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ARTICLE

Flexible Cross-Linked Organosilicon Thin Films by Initiated Chemical Vapor Deposition

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ABSTRACT: Highly cross-linked but flexible polyhexavinyldisiloxane (p-HVDSO) thin films were deposited by initiated chemical vapor deposition (iCVD) for applications where smooth, adhesive, and flexible coatings are required, like biological implantations or thin film electronics. The substrate temperature and the initiator flow rate dependencies were investigated as routes to enhance the cross-linking degree of the network. The most cross-linked film was obtained at substrate temperature of 60 °C and monomer/initiator ratio of ~1. Kinetic analysis of the deposition process indicates that the film formation rate is limited by the saturation reactions of the vinyl groups, with an activation energy of 53.8 kJ/mol with respect to the substrate temperature. Atomic force microscopy showed microscopically flat surfaces, while tape test and bending cycles revealed high adhesion and flexibility. The possibility of obtaining a tunable cross-linking degree through methylene bridges by changing the substrate temperature makes the p-HVDSO films suitable for a wide range of applications.

Introduction

Organosilicon polymers, deposited by dry polymerization techniques like chemical vapor deposition (CVD), are widely used in various applications ranging from bioscience to dielectric film for integrated circuits.[1] Their importance resides in the possibility of easily tuning the structure and the properties of these polymers by changing the deposition conditions or the precursors. The polymer compositions can be adjusted according to the application. Organosilicon polymers are also easily deposited due to their sufficiently volatile precursors.

This work is focused on the deposition of organosilicon thin films by initiated CVD (iCVD) (for an extensive review see ref 2). The advantage of using iCVD resides in the possibility of easily controlling the reaction pathways and the polymer chemistry according to the application. iCVD is an all-dry polymerization technique which involves the reactions between the radical-generating species and a monomer with unsaturated bonds to create monomer radicals which are adsorbed on the substrate surface where they polymerize. This process is a free-radical polymerization process with the advantages of separating the initiation temperature (generally more than 200 °C) from the polymerization temperature (generally less than 100 °C) and taking place in both the vapor and solid phases, without any solvent or wet steps. Hence, solvent- or temperature-sensitive substrates can be coated by iCVD, including polymer,[3] paper,[4] membranes,[5] and biological implants.[6]

The polymerization mechanism generally involves three steps: initiation, propagation, and termination; a schematic of the deposition mechanism is given by Lau et al.[7,8] The process is initiated when radicals are created by heating a filament array up to 200−300 °C. Temperatures in this range are high enough to break only the labile bonds such as peroxide linkage contained in initiator species and thus to create radicals. The radicals initiate the polymerization by reacting with the unsaturated bonds of the adsorbed monomer and thus creating polymer chains with radical ends which then propagate reacting with other monomer molecules. The substrate temperature is maintained below 100 °C to promote adsorption of the monomer. Finally, the termination step consists of capping the chain radical ends with the initiator radicals or by recombination of two polymeric chains.

The advantage of using iCVD over other deposition techniques (e.g., CVD or PVD) is the ability to control the possible reaction pathways and thus fully retain the functional groups of the monomer without the breaking and recombination of dangling bonds due to plasma ion bombardment or to precursor pyrolysis. The complete absence of any ion bombardment and the low polymerization temperatures allow to maintain a high carbon content in the organosilicon polymers and thus preserve the "organic character" of the selected precursor.

Previously, iCVD organosilicon films were deposited from the cyclic siloxane monomer: the trivinyltrimethylcyclotrisiloxane (V_3D_3). The V_3D_3 polymer (p-V_3D_3) thin films[9] showed good flexibility and solvent resistance in polar and nonpolar solvents. However, the deposition rate was very low (7−10 nm/min) due to the steric hindrance of the large $(Si-O)_3$ rings. To increase the deposition rate, Achyuta et al.[10] copolymerized the V_3D_3 with a linear spacer (hexavinyldisiloxane, HVDSO). The resulting iCVD copolymer had a 4-fold higher deposition rate and the same beneficial properties of V_3D_3 homopolymer: high cross-linking, good adhesion to silicon substrate, and solvent resistance. In this case, the polymerization occurred via successive additions of initiated radicals of the monomer and of the spacer. The spacer enhanced the deposition rate because of its six reactive sites (i.e., the vinyl bonds) and also because it is easily included in the growing polymer chains due to its less bulky linear structure.

In this work we demonstrate the synthesis of an organosilicon polymer starting directly from a linear monomer unit, the HVDSO, and using *tert*-butyl peroxide (TBPO) as initiator. Differently from p-V_3D_3, the p-HVDSO does not contain $(Si-O)_n$ rings; thus, densely packed polymeric chains are expected. The iCVD starting from HVDSO is expected to produce a

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Table 1. Reactor Conditions for the Deposition of p-HVDSO

sample name	reactor pressure (Torr)	substrate temperature (°C)	filament temperature (°C)	HVDSO flow rate (sccm)	TBPO flow rate (sccm)	N_2 flow rate (sccm)	P_M/P_{sat}
A1	0.15	20	280	2.6	2	1	0.3
A2	0.3	30					
A3	0.6	40					
A4	1	50					
A5	1.8	60					
B1	0.8	40	280	2.6	1	5	0.3
B2					2	4	
B3					3	3	
B4					4	2	
B5					5	1	

cross-linked network preserving the high carbon content of the monomer. The aim of this paper is also to show how and if the degree of network cross-linking can be tuned by changing two key parameters of the deposition process: the substrate temperature and the initiator flow rate. The possibility of tuning the cross-linking degree of p-HVDSO deposited by iCVD would enable its usage in various applications: high cross-linked films may function as an organic interlayer in multilayered impermeable coatings while less cross-linked films may be chemically functionalized through the reaction with the unreacted vinyl groups.

