluted SiOSi absorption peak¹¹. As described in reference¹¹, deconvolution of the SiOSi region between $1300\text{-}900\text{ cm}^{-1}$ can only be modeled by three peaks assigned to cage (1138 cm^{-1}), network (1063 cm^{-1}) and suboxide (1024 cm^{-1}) fractions.

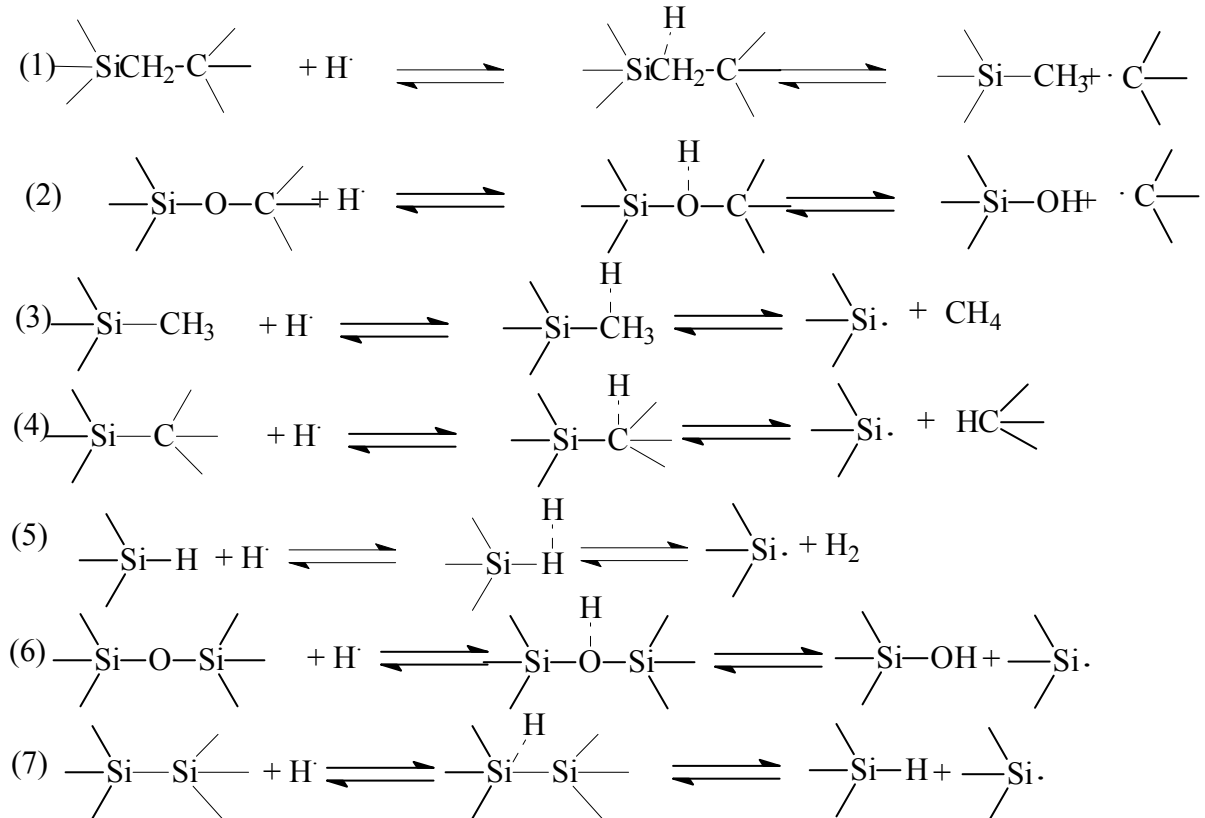
The high temperature HB treatment of the P1-1 sample produced much smaller and different changes in the oxide's bond structure of the films. These changes consist mainly of higher loss of CH_x than from the CG, CB treatments, as indicated by the reduction in peak intensity at about 2900 cm^{-1} , increased SiMe_3O and/or SiEt (1242 cm^{-1}), loss of cage (1138 cm^{-1}), gain of network oxide (1074 cm^{-1}) and decreased suboxide at 1037 cm^{-1} but increased suboxide at 1004 cm^{-1} attributed to increased Si alkyl contributions.

