FTIR-ATR spectroscopy in thin film studies: The importance of sampling depth and deposition substrate

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ABSTRACT
Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflectance mode (ATR) was used to characterize SiO$_x$H$_y$ thin films deposited on either polypropylene foil or silicon wafers through a cold atmospheric plasma discharge. Compared to a classical transmission spectrum with transverse (TO) vibrational modes, the FTIR-ATR spectra revealed modified and/or exhibited additional features caused by either the non-orthogonal angle of incidence of the infrared radiation with respect to the sample normal or the partial light reflection on the deposition substrate. On one hand, recording the infrared spectra with an angle of incidence other than 90° produced a longitudinal (perpendicular to the sample normal) component in the electric field of the incident light, which enabled the detection of longitudinal (LO) vibrational modes. On the other hand, the transverse vibrational modes of thin films deposited on silicon were slightly extinguished with a concomitant increase of the spectral intensity of the LO features, due to both the partial withdrawing between the incident and reflected electric fields of the infrared light lying in the sample plane and, the addition of those perpendicular to this sample plane. These data thus clearly show the enormous potential of FTIR-ATR to characterize thin film molecular order, provided that a prior comprehensive analysis is performed on the sampling depth and the light reflection on the deposition substrate.

KEYWORDS
Fourier transform infrared spectroscopy Molecular order, longitudinal optical vibrational mode LO/TO, SiO$_x$H$_y$ thin film

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1 INTRODUCTION

The plasma deposition of thin films is now used in several spheres of human activity. Indeed, thin films from a few to several hundred nanometers in size are being developed for various types of applications, including gas barriers [1], antireflective coatings [2], drug delivery [3, 4], or materials with improved biocompatibility [5, 6], to name only a few. Their activity is most likely driven by such intrinsic properties as high refractive index [7], high hydrophobic or hydrophilic properties [8, 9], and electrical conductivity [10]. These films are preferably as thin as possible to prevent any undesirable effects which could lead to optical artefacts [11], delamination under mechanical constraints [12], or mechanical mismatch with the substrate material [13]. Thin film characterization techniques therefore require state-of-the-art analytical instruments to probe their chemistry and organization at the nanometer scale.

Among these techniques, FTIR spectroscopy has been proven to be highly effective. The easiest way to record thin film FTIR spectra is to deposit them on substrates that are transparent in the mid-infrared region while measuring the normal angle incidence signal with respect to the sample surface. Such a configuration makes it possible to observe the transverse optical (TO) vibrational modes [14]. However, FTIR spectra recorded at an angle by either transmission or reflection (provided that the substrate is reflective) by physically tilting the sample or using polarized light also reveals features assigned to longitudinal optical (LO) vibrational modes, thereby providing information on a film’s molecular organization [14-17].

The attenuated total reflectance (ATR) spectral acquisition mode is another tool commonly used to record the infrared spectra of thin films and coatings. Its ease of manipulation and the possibility of depth profiling by recording spectra at various light incidence angles has rapidly made it a technique of choice. FTIR-ATR basically takes advantage of the fact that an incident ray is reflected at the interface between two materials of different refractive indexes. In a typical experiment, the layer of interest is placed against an ATR crystal made of a material with a high refractive index (Ge, Si, ZnSe, Diamond, etc.).

FTIR-ATR has been used in several studies to investigate thin films [18-22]. However, comparing thin film FTIR-ATR spectra from one study with those of another was shown to be a tedious task, as the apparently similar plasma conditions produced significant variations in the infrared spectra and consequently, to inconsistent spectral assignments [20, 22]. A closer examination of the relevant literature led to the conclusion that these spectral discrepancies were likely related to the light of incidence at which the spectra were recorded as well as to the light reflection on the deposition substrate [14-19, 23, 24].

The goal of this study was therefore to investigate the influence of the substrate on the FTIR-ATR spectra of plasma-deposited thin films. Particular attention was given to the interaction between the evanescent wave and the deposition substrate, with a focus on the importance of substrate capability to reflect the incoming light radiation. The investigated plasma was a dielectric barrier discharge (DBD) operated under atmospheric pressure in nitrogen with a mixture of hexamethyldisiloxane (HMDSO) and nitrous oxide (N₂O) for the deposition of silica-like thin films.

