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Initiated-chemical vapor deposition of organosilicon layers: Monomer adsorption, bulk growth, and process window definition

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Organosilicon layers have been deposited from 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V3D3) by means of the initiated-chemical vapor deposition (i-CVD) technique in a deposition setup, ad hoc designed for the engineering of multilayer moisture permeation barriers. The application of Fourier transform infrared (FTIR) spectroscopy shows that the polymerization proceeds through the scission of the vinyl bond and allows quantifying the degree of conversion of vinyl groups, which is found to be larger than 80% for all the deposited layers. In situ real-time spectroscopic ellipsometry (SE) allows following all the i-CVD growth stages, i.e., from the initial monomer adsorption to the layer bulk growth. Finally, the combination of SE and FTIR has allowed defining the process window for the deposition of stable and highly cross-linked poly(V3D3) layers by tuning a key process parameter, i.e., the surface monomer adsorption. © 2012 American Vacuum Society.

I. INTRODUCTION

In the past years, initiated-chemical vapor deposition (i-CVD) has proven to be a very well suited approach toward vacuum deposition of polymeric films for application in many fields where specific surface and bulk properties are desired, i.e., hydrophobicity/hydrophilicity, antimicrobial, binding of biological ligands, biopassive dielectrics, low-k materials and, recently, as responsive materials and organic interlayers in multilayer moisture and oxygen barrier systems.

The advantage of the i-CVD approach with respect to the widely known hot wire CVD is the lower thermal budget required for the polymerization process to occur. The unsaturated bonds of the monomer unit are activated by the free radicals generated during the thermal dissociation of an initiator molecule (i.e., a peroxide), requiring only “mild” grid temperature conditions, typically 500–800 K, and, therefore, making the process compatible with the treatment of sensitive materials such as paper, polymers, and membranes. The monomer structure retention, within the deposited layer, allows defining the i-CVD as an outstanding deposition tool for vacuum polymerization, compared to other well known CVD polymerization processes, such as (pulsed) PECVD. Also the potential for scaling-up and compatibility with roll-to-roll solutions have been discussed for the i-CVD process.

Previous studies have shown that the deposition rate and the number-average molecular weight in the i-CVD process are linearly dependent on the monomer surface concentration, pointing out a polymerization process predominantly occurring at the substrate surface. The monomer surface concentration can be related to a nondimensional parameter given by the ratio of the monomer partial pressure (PM) and its saturated vapor pressure (Psat). PM/Psat. The PM/Psat and, hence, the monomer surface concentration, can be controlled by varying the deposition parameters, such as the monomer partial pressure PM or the substrate temperature (which will lead to changes of the monomer saturation vapor pressure Psat). The ratio PM/Psat then, represents a key parameter for any i-CVD process to be set up. It is therefore fundamental to have in situ real-time diagnostics to study the overall i-CVD process and, in particular, to quantify the monomer surface adsorption and, consequently, define the i-CVD process window for a given deposition process. Generally, the i-CVD process window can be defined as a range in which the PM/Psat parameter is large enough to sustain the polymerization process, without leading to an excess of monomers at the surface, resulting either in an incomplete polymerization or in monomer condensation. Considering these guidelines, on the basis of studies on the relationship between the monomer surface adsorption and the deposition rate of the polymer and number-average molecular weight, the recommended i-CVD process window has been defined by a PM/Psat value leading to one up to three monolayers of adsorbed monomer on the surface. However, other aspects, related to the monomer reactivity and the final stability and quality of the deposited layer, may need to be taken into account when defining the i-CVD process window. On the base of our studies, it has been observed that highly cross-linked polymer structures can be obtained by...
reducing the presence of unreacted monomer units or short oligomers at the end of the deposition process.

The implementation of \textit{in situ} real-time diagnostics in order to define an i-CVD process window is, therefore, fundamental. So far, in literature, quartz crystal microbalance (QCM) measurements have been used for the determination of the monomer surface concentration,\textsuperscript{12–14} while the film growth development has been followed by means of laser interferometry.\textsuperscript{15–18} During QCM measurements, the mass adsorption on the quartz crystal, generally gold coated, results in a frequency shift that can be directly related to the mass of the adsorbed monomer.\textsuperscript{12–14} As only physisorption is considered to control the monomer/surface interaction,\textsuperscript{12–14} at each value of \(P_M/P_{sat}\), the amount of adsorbed monomer is taken as the average of the measured monomer surface concentration during the adsorption and desorption of the monomer from the surface of the QCM.\textsuperscript{12–14}

Laser reflection interferometry measures the periodic interference of light waves reflected from the growing film surface and the film/substrate interface. However, in order to continuously monitor the film growth, a calibration needs to be performed by comparing the interferometry results with data collected using an independent method. This means that only the layer thickness can be monitored in real-time, as an assumption on the growing layer optical constants has to be made.

