行政院國家科學委員會專題研究計畫期中報告

極低介電常數材料(k<2.2)與銅製程在超大型積體電路上之應用研究(1/2)

Study on the integration of ultra low k(k<2.2) and copper interconnect in ULSI application (1/2)

計畫編號：NSC　91－2215－E－009－044
執行期間：91 年　8　月　1　日至　92 年　7　月　31 日

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一.中文摘要

隨著半導體技術的進步，元件的尺寸不斷的縮小，並且進入了深次微米的領域內。為了增加積體電路的性能，降低導線的線寬和增加金屬導線層的數目，便成為超大型積體電路技術所採用的方式。但此時，訊號傳遞的時間延遲和高功率的消耗便成為很嚴重的問題，大大降低了元件的表現性。為了解決此問題，便引入了低介電材料和銅導線來取代傳統的製程。在眾多的低介電材料中，PPSZ (porous organo-silsesquiazane)薄膜，是一種具有多孔隙度的極低介電常數材料(k~2.2)。在本年度的計畫中，將對此材料的物性、熱穩定性及電性進行探討，結果發現此材料不但有極低的介電常數，而且有很好的熱穩定性。

關鍵詞: PPSZ, 低介電數材料, 多孔隙度

Abstract

As the feature of the integrated circuit (IC) is scaled down, the resistance and capacitance of multilevel interconnect are increased due to the thinner metal wires and shorter distance between them. The interconnect RC delay and power dissipation will be increased and become an issue of performance. Therefore, conductors with lower resistivity and dielectrics with lower dielectric constant are thus deeply needed for ultra-large scale integrated circuits (ULSIs) generation. In this thesis, we use new low-k dielectric PPSZ (porous organo-silsesquiazane, k=2.2) to replace traditional SiO_2 (k=4.0). In order to be useful, the intrinsic properties of new low-k dielectrics such as fundamental physical, electrical, thermal stability of the spin on glass (SOG) have been found. And we used PPSZ as the insulator and Cu as the conductor to evaluate the electrical properties of PPSZ.

Key word: PPSZ, low-k, porous

二.緣由與目的

When the progress of integrated circuit (IC) process technology continuously scaled down to deep sub-micron regime, the speed of signal propagation is determined by the technology of multi-level interconnection instead of intrinsic transistor delay. The key issues of resistance-capacitance (RC) time delay are related to the wiring metal and the inter-metal dielectrics (IMD). In order to reduce the resistance and enhance the reliability, Cu has been recognized as the most suitable alternative for Al as wiring material.[1-2] Besides, low dielectric constant (low-k) materials, replaced traditional silicon dioxide as IMD, are thus inevitable for decreasing the parasitic capacitance. Low-k dielectrics can also lower the power consumption and the crosstalk between metal lines.[3-5] In recent years, there are many low-k materials have been developed including organic and inorganic ones. The method to form dielectrics is uncertain, too. Both the conventional chemical vapor deposition (CVD) [6-9] and spin-on procedure compete with each other. The former has a long and successful history, but seem to suffer uncertain extendibility to ultra low k materials (k<2.2). The latter, in spite of its track record for photoresist, has raised some questions in applications to on-chip dielectric insulators. However, switching two methods is not an attractive option for new device generation. In accordance with the requirement of low permittivity, many of major SOG suppliers are developing new types of SOG. As traditional materials had the permittivity larger than 2, the porous material could get lower than 2. In this paper, we will investigate an organic porous organo-silsesquiazane (PPSZ) from Clariant Inc. The material is similar to porous methylsilsesquioxane (MSQ) material. Compare to conventional siloxane-based spin-on glass, this material with lower dielectric constant due to the presence of $Si\text{-}CH_3$, C-H bonds, and porous structure instead of partial Si-O bonds. The intrinsic material property of low-k material is first discussed. In addition, the integration issues such as enhancement of thermal stability, the impact of O_2-plasma ashing, the damage of the PR wet stripper on the dielectric quality and the resistance to copper penetration are all investigated. We also provide plasma treatments to improve the impact of the above-mentioned issues.

