

Production of Selective Membranes Using Plasma Deposited Nanochanneled thin Films

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The hydrolyzation of thin films obtained by tetraethoxysilane plasma polymerization results in the formation of a nanochanneled silicone like structure that could be useful for the production of selective membranes. Therefore, the aim of this work is to test the permeation properties of hydrolyzed thin films. The films were tested for: 1) permeation of polar organic compounds and/or water in gaseous phase and 2) permeation of salt in liquid phase. The efficiency of permeation was tested using a quartz crystal microbalance (QCM) technique in gas phase and conductimetric analysis (CA) in liquid phase. The substrates used were: silicon for characterization of the deposited films, piezoelectric quartz crystals for tests of selective membranes and cellophane paper for tests of permeation. QCM analysis showed that the nanochannels allow the adsorption and/or permeation of polar organic compounds, such as acetone and 2-propanol, and water. CA showed that the films allow salt permeation after an inhibition time needed for hydrolysis of the organic radicals within the film. Due to their characteristics, the films can be used for grains protection against microorganism proliferation during storage without preventing germination.

Keywords: *plasma, polymerization, TEOS, nanochannels*

1. Introduction

Plasma processing is a widely spread technique due to several advantages, such as obtaining new reactions probably at much lower temperatures or even room temperature if the reagents are under plasma conditions. Among the reactants useful for plasma deposition, organic silicon compounds play an important role once they are environmentally correct substances that can be easily manipulated. TEOS (tetraethoxysilane) is a common reactant for production of silicon oxide thin films due to the good adhesion in several substrates^{1,2} and the required low deposition temperature^{3,4,5}. However, the removal of organic radicals of TEOS molecule is not easy even in plasma conditions^{6,7} and the electrical properties usually are not adequate for MOS devices production⁸. Nonetheless, at room temperature TEOS plasma polymerization is simple and it is possible to obtain nanochanneled silicone like structures through the hydrolyzation of these thin films⁹. Plasma polymerized TEOS films are hydrophobic, but in contact with water they form nanochannels with 20 nm depth, which increase the superficial area of the film, making it possible not only the use for sensors development¹⁰ but also the retention of metals, in liquid phase, and volatile organic compounds (VOC's), in gaseous phase. Moreover, the use for grains protection allows not only¹¹ conservation during storage but also enhancement of water affinity to accelerate germination.

Therefore, due to their morphological and physical-chemical characteristics these films can be used as selective membranes. In particular, they may be used for protection of natural polymers. Thus, the aim of this work was testing the permeation properties of hydrolyzed thin films for: 1) polar organic compounds and/or water in gaseous phase and 2) permeation of salt in liquid phase.

2. Experimental Procedures

Plasma polymerized thin films were deposited using TEOS (Merck Ltd., USA, industrial grade) and a homemade plasma reactor. TEOS was admitted in the reaction chamber by differential pressure and the deposition conditions were 0.2 Torr, 200 W, 5 minutes. The reactor as well as operation conditions have been described elsewhere¹². The films were deposited: 1) on silicon wafers 3", <100>, 10-20 Ωcm for characterization of the films, 2) on piezoelectric quartz crystals with frequency of 4.096 MHz (Hosonic Ltd., Brazil) to test the permeation characteristics of the films, 3) on cellophane paper (Baitaca Industrial do Brasil Ltd., Brazil) to test the permeation of ionic species.

The films deposited on silicon wafers were characterized by profilometry (Dektak 3030 profilometer, Veeco Instruments Inc., USA), infrared spectroscopy analysis (FTIR, FTS-40 - Bio-Rad Laboratories, Hercules, CA, USA), measuring the contact angles formed by 4 μL drops of water (to test the hydrophobic character of the films) and of NaOH (to test the affinity of the films for basic solutions) using a Rame-Hart goniometer. The film surface was analyzed by atomic force microscopy (AFM, Nanoscope E, Digital Inc., CA, USA). The ionic adsorption tests were made using CuSO₄ aqueous solution and the adsorption efficiency was accessed by FTIR.

Evaluation of ionic species permeation using as substrate cellophane paper modified or not by deposition of TEOS thin film was performed. The tests used an experimental setup formed by two compartments separated by the substrate to be tested. Both compartments have an electrode in order to measure and/or compare the solution conductivity as a function of time. On the performed tests one of the compartments receives water and the other a 0.025 M NaCl aqueous solution.