Nowadays, \textit{in situ} spectroscopic ellipsometry (SE) is widely acknowledged as an analytical tool providing real-time monitoring on film growth processes,\textsuperscript{19–26} since it is a nondestructive, versatile technique easily implemented in a deposition setup. With respect to the above-mentioned techniques, SE allows the real-time, direct determination of both layer thickness and optical constants\textsuperscript{27} of the growing layer. Since the thickness sensitivity with SE reaches the atomic level, this technique is also suitable for the determination of the thickness of the adsorbed monomer at the surface in the i-CVD process. For example, Karpovich and Blanchard\textsuperscript{28} studied the adsorption of different vapors on a gold coated QCM crystal by means of SE and QCM showing a linear relationship between the SE measured adsorbed vapor layer thickness and the QCM measured adsorbed vapors layer volume.\textsuperscript{28}

When applied to the i-CVD process, therefore, \textit{in situ} SE represents an “all in one” diagnostic tool providing information on the whole process, i.e., starting from the monomer adsorption stage to the polymerization process and polymer bulk growth.

This paper reports on the real-time study of the i-CVD process of poly(V\textsubscript{3}D\textsubscript{3}) layers by means of \textit{in situ} SE measurements. Poly(V\textsubscript{3}D\textsubscript{3}) polymers have been synthesized by means of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V\textsubscript{3}D\textsubscript{3}) as monomer and di tert-butyl peroxide (d-TBPO) as initiator. Poly(V\textsubscript{3}D\textsubscript{3}) have proven their potential as biopassivating material being highly cross-linked, showing good adhesion to silicon substrates, and being insoluble both in polar and apolar solvents.\textsuperscript{5,29} In our case, poly(V\textsubscript{3}D\textsubscript{3}) layers were deposited as organic interlayers for an organosilicon-based organic/inorganic multilayer moisture and oxygen barrier system, where highly cross-linked organic interlayers are desirable.\textsuperscript{5,9}

The use of \textit{in situ} SE, as a tool to study the polymer growth mechanism during all its stages, is reported for the first time to the authors’ knowledge. The monomer surface adsorption has been studied by means of adsorption/desorption isotherms followed by \textit{in situ} SE measurements on the same substrates used for the deposition of the polymeric layer (i.e., Si/SiO\textsubscript{2} substrate). Different than studies already reported in literature,\textsuperscript{12–14} the desorption isotherm has also been taken into account as it allows highlighting a possible chemisorption process, between monomer and substrate. Furthermore, the polymer growth has been followed as a function of the deposition time. The use of the \textit{in situ} and \textit{ex situ} SE coupled with other diagnostic tools (namely, FTIR) has allowed for the definition of the i-CVD process window for the monomer here under investigation, by limiting the monomer surface adsorption to 1/3 of the monomer monolayer thickness, for the deposition of stable, highly cross-linked polymers.

The paper is organized as follows. Section II reports on the deposition chamber, the deposition procedure, and analytical techniques used to characterize the polymers’ chemistry, structure, and degree of conversion of vinyl groups. Section II also provides a description of the methodology used for the \textit{in situ} study of the poly(V\textsubscript{3}D\textsubscript{3}) layer with SE and a description of the V\textsubscript{3}D\textsubscript{3} monomer adsorption/desorption (ads/des) measurement procedure. Section III is divided into two main parts. Section III A presents the results on the poly(V\textsubscript{3}D\textsubscript{3}) characterization. Section III B discusses the \textit{in situ} SE study of the poly(V\textsubscript{3}D\textsubscript{3}) film growth in all its stages, together with the studies on the polymer stability and the definition of the i-CVD process window.

II. EXPERIMENT

A. Deposition chamber

The deposition chamber is a custom-built cylindrical vacuum reactor shown in Fig. 1. This setup allows performing both i-CVD and PECVD processes, in order to develop organic and inorganic layers, respectively. The chamber measures 40 cm in diameter and 58 cm in height. The walls of the setup are heated up at a constant temperature of 353 K to avoid monomer condensation and minimize monomer adsorption. Monomer and initiator are mixed in a buffer and injected into the deposition chamber through a ring placed above the grid. The vessel is pumped through the bottom by means of a rotary vane pump (Adixen) in combination with a turbomolecular pump (Pfeiffer). The pressure is monitored by three pressure gauges for different ranges: a Penning (Pfeiffer) pressure gauge to cover the range from \(10^{-7}\) mbar up to atmospheric pressure, which is used to measure the base pressure of the setup, and two capacitive (Pfeiffer) pressure gauges to monitor the pressure during the process (\(10^{-8}\text{–}10^{-10}\) mbar) and the pressurization of the system (1 mbar–atmospheric pressure). During the deposition process the pressure is controlled through a butterfly valve (VAT).

The grid consists of a single tungsten wire (\(\Omega = 0.2 \text{ mm}\)) coiled to form 15 lines, spaced 2 cm from each other, resistively heated by a dc current. A feed-loop system to read and
autoadjust the grid temperature to the set value is embedded into a custom-built power supply system. The grid is mounted on a magnetic movable arm through which is removed from the deposition chamber and placed in a separate vacuum chamber, in order to avoid deposition on the wire during the PE-CVD process. The 225 cm² copper made substrate holder is connected to a temperature control system, composed by resistive heating elements (Eurotherm) and three Peltier cooling elements, which allow for the temperature control from 383 K to below room temperature. The substrate holder is connected to a moving system in order to vary the grid–substrate distance. During this work, the latter was fixed to 2 cm. The substrate holder is grounded and acts as an electrode during the PECVD process when the plasma is ignited by applying a radio frequency to the rf electrode (area $= 314 \text{ cm}^2$, Fig. 1) placed at a distance of 6.8 cm from the grounded electrode. The setup, which has a quartz window for visual inspection, is equipped with SE windows mounted in sliding flanges in order to study the deposition process at any substrate height.