Previous kinetic studies on iCVD[7,8] demonstrated that this technique is strictly governed by the amount of monomer absorbed on the surface, quantified through the ratio between the monomer partial pressure (P_M) and the saturation pressure (P_{sat}). To compare the chemistry and the deposition rate of the polymers obtained at different substrate temperatures or initiator flow rates, a constant P_M/P_{sat} value of 0.3 was maintained for all the experiments. A P_M/P_{sat} value of 0.3 was sufficient to obtain reasonable deposition rate avoiding any condensation of the liquid phase.

Most possible applications of organosilicon films require that the coatings must show relatively high density/cross-linking, low surface roughness, structural integrity under physical stress, and good adhesion to substrate. For example, for biomedical implantations good flexibility and adhesion are vital coating properties in order to prevent delaminations which would result in corrosion or malfunction.[11] For thin film electronics, planarizing adhesive coatings are required especially for nonpolishable substrates.[12] In this study, some physical properties of p-HVDSO films were evaluated such as the flexibility (in terms of integrity after bending), the adhesion to the substrate, and the surface roughness.

Experimental Section

Deposition setup. The deposition chamber was a custom-built cylindrical vacuum reactor as previously described.[13] The chamber sizes were 24.6 cm in diameter and 3.8 cm in height. The reactor had a removable quartz top (2.5 cm thick) to allow visual inspection and laser interferometry. The reactor was pumped by a mechanical Fomblin pump (Leybold, Trivac), and the pressure was monitored with a MKS capacitive gauge.

The liquid monomer (hexavinyldisiloxane, 95% Gelest) and initiator (*tert*-butyl peroxide, TBPO, 98%, Aldrich) were used without any further purification steps. The monomer was vaporized maintaining the liquid jar at 80 °C and was then introduced into the reactor through a needle valve. The initiator was kept at room temperature and introduced through a mass flow controller (MKS Instrument). The labile peroxide bond of the initiator was thermally broken by a filament array of 14 parallel nickel chromium filaments (Goodfellow) at a distance of 1.5 cm from the substrate. The filaments were heated up to 280 °C using a dc power supply (Sorensen). The filament (T_{fil}) and the substrate temperatures (T_{sub}) were monitored by two thermocouples (Type K, Omega Engineering). The substrate temperature was adjusted (with an error of ± 2 °C) using a chiller/heater (NESLAB). The film growth was monitored real-time by reflecting a He−Ne laser (JDS Uniphase) off the substrate and the film and recording the interference laser signal intensity as a function of time. Each film was deposited up to a thickness of 200 ± 10 nm.

Two sets of experiments were performed: A1−5 changing the substrate temperature (20−60 °C) and the pressure (0.15−1.8 Torr) and B1−5 changing the initiator (1−5 sccm) and nitrogen (5−1 sccm) flow rates. For this second set of experiments a total flow rate of 8.6 sccm was maintained to keep the residence time of the active species in the reactor chamber constant. All the parameters were adjusted to keep the ratio P_M/P_{sat} fixed at 0.3. The monomer flow rate and the filament temperature were kept at 2.6 sccm and 280 °C, respectively. The deposition conditions are summarized in Table 1.

Film Characterization. Chemical characterization of the films was performed by Fourier transform infrared (FT-IR) spectroscopy through a Nexus 870 FTIR, Thermo Nicolet spectrometer equipped with a DTGS-TEC detector in transmission mode. The spectra were acquired from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} repeating 256 scans. The spectrum of a bare Si wafer was used as the background. In order to minimize the effects of water vapor and carbon dioxide absorption, the spectrometer was purged with nitrogen for 15 min between each measurement. To investigate the quantity of vinyl group retained in the polymer matrix, the C−H stretching band (3300−2700 cm^{-1}) was regressed using five Gaussian components using the "Fit multi-peaks" procedure of OriginLab software.

The film thicknesses were measured by ex-situ variable angle spectroscopy ellipsometry (VASE, JA Woollam M-2000). The measurements were done at three different angles (65°, 70°, and 75°) in the wavelength range of 200−1000 nm. The applied optical model consisted of four components: the silicon substrate, the native SiO_2 layer of 5 nm, the film bulk, and the surface roughness layer. The bulk components were modeled by the Cauchy function adding the Urbach tail to model the absorption. The top roughness layer was modeled using the Bruggeman effective medium approximation (BEMA). This layer is generally used to simulate the situation in which small particles of one material are suspended in a matrix of the host material, so it is often used to reproduce interfacial mixing or surface roughness. The BEMA layer was made of two components: 50% bulk film and 50% voids. The model also incorporated possible thickness inhomogeneity within the sampled area.

The elemental analysis was done using X-ray photoelectron spectroscopy (XPS). The XPS spectra were obtained using a SSX-100 (Surface Science Instruments) spectrometer equipped with a monochromatized Al Kα source. Survey scans were conducted at an X-ray incident angle of 0° with penetration depths of ~10 nm.

Surface film morphology was investigated by atomic force microscopy (AFM, Digital Instruments, D3100-1). Images were acquired in tapping mode using conical gold-coated silicon tips. Root-mean-square roughness was measured on 3×3 μm^2 surface areas.