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The films were also deposited on beans (Cerealista Cristo Rei Ltd., Brazil). In order to test the resistance of the films deposited, the treated beans were: 1) immersed up to 40 minutes in water, 2) kept in a desiccator in saturated vapor water environment. The surface of the beans after these treatments was observed using optical microscopy.

3. Results and Discussion

The results are presented in three parts: 1) main physical-chemistry properties of TEOS plasma polymerization, 2) characterization of the selective membranes and 3) use of the films for grains surface protection.

3.1. Main physical-chemistry properties of TEOS plasma polymerization

TEOS plasma polymerization showed films with deposition rates from 60 Å/min to 400 Å/min if pressure and power are varied from 80 mTorr to 400 mTorr and 200 W to 400 W, respectively. However, an increase of pressure results in an increase of deposition rate but leads to particle formation, which is undesirable. An increase of power leads to high consumption of reagents and deposition desuniformity. The films obtained in the optimal conditions (200 W, 200 mTorr) presented SiOSi, SiOH and CH_n bands and were hydrophobic. Table 1 shows typical results of FTIR analysis of films that were immersed in water for different duration of time. It can be noticed a trend that as the time of immersion increases, the relative intensity of SiOH increases indicating the hydrolysis of the organic radicals within the film. However, the hydrolysis reaction is not 100% efficient, once the decrease of CH_n relative intensity is not high and depends on film thickness. On these films, the contact angles for a drop of water ranged from 70° to 80° and the variation is highly dependent of the chamber cleanness conditions.

When oxygen was also admitted to the plasma reactor on the best conditions formerly determined (200 W, 200 mTorr) the deposition rates increase. Addition in O₂:TEOS ratio of 10, 50 and 90% leads to deposition rates of 80 Å/min, 596 Å/min and 880 Å/min, respectively. The infrared spectrum shows the same species found for the TEOS polymerization. However, the OH/SiOSi relative intensity increases to 90% O₂ mixture (0.845) probably due to trapped water, once deposition occurs at room temperature. Moreover, CH_n/SiOSi relative intensity also changes to 0.142 and 0.176, to 50 and 90% O₂ mixture, respectively. The results were expected because oxygen can oxidize TEOS molecule and produce water on these plasma conditions⁷, nonetheless the organic radicals are still detected in all conditions.

The contact angles formed by drops of water on the surface of all films are only slight different and correspond for TEOS and TEOS + O₂ films approximately to 70° and 60°, respectively. The lower contact for TEOS + O₂ films is probably due to the higher SiOH relative intensity. On the other hand, for all films contact angle for saturated NaOH aqueous solution showed variation from 60° to zero

Table 1. Relative intensity of the main species obtained by infrared spectroscopy for a sample immersed in water at the room temperature. Deposition conditions: 0.2 Torr, 200 W, 5 minutes.

OH (3400 cm ⁻¹)	Species			Immersion time (minutes)
	CH _n	SiOSi	SiOH	
0.3704	0.1063	1	0.0201	0
0.3411	0.1004	1	0.0309	5
0.2938	0.1041	1	0.0311	10
0.3039	0.0960	1	0.0308	15
0.2890	0.0972	1	0.0277	30
0.3603	0.1031	1	0.0346	2 days

in less than three minutes. Figure 1 shows the aspect of the film after contact with NaOH aqueous solution, as can be seen in the figure the film was partial or total removed.

The characterization of the deposited films by FTIR and contact angle measurements indicate that the production of a hydrophobic film is possible even in presence of the oxygen molecule. The results also indicate that it is possible to tailor slightly the hydrophobic/hydrophilic character of the film controlling the O₂:TEOS ratio. However, these films are non resistant to basic solutions and can be easily hydrolyzed, as shown in Equation 1. This hydrolysis is well known in wet polymerized thin films¹³. Only water might provide the hydrolysis reaction, which occurs during the immersion, but this reaction will not allow complete removal of organic radicals of the film.