The monomer (1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane: V$_3$D$_3 > 95\%$, Gelest) and the initiator (di-tert-butyl peroxide: d-TBPO 98\%, Aldrich) are used without any further purification. Monomer and initiator are vaporized in stainless steel bubblers set at a temperature of 373 and 298 K, respectively, and the flow rates are controlled by two vapor source controllers (VSC 1150C, MKS). The monomer and initiator lines to the vessel are heated up at a constant temperature of 393 and 308 K, respectively, to avoid vapor condensation. Four inch c-Si wafers are used as substrates for the deposition of the poly(V$_3$D$_3$) layers without any cleaning procedure prior to the deposition.

During a typical i-CVD deposition, the monomer and initiator are injected into the deposition chamber, then the pressure is set to the deposition value and the deposition is started by setting the grid temperature. The deposition process is concluded by switching off the initiator and monomer flow rates and the grid power; then the chamber is gradually evacuated to the base pressure. Finally, the system is brought to atmospheric pressure by pressurizing it with a controlled flow of N$_2$ gas. The deposition conditions of the i-CVD layers are listed in Table I.

### B. Layer characterization

The chemical characterization of the poly(V$_3$D$_3$) layers is performed by means of Fourier transform infrared (FTIR) spectroscopy with a Bruker Tensor 27 spectrophotometer. The FTIR spectra are acquired in transmission mode in the range of 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and the number of scans varying from 256 to 2000 (depending on the film thickness) in order to reduce the signal to noise ratio. Before the spectra acquisition the spectrometer is purged for 15 min with N$_2$ to minimize the effect of H$_2$O and CO$_2$ absorption. The monomer spectrum is acquired with the same spectrometer by placing a drop of the liquid monomer between two IR transparent KBr windows. The deconvolution of the CH$_x$ (3150/2800 cm$^{-1}$), and the Si–O–Si (1150/900 cm$^{-1}$) related absorption bands is performed by ORIGINLAB software. Lorentzian functions are applied for the deconvolution of the liquid monomer absorption band, since collision broadening contributes mainly to the vibrational modes, while Gaussian functions are used for the deconvolution of the polymer absorption bands, as, in this case, the Doppler broadening, due to molecules thermal motion, dominates.

To determine the degree of conversion of vinyl groups, the $\delta$CH$_2$ asymmetric stretching at 3057 cm$^{-1}$, together with the Si–CH$_3$ bending signal at 1260 cm$^{-1}$ (as reference) are used, since the latter is present in both polymer and monomer and remains unaffected during the polymerization process. Without the reference signal no quantitative comparison (monomer versus polymer) can be made. The degree of conversion of vinyl groups is calculated by means of

**Table I. Conditions of deposition of the poly(V$_3$D$_3$) layers.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>V$_3$D$_3$ (SCCM)</th>
<th>d-TBPO (SCCM)</th>
<th>$T_{wall}$ (K)</th>
<th>$T_{sub}$ (K)</th>
<th>$P$ (mbar)</th>
<th>$P_{V3D3}/P_{satV3D3}$</th>
<th>$T_{walls}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>2</td>
<td>313</td>
<td>313</td>
<td>0.7</td>
<td>0.374</td>
<td>353</td>
</tr>
<tr>
<td>2</td>
<td>323</td>
<td>0.201</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>328</td>
<td>0.150</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>4</td>
<td>333</td>
<td>0.113</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>343</td>
<td>0.065</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>353</td>
<td>0.040</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** (Color online). Schematic of the i-CVD /PECVD deposition setup.
where area ($\nu^\beta = \text{CH}_2$) and area($\delta^\prime \text{Si} - \text{CH}_3$) are the deconvoluted peak areas associated with the CH$_2$ asymmetric stretching mode of the vinyl group (at 3057 cm$^{-1}$) and the area of the symmetric bending absorption band (1260 cm$^{-1}$) in the polymer and monomer, respectively. All the reported FTIR spectra are baseline corrected and normalized with respect to the layer thickness.

C. Film growth and monomer ads/des isotherms studies

The thickness and the optical properties of the poly(V$_3$D$_3$) layers are determined by means of in situ and ex situ SE. The layer growth and monomer ads/des isotherms are studied by means of in situ SE. Ex situ measurements are acquired either at a single (70°) or at three angles of incidence (65°, 70°, 75°), in a wavelength range of 190–1000 nm by means of a J.A. Woollam Co. M-2000D ellipsometer. In situ SE measurements are acquired at an angle of incidence of 71.5° with a wavelength range of 245–1000 nm by using a J.A. Woollam Co. M-2000 F ellipsometer. The optical model used for the film growth studies consists of (1) silicon substrate, (2) SiO$_2$ native oxide layer (1.5–2 nm), and (3) poly(V$_3$D$_3$) layer modeled with the Cauchy dispersion formula and Urbach tail as reported in the following:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},$$