2 MATERIALS AND METHODS

2.1 Materials

Commercial polypropylene films (PP) 20 µm in thickness were purchased from Goodfellow Corporation (Lille, France), while double side polished silicon wafers (350-400 µm in thickness, orientation (100)) were obtained from Siltronix (Archamps, France). The gases used for the DBD process were nitrogen (99.998% purity) and nitrous oxide (99.998% purity) purchased from Air Liquide (Toulouse, France). The monomer hexamethyldisiloxane (HMDSO) was purchased from Fluka (Saint-Quentin-Fallavier, France).
2.2 Methods

2.2.1 Plasma deposition

The DBD set-up has been described elsewhere [25]. The discharge was ignited under atmospheric pressure between two parallel electrodes (5 cm x 2 cm) made of metalized paint deposited on alumina plates. The deposition process on both the PP and the silicon consisted of a gas flow (mixture of HMDSO and \( \text{N}_2\text{O} \) diluted in \( \text{N}_2 \)) brought between two alumina plates to continuously renew the gaseous atmosphere. A vapor source controller (Bronkhorst, Montigny-lès-Cormeilles, France) was used to deliver the necessary HMDSO flow rate at room temperature and the gas flows were regulated by means of mass flow meters. The deposition standard conditions for the \( \text{SiO}_x \) inorganic layer were 10 ppm HMDSO and 240 ppm \( \text{N}_2\text{O} \) diluted in \( \text{N}_2 \) flowing at 3.5 liters per minute. The DBD operated primarily in the homogeneous Townsend mode. This plasma regime was obtained by fixing the gas at 1 mm and inducing the discharge with an AC sinusoidal high voltage at a frequency of 2 kHz. Also investigated were filamentary discharges which were generated at the same frequency using a square wave function as the high voltage curve profile. The power dissipated in the discharge was calculated from the charge and voltage measurements and was kept constant in both discharge regimes by adjusting the voltage amplitude. The dissipated power was approximately 0.3 \( \text{W/cm}^2 \), reaching a mean deposition rate of 15 nm/min with the Atmospheric Pressure Townsend Discharge (APTD), as determined by profilometry (KLA-Tencor Alpha Step IQ Surface Profiler, Meylan, France). The deposition rate was measured by hiding a part of the sample with kapton rubber while performing a plasma deposition for 20 min, followed by a measurement of the height of the step between the naked substrate and the plasma-deposited film. Under the experimental conditions chosen here, the deposition rate was rather constant over the 2 cm-long discharge.

2.2.2 FTIR-ATR measurements

FTIR-ATR spectra were recorded using a Nicolet Nexus spectrometer equipped with a germanium-coated KBr beamsplitter and a nitrogen-cooled MCT-A detector at a spectral resolution of 4 cm\(^{-1}\) (Thermo Scientific, Courtaboeuf, France). Samples were mounted on the germanium crystal of a Veemax variable angle ATR attachment (Pike, Paris, France) for further spectrum recording with 32 scans. For comparison purposes, a transmission FTIR spectrum of a \( \text{SiO}_x\text{H}_y \) thin film deposited on a silicon wafer was also recorded using the same spectrometer. The FTIR-ATR data presented thus far resulted from the measurement of more than fifty films. For the peak height intensity ratio measurements, the spectra were corrected using a straight baseline between 980 and 1250 cm\(^{-1}\).

3 RESULTS AND DISCUSSION

Fig. 1 shows the FTIR transmission spectrum of an ATPD-deposited \( \text{SiO}_x\text{H}_y \) layer on a silicon wafer recorded with a normal angle of incidence. Despite the apparent simplicity, interpreting this spectrum was fairly complex due to the presence of several features, some of which were overlapping. In addition, most of the fundamental features were observed as two peaks due to the in-phase (ip) and out-of-phase (oop) vibrational interactions between neighboring chemical moieties. Generally speaking, oop components of a fundamental vibration occur at higher frequencies [16].
Accordingly, the most intense peak of the SiO$_x$H$_y$ infrared spectrum located at 1070 cm$^{-1}$ was assigned to the in-phase asymmetric stretching vibrational mode of the neighboring SiO$_2$ moieties (-O-Si-O-). Its out-of-phase counterpart was located in the shoulder left of the 1070 cm$^{-1}$ main feature and is generally observed near 1210 cm$^{-1}$ [16], while the broad feature at 920 cm$^{-1}$ is generally assigned to Si-O-(H) spectral mode vibration [26]. Again, the relatively important bandwidth of this infrared peak indicates the occurrence of both in-phase and out-of-phase features behind this spectral component. Finally, the ip and oop components of the symmetric SiO$_2$ bending vibrational mode were fairly well resolved and were observed at 790 cm$^{-1}$ and 814 cm$^{-1}$, respectively [16].