三.結果與討論

As shown in Fig. 1, the formation of PPSZ film is exhibited. Porous Methyl-silsesquiazane will be transformed to porous methyl-silsesquioxane with the addition of water. The water provides the oxygen to replace the nitrogen of methyl-silsesquiazane. In Fig. 2, FTIR of PPSZ formation is shown. The broadening of Si-OH bond is due to the adsorption of water. After curing in furnace, the water can be eliminated and the standard PPSZ film is achieved. During the hydration between 4 and 14 hours left in the cleanroom, it is obvious that the Si-N peaks are almost disappeared and Si-O “network” is enhanced fast. Besides, Si-C bonds are gradually enhanced which determine the quality of PPSZ film. Fig. 3 shows the leakage current density of PPSZ with different curing temperature. Identically, the leakage current density did not vary sharply and kept in an acceptable range. Fig. 4 shows the dielectric constant of PPSZ film with Al and Ti/Cu electrode. It is found the k value is about 2.2. Fig. 5 shows the temperature dependence of stress of PPSZ film and the thin film stress is positive that can be referred to tensile stress. It is shown that as the temperature is heated up, the tensile stress is decreasing. This means the expansion coefficient of PPSZ film is smaller than the Si

substrate. Also, the reversible curve is observed. It suggests that the quality of PPSZ is good and is not damaged under the test of the thermal cycle. In the study of thermal stability, the results as Fig. 6 show FTIR spectra with different temperature. There is nearly no degradation even if leaving the sample in the furnace at 500 ℃. In Fig. 3, the J-E relation shows good leakage characteristics and there's no obvious increase in the leakage current. The above indicates PPSZ is good in thermal stability and can tolerate the thermal treatment in interconnect. Until leaving PPSZ in the furnace at 550 ℃ for 30 minutes, we observed PPSZ was initially damaged that product some hole at the film and the decline of C-H and Si-C bonds were exhibited as Fig. 6. In Fig. 7, it shows the temperature dependence of thickness after curing in the furnace. The variation of thickness is not severe until the hole on PPSZ appears. The insert shows the local topography of 50-times magnification of the hole photographed by optical microscope and indicates the damage was caused by the strict thermal treatment. The damaged sample was characterized by TDS compared with the standard sample, cured at 400 ℃ for 30 min. Fig. 8 and Fig.9 exhibit the water and CO_2 content of PPSZ film. It is observed the damaged sample absorbed more water and CO_2 than the standard one. From the above discussions, we know PPSZ can meet the thermal requirement in interconnect with good thermal stability.

In the study of plasma treatments on the issues of process integration, we performed O_2, NH_3, and H_2 plasma treatments. Figure 10 to Figure 13 summarize the results of H_2 plasma treatment on the porous silica film. Figure 10 shows that the thickness of the film has not decreased obviously after undergoing H_2 plasma treatment, and it was almost not changed. It can be seen that during the treatment process, the H_2 plasma has not damaged the thin film. Although the thickness of the film decreases slightly with the increase in the length of treatment time, the variation in thickness after H_2 plasma treatment is still low compared with other plasma treatments. Because the treated film has not been damaged or intensely impacted on the film properties, the film properties are slightly similar to the properties of untreated film. Figure 11 shows the changes in the FTIR spectra of PPSZ films before and after 1 minutes, 2 minutes and 3 minutes H_2 plasma treatment. It can be seen that when the treatment time is prolonged, the Si-C bond only shows a slight tendency to decrease on the spectrum, but the film structure as a whole does not change much in general. Figure 12 shows that the leakage current density of porous silica with H_2 plasma treatment for 1 to 3 minutes without post annealing. The leakage current shows a little increase as porous silica film is treated by H_2 plasma. Fig. 13 shows that the dielectric constant was decrease with H_2 plasma treatment for 1 to 3 minutes. The Si-H bond was increased with H_2 plasma treatment for 1 to 3 minutes in Fig. 14. Fig. 15 to 18 show the results of PPSZ films after O_2 plasma treatment. As shown in Fig. 15, the thickness of the film has decreased by approximately 20% when the step of the process is from the cured PPSZ film to 90 seconds O_2 plasma treatment. And the thickness decreased abruptly. Fig. 16 shows the changes in the FTIR spectra of PPSZ before and after O_2 plasma treatment. Obviously, the both peaks, Si-C and C-H, were large decrease after 90 sec O_2 plasma treatment. The intensity of Si-OH bond signal is increased gradually when O_2 plasma is applied to PPSZ film. This indicates that oxygen radicals can diffuse deep into the porous inner structure of the film to break a large number of Si-C bonds in the SiO_2 porous