A low amount of oxygen during plasma deposition does not favor silicon oxide formation. As show in Equation 2 a huge amount of oxygen, that would correspond to more than 90% of O₂, is required for total TEOS oxidation. Moreover, once TEOS adsorption on silicon wafer is favored for SiO interactions between surface and molecule, the small amount of oxygen used was not enough for appreciable SiOSi formation. On the other hand, the presence of oxygen in the gaseous phase favored oxidation of organic radicals and formation

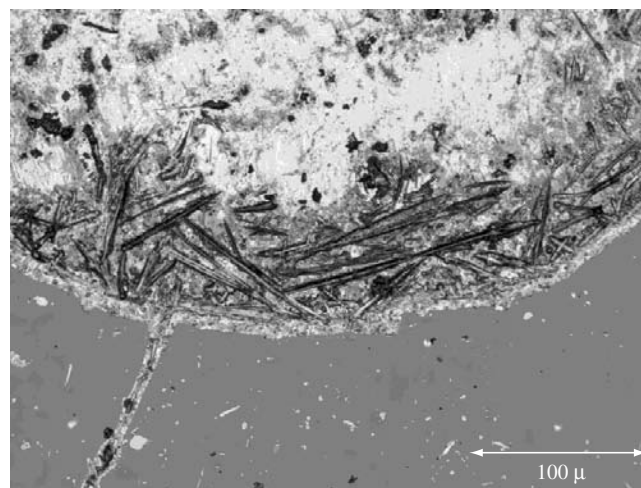


Figure 1. Optical microscopy of the film after contact with NaOH aqueous solution.

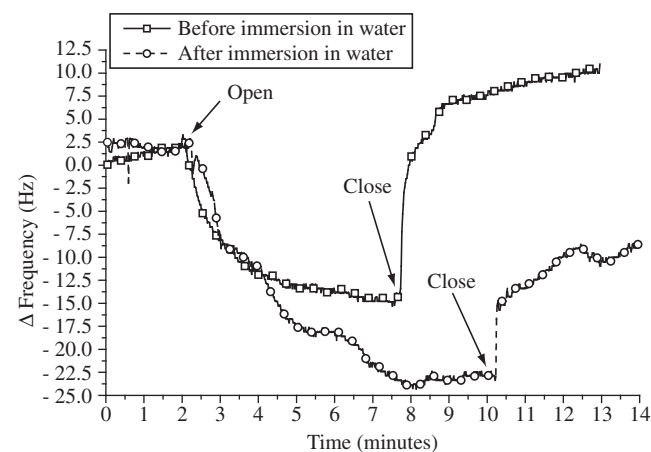


Figure 2. QCM analysis before and after immersion in water for one hour. Arrows indicate water admission (approximately 2 minutes) and removal (approximately 8 and 10 minutes).

of SiOH species. The SiOH on the surface allowed obtaining lower contact angle formed by drops of water. Thus, it is possible to change the hydrophilic character of the film surface during deposition only by changing the O_2 :TEOS ratio.

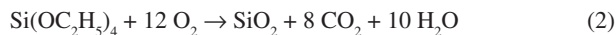


Figure 2 shows the frequency variation obtained using QCM measurements and water carried by nitrogen. TEOS thin film was deposited directly on the piezoelectric quartz crystal and was analyzed in two conditions: before and after immersion in water for one hour. On this analysis the variation of frequency is related to adsorption or/permeation. A surface phenomenon, such as adsorption, normally leads to a small and quick variation whereas permeation, which needs diffusion of the reactant within the film, presents a slow and constant variation during a long time. When comparing the behavior of the film before and after immersion some differences can be observed. For samples not previously immersed in water, it is possible to notice a small and quick variation for water admission probably due to adsorption in the surface once the signal quickly returned when water is closed. However, for TEOS film previously immersed on water, although water admission varies the frequency in a similar manner that obtained in as deposited films the signal shows a slightly slower variation, probably due to permeation. Moreover, after water is removed the signal does not return to the same baseline. This difference of behavior is due to the hydrolysis of the film that leads to the formation of SiOH bands on the surface and probably within the film. Therefore, after the immersion strong hydrogen bond interactions may occur and some water remains on the film, preventing the baseline to return to the initial value.

Figure 3 shows the microstructure of the films before and after immersion in water. It can be seen that the film presents channel of a dimension of 449 Å deep and 236 Å wide before and 508 Å deep and 213 Å wide after immersion indicating that the nanochannels of the films increase in size when hydrolyzed.

The adsorption of ionic species was also tested. The film was characterized by infrared analysis before and after immersion in saturated aqueous solution of CuSO_4 during one hour. A band could

be noticed in 640 cm^{-1} after the immersion however this band could be easily removed for dip in water. Therefore diffusion of the saturated solution into the small channels does not allow the ionic species migrate through the film. Figure 4 shows the typical results.