$$k(\lambda) = z \exp(\beta \left(12400 \left(\frac{1}{\lambda} - \frac{1}{\gamma'}\right)\right),$$

where $A$, $B$, $C$ are the Cauchy fit parameters together with $z$ (extinction amplitude) and $\beta$ (the exponent factor) of the Urbach function. The value of the band edge ($\gamma'$) is fixed to 400 nm. The use of the Urbach function is motivated by the fact that the poly(V$_3$D$_3$) layers contain carbon and hence show an absorption tail at lower wavelengths. For the in situ SE data the silicon substrate temperature is fitted prior to the deposition process and the ads/des studies, and kept constant to the fitted value. The fitted values of the silicon substrate temperature have been found to be in excellent agreement (within ±2 K) with the substrate holder temperature for all analyzed samples. The V$_3$D$_3$ monomer ads/des measurements are performed in the deposition setup directly on c-Si substrates by monitoring the adsorbed monomer thickness by means of in situ SE measurements. The used optical model is composed of: 1) silicon substrate; 2) SiO$_2$ native oxide layer (1.5–2 nm); 3) V$_3$D$_3$ monomer layer, modeled with the Cauchy dispersion being the thickness the only fit parameter and the monomer refractive index fixed to the constant value of 1.422 at 589.3 nm, as reported in literature. The choice of studying the surface monomer adsorption by monitoring the changes in thickness is motivated, as will be shown in Sec. III, by the fact that the silicon substrate is a nonporous substrate. The refractive index has been kept fixed to the values found in literature during the measurements. As for the investigated thickness ranges (<10 Å) there is complete correlation between thickness and refractive index.

Two sets of ads/des isotherms are performed, namely equilibrium ads/des measurements and ads/des measurements by mimicking the deposition conditions. In both cases monomer and initiator are injected into the deposition chamber with the same ratio as used during the deposition (see Table I) with the setup at the base pressure of 10$^{-6}$ mbar and the pressure is increased up to the value of 0.7 mbar. (The initiator (d-TBPO) is also present in this step, but $P_{\text{sat(d-TBPO)}} = 118.8$ mbar against $P_{\text{sat(V3D3)}} = 1.56$ mbar at 313 K. This corresponds to a value of $P_{\text{(d-TBPO)/P_{sat(d-TBPO)}}} = 10^{-3}$ and $P_{\text{(V3D3)/P_{sat(V3D3)}}} = 0.374$, for a substrate temperature of 313 K and a final pressure of 0.7 mbar. Under the same conditions, ads/des isotherms, in which the monomer has been replaced by He as buffer gas have been also measured, to quantify any initiator surface adsorption. This resulted in no initiator adsorption. Moreover, a comparison of the ads/des isotherms in which the system V$_3$D$_3$/d-TBPO has been replaced by the system V$_3$D$_3$/He has been performed resulting in the same ads/des isotherm shape and final V$_3$D$_3$ thickness uptake.) In the case of the equilibrium isotherms, the pressure is increased by 0.02 mbar steps, at each step the adsorbed monomer thickness is acquired after the pressure has stabilized. The desorption measurement is carried out in a similar fashion. In the case of the ads/des isotherms performed by mimicking the deposition conditions, the pressure is continuously increased from the base value to the set value of 0.7 mbar and the adsorbed monomer thickness is monitored in real time; a similar approach is followed during the desorption step. In the case of the equilibrium ads/des isotherms the substrate temperature is of 313 K which allows to tune the $P_{\text{ad/P_{sat}}}$ parameter in the range of 0–0.374. In the case of the ads/des isotherms carried out by mimicking the deposition conditions the same study has been performed also at a substrate temperature of 313 K, 333 K and 353 K. The values of the monomer saturation vapor pressure ($P_{\text{sat}}$) have been derived by means of the Clausius-Clapeyron relation considering the value of saturation vapor pressure at 298 K, i.e. $P_{\text{sat}} = 0.571$ mbar and the monomer boiling point (462 K at atmospheric pressure 1013 mbar). For all the SE measurements, the data analysis is performed by using J.A. Woollam Complete EASE$^\text{TM}$ software version 4.27 and the mean squared error between the experimental data and
the model is minimized by adjusting the fit parameters using the Levenberg–Marquardt algorithm.

D. Other diagnostic tools

The layer morphology is studied by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements. AFM measurements are performed with a Solver Pro Scanning Probe Microscope (NT-MDT) in semicontact mode using tips (NSG-10) with a radius of curvature of 10 nm with a scan area of 4 μm². The measurement and analysis are performed with NOVA software (NT-MDT) in order to describe the surface morphology of the sample. SEM measurements are performed with a JEOL 7500FA microscope with electron energy of 5 kV.