In normal incidence transmission infrared spectroscopy, the electric field of the infrared radiation is exclusively oriented parallel to the sample plane, enabling a probe of the vibration of SiO groups (referred to as transverse optical (TO) components) lying in the sample plane [14].

Using an ATR attachment to study thin films calls for a cautious analysis of the resulting infrared spectra, for two fundamental reasons. First, the inherent angle between the infrared beam and the sample provides a longitudinal (perpendicular to the sample normal) component in the electric field of the incident light [14]. For SiO$_x$H$_y$ thin films, this implies that the SiO bonds (or more precisely, their dipolar moments) oriented perpendicularly to the sample plane can be excited by the infrared radiation, which enables the probing of the LO modes. In the past, an infrared analysis of thin layers with a light incidence different than 90° was used to somewhat characterize the order within these samples, with a theoretical and perfectly ordered film considered as having all the dipolar moments of its chemical groups lying in the sample plane and thus exclusively producing TO modes. While this observation was shown to be very useful in analyzing thin film molecular organization [20], it also added significant complexity to the overall infrared spectrum, as each of the so-called in-phase and out-of-phase TO vibrational modes observed for normal light of incidence had its LO counterpart when the light incidence was different than 90° [16].

Second, ATR infrared spectra of thin films are also influenced by light reflection on the deposition substrate. For samples thinner than the ATR sampling depth and deposited on partly reflective substrates, the evanescent wave is partially reflected by the substrate. In this case, the electric field component of the incident light lying in the sample plane is – at least partially – cancelled by that of the reflected beam, while the incident and reflected electric fields perpendicular to the sample plane add up [14]. From an FTIR-ATR spectroscopy point of view, this leads to a decrease in the intensity of the TO vibrational features with a concomitant increase of the LO peak intensity.
Fig. 2 depicts the effect of the infrared light angle of incidence and light reflection on the deposition substrate, which required that we consider the ATR sampling depth (dp determined through the Harrick’s equation) and the evanescent wave intensity decay (defined through a classical exponential decay function) [27]. This drawing was adapted to the ATR spectral recording mode from previous observations made by Dupont et al. while attempting to describe the FTIR reflection spectra of thin films [14].

For the layers deposited on non-reflective PP, the spectral modifications with respect to the transmission spectra were only related to the light angle of incidence. As seen in Fig. 2a, the signal recorded in the ATR spectra of very thin films (75 nm in this case) arose from the entire sample and included the film/PP interface. When samples thicker than the sampling depth (ST > dp; typically, 1000 nm for a 30° angle of incidence at 1000 cm⁻¹, Fig. 2b) were deposited on low refractive index substrates, most of the signal came from the air/film interface, with no contribution from the film substrate interface. In both cases, the recorded FTIR-ATR spectra resulted from the interaction of both the parallel and the perpendicular component of the incident electric field (E1). As a result, FTIR-ATR may be used to probe thin film molecular order as a function of the distance from the substrate/film interface.

The situation was significantly different when layers were deposited on partially reflective Si. As depicted in Fig. 2c, the effect of the reflection of the evanescent wave (E2) on the reflective substrate was added to that of the infrared light angle of incidence for layers thinner than the sampling depth (ST < dp), subsequently decreasing the TO and increasing the spectral intensity of the LO features, as E2∥r partially cancels E2∥i while E2⊥r adds up to E2⊥i. Because of the evanescent wave decay, the partial extinguishing of the TO component and the LO feature intensity increase is likely to be observed up to ST = dp. In theory, light reflection by the substrate has no more influence on the shape of the FTIR-ATR spectrum (because the infrared light indeed does not reach the substrate).
when ST becomes larger than $d_p$, and therefore gives rise to the situation depicted in Fig. 2b. In practice, TO mode extinction and LO feature enhancement occurred for film thicknesses of $ST < d_p$, as $E2r$ appeared to be considerably lower than was $E2i$, as schematically depicted in the offset of Fig. 2c.

Fig. 3 highlights these two phenomena. Fig. 3b displays the FTIR-ATR spectrum recorded at a $30^\circ$ angle of incidence by a SiO$_x$H$_y$ thin layer deposited for 5 min (sample thickness approximately 75 nm) on polypropylene (PP). Of note is that the refractive index of PP (1.49) was somewhat identical to that of the deposited layer (1.46) and accordingly, the evanescent wave penetrated through the PP substrate once it had crossed the SiO$_x$H$_y$ thin layer, with almost no reflection. A comparison of the spectrum in Fig. 3b with a normal incidence infrared spectrum (Fig. 3a) shows the effect of the angle light incidence on the so-called intensity of the TO and LO vibrational modes. Indeed, the spectrum shown in Fig. 3b clearly exhibited a significant increase in the intensity of the shoulder located left of the main infrared feature at 1070 cm$^{-1}$. This was due to the appearance of an LO vibrational mode, generally observed near 1160 cm$^{-1}$ (out-of-phase) associated with the TO mode at 1210 cm$^{-1}$ [16]. Although difficult to detect (this feature is further evidenced later) a very small band occurred at 1275 cm$^{-1}$, which was assigned as being the LO mode (in-phase) associated with the 1070 cm$^{-1}$ TO mode [16].