The spectrum of the samples CB treated for 10 minutes appeared to be very similar to that of the samples treated for 5 minutes. The subtraction of the two spectra showed that the longer treatment in the hydrogen plasma caused a further reduction of the suboxide SiOSi , cage SiOSi and SiMe_n and enhancement of the network oxide.

The effect of the plasma treatments on the FTIR spectrum of the P1-2 film was much smaller than that produced on the spectrum of the P1-1 film. Thus, the effect of the CB treatment on the bond structure of the P1-2 film was similar to that of the HB treatment on the structure of the P1-1 film. The difference in the behavior of the two films prepared from same precursors may be attributed to different degree of porosity and possibly different pore sizes expected to be in the two films of different dielectric constant. Other factors which might affect the film's behavior include the higher relative carbon content of P1-1 and higher relative cage content of P1-1. A comparison of FTIR spectra normalized to the SiOSi highest peak as shown in Figure 5 reveals that P1-1 has the largest ratio of CH_x to SiOSi and thus the highest relative carbon content. Additionally, a deconvolution of the SiOSi peak region¹¹ reveals that P1-1 has a large cage fraction of SiOSi . More significantly, P1-1 has the largest relative cage content of the films examined and it is stable after H plasma treatment as shown in Figure 6, which plots the relative cage, network, and suboxide fractions of the P1 and P2 films before and after CB treatment. Sample P1-1, characterized by lower k value than P1-2, is expected to have higher degree of porosity and potentially larger pores¹⁰, possibly attributable to the relatively large CH_x and cage fractions.

The changes induced by the hydrogen plasma treatments (CB and HB) on the FTIR spectra of the P2-1 film, shown in Figure 7, have a similar trend to those observed for the P1-1 film, prepared with a different porogen, but were significantly smaller (compare Figure 4). Thus the CB treatment of the P2-1 film caused much less conversion into Si-Me₃ bonds compared to P1-1. This was in spite the fact that the dielectric constant of P2-1 (k=1.8) was slightly smaller than that of P1-1 (k=2.0). Changes similar to P2-1 were observed for the CB and HB treated P2-2 and P2-3 films and were almost unrelated to the values of the dielectric constants (k~2.05 and 2.40 for the latter films). As the P2-3 film is expected to have lower porosity than the P2-1 and P2-2 films, the results discussed above indicate that the modification induced in the P2 films are not related to their porosities. The negative peak observed at 777 cm⁻¹ in Figure 7 reflects the loss of SiMe₁ bonds¹¹ due to the plasma treatment. The most apparent difference in the P1 and P2 films is the relative CH_x content. P2 films have far less relative CH_x than P1 films and this may account for the observed differences after H plasma treatments. Large relative CH_x contents in the films potentially acts as a network disrupter by limiting SiOSi linkages and apparently decreases the films inertness to hydrogen plasma treatments.

Protonation by the atomic hydrogen generated in the plasma can lead to extensive bond breaking in the SiCOH matrix including disruption of C-C bonds as listed in the possible reactions below:



The bond breakage caused by the H atoms in the plasma can occur anywhere within the SiCOH matrix, thus the undesignated Si linkages in the reactions, and leads to formation of terminal Si-methyl species and to many crosslinking opportunities. Reaction 1 results in the formation of terminal (non crosslinking) Si-methyl and the

generation of a carbon radical which can react with any other activated silyl site as formed in reactions 5-7 to generate an additional terminal Si - alkyl. Breaking of C-O bonds as depicted in reaction 2 would also lead to the formation of carbon radicals. Activated silyl sites are formed by breaking Si-C, Si-H, Si-Si and possibly Si-O bonds as shown in reactions 3-7 catalyzed by hydrogen protonation reactions in the plasma. The activated silyl sites are then available to react with carbon radicals to form terminal carbon species or to react with other activated silyl species to form Si-Si crosslinks or possibly with SiOH to generate a SiOSi crosslink.