III. RESULTS AND DISCUSSION

A. Poly(V₃D₃) layer characterization

In Fig. 2 the comparison between the FTIR absorption spectra of the deposited poly(V₃D₃) layer and the liquid phase monomer is reported. A list of the absorption modes for both monomer and polymer spectra is reported in Table II. The spectra comparison shows that the polymerization occurred via the cleavage of the vinyl groups present in the monomer, as can be observed by the quantitative decrease of the vinyl-related signals such as the \( \nu_{\text{as}} \) CH₂ asymmetric deformation (at 1408 cm⁻¹), the C=C stretching (at 1597 cm⁻¹) and, in the CH₃ region (=CH₂ asymmetric and

![Fig. 2. V₃D₃ monomer and poly(V₃D₃) FTIR spectra comparison.](image)

| Wave number polymer (cm⁻¹) | Wave number monomer (cm⁻¹) | Chemical bond | Vibration mode⁴
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3057</td>
<td>3058</td>
<td>CH₂ in vinyl</td>
<td>( \nu_{\text{as}}^b )</td>
</tr>
<tr>
<td>3018</td>
<td>3017</td>
<td>CH₂ in vinyl</td>
<td>( \nu_{\text{s}}^b )</td>
</tr>
<tr>
<td>2974</td>
<td>2976</td>
<td>CH in vinyl</td>
<td>( \nu_{\text{as}}^b )</td>
</tr>
<tr>
<td>2962</td>
<td>2966</td>
<td>CH₁ in C sp³</td>
<td>( \nu_{\text{s}}^b )</td>
</tr>
<tr>
<td>2935</td>
<td>2935</td>
<td>CH in vinyl</td>
<td>( \nu_{\text{s}} )</td>
</tr>
<tr>
<td>2910</td>
<td>2910</td>
<td>CH₂ in C sp³</td>
<td>( \delta_{\text{as}}^b )</td>
</tr>
<tr>
<td>2878</td>
<td>2905</td>
<td>CH₁ in C sp³</td>
<td>( \delta_{\text{as}} )</td>
</tr>
<tr>
<td>2861</td>
<td>–</td>
<td>CH₂ in C sp³</td>
<td>( \delta_{\text{s}} )</td>
</tr>
<tr>
<td>–</td>
<td>1926</td>
<td>CH₂ in vinyl</td>
<td>Overtone of 963 cm⁻¹ signal⁸</td>
</tr>
<tr>
<td>1597</td>
<td>1597</td>
<td>C=C in vinyl</td>
<td>( \nu_{\text{s}} )</td>
</tr>
<tr>
<td>1460</td>
<td>–</td>
<td>CH₂ in C sp³</td>
<td>( \delta_{\text{as}}^b )</td>
</tr>
<tr>
<td>1408</td>
<td>1408</td>
<td>CH₂ in Si–(CH₂)–Si and in vinyl</td>
<td>( \delta^i )</td>
</tr>
<tr>
<td>1260</td>
<td>1261</td>
<td>Si–CH₃</td>
<td>( \delta_{\text{s}} )</td>
</tr>
<tr>
<td>1016</td>
<td>1002</td>
<td>Si–O–Si in (SiO)₃</td>
<td>( \nu^a )</td>
</tr>
</tbody>
</table>

1002 1002 cm⁻¹ (SiO)₃ short polymer chains

\( \nu^a \)

995 995 cm⁻¹ (SiO)₃ short polymer chains

\( \nu^a \)

970

963 963 cm⁻¹ Si–(CH₃)–Si \( \omega^c \)

798 804 804 cm⁻¹ CH₂ in vinyl \( \omega^i \)

617 621 621 cm⁻¹ Si–CH=CH₂ \( \delta^b \)

\( \nu_{\text{as}}, \nu, \rho, \omega \) denote stretching, bending, rocking, and wagging vibration modes, respectively. \( a \) and \( s \) denote asymmetric and symmetric vibrations, respectively.

⁴References 5 and 34.
⁵Reference 8.
⁶References 8, 34, and 35.
⁷References 8 and 35.
⁸Reference 34.
⁹Reference 36.
¹⁰References 8, 34, and 37.
¹¹References 8, 34, and 36.
¹²References 36 and 37.
¹³References 8, 34, 36, and 37.

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symmetric stretching at 3057 and 3018 cm\(^{-1}\)), the \(=\text{CH}\) asymmetric and symmetric stretching at 2974 and 2935 cm\(^{-1}\) in the polymer spectrum with respect to the monomer spectrum. The absorption at 1408 cm\(^{-1}\), still present in the polymer spectrum, is also attributed to the deformation of the methylene group bonded to silicon.\(^5\) As the polymerization process occurs through the activation of the vinyl groups, the features associated with the generated polyethylene chains, such as the asymmetric and symmetric stretching modes of the methylene groups at 2910 and 2861 cm\(^{-1}\) and the asymmetric bending mode of the methylene groups at 1460 cm\(^{-1}\), appear in the polymer spectrum. The retention of the other monomer functional groups (i.e. the methyl group bonded to silicon and the cyclotrisiloxane ring) is witnessed by the Si-CH\(_3\) symmetric bending signal at 1260 cm\(^{-1}\) Si-O-Si asymmetric stretching at 995 cm\(^{-1}\), which do not undergo any changes upon polymerization. A shift of the peak associated with the cyclotrisiloxane ring from 1016 cm\(^{-1}\) in the monomer to 995 cm\(^{-1}\) in the polymer occurs. In literature a similar observation has been reported for the polymerization of the tetravinyl-tetramethyl-cyclootetrasiloxane, showing a shift of the cyclootetrasiloxane band from 1075 cm\(^{-1}\) (monomer) to 1065 cm\(^{-1}\) (polymer).\(^6\) The ring opening can be excluded since this would imply a broadening of the absorption band and the appearance of a shoulder at 1080 cm\(^{-1}\),\(^3\) related to linear Si-O-Si chains, which is not present in the polymer spectrum in Fig. 2. The cyclotrisiloxane functionalities are known to absorb at 1010–1020 cm\(^{-1}\), but this absorption band can be shifted well below 1000 cm\(^{-1}\) due to strain in the ring structure\(^3\) upon polymer chain formation. To further investigate this point, the deconvolution of the Si-O-Si asymmetric stretch band (900–1150 cm\(^{-1}\)) related to the (SiO)\(_3\) ring has been performed for the layer deposited at different temperatures and the results are shown in Fig. 3: the band centered at 1002 cm\(^{-1}\) is associated with the Si-O-Si asymmetric stretching of the cyclosiloxane bonded to short polymeric chains (low tension into the ring structure\(^3\)); the one at 995 cm\(^{-1}\) is associated with the same vibration, where the ring is bonded to long polymeric chains (higher degree of cross-linking and tension on the ring structure\(^3\)); the third peak can be more likely assigned to the wagging of the methylene bridge (Si-(CH\(_2\))\(_2\))Si.\(^8\) A temperature increase induces an increase in the absorption band associated with the highly cross-linked, long polymeric chains. The effect of the substrate temperature on the deposited layer will be further addressed in the next section.