![Figure 3](image)

**Figure 3.** (a) FTIR transmission spectrum of a SiO$_x$H$_y$ thin layer deposited by DBD on a silicon wafer; (b) FTIR-ATR spectrum of a 75 nm-thick SiO$_x$H$_y$ layer deposited on polypropylene recorded with a $30^\circ$ angle of incidence; (c) FTIR-ATR spectrum of a 75 nm-thick SiO$_x$H$_y$ layer deposited on silicon recorded with a $30^\circ$ angle of incidence.

Fig. 3c exhibits the infrared spectrum of a SiO$_x$H$_y$ thin layer deposited for 5 min on a silicon wafer (Si). Here, the refractive index of Si was 3.4, meaning that the light crossing the SiO$_x$H$_y$ thin layer was partially reflected by the silicon substrate, therefore theoretically leading to a partial extinguishing of the TO vibrational modes along with a concomitant increase of the intensity of the LO features, as observed by the increase of the LO/TO mode intensity ratios. This was particularly evident upon analysis of the spectrum in Fig. 3c, which exhibited a very broad feature spanning from 1000 to 1250 cm$^{-1}$. This wide, featureless band shape was likely the result of the decrease of the 1070 and 1210 cm$^{-1}$ TO modes, with intensities becoming similar to that of the 1160 cm$^{-1}$ LO mode. Of interest is that the so-called 1275 cm$^{-1}$ feature, hardly detectable in the spectrum of the SiO$_x$H$_y$
film deposited on the PP, became clearly evidenced when the film was deposited on silicon due to the combination of the “angle of incidence” and the “reflection” effects.

It must be emphasized here that the 1275 cm$^{-1}$ peak has at times been assigned to the Si-(CH$_3$)$_x$ stretching mode vibration in the spectra of plasma-deposited films made with HMDSO as the precursor [22] and has been attributed to the presence of residual carbon within the layer structure. However, this assignment was ruled out in the present study, as no such feature was observed in the FTIR transmission spectra of the SiO$_x$H$_y$ layers recorded at a normal angle of incidence (Fig. 3a). In addition, previously published XPS data on coatings deposited under similar conditions concluded to the absence of carbon [25].

The observations of the spectra in Fig. 3 thus have serious implications when attempting to interpret SiOxHy or any other thin film molecular organization by FTIR-ATR spectroscopy. For instance, the analysis must consider light reflection on the substrate as well as the ATR sampling depth.

Fig. 4a shows the FTIR-ATR spectra measured at 30° of light incidence of SiO$_x$H$_y$ layers of various thicknesses (from 75 to 600 nm) deposited on PP, along with a transmission spectrum provided as reference. Compared to the SiO$_x$H$_y$ transmission spectra, the LO component located near 1160 cm$^{-1}$ clearly emerged from the spectrum of the 75 nm film and gradually decreased with the increase in film thickness. This qualitative observation is supported by data presented in Fig. 4c, which show the relationship between the $A_{1160}/A_{1070}$ intensity ratio and the SiO$_x$H$_y$ film thickness. As can be seen in this figure, the band intensity ratio decreased with the film thickness, therefore indicating that the film molecular order was low near the substrate/film interface and increased as the film deposition process went on.

![Figure 4](image_url)

Figure 4. (a) FTIR-ATR spectra of SiO$_x$H$_y$ thin films of various thicknesses deposited on polypropylene; (b) FTIR-ATR spectra of SiO$_x$H$_y$ thin films of various thicknesses deposited on silicon; (c) $A_{1160}/A_{1070}$ peak height intensity ratio as a function of the SiO$_x$H$_y$ layer thickness deposited on polypropylene (○) and silicon (●). All spectra were recorded at a 30° angle of incidence.
The significance of such an analysis is quite difficult when the layers were deposited on silicon because the so-called “reflection” effect gradually decreased with sample thickness, due to the exponential evanescent wave intensity decay. In other words, the film molecular disorder was somewhat overestimated for thin layers because of the more significant partial extinction of the TO vibrational modes. For example, at an incidence angle of 30° and a frequency of 1100 cm⁻¹, simple calculations enabled us to determine that 90% of the incident evanescent wave intensity reached the Si substrate after crossing a 100 nm thin film, while this value dropped to approximately 55% when a 600 nm layer was used.