Formation of SiMe₃O and other Si-alkyl terminal sites as discussed earlier is vividly observed for P1-1 which has the largest relative carbon content and is the thickest film. After CB and CG plasma treatments, little relative change is seen in CH_x, or SiC absorption peaks yet increased SiMe₃O and/or other Si-alkyl terminal sites are observed. Presumably the large carbon content in P1-1 is either unbound hydrocarbon in the SiCOH matrix or more likely P1 films contains more and longer covalently bonded hydrocarbon chains than P2 films. The increased carbon content increases the probability of generating carbon radicals in P1-1 films via reactions 1 or 2. The carbon or methyl radicals generated in reactions 1 or 2 is free to react with any activated silyl sites to form a terminal Si-alkyl site.

As shown in Figure 8, from the deconvolution of the SiC region (900-700 cm⁻¹) of P1-1, retention of SiH and Si-alkyl₂ and Si-alkyl₃ (alkyl is methyl, ethyl or longer hydrocarbon) is confirmed by the little apparent change in the absorption at 890 and 840 cm⁻¹ attributed to HSiO₃, Si-alkyl₂ and Si-alkyl₃. After CB treatment an increase in the absorption at 802 cm⁻¹ attributed to Si-alkyl₂ and a decrease in the absorption at 775 cm⁻¹ attributed to Si-alkyl₁ is observed. A decreased absorption at 775 cm⁻¹ was also observed in the subtraction spectrum. These results suggest a segregation of carbon in the SiCOH matrix with a preferential loss of methyl from SiMe₁ sites and formation of SiMe₂ sites. The preferential loss of Me from SiMeO₃ sites and increased SiMe₂ is suggestive of some segregation in the film with high carbon content sites coalescing. These reaction scenarios are more effective in the plasma treatments at low temperatures and in thicker films, where the outdiffusion of carbon radical species is minimized the potential of reacting with active sites generated in the SiCOH matrix by the hydrogen plasma is maximized.

The increased dielectric constant after all of the hydrogen plasma treatments is at least partially attributed to molecular rearrangement of the SiCOH matrix. Where the bond breaking catalyzed by protonation of the hydrogen plasma, resulted in the formation of active silyl sites which could crosslink resulting in formation of additional SiOSi and Si-Si bonds and the resultant densification of the film.

The results presented above show that the effects of hydrogen plasma treatment on the bonding structure of the pSiCOH films are dependent on the history of the film preparation, specifically the precursors used for the preparation of the films in the present case. Additionally, the chemical composition of the film plays a role in determining the effect of hydrogen plasma treatment with a high carbon containing film such as P1-1 being more susceptible to hydrogen plasma densification. Furthermore, for one type of films (P1) the results of the plasma treatment are affected by the porosity in the films (as indicated by the k values), while for other type of films (P2) they are not.

C. Plasma effects on pSiCOH properties

The modifications induced by the plasma treatments on other film properties are presented in Figures 9 - 11. All plasma treatments resulted in an increase in the index of refraction of the dielectric films. As shown in Figure 9, with one exception potentially associated with an experimental error, the room temperature treatments resulted in higher increases in the index of refraction than the 180 °C treatments. The increases in the index of refraction are generally lower for the P2 than for the P1 films.

The behavior of the films shrinkage, shown in Figure 10, is opposite to that of the index of refractions. The shrinkage of the films treated at room temperature is smaller than that of the films treated at 180 °C and the shrinkage of the P1 films is much smaller than that of the P2 films. We see again the influence of the precursor used for the preparation of the films on the results of the hydrogen plasma treatments. The shrinkage of the films is expected to indicate a densification of the films as a result of the changing in the bonding structures induced by the plasma treatment, as described above. This densification will cause an increase in the dielectric constant of the films. However, it is possible that at least a fraction of the observed shrinkage may be related to the etching of the films by the hydrogen plasma.