As reported in Sec. II, the degree of conversion of vinyl groups can be inferred from the area of the signal related to the \(=\text{CH}\)\(_2\) asymmetric stretching signal at 3057 cm\(^{-1}\), obtained from the deconvolution of the CH\(_2\) (3150–2800 cm\(^{-1}\)) as reported in Fig. 4, and the area of the absorption band centered at 1260 cm\(^{-1}\) associated with the Si-CH\(_3\) bending. According to Eq. (1), a degree of conversion of vinyl groups (the error in the given value of the degree of conversion of vinyl groups is the standard deviation of the results obtained by calculating the degree of conversion of vinyl groups by using at least four polymer spectra for each temperature) of 82\% \pm 3\% (s.d.) and 87 \% \pm 1\% (s.d.) has been calculated for the layers deposited at 313 and 333 K, respectively. For higher temperatures the \(=\text{CH}\)\(_2\) signal was further reduced within the noise level and thus a degree of conversion of vinyl groups larger than 87\% can be assumed for a substrate temperature higher than 333 K.

### B. Film growth study and process window definition

Figure 5 reports all the i-CVD process steps as followed by means of \textit{in situ} SE. Beside the linear polymer growth...
process [see Fig. 5(a)], two other characteristic steps can be highlighted: the initial thickness uptake, which is related to the monomer surface adsorption during the setting of the deposition conditions [see Fig. 5(b)] and, under certain experimental conditions (Table I, sample 1), a thickness reduction of the deposited layer, occurring upon chamber evacuation and pressurization, as highlighted in Fig. 5(c). In the remainder of Sec. III, the phenomena of thickness losses and the monomer surface adsorption will be further addressed with the purpose of the defining the i-CVD process window.

### 1. V₃D₃ monomer ads/des isotherm studies

Figure 6(a) shows the equilibrium ads/des isotherms on silicon (Si/SiO₂ native oxide ~ 1.5 nm) substrate at a temperature of 313 K in the $P_M/P_{sat}$ range of 0–0.374. The $P_M/P_{sat}$ upper limit coincides with the values corresponding to the experimental conditions that led to a thickness loss [see Fig. 5(c)]. Although the $P_M/P_{sat}$ range is not extended to 1, the shape of the isotherms clearly resembles that of a type II isotherm, which, according to the IUPAC classification of the ads/des isotherm, corresponds to a nonporous substrate, as expected to occur on a silicon wafer. From the adsorption curve, the inflection point, indicative of monolayer adsorption, is observed after a first initial increase for low $P_M/P_{sat}$ (<0.1). After that monolayer thickness has been reached, the adsorbed monomer thickness further increases, pointing out to a multilayer adsorption development. Since for the i-CVD processes the monomer adsorption is reported to be governed by a physisorption mechanism, the desorption is expected to be reversible. However, a hysteresis behavior develops, which points out chemisorption processes in the presence of the native SiO₂ layer, and the (SiO)₃ siloxane ring of the monomer. The adsorbed monomer monolayer thickness, $t_0$, can be obtained by fitting the adsorption isotherm with the Brunauer–Emmet–Teller (BET) equation reported in the following:

$$t_{admon} = \frac{t_0 c k(P_M/P_{sat})}{(1 - k(P_M/P_{sat}))(1 + (c - 1)k(P_M/P_{sat}))},$$  \hspace{1cm} (3)
which relates the thickness of surface adsorbed monomer to the $P_M/P_{sat}$ ratio, via the BET constant $c$ and a correction factor $k$ that takes into account that even at $P_M/P_{sat} = 1$ a finite number of multilayers is adsorbed. Due to the restricted $P_M/P_{sat}$ range in our work, $k$ has been fixed to 1. A value of $t_0 = 0.497$ nm ± 0.004 nm ($R^2 = 0.989; \ c = 47 \pm 3$), has been obtained, close to the $V3D3$ molecular radius of 0.404 nm as estimated from the monomer van der Waals volume calculated as the sum of atomic and bond contributions.\footnote{Since this estimation does not take into account any geometry of the molecule (it assumes a sphere, and therefore overestimates the dimension) and the fact that the monolayer thickness is comparable with the molecular radius, it is hypothesized that the preferred direction of adsorption for the molecule is probably horizontal, with the cyclotrisiloxane ring parallel to the substrate. This is confirmed by the chemical structures of the $V3D3$ molecule, which exists in a mixture of cis and trans configurations,\cite{39,42} as reported in Fig. 6(b) in which, in both configurations, the cyclotrisiloxane ring shows a planar structure with only a slight distortion of the Si–O–Si bonds in the case of the trans configuration. (The isotherm shape found in this work differs from the ones reported in literature for similar studies.\cite{13,14} Although a comparison between the different isotherms is difficult to be made, as their shape (and hence the BET curve) depends on the adsorbing molecule chemistry, the substrate chemistry/porosity and, hence, the substrate/adsorbing molecule interaction,\cite{39,43} some conclusions can still be drawn. The shape of the BET equation is function of the BET constant $c$ and, for a non-porous substrate (as Si/SiO$_2$ and gold substrates), it shifts from a Type II to a Type III isotherm, characteristic of weak monomer/substrate interactions, for $c < 2$. In the case reported in literature, a value of $c = 1.950$ and $c = 2.536$ for ethyl acrylate and butyl acrylate,\cite{14} respectively, on gold coated quartz crystal are reported in comparison with the fitted valued of $c = 47 \pm 3$ found in this work for the $V3D3$ on Si/SiO$_2$ substrate, pointing out that differences in the substrate/adsorbing molecule interaction are playing a role. As a matter of fact a value of $c = 12$ (Type II isotherm) has been also reported in literature for the adsorption study of glycidyl methacrylate monomer on Si/SiO$_2$ substrate.\cite{14} The equilibrium conditions considered in the previous experiment are slightly different from the real deposition conditions, Therefore, additional ads/des isotherms have been performed by mimicking the deposition conditions [i.e., continuous pressure increase, in the same way as the thickness uptake shown in Fig. 5(b)]. Figure 7 shows the ads/des isotherms acquired at 313 K; the adsorption isotherm is still of type II, but the amount of adsorption is reduced since the equilibrium is not reached at every pressure step. Also, the hysteresis behavior is limited. Nevertheless, also in this case the thickness of the surface adsorbed monomer is well beyond the inflection point or the so-defined monolayer thickness, although this is lower than the one found under equilibrium conditions. The values of the adsorbed monomer thickness at the same final pressure of 0.7 mbar obtained from the ads/des isotherm studies performed at substrate temperatures of 333 and 353 K are also reported in Fig. 7, and they coincide, within the experimental error, with the data points of the adsorption isotherm obtained at 313 K.

2. Thickness loss characterization

As shown in Fig. 5(c), under specific deposition conditions (Table I, sample 1), the deposited layer undergoes a thickness loss ($\Delta t$) upon chamber evacuation. $\Delta t$ is defined as the difference between the film thickness as result of the deposition process (as-deposited) and the ex situ film thickness as measured with SE after chamber evacuation and exposure of the film to the environment. This phenomenon can be related to the presence, within the layer, of unreacted monomer units or short oligomers at the end of the deposition process, which are removed from the deposited layer during the chamber evacuation (the monomer condensation is less likely to occur since, under our experimental conditions, the monomer partial pressure is still lower than its saturation pressure: $P_{V3D3} = 0.583$ mbar < $P_{satV3D3} = 1.56$ mbar at 313 K). Parallel studies on the same system $V3D3$/d-TBPO (Ref. 29) and on the $V3D3$/HVDSO/d-TBPO system (Ref. 17) report on the existence of a pressure dependent substrate temperature threshold below which unreacted monomer or short oligomer units may be trapped in the growing layer and pumped away during the chamber evacuation and leaving, in this case, micrometric size disk-shaped holes in the layer surface\cite{29} or even holes of visible size,\cite{17} therefore, pointing out a bulk-related phenomenon. However, under our experimental conditions, those defects were not detected on the surface of the deposited layers even for the highest thickness loss recorded by in situ SE, as pointed out by the SEM image in Fig. 8, showing a smooth and homogeneous surface. Furthermore, neither thickness losses are monitored, nor in situ real-time studies are carried out to further investigate this observation; therefore, a detailed study of this phenomenon has been carried out and reported below.