3.2. Characterization of the selective membranes

Figure 5 shows the frequency variation for QCM measurements when admitted water, 2-propanol and acetone. A different behavior can be seen for acetone. A sharper decrease in frequency variation quickly followed by saturation is observed for acetone indicating that only adsorption is occurring whereas permeation is likely to occur for water and 2-propanol due to the slower decrease in frequency.

Figure 6 shows the conductivity as a function of time measured on the compartment that received water and using cellophane paper as substrate. For substrates recovered by TEOS thin films, although it can be noticed a time delay on the measurements, probably due to hydrolysis of the thin film, the substrate do not avoid the increase

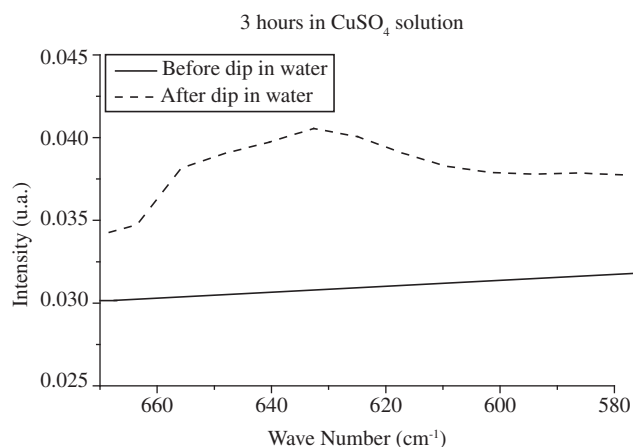


Figure 4. FTIR band in 640 cm^{-1} obtained after the immersion of TEOS film in water.

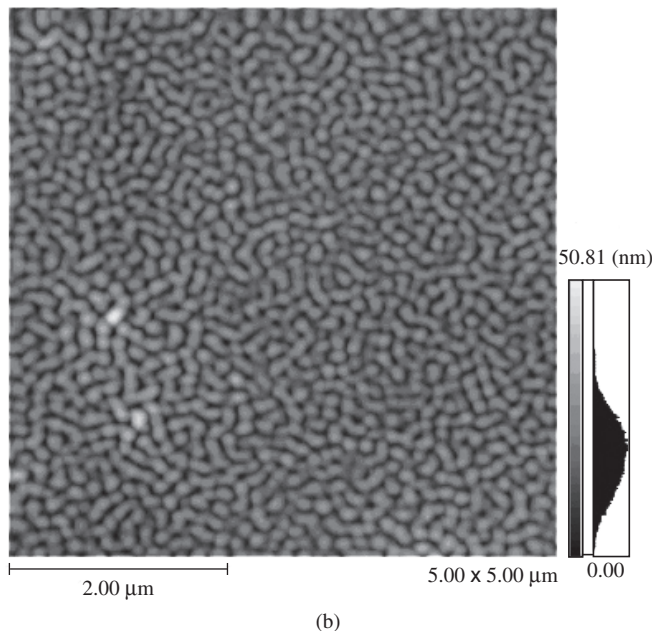
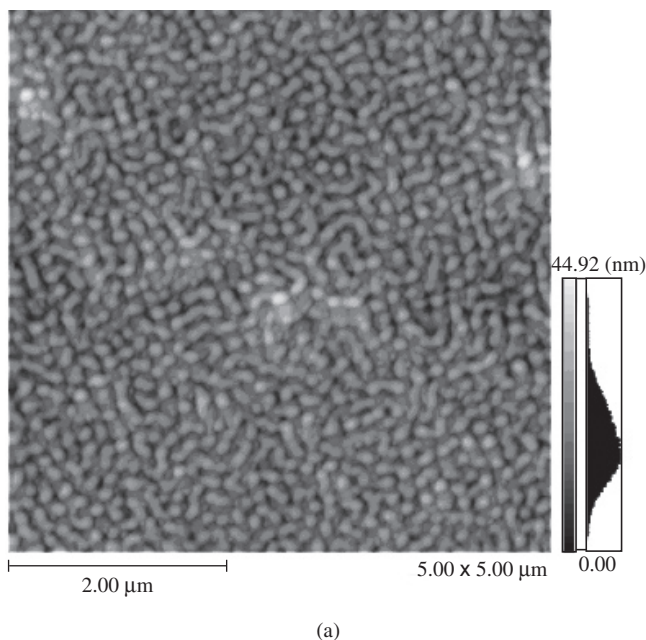


Figure 3. AFM before a) and after b) immersion in water.