Figure 11 shows indeed an increase of the dielectric constants of all films after the hydrogen plasma treatments. The CG and CB treatments induced larger changes in the dielectric constant than the HB treatment, in spite of the larger shrinkage produced by the latter. The larger changes in the dielectric constant of the cold treated films shown in Figure 11 may be associated with larger amount of SiOH bonds in these films, but it might also indicate that some of the measured shrinkage is associated with etching of the film in addition to its densification, especially in the films treated at high temperature. Figure 11 illustrates again the effect of the porogen used for the preparation of the films on the final properties. Thus the P2-3 film had smaller changes in the dielectric constant than the P1-2 film, both having the same initial dielectric constant (see Table I). This is in contrast with the larger shrinkage observed for P2-3 compared to P1-2. This discrepancy might again be explained assuming that the shrinkage of the P2 films is caused by loss of material by plasma etching, in addition to the densification of the film.

Interestingly the P2-3 films which shrank 7% under CB treatment have a much smaller cage fraction than the P1-1 films which only shrank 1% under same treatment. Possibly a stable cage structure is key to limiting shrinkage in SiCOH films; the cage structure in P1 films may be related to the high carbon content of the films as well. Additionally, SiH is retained for P1-1 but not for P2-2 after CB treatments. Possibly, hydrogen bonding in the SiCOH cage matrix of P1 films is stabilizing the SiH sites in the SiCOH matrix rendering them resistant to the H plasma treatment. Most likely, the large carbon content in the P1 films is contributing to the stability of the cage matrix and retention of SiH, possibly through alkoxide (R_3SiOCR_3 where R can be Si, C, O, or H) bonding sites.

IV. CONCLUSIONS

Exposure of porous pSiCOH films to hydrogen plasmas results in a modification of their bonding structure. The treatment at room temperature also causes some formation of SiMe₃ bonds. Preferential loss of methyl is observed from SiMeO₃ sites.

The structural modifications induced by the plasma treatments result in film shrinkage, increase in index of refraction and increase in the dielectric constants of the films. The modifications of these properties are dependent on the substrate temperature during the plasma treatment, but not on the substrate bias during the room temperature treatments.

The greater increase in the dielectric constant of the P1 films was attributed to the larger chemical change and molecular rearrangement after hydrogen plasma treatment than for the P2 films as evidenced by the increased FTIR intensity of the SiMe region, and formation of SiMe₃ and SiOMe sites, without apparent loss of CH_x. Hydrogen plasma treatment possibly formed carbon radicals which reacted with silicon radicals in the matrix to generate SiC bonds without loss of CH_x.

The increase of the dielectric constants is the result of several factors including, molecular rearrangement leading to increased crosslinking, and film densification

The results of the hydrogen plasma treatments on the film properties are affected by the precursors used to prepare the films.

ACKNOWLEDGMENTS

The authors are thankful to C. Wang and D. Restaino for supplying the films used in this study.

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Table I: Definition of samples and values of dielectric constants

Sample	Porogen	k - original	k - CG	k -CB	k-HB
P1-1	POR1	2.00	2.80	2.58	2.47
P1-2	POR1	2.40	3.04	2.84	2.64
P2-1	POR2	1.80			
P2-2	POR2	2.05			
P2-3	POR2	2.40	2.61	2.59	2.56

Table II: Plasma treatment conditions

Treatment	Temperature (C)	Bias (-VDC)
CB	25*	150
CG	25*	0
HB	180	150

*) The temperature is defined at the beginning of the experiment; it increased during the plasma treatment to ~40 °C.

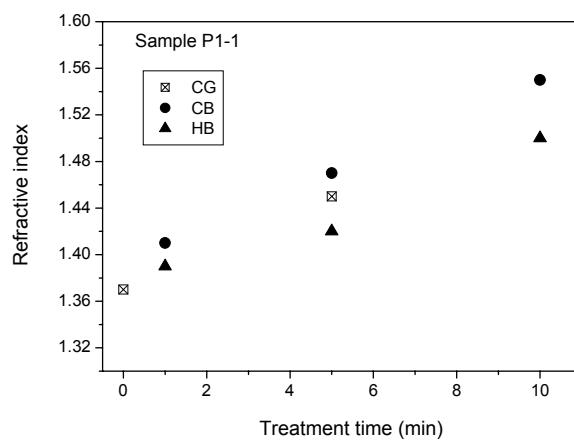


Figure 1. The refractive index of P1-1 as a function of the treatment time and type of plasma treatment.