film. On the side, the Si-OH peak was abruptly produced and getting increase with the time of O_2 plasma treatment. That is well known that the Si-OH will be induced to absorb the moisture and make the dielectric constant of film increased. Fig. 17 and Fig. 18 show the changes in the leakage current density and dielectric constant of porous silica before and after the O_2 plasma treatment. There is an obviously rising of dielectric constant after the O_2 plasma treatment. This is because of the absorption of moisture. Besides, the leakage current density is almost breakdown. The PPSZ film is sensitive to oxygen plasma and easily degraded. The PPSZ has large surface area and the rate of chemical reaction is proportional to the surface area. So the PPSZ is much weaker than MSQ or HSQ. We can say that the degradation due to the ozone plasma is a key issue to integrate PPSZ with conventional processes. Fig. 19 to Fig. 22 depict the properties of PPSZ after O_2 plasma treatment followed by H_2 plasma treatment. Fig. 19 shows the variation of thickness after treatments. Fig. 20 shows the FTIR of the film after two step treatments. The Si-C and C-H peaks don't keep well if H_2 plasma is treated first. In Fig. 22 and Fig. 23 show the leakage and dielectric constant are not improved. The time of H_2 plasma treatment was probably not enough to form a passivation layer and to prevent film from the degradation caused by oxygen plasma.

四. 結論

A notable organic spin on polymer material PPSZ has been developed for interlevel dielectric applications. PPSZ polymer exhibits excellent local planarization due to its ability to flow during the bake cycle. The polymer gives low stress, crack-free films that have a low dielectric constant after cure. The magnitude of the dielectric constant of a material is determined mainly by the strength of the dipole moment and the density. Substitution of Si-CH_3 for highly polarized Si-O is another possible reason for the decrease of dielectric constant.[10] In the study of thermal stability of PPSZ, it is found that the thermal stability of PPSZ is good. The film is stable and has low dielectric constant and low leakage current till 550°C curing temperature. PPSZ can tolerate the thermal treatment in interconnect with good thermal stability. Also, in this project, we investigated the impact of plasma treatments. It shows that O_2 would bring damage to PPSZ films.

五.參考文獻

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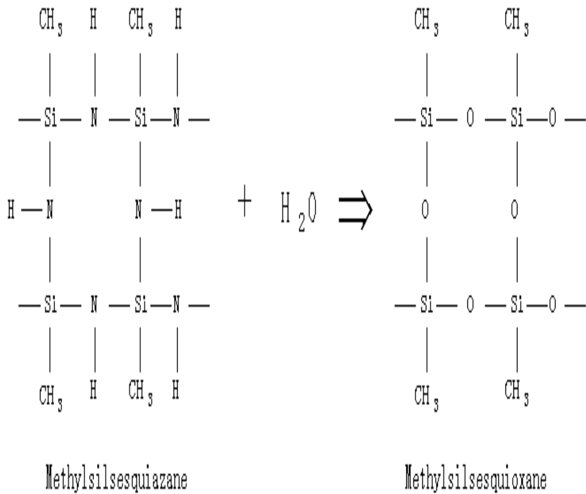

Fig.1: The formation of PPSZ film is exhibited.