Flexibility tests were carried out using a dynamic mechanical analyzer (TA Instruments, Q800 model) using a three-point bending load scheme. This load cell consists of two lateral fixed ends to clamp the sample and one moveable part in the center whose displacement (up and down) causes the bending of the sample. To test the flexibility, the samples were deposited on plastic substrates: 2,6-poly(ethylene naphthalate) (PEN, Teonex Q65FA 125 μm manufactured by DuPont Teijin). The samples (size $70 \times 5 \times 0.6$ mm^3) were subjected to 30 dynamic loading

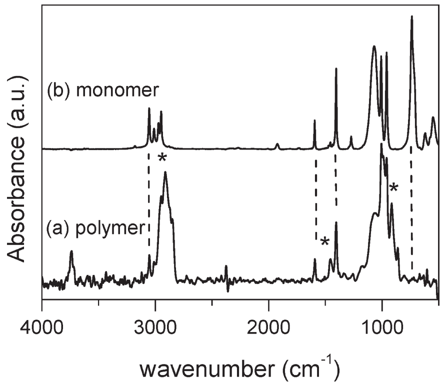


Figure 1. FT-IR spectra of HVDSO monomer (b) and the resulting polymer (a). The dashed lines represent the location of the main absorptions of the vinyl groups, and the asterisks represent the methylene bridges absorptions in both monomer and polymer spectra.

Table 2. Absorption Band Assignments for Infrared Spectra According to Refs 9 and 15

wavenumber polymer (cm^{-1})	wavenumber HVDSO (cm^{-1})	group	vibration mode
3050	3050	CH_2 in vinyl	asymmetric stretch
3010	3010	CH_2 in vinyl	symmetric stretch
2960	2972	CH in vinyl	asymmetric stretch
	2950	CH in vinyl	symmetric stretch
2915		CH_2 in Csp3	asymmetric stretch
2856		CH_2 in Csp3	symmetric stretch
	1922	CH_2 in vinyl	symmetric wag
1594	1594	C=C	stretch
1456		CH_2	asymmetric stretch
1400	1404	CH_2 in $Si-(CH_2)_x-Si$ and in vinyl	bending
1250	1270	$SiOC_3$	symmetric stretch
1063	1066	Si−O−Si	asymmetric stretching
1000	1008	C=C	twisting
990		$Si-(CH_2)_x-Si$	wagging
960	960	CH_2 in vinyl	wagging
850		C−H	bending
680	620	$Si-CH=CH_2$	wagging

cycles applying a dynamic force of 0.05 N with a rate of 0.1 N/min at room temperature. The displacement in the center of the sample was 8 mm, and the estimated bending angle was around 17°.

Adhesion to silicon wafer was tested by following the standard procedure reported in ASTM International tape test D3359-02.[14] For this test, adhesive tape (3 M Scotch tape #600 as recommended in ASTM procedure) was applied on the sample surface and rapidly removed. The percentage of delamination was determined by dividing the test surface into equally spaced grids and then manually counting the number of grids, which showed delamination. The surface morphology and surface damage, such as delamination, and cracking was examined by optical microscopy (Zeiss, Model AxioSkop 2 MAT). Coating adhesion was evaluated for films with the same thickness of 200 ± 10 nm, since the adhesion is greatly influenced by the variation of this parameter.

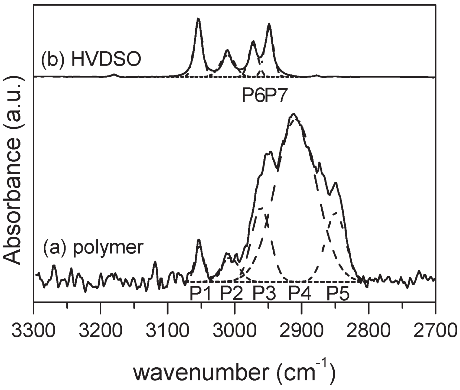


Figure 2. Enlargement of the 3300−2700 cm^{-1} region of the FTIR spectra of HVDSO monomer and sample A5. The decomposition in the major components is also represented for each band.

Results and Discussion

Chemical Characterization. Figure 1a,b shows FTIR absorption spectra for the monomer (HVDSO) and its polymer deposited in condition A5 as reported in Table 1.

The assignments of the main absorption frequencies are summarized in Table 2.

The spectrum of the monomer (Figure 1b) is dominated by the characteristic absorptions of the vinyl bonds[15] (e.g., sp2-C−H stretching band at 3050−2950 cm^{-1}, sp2-C−H bending at 1400 cm^{-1}, or wagging mode of $Si-CH=CH_2$ groups at 620 cm^{-1}). From the comparison between the spectra of the polymer and the monomer, it is observed that the bands related to vinyl groups are largely reduced after polymerization, and new bands related with methylene bridges appear in the polymer[15] (e.g., sp3-C−H stretching band at 2950−2856 cm^{-1}, sp3-C−H asymmetric stretch at 1456 cm^{-1}). These key differences clearly indicate that the polymerization process involves the saturation of a considerable percentage of the vinyl groups contained in the monomer. A careful examination of the C−H bond absorption region (2700−3300 cm^{-1}) shows that the vinyl bonds are mostly saturated during the polymerization, but not completely, probably because of steric hindrance and chain orientation. An enlargement of this region is given in Figure 2.