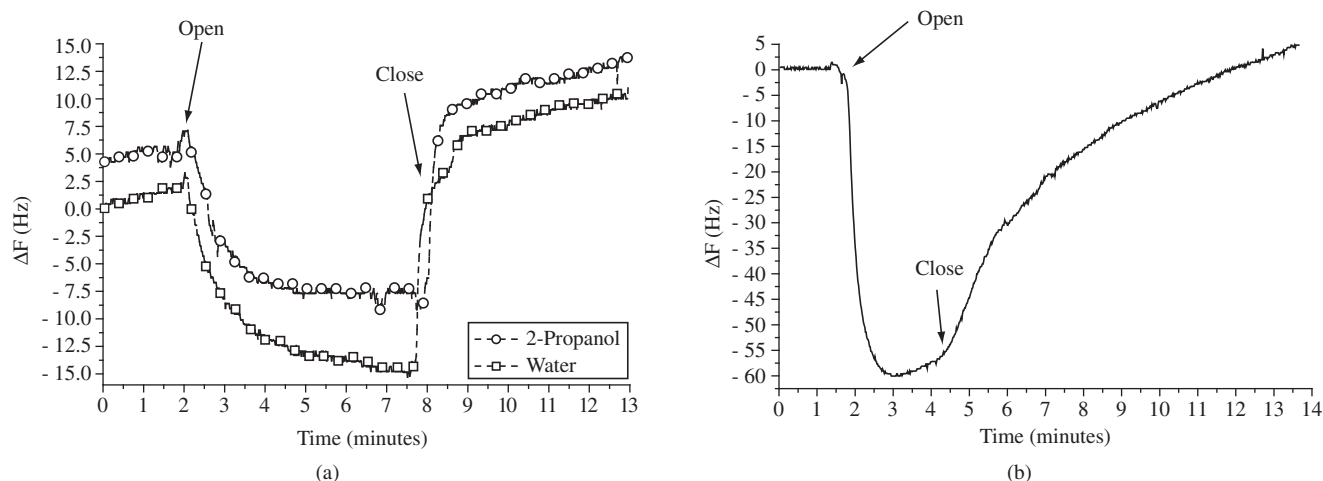


Figure 5. Frequency variation for QCM measurements of water, 2-propanol a) and acetone b) carried by nitrogen as a function of time. Arrows indicate admission or removal of the reactants.

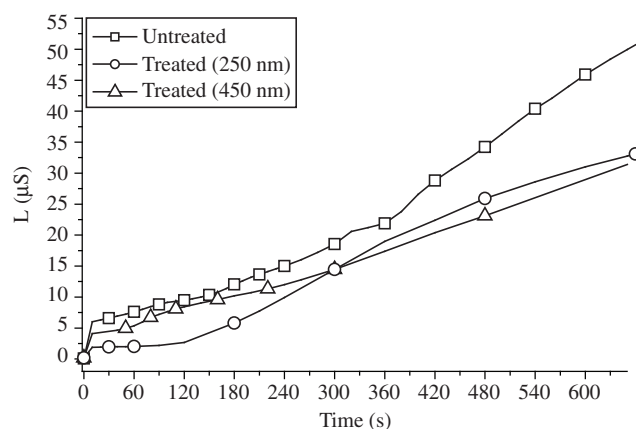


Figure 6. Conductimetric measurements as a function of time for treated and untreated cellophane substrates. The measurements used 0.025 M NaCl aqueous solution.

in conductivity and present a similar behavior when compared with cellophane untreated surfaces. Therefore, some ion migration should occur in the substrate. The two different thicknesses used (250 nm and 450 nm) do not influence the delay time most likely due to the high amount of water available on the system.

Cellophane is a lignocellulosic material similar to the surface found in grains. Increases on conductivity values as a function of time imply that ions are reaching the compartment, which means that the substrate is not protect for these species. In such conditions, probably these films can be used for surface protection during storage without avoiding other phenomena, such as germination, that need permeation of ionic species.