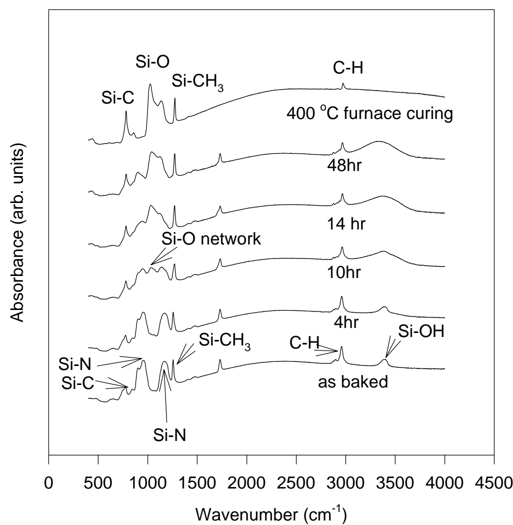

Fig. 2: FTIR of PPSZ Hydration Process at various hours

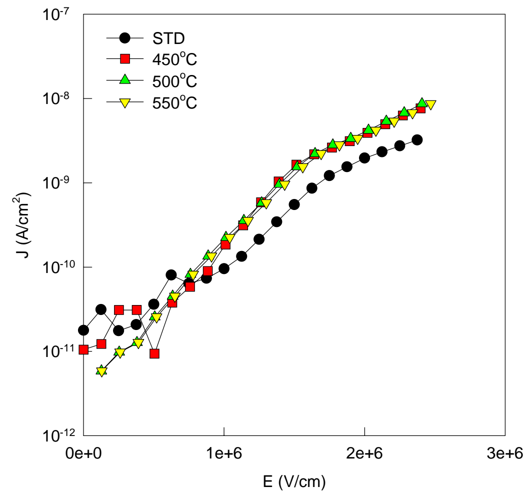

Fig. 3: J-E curve of PPSZ with different temperature.

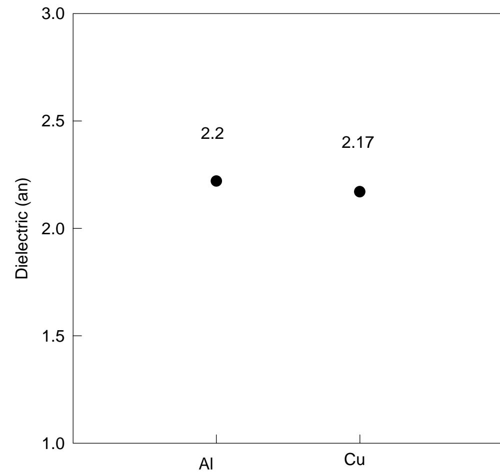

Fig. 4: The dielectric constant of PPSZ film with Al and Ti/Cu electrode.