The least-squares regression of the polymer C−H stretching band is obtained with five Gaussian components falling at 3050 (P1), 3010 (P2), 2960 (P3), 2910 (P4), and 2850 cm^{-1} (P5), while for the monomer four components can be well distinguished at 3050 (same as P1), 3010 (same as P2), 2980 (P6), and 2950 cm^{-1} (P7). The two components P1 and P2 are due to the asymmetric and symmetric stretching mode of sp2-C−H in vinyl CH_2 groups both in the polymer and in the monomer band.[15] The components at 2980 (P6) and 2950 cm^{-1} (P7) detected in the monomer can be assigned to sp2-C−H asymmetric and symmetric stretching in vinyl CH groups, and they merge into one broad component (P3) at 2960 cm^{-1} in the polymer spectrum. This last component can be assigned also to the asymmetric stretching of methyl groups derived from the initiation and termination reactions with the *tert*-butoxy (TBO) radicals created by the thermal decomposition of the initiator as explained in the Scheme 1.

It should be noted that a small fraction of the methyl groups detected might be derived also from the β-scission of the TBO radicals, occurring at filament temperatures higher than 250 °C.[13] The last two components P4 and P5, in the polymer CH band, are due to the asymmetric and symmetric stretching of methylene groups and they have the highest intensity with respect to the other components. The presence of large amount of methylene bridges is a signature of a densely cross-linked polymer.

Table 3 shows the atomic percentage of carbon, silicon, and oxygen present in iCVD film as calculated from the XPS spectrum of the sample A5.

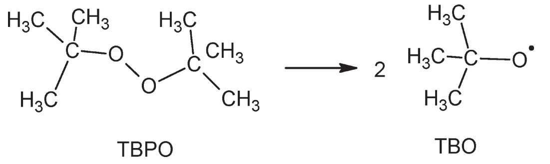
The observed carbon-to-silicon ratio of 6.6:1 in the films is higher than 6:1 present in the pure monomer; similarly, the oxygen-to-silicon ratio 0.8:1 in the polymer is higher than 0.5:1 in the monomer. These differences are due to the initiation and termination reactions which result in the inclusion of TBO terminating groups in the polymer chain. The C 1s XPS signal is decomposed in three components:[16] sp2-C at 284.4 eV, sp3-C (structurally bonded and hydrocarbon contamination) at 285 eV, and C−O at 286.8 eV. Good correlation between the predicted and experimental XPS spectra of the films is obtained by assuming each component had a 60/40 Gaussian/Lorentzian line shape having a full width at half-maximum fixed at 2 eV. The percentage of vinyl groups, obtained from the fitting, is 7 ± 1%. The ratio between the band area of sp2-C and Si signals is 0.6; as a consequence, only 1.2 vinyl bonds over six in the monomer molecule remain unreacted in the polymer matrix.

These spectroscopic evidences support the conclusion that polymerization occurs as a result of the reaction of the vinyl bonds present in the monomer to form saturated carbon chains. The polymerization mechanism is similar to the one already presented for another iCVD polymer obtained from vinyl organosilicon monomers[9] and is summarized in Schemes 1−3.

Table 3. Elemental Ratios Present in Polymer Film As Measured by XPS of Sample A5

element	atomic percentage (%)
Si 2p (%)	12
C 1s (%)	79
O 1s (%)	9

Scheme 1

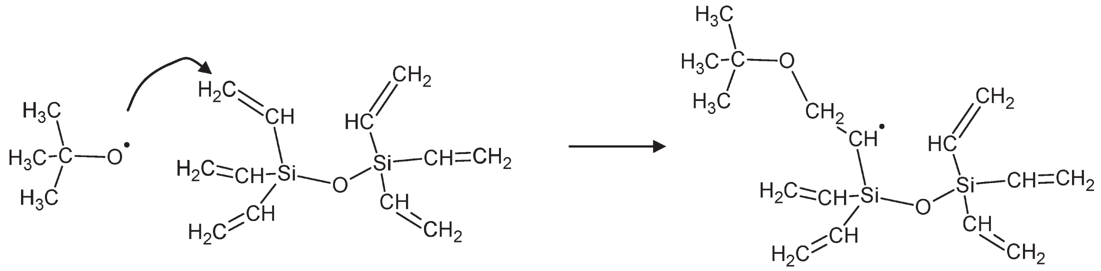


The TBO radicals react with the vinyl groups of the HVDSO, creating radical ends on the monomer (Scheme 2). Thus, the polymerization process propagates via successive addition of monomer molecules to the radical chain as shown in Scheme 3, resulting in the saturation of the vinyl bonds and the formation of methylene bridges ($2Si-CH=CH_2 \rightarrow Si-CH-(CH_2)_2-CH-Si$). The termination reactions are not shown, but they involve the capping of the radical ends of the growing polymer chain by reacting with TBO radicals or with other chain fragments.

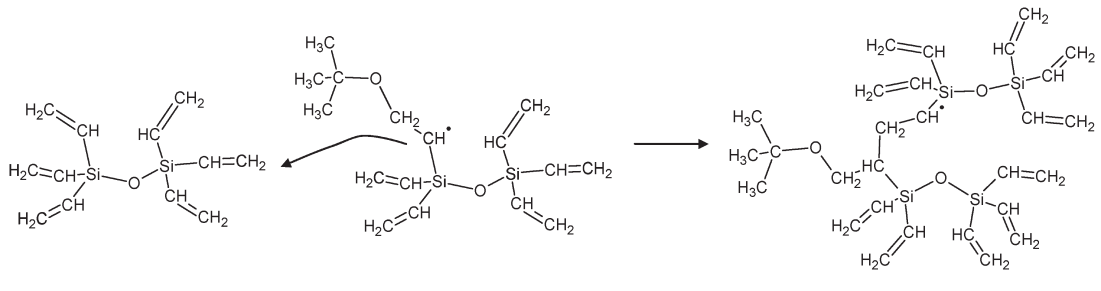
The presence of six vinyl groups allows the formation of a dense network of methylene bridges. The effect is the high cross-linking degree, which results in the insolubility of the p-HVDSO in common solvents (water, acetone, tetrahydrofuran); thus, the polymer chain length cannot be directly measured by conventional techniques, like gel permeation chromatography.