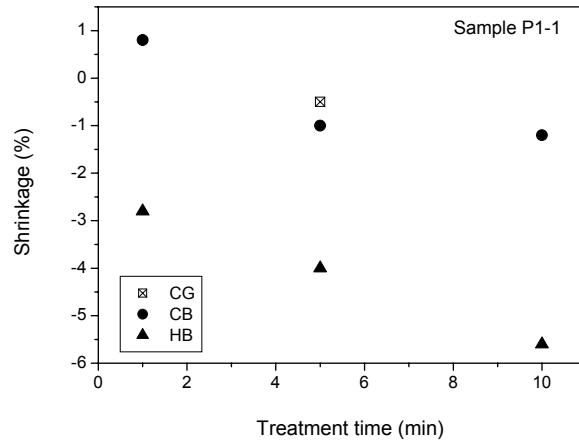


Figure 2. Changes in the thickness of P1-1 as a function of the treatment time and type of plasma treatment.

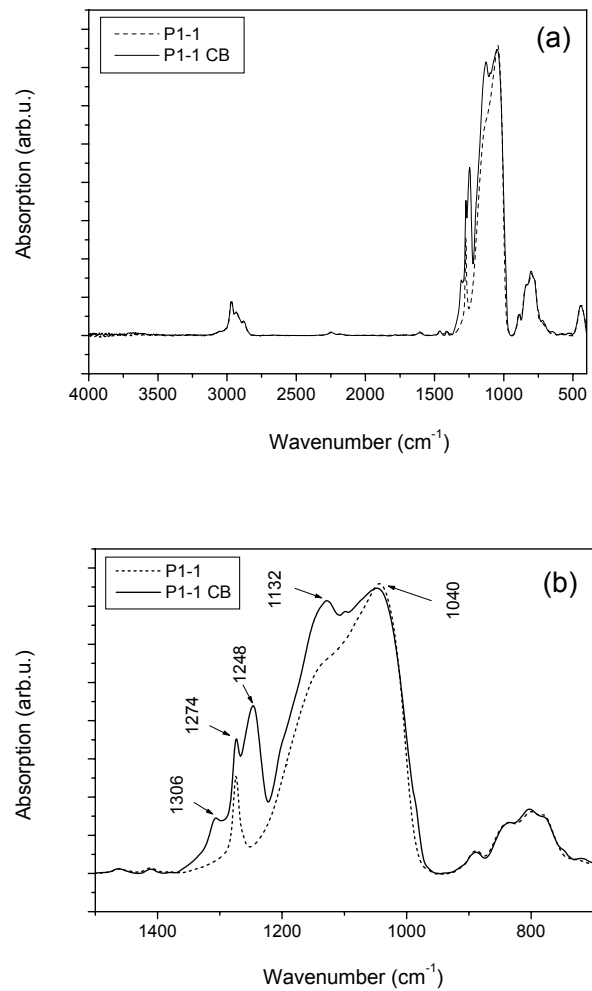


Figure 3. FTIR spectra of sample P1-1: broken line - as-received films; solid line – after CB treatment. Figure 3.b shows an expanded section of Figure 3a.

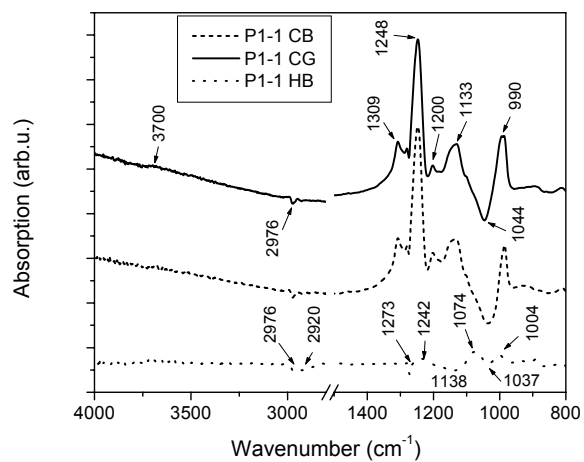


Figure 4. FTIR spectra of plasma treated P1-1 specimens after subtraction of the spectrum of the as-received sample.