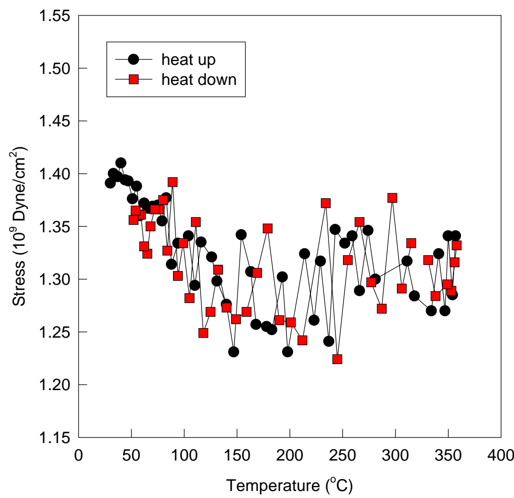

Fig. 5: The temperature dependence of stress of PPSZ film

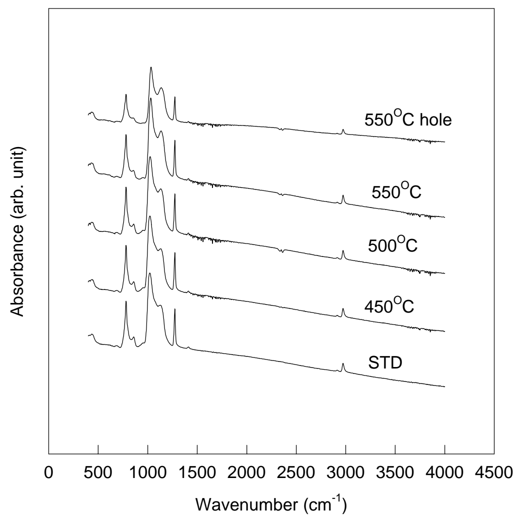

Fig. 6: FTIR of PPSZ at different temperature

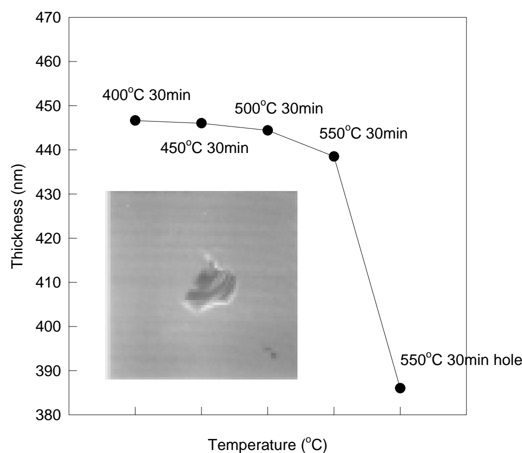

Fig. 7: The temperature dependence of thickness after curing in the furnace. The insert shows the local topography of 50-times magnification of the hole photographed by optical microscope.

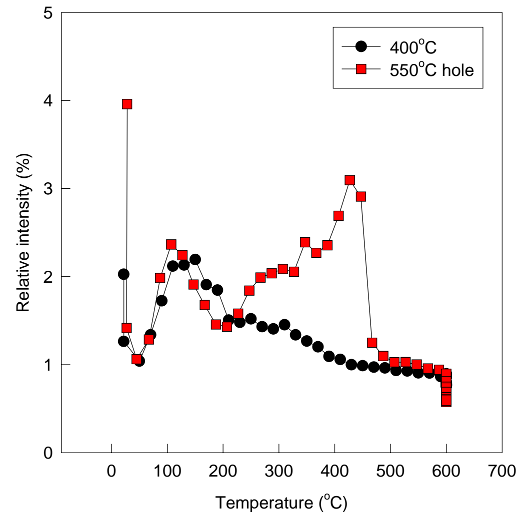

Fig. 8: The water content of PPSZ film measures by TDS.

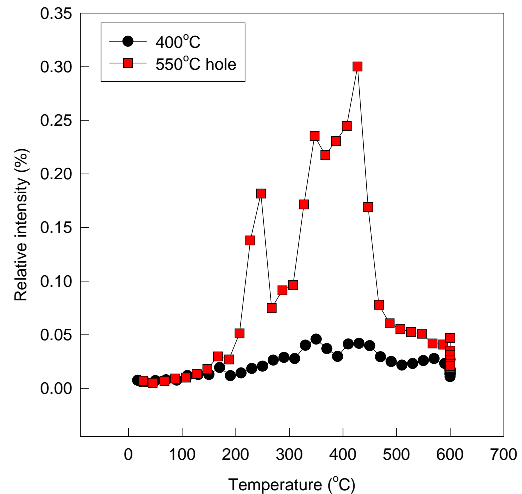

Fig. 9: The CO_2 content of PPSZ film measures by TDS.