3.3. Surface protection

Due to the interesting characteristics the films showed they were deposited on grains and tested as protective membranes on grains in particular on beans. During plasma deposition, due to the low pressure, the beans showed a high degasification rate generating nitrogen, oxygen and water at their surface and practically preventing the adhesion of the film during plasma deposition. Therefore it is almost impossible with the vacuum system available in commercial equip-

ment to reach a pressure for a satisfactory plasma deposition once the beans had been admitted to the chamber. In order to eliminate this drawback a different way of deposition was attempted considering that TEOS molecule can easily adhere on cellulose and that TEOS plasma can be carried out even near atmospheric pressure. A huge amount of TEOS (approximately 1 Torr) was admitted in the chamber without any flow, i.e. in a closed chamber, and plasma was obtained. This method of deposition will be called closed chamber mode in the rest of the paper. In doing so TEOS molecules adsorb on the surface of the grain although the degasification still persists and liberates mainly oxygen and/or water. Immediately after the plasma ignition TEOS and oxygen, or even water, can quickly react producing oligomers on or near the surface that can easily adhere to the surface. Once this pretreatment of the beans, called subsequently passivation, is conducted it is possible to perform a normal plasma deposition using processing parameters similar to the ones used for obtaining TEOS films, as previously described. The films obtained after this passivation were characterized by profilometry, FTIR and evaluating the contact angle formed by a drop of water, using a silicon wafer that was inserted in the plasma reactor together with the beans. The overall deposition rate was 400 Å/min, however the process uses two different steps and the first one shows a much lower deposition rate once just a thin film (approximately 100 Å) was observed by optical microscopy after 5 minutes of plasma deposition. Infrared spectrum showed SiOSi and CH_n but also SiOH due to the oxygen presence in chamber that cannot be avoid even with this deposition method. The relative intensities observed were 0.175 and 0.0811 for $CH_n/SiOSi$ and SiOH/SiOSi, respectively. Moreover, the contact angles measurements with a drop of water showed values around 70°. Therefore, for all practical purposes the film produced is quite similar to the ones obtained without beans present on the chamber.

Figure 7 shows the silicon surfaces used as reference and inserted in the plasma reactor together with the beans when the deposition is carried out before and after the closed chamber mode has been used. It can be seen that a continuous film is only obtained when the closed chamber mode is used.

In order to determine the importance of this deposition method, other passivation procedures were tested and Table 2 summarizes the principal results. The use of heating and nitrogen plasma as well can facilitate desorption of adsorbed gases and water. However, none of the methods favored this desorption and the obtained results to TEOS

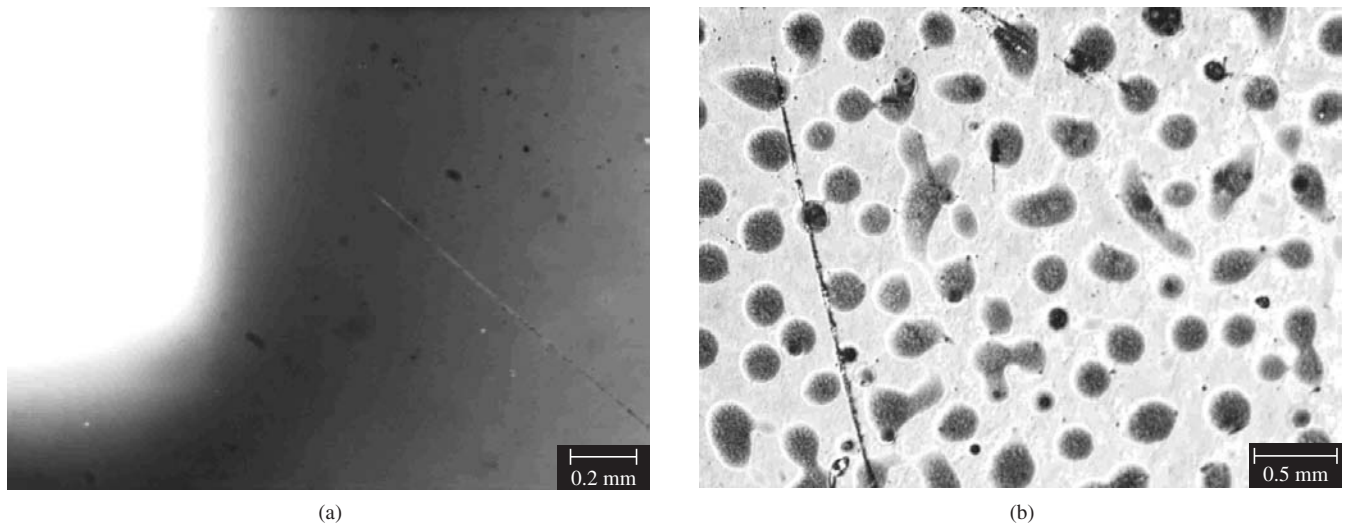


Figure 7. Optical microscopy of silicon wafer surface when closed chamber is a) or is not b) used.