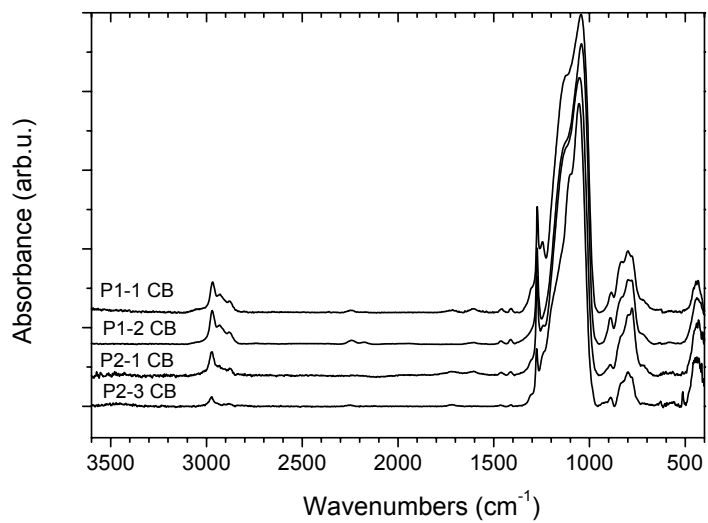


Figure 5. FTIR spectra of P1-1, P1-2, P2-1 and P2-3 films after CB treatment, normalized to the SiOSi peak intensity. P1 films contain relatively more CH_x than P2 films.

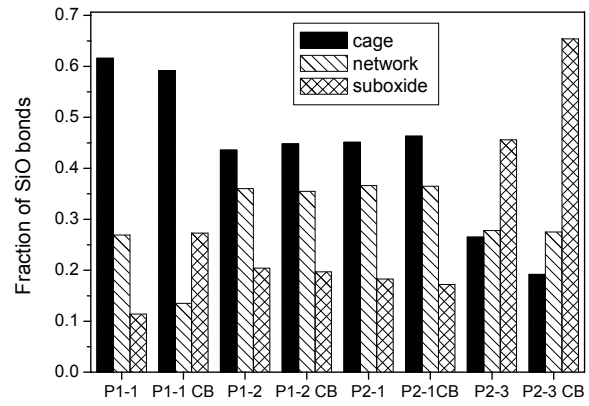


Figure 6. Fractions of SiO bonds in as deposited films and after CB treatment.

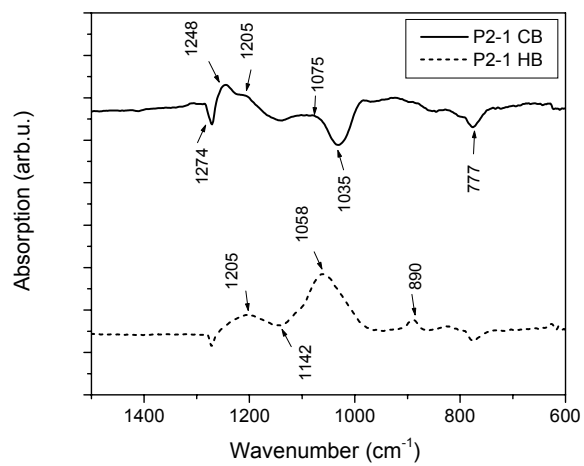


Figure 7. FTIR spectra of plasma treated P2-1 specimens after subtraction of the spectrum of the as-received sample.