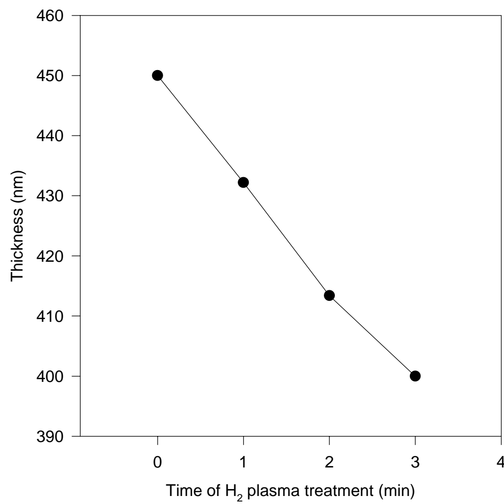

Fig. 10: The variation thickness of PPSZ with different H_2 plasma post treatment time.

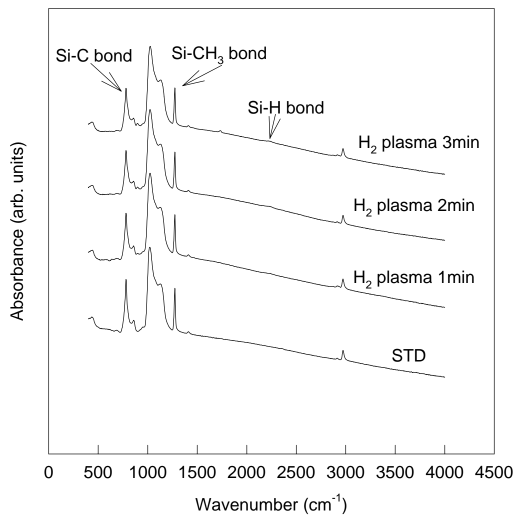

Fig. 11: The FTIR spectra of PPSZ with different H_2 plasma post treatment time.

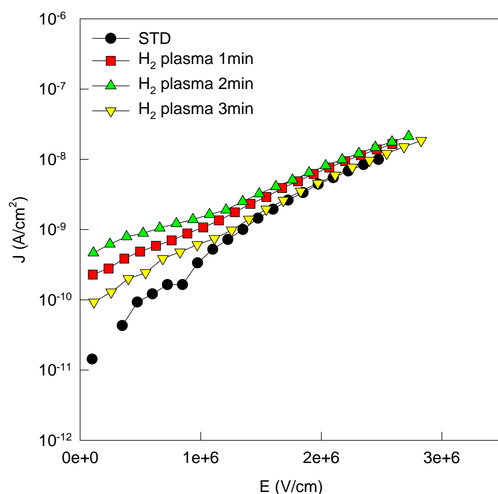

Fig. 12: The leakage current of PPSZ with different H_2 plasma post treatment time.

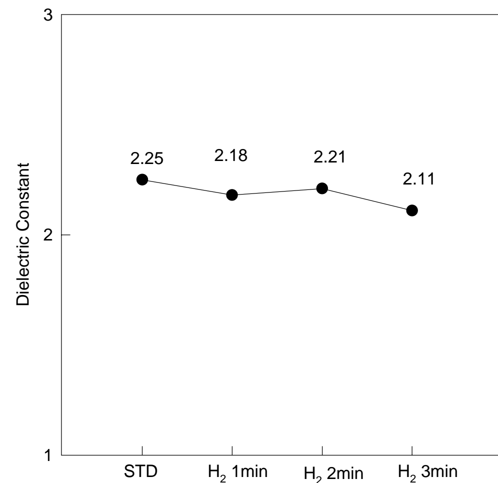

Fig. 13: The dielectric constant of PPSZ with different H_2 plasma post treatment time.

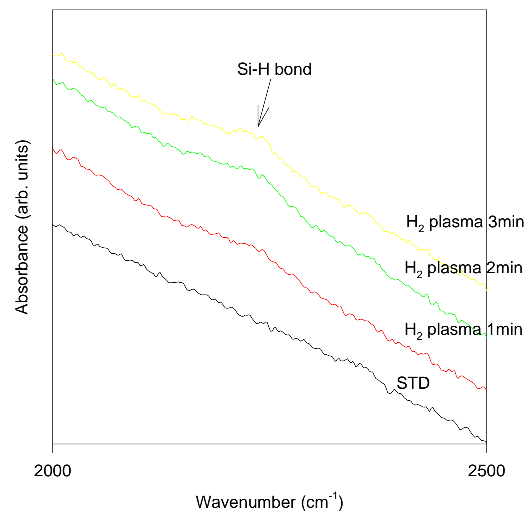

Fig. 14: The FTIR spectra of PPSZ with different H_2 plasma post treatment time.