Cross-Linking Reactions. Two sets of experiments (A1−5 and B1−5 as reported in Table 1) were performed to study the effects of substrate temperature and initiator flow rate on the cross-linking degree of the p-HVDSO network. In the first set (A1−5) both the substrate temperature and the pressure were varied in order to keep the amount of monomer adsorbed on the surface constant. In fact, the iCVD processes are strongly dependent on the adsorption,[7,8] with monomer concentration at the surface being an important rate-determining factor. The amount of monomer adsorbed on the surface can be qualitatively related to the ratio between monomer partial pressure (P_M) and saturation pressure (P_{sat}); in fact, numerous absorption isotherms relate the amount of material adsorbed on the surface to P_M/P_{sat}. Moreover, at low P_M/P_{sat} the relation becomes linear in agreement with the Henry's law limit. The increase of the substrate temperature leads to low surface adsorption because of the negative activation energy of the adsorption process; on the other hand, it can enhance the rate of the surface reactions which are characterized by positive

Scheme 2



Scheme 3



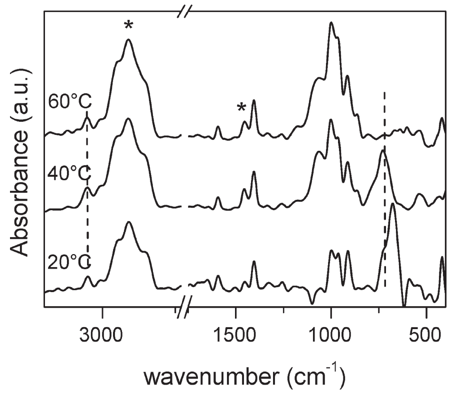


Figure 3. FT-IR spectra of iCVD films deposited varying substrate temperatures (20−60 °C) and the pressure to leave the P_M/P_{sat} constant. Sample A1−A3−A5 as reported in Table 1. The principal differences between the two spectra are highlighted by dashed lines for the vinyl groups and asterisks for the methylene.

activation energies. To isolate this last kinetic aspect from the adsorption limitation, the pressure was increased (increasing P_M) with the substrate temperature (increasing P_{sat}), and thus a constant P_M/P_{sat} value of 0.3 was maintained for all experiments. In the second experimental set (B1−5) as the initiator flow rate was increased, the nitrogen flow rate was decreased to keep the total flow rate constant at 8.6 sccm, and thus the residence time of the active species in the reactor and the monomer partial pressure (P_M) were kept constant.

Figure 3 shows the spectra of the films deposited at the substrate temperatures of 20, 40, and 60 °C (conditions A1−A3−A5 as reported in Table 1).

The main difference between these spectra is the reduction of the unreacted vinyl bonds in the polymer matrix and the increase of the methylene groups with substrate temperature. In fact, the Si−CH=CH$_2$ wagging, at 680 cm^{-1}, gives a strong absorption for the polymer A1 deposited at 20 °C and completely disappears for the sample A5, deposited at 60 °C. The signal at 1456 cm^{-1} due to methylene asymmetric stretching increases with temperature. Also, the shape of the CH$_x$ absorption band between 2700 and 3200 cm^{-1} changes. The component at 2915 cm^{-1} due to the sp3-CH$_2$ increases in intensity with the temperature, while the shoulder over 3000 cm^{-1} due to vinyl bonds decreases. Furthermore, the broad band between 800 and 1100 cm^{-1} changes with the substrate temperature. The contributions to this band are from Si−O−Si bonds (stretching at 1070 cm^{-1}, bending at 914 cm^{-1}), sp2-C−Si (twisting at 1006 cm^{-1}, wagging at 962 cm^{-1}), and sp3-C−Si (rocking at 988 and 859 cm^{-1} in Si(CH$_x$)$_3$ groups). Because of the saturation reactions, the sp2-C contributions should decrease and the sp3-C contributions should increase. However, the dependency of each separate component on temperature cannot be easily determined due to the large number of contributions in this band.

Figure 4 reports the semilog plot of the deposition rate as a function of inverse substrate temperature according to the Arrhenius law. Using the least-squares linear regression to the data, an apparent activation energy of 53.8 ± 8 kJ/mol for the deposition is calculated from the slope of the regressed line. On the right *y*-axis of Figure 4, the negative logarithm of the amount of the unreacted vinyl bonds is plotted. The percentages shown are calculated by the ratio between the band areas of the Si−CH=CH$_2$ wagging absorption in the polymers and in the monomer. The amount of unreacted vinyl groups incorporated in the polymer matrix decreases as substrate temperature increases, and an apparent activation energy of 56.8 ± 8 kJ/mol is calculated from the negative logarithm of the amount of the unreacted vinyl bonds. Comparable apparent activation energies suggest that the main reaction pathway for the formation of the p-HVDSO is through the saturation of the vinyl bonds of the monomer molecules which becomes the rate-limiting step for the conditions studied here keeping the amount of adsorbed monomer on the surface constant. Previous kinetics analyses on iCVD processes starting from acrylate and methacrylate monomers, where the amount of adsorbed monomer on the surface is allowed to vary, report negative apparent activation energies. In these studies, increasing the stage temperature both increases the propagation rate on the surface and decreases the equilibrium concentration of absorbed species on the substrate. The negative apparent activation energy indicates that the decrease in the surface concentration of reactive species dominates over the increase in the reaction rate constant, indicating adsorption control. Here, the vinyl bonds of the HVDSO are less reactive than those in acrylate and methacrylate systems. Hence, the rate-limiting step here is the slow kinetics of vinyl bond reaction rather than adsorption of the monomer on the surface. In the case of an adsorption controlled system, an activation energy similar in magnitude to the one obtained for the p-HVDSO was found by Achyuta et al.[10] for the copolymerization of V$_3$D$_3$ and HVDSO (−41 kJ/mol).