Table 2. Summary of the principal results for the attempted passivation procedures.

Passivation procedures	Results
Deposition without any previous pretreatment	For only 50 beans inside the chamber, base pressure reaches 70 mTorr in half one hour of vacuum pumping but stabilizes on this value for several hours. Difficult to estimate deposition rate. Discontinuous films SiOH present on FTIR spectra
Deposition after heating the beans in an oven at 120 °C during 5 minutes	Similar results when compared to deposition without any previous pretreatment SiOH present on FTIR spectra
Nitrogen plasma during 5 minutes before TEOS deposition	Similar results when compared to deposition without any previous pretreatment SiOH present on FTIR spectra
Closed chamber followed by “normal deposition” (as described previously)	Base pressure after closed chamber deposition is lower than 10 mTorr and is achieved in a few minutes. TEOS deposition can be carried out without any difficult Continuous films SiOH present on FTIR spectra

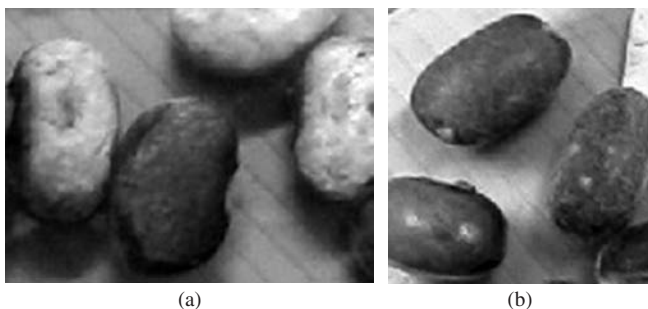


Figure 8. Grains surface of untreated a) and treated b) beans kept inside a desiccator with saturated water vapor during ten days.

deposition are similar with or without any previous pretreatment except for closed chamber deposition.

Several batches of grains were processed with or without the use of the passivation process. The process conditions (200 mTorr, 200 W) were the same for all batches but without passivation pro-

cess the TEOS film is obtained at a base pressure of 70 mTorr. The reference silicon wafers showed discontinuous films for all samples without passivation process. Where the passivation process was used, infrared spectra of the reference silicon wafers showed a high relative intensity for SiOH and OH when compared with films produced without grains inside the chambers. The observed high intensity is probably due to the high amount of oxygen available at the beginning of the passivation process.

Figure 8 presents the visual aspect of beans that were kept inside a container in a saturated water vapor environment for ten days. Figure 8a presents untreated beans whereas Figure 8b presents beans on which film of TEOS had been deposited previously to exposure to saturated vapor. It can be seen in Figure 8a the presence of white spots, which are due to microorganism attack. These white “spots” were not observed on the beans that were plasma treated indicating that the TEOS film can be used to protect the grains against microorganism attack. The immersion of the grains in water showed that the surface wrinkles after three minutes. Therefore, once the grains kept the ability of water adsorption, the germination is still possible.

These results are in good agreement with the observed behavior of the TEOS selective membrane for ionic and organic compounds using cellophane substrate.

4. Conclusions

TEOS selective membranes allow the permeation of ionic species as organic compounds as well. Therefore the use of TEOS plasma polymerization for protection of natural polymers offers a wide range of possibilities, such as protection during storage of grains without preventing later germination, when severer conditions are used.

As mentioned before, natural polymers, such as grains, present a high degasification rate. Therefore, one of the drawbacks on plasma deposition using natural polymers is the achievement of the base pressure. On the other hand, deposition with high pressure and high degasification rate favor silicon oxide and particle formation, due to the high oxygen concentration. Therefore, the passivation process developed presents several advantages not only on grain protection but also natural polymer surface modification.

Acknowledgments

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