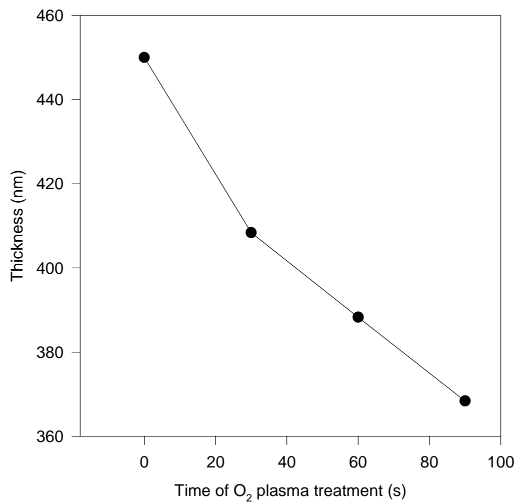

Fig. 15: The variation of thickness of PPSZ with different O_2 plasma post treatment time.

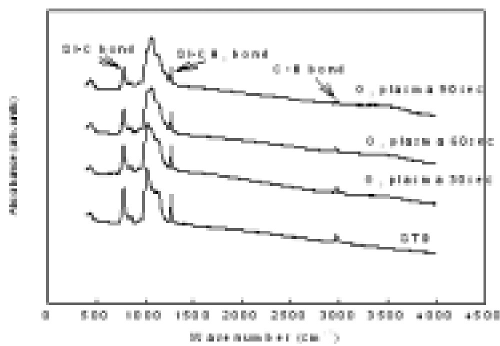

Fig. 16: The FTIR spectra of PPSZ with different O_2 plasma post treatment time.

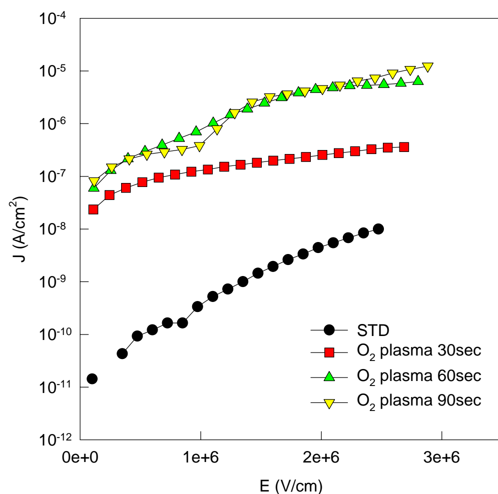

Fig. 17: The leakage current of PPSZ with different O_2 plasma post treatment time.

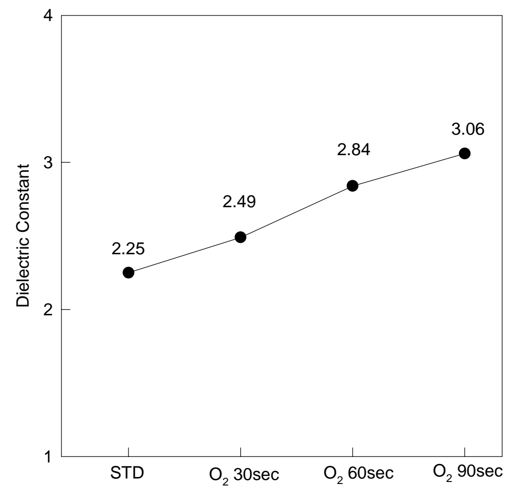

Fig. 18: The dielectric constant of PPSZ with different O_2 plasma post treatment time.