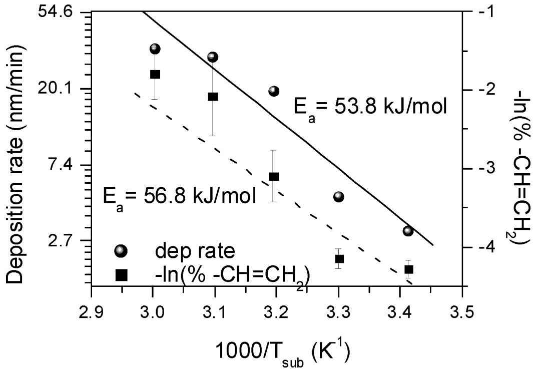


Figure 4. Semilog plot of the deposition rate data (left *y*-axis) and the negative natural logarithm of the percentage of unreacted vinyl groups in polymer matrix (right *y*-axis) as a function of the reciprocal of the substrate temperature (sample A1−5).

To investigate the effect of the initiator flow rate on the polymerization reactions, five films were deposited at the conditions B1−5, as reported in Table 1. Figure 5 shows the spectra of samples B1−B3−B5. As the initiator flow rate is increased, the intensity of the C−O peak at 1100 cm^{-1} increases while the intensity of Si−CH=CH$_2$ wagging absorption (680 cm^{-1}) decreases. The asymmetric stretching of the saturated CH$_2$ (1456 cm^{-1}), on the other hand, does not change with the initiator flow rate. This suggests that increasing the amount of initiator in the process provokes the saturation of vinyl groups in the matrix through the reaction with TBO radicals more than through cross-linking reactions between the monomer molecules adsorbed on the surface. For this set of experiments, the deposition rate and the percentage of vinyl bonds retained in the polymers are reported in Figure 6 as a function of the initiator flow rate.

Generally, the deposition rate is proportional to the concentration of TBO radicals in the gas phase. As demonstrated by Ozaydin-Ince et al.,[13] the radical concentration is a function of the filament temperature and for a given T_{fil} the radical concentration and hence the deposition rate should

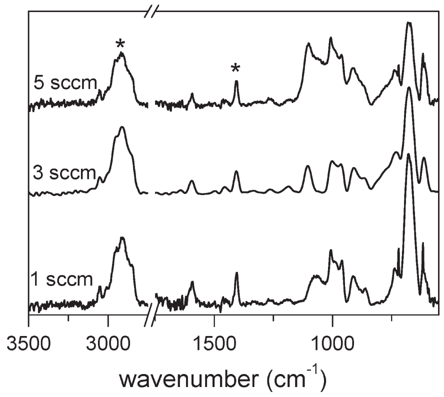


Figure 5. FT-IR spectra of iCVD films deposited varying initiator (1−5 sccm) and complementarily N_2 flow rate (5−1 sccm) to leave constant the total flow. Sample B1−B3−B5 as reported in Table 1. The principal differences between the two spectra are marked with dashed lines (sp2-C) and asterisks (sp3-C).

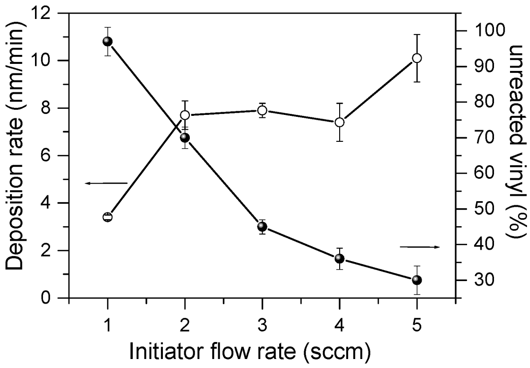


Figure 6. Deposition rate data and percentage of sp2-C retained in polymer matrix as a function of initiator flow rate (sample B1−5).

increase with the initiator flow rate at the kinetic limited regime and for low initiator flow rates, as long as the residence time of the active species in the reactor is constant. At high initiator flow rates a transition to a zero-order dependence of the deposition rate with respect to radical concentration is generally observed. This behavior seems to be strongly confirmed for p-HVDSO; in fact, between 1 and 2 sccm the deposition rate depends strongly on the initiator flow rate, while for initiator flow rates higher than 3 sccm, the dependence is weaker. This transition can be due to various kinetic reasons which are beyond the scope of this article. One simple explanation can be that when the amount of TBO radicals is considerably high (flow rate >3 sccm), the rate-limiting factor is the amount of monomer adsorbed on the surface; thus, the high quantity of radicals cannot initiate new chains but just terminate the existing ones. In addition, another factor which at high initiator flow rate could contribute to the slowdown of the deposition rate is the possible initiator radical recombination. Moreover, the large quantity of activated TBO radicals at high initiator flow rates can explain the increase in the C−O signal in the IR spectra (Figure 5): the C−O bond is not contained in the monomer structure; thus, it can only be due to the reactions with the TBO radicals. The sp2-C percentage (in Figure 6) decreases sharply as the initiator flow rate increases. This means that increasing the initiator flow rate causes the formation of more activated radicals in the vapor phase, which then react with the double bonds of monomer molecules and the growing chains, creating a quantity of activated chains in the polymer. Above 3 sccm the further increase of the TBO radicals induces the saturation of fewer double bonds, confirming that fewer chains are initiated due to the deficiency of the monomer molecules. Hence, it can be concluded that increasing the initiator flow rate leads to more capping with terminal TBO groups but does not enhance the network cross-linking as the number of methylene bridges is almost constant.