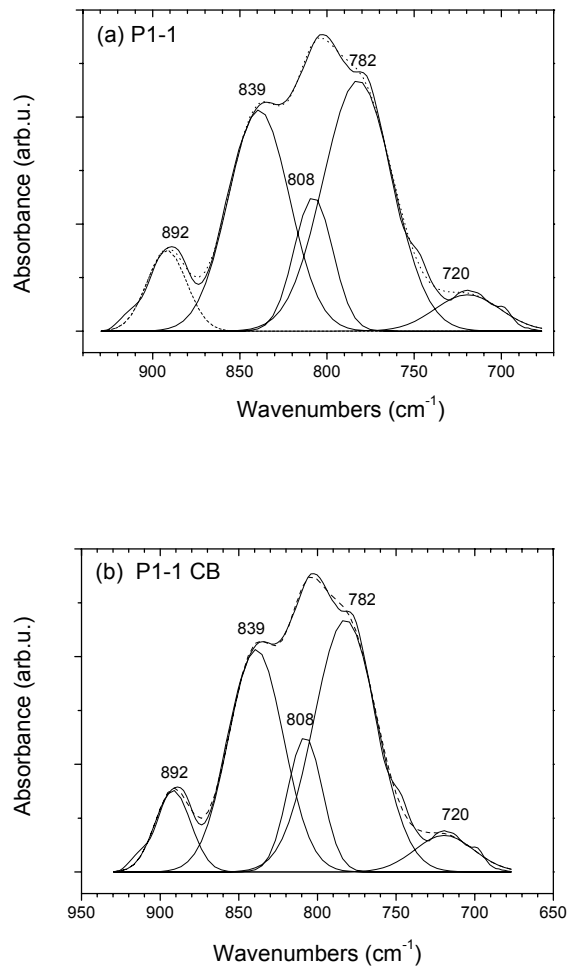


Figure 8. Deconvolution of SiC region 950-650 cm⁻¹ of FTIR spectra of P1-1 as deposited (a) and after CB treatment (b).

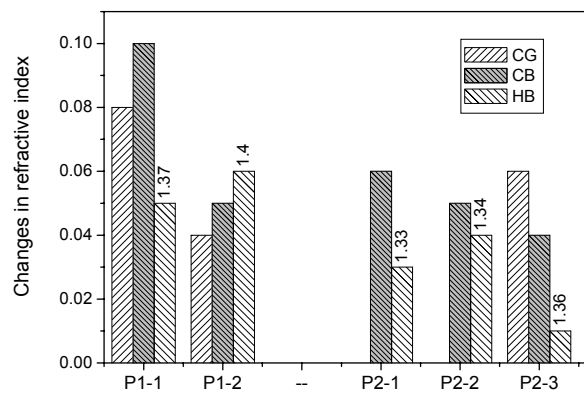


Figure 9. Changes in refractive index caused by 5 minutes hydrogen plasma treatments. Numbers on columns indicate refractive index of as-received films.

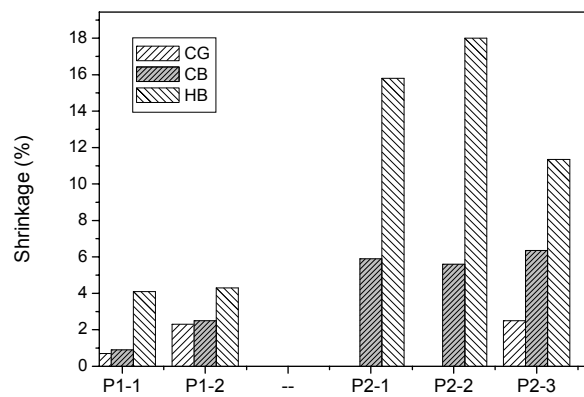


Figure 10. Shrinkage caused by 5 minutes hydrogen plasma treatments.

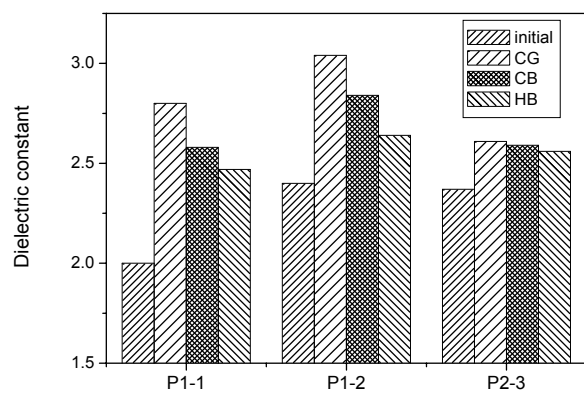


Figure 11. Changes in the dielectric constants caused by 5 minutes hydrogen plasma treatments.