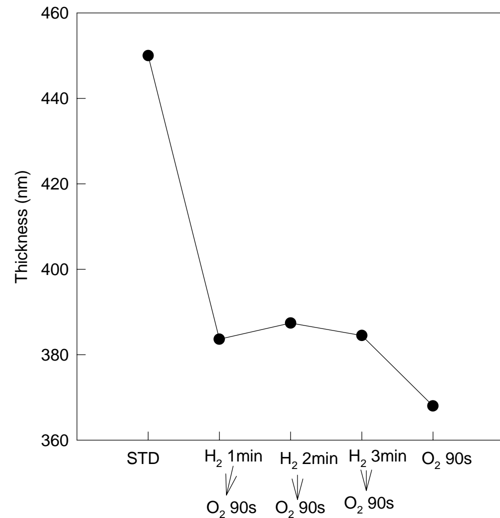

Fig. 19: The variation thickness of PPSZ with different H_2 plasma post treatment time, then O_2 plasma 90 second.

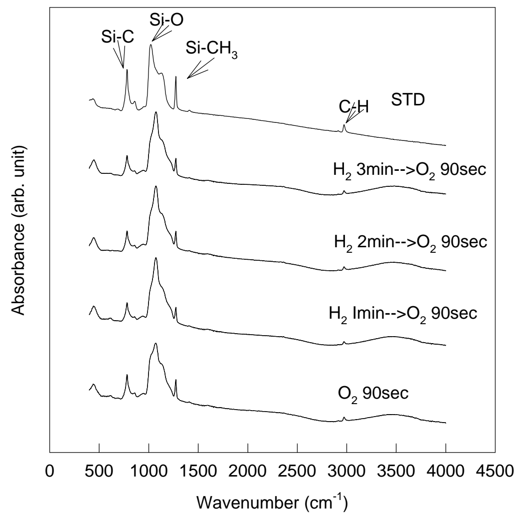

Fig. 20: The FTIR spectra of PPSZ with different H_2 plasma post treatment time, then O_2 plasma 90 second.

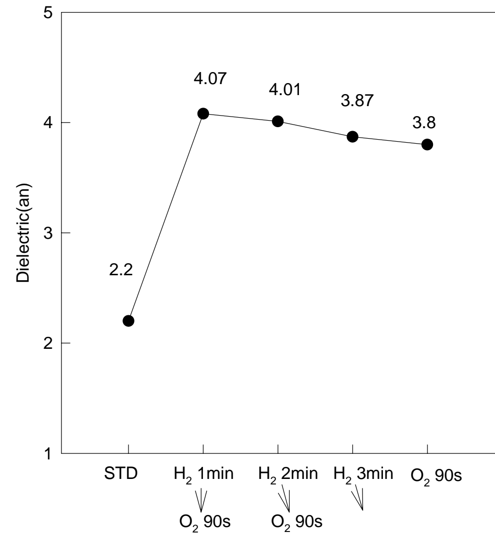

Fig. 22: The dielectric constant of PPSZ with different H_2 plasma post treatment time, then O_2 plasma 90 second.

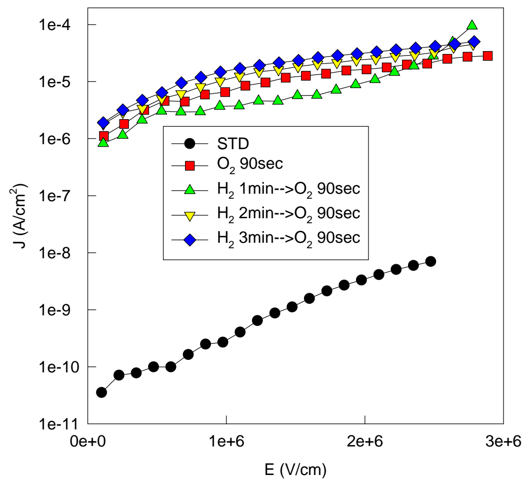

Fig 21: The electric current of PPSZ with different H_2 plasma post treatment time, then O_2 plasma 90 second.

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