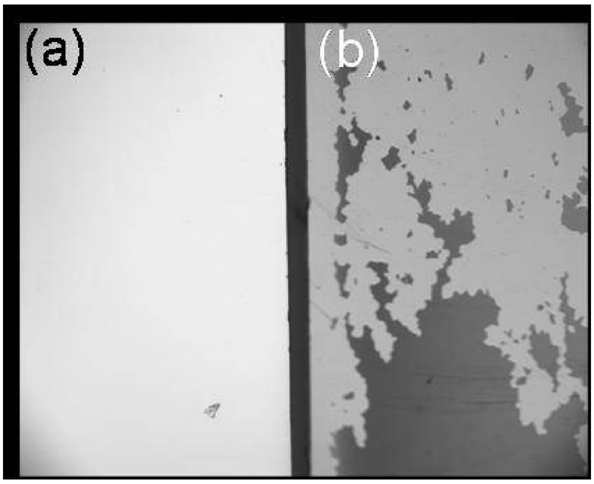


Figure 7. Optical micrograph of sample A5 (a) and B1 (b) after tape test.

Physical Properties. Tape tests were performed on all the samples of Table 1 to study the adhesion of p-HVDSO coating to silicon substrate. All samples passed the test without showing any delamination or cracking except for the sample B1. Figure 7 shows the micrographs of the samples deposited in conditions A5 (a) and B1 (b) after the test.

As can be seen in Figure 7a, there are no defects or delamination on the surface of A5 sample. On the contrary, the tape test of B1 (Figure 7b) resulted in the lifting off of the 60% of the film. The severe delamination of B1 might be related to the low cross-linking degree of this polymer; in fact, it contains the largest amount of unreacted vinyl group (sp2-C around 97%), resulting probably in weak physisorption. The adhesion of iCVD polymers can be improved by covalently bonding the coatings to the substrates, using a linker, such as silane or thiol compounds or using grafting methods. The results of the adhesion tests on p-HVDSOs presented in this work are very encouraging; in fact, no substrate pretreatment or grafting was performed before deposition to enhance the adhesion.

Bending test was performed to evaluate the flexibility of the sample A5. High cross-linking degree might lead to an overconstrained and rigid network leading to instability under physical stresses. Sample A5 showed good flexibility and even after 30 loading cycles did not show any cracks or delaminations. Studies of Philips et al.[17] and the successive works[18,19] correlated the constraint degree of the network to the cross-linking through the mean connectivity number ($\langle r \rangle$), which is the average number of possible network forming bonds per atom. Following the formalism of He et al.,[18] this number can be expressed as

$$\langle r \rangle = \frac{\sum_r r n_r}{\sum_r n_r} \tag{1}$$

with n_r being the number of atoms having r network forming bonds. Generally amorphous films have a connectivity number between 2 and 3. When the connectivity number of

Table 4. Network Forming Atoms (n_r) and Network Forming Bonds (r) per Each Functional Group Incorporated in the Polymer Matrix

functional group	n_r	r
$-OCH(CH_3)_3$	5	9
$-CH{=}CH_2$	2	3
$-CH_2-CH_2-$	2	4
$-Si-O-Si-$	3	10

the network is between 2 and 2.4 (corresponding to low cross-linking of the polymer chains to form a network), there are many ways in which the network can be deformed without changing the bonding angles or lengths, and the polymer is underconstrained and flexible. He et al.[18] found that a connectivity number of 2.4 corresponds to the best balance between constraint and cross-linking; in fact, in this case the elastic constant of the network is zero, and the number of constraints introduced by short-range bond bending and stretching forces exactly balance the degrees of freedom in the material.

In the case of p-HVDSO, the connectivity number can be calculated by counting the network forming bonds per atom in each functional group and then summing over the number of that specific functional group per each monomer unit. There are two kinds of possible reaction for the monomer molecule: the addition of an initiator radical to the vinyl bonds and the methylene bridge formation by vinyl polymerization. Thus, the functional groups, which may be included in the matrix, are the TBO radicals, the vinyl groups, the methylene bridges, and the siloxane units (SiOSi). For each functional group, the network forming atoms (n_r) and the network forming bonds (r) were counted, as reported in Table 4.

Note that H atoms do not contribute to the network connectivity[20,21] because they form just one bond. Let x and I/M be the fraction of unreacted vinyl bonds and the number of initiator unit incorporated in the matrix per monomer molecule, respectively. For each monomer unit, there will be $6x$ unreacted vinyl bonds, $6(1 - x)$ reacted (i.e., methylene bridges), I/M initiator units, and 1 siloxane bond. The fraction of unreacted vinyl bonds (C_{sp2}/Si) was estimated from XPS and IR analysis, being around 6−7%, thus 0.12 per monomer molecule. The number of initiator radicals per monomer molecule was determined assuming that the increment of C in the polymer ($C/Si = 6.6$ from XPS) over the monomer stoichiometry ($C/Si = 6$) was due to the incorporation of initiator fragment in the matrix, neglecting any surface contamination during XPS analysis.