![Fig. 7. V3D3 ads/des isotherm carried out by mimicking the deposition conditions on silicon substrate at a substrate temperature of 313 K together with the values of the adsorbed monomer thickness at substrate temperatures of 333 and 353 K.](image-url)
The proof that the thickness reduction is a bulk-related phenomenon derives from the absolute values of the $\Delta t$ (i.e., the thickness loss) increasing linearly as function of the deposition time, as shown in Fig. 9. This rules out a surface-related phenomenon, as in the latter case, the $\Delta t$ values would result independent from the deposition time/layer thickness. Furthermore, the relative $\Delta t$ (defined as the ratio between the $\Delta t$ and the as-deposited layer thickness) reaches a plateau for long deposition time as reported in Fig. 9: this suggests that, under the hypothesis that the thickness reduction is attributed to unreacted monomer, the latter participates in the polymerization process also in the bulk of the growing layer. Within 20 min of deposition, the equilibrium between the reacted and unreacted monomer is reached in the polymerization process. To support the hypothesis on the propagation of the polymerization in the layer bulk, a comparison between a continuous and a step-by-step deposition (i.e., the i-CVD layers are deposited in 5 min steps and the chamber is evacuated between two steps) is reported in Fig. 10. The layers that have been obtained from alternating deposition and evacuation steps are characterized by larger thickness losses. On the contrary, when the deposition is a continuous process, the overall thickness loss is smaller. This allows one to conclude that the polymerization process occurs not only at the surface of the growing layer but also in the bulk by diffusion of the nonreacted monomer and reaction with polymer chains at the unsaturated sites.

3. Process window definition

The i-CVD process window can be defined by studying the effect of process key parameters through which the monomer adsorption can be controlled and also the monomer reactivity can be enhanced. Among all deposition parameters, the substrate temperature fits these requirements. By keeping the rest of the deposition parameters constant, i.e., wire temperature, monomer to initiator ratio, and pressure, increasing the substrate temperature would lead to a reduction of the surface monomer adsorption and to an increase of the monomer reactivity.

This is confirmed by the decrease of the thickness losses with the increasing of the substrate temperature as shown in Fig. 11, which also reports the trend of the surface adsorbed monomer thickness determined by means of in situ SE ads/des measurements done by mimicking the deposition conditions at substrate temperatures of 313, 333, and 353 K. Clearly, a correlation between the reduction of the surface monomer adsorption thickness and the thickness losses is evident. As the temperature increases, the monomer surface...
concentration is reduced; furthermore, its reactivity is enhanced, promoting the polymerization process and reducing the thickness losses. Yet, it is necessary to understand how the substrate temperature, by reducing the thickness losses, affects the layer quality.

In Fig. 12 the layer refractive index values, measured for both the as-deposited and in vacuum condition, are presented. A difference in refractive index values for the layer that showed high thickness losses ($T_{\text{sub}} = 313$ K) is highlighted. In particular, the refractive index is increasing from the as-deposited layer to the layer after evacuation. This can be related to layer densification upon evacuation, due to the matrix collapse accompanying the layer thickness reduction. The overall increase of both values of the refractive index may suggest a layer restructuring with the substrate temperature. As matter of fact, it has already been shown earlier in this paper that an increase in temperature is responsible for an increase of the polymer matrix cross-linking through the increase of the signal related to the ($\text{SiO}_3$) ring bonded to long highly cross-linked polymer chains (Fig. 3) and for an increase in the degree of conversion of vinyl groups. An improvement in the polymer morphology is also observed by comparing the rms surface roughness of the layers deposited at different substrate temperatures, corresponding to high and low $\Delta t$ (e.g., and 313 and 333 K), which decreases from 0.94 nm ±0.02 nm to 0.51 nm ±0.02 nm.

The previous results can be summarized by the i-CVD process window definition for the polymerization of the poly ($V_3D_3$) layers as reported in Fig. 13. By tuning the $P_M/P_{\text{sat}}$ parameter with the substrate temperature a well cross-linked polymer structure exhibiting no thickness loss upon evacuation can be achieved by setting the monomer adsorption on the substrate, which should be limited to a thickness corresponding to the inflection point in the isotherm. This translates in an adsorbed monomer thickness restricted to one-third of the monolayer thickness.

### IV. SUMMARY AND CONCLUSIONS

The implementation of the i-CVD process in a novel deposition setup has been successfully accomplished by the deposition of poly ($V_3D_3$) layer by using 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane and di-tert-butyl-peroxide as initiator. The comparison of the FTIR spectra of monomer and polymer showed that the polymerization process occurred only through the cleavage of the vinyl groups present in the monomer and the retention of the other monomer functional groups, namely, the cyclotrisiloxane ring and the methyl groups attached to the silicon atoms of the cycle. A degree of conversion of vinyl groups above 80% has been found for all the poly ($V_3D_3$) layers. The film growth has been studied in situ by means of spectroscopic ellipsometry as real-time diagnostics to follow all stages of the i-CVD process from the initial monomer adsorption to the linear film growth and to the thickness losses due to the presence of unreacted monomer units at the end of the deposition process. Furthermore, in situ SE measurements allowed characterizing the thickness losses as bulk-related phenomenon and brought new information on the polymerization process, which propagates not only at the surface of the growing layer but also in the bulk. Finally, together with other complementary analysis (FTIR), in situ SE measurements made it possible to define the process window for the deposition of stable ($\Delta t \to 0$ nm) and highly cross-linked poly ($V_3D_3$) layers, which can be obtained by tuning the surface monomer adsorption below one-third of the monolayer thickness. The poly ($V_3D_3$) layers showing limited thickness losses and high degree of cross-linking (i.e., $T_{\text{sub}} = 333$ K) are presently tested as organic interlayer for inorganic/organic multilayer moisture diffusion barrier systems.

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