Hence, applying eq 1, the mean connectivity number was estimated to be around 2.1 for sample A5.

As a consequence, this polymer has high cross-linking degree, but there are still some vinyl terminal groups per silicon atom which lower the degree of constraint and reduce the elastic modulus, as reported in the previous studies.[18,19] This allows the polymer to be flexible and not crack if bent.

Finally, Figure 8 shows the atomic force micrograph (AFM) of sample A5. The surface appears to be very smooth with root-mean-square roughness of 0.7 nm. Low roughness of thin polymer films is often reported for organosilicon amorphous materials.[6] This is also consistent with the film flexibility discussed previously: a semicrystalline material would display some degree of cracking under strain as discussed also for the p-V_3D_3 case.[6] The low roughness, moreover, makes this coating suitable for a number of applications in which smooth films are required (i.e., smoothing organic interlayer for multistacks[22]).

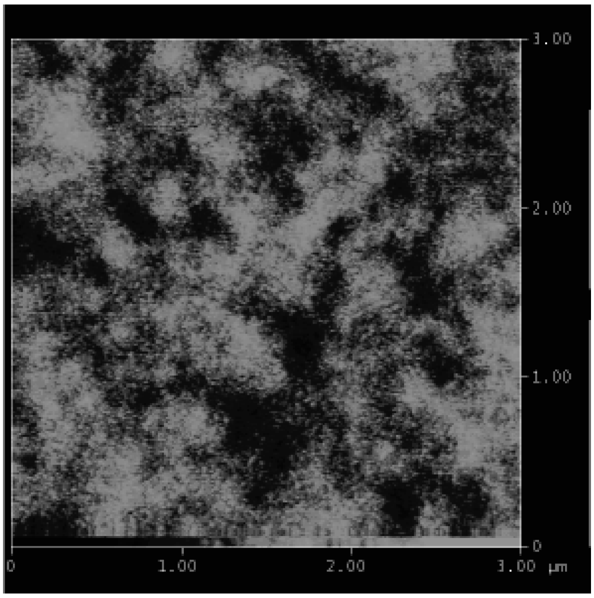


Figure 8. AFM image of p-HVDSO deposited in condition A5 as reported in Table 1. RMS = 0.7 nm.

Conclusions

Self-cross-linked organosilicon coatings were iCVD polymerized starting from HVDSO as monomer and TBPO as initiator. The choice of depositing organosilicon polymer by iCVD was dictated by the possibility of having a control on the reaction pathways and obtaining a dense network, preserving the organic character of the monomer.

Spectroscopic studies showed that the resulting polymer contains a large amount of methylene bridges, and only 1.2 unreacted vinyl bonds over six in the monomer structure are retained in the polymer matrix. Not all the vinyl groups of the monomer react to form linear hydrocarbon chains because of steric hindrance and chain orientation.

The substrate temperature and the initiator flow rate were found to significantly affect the number of vinyl bonds reacting. Increasing the temperature the saturation reactions occur via cross-linking among the growing polymeric chains adsorbed on the surface; in fact, corresponding to a decrease in sp2-C IR absorptions, an increase in sp3-CH_2 groups was detected. On the other hand, increasing the initiator flow rate, the vinyl groups are saturated mainly by capping reaction with TBO radicals; thus, more C−O bonds and constant methylene groups are detected. The deposition rate was found to increase significantly with the substrate temperature. As the amount of monomer molecules adsorbed on the surface was constant for all the experiments, the higher deposition rates can be explained only with higher reaction rate constant, according to the Arrhenius law. Spectroscopic evidence showed that the surface reactions that are promoted by the substrate temperature are mainly the saturation reactions of vinyl groups to form a polymeric network cross-linked by methylene bridges.

In this sense, the choice of using iCVD was crucial; in fact, it allowed depositing cross-linked polymer with full retention of their organic functional groups, avoiding the structural damages (e.g., dangling bonds or etching of labile functional groups) due to ion bombardment of plasma process, generally used to enhance the cross-linking of plasma polymer. Moreover, iCVD created a versatile polymer for which the degree of network cross-linking and the number of vinyl terminal groups can be easily tuned according to the application by changing the substrate temperature or initiator flow rate, as demonstrated.

When the majority of the vinyl moieties are reacted, the resulting material is an amorphous network, with low surface roughness and high structural integrity under physical stress. The p-HVDSO resulted to be self-adherent to silicon substrate; in fact, it passed the tape tests, even without any surface treatment prior to deposition. The high cross-linking of this polymer resulted also in insolubility of the coatings in common solvents. Although highly cross-linked, p-HVDSO films showed high flexibility, in terms of integrity after bending. This is due to the presence of some terminal vinyl groups in the matrix which seem to reduce the degree of network constraint and elastic modulus, allowing deformation without any cracking or delamination. These properties make the p-HVDSO films suitable for several applications, like coatings of biomedical implants or organic coatings for thin film electronics.

Future work with these polymers will focus on the integration of these layers in silica/organosilicon multistacks for applications like ultrahigh barrier layer. The fundamental understanding of the control over iCVD-controllable and stable cross-linking while retaining film flexibility can be extended to future work with monomers containing multiple vinyl groups and is expected to find utility in the modification of membranes as well as micro- and nanoelectrical and mechanical systems (MEMS). The retained vinyl groups on the surface could be used as reactive sites for further functionalization (to enhance the adhesion of successive layers or to enhance biomolecules immobilization).

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