This behavior is clearly evidenced in Fig. 4b, which presents the FTIR-ATR spectra of SiO₂Hₓ layers of various thicknesses deposited on Si. As mentioned above, for thin films (below 100 nm), the SiO₂Hₓ film gave rise to a broad, featureless infrared spectrum most likely caused by a concomitant decrease in intensity of TO modes due to the “reflection” and the appearance of LO modes. This statement is further supported by the appearance of the low intensity feature at 1275 cm⁻¹ which was the LO mode associated with the 1070 cm⁻¹ TO mode. With increased film thickness, the spectra gradually returned to a shape similar to that of the SiO₂Hₓ transmission yet remained somewhat broader. In addition, the relative intensity of the 1275 cm⁻¹ feature gradually decreased with film thickness, most likely as a result of the decreased intensity of the incident evanescent wave when the film thickness was increased.

For comparison purposes, the A₁₁₆₀/A₁₀₇₀ peak height intensity ratio is also reported in Fig. 4c. These data clearly show that the disorder within the SiO₂Hₓ thin layers was overestimated for the 100 nm-thick film because of the so-called “reflective” effect, as depicted in Fig. 2c. However, this overestimation of the thin film disorder appeared to become negligible for film thicknesses greater than 150 nm, because at this film size, the A₁₁₆₀/A₁₀₇₀ peak height intensity ratio became almost identical for the SiO₂Hₓ layers deposited on either polypropylene or silicon. This is also an indication that in practical measurement conditions, the value of E₂r is considerably lower than that of E₂i.

Overall data on the SiO₂Hₓ layers deposited on either polypropylene or silicon highlight the fact that care must be taken when analyzing the FTIR-ATR spectra of thin layers. On non-reflecting substrates, the incidence angle provided by the ATR measurements emphasizes the LO modes which can be advantageously used to characterize the order within thin layers. This so-called “angle of incidence” effect is thickness-independent and may thus provide firsthand information regarding thin film molecule organization as a function of their distance from the interface or, in other words, on film organization at various stages of its deposition.

On reflective substrates, a “reflective” effect adds up to the LO mode enhancement provided by the ATR incidence angle. Accordingly, FTIR-ATR spectra recorded on reflective substrates result in a concomitant LO mode enhancement due to the infrared beam incidence angle and a TO mode extinguishing/LO mode enhancement caused by this “reflective” effect, which is film thickness-dependent. In this context, following the molecular organization of thin films during their growth becomes virtually impossible. Nevertheless, FTIR-ATR measurements performed on thin films deposited on reflective substrates may prove to be beneficial in exacerbating molecular disorder differences in layers that are known to be almost identical in thickness.

Fig. 5 shows such an example of the usefulness of FTIR-ATR for thin film analysis and displays the spectra of SiO₂Hₓ thin films deposited on polypropylene in either homogeneous or filamentary discharge regimes, using the same discharge power, gas mixture, and deposition time. As demonstrated in previously published data, thin films deposited in homogeneous APTD discharge environments are denser than those made under filamentary conditions containing a significant amount of powders [28]. As a result, films deposited using APTD are expected to be more ordered compared to those deposited using filamentary discharge. This statement is clearly supported by the spectra shown in Fig. 5, as the homogeneously deposited film exhibited 1210 cm⁻¹ (TO) and 1160 cm⁻¹ (LO) modes of approximately the same intensity, with almost no contribution observed at 1275 cm⁻¹. In contrast, the spectrum of the SiO₂Hₓ layer deposited in a filamentary regime clearly displayed a lower 1210 cm⁻¹/1160 cm⁻¹ ratio along with the clear appearance of the 1275 cm⁻¹
These observations all converge toward the so-called “molecular disorganizing effect” produced in filamentary atmospheric plasmas.

Figure 5. FTIR-ATR spectra recorded at a 60° angle of incidence of 75 nm-thick layers of SiO\textsubscript{x}H\textsubscript{y} deposited on polypropylene in (a) a homogeneous and (b) a filamentary plasma regime.

4 CONCLUSIONS

This study clearly demonstrates the enormous potential of FTIR-ATR spectroscopy for the study of thin film molecular organization, provided that a prior comprehensive analysis is performed on the sampling depth and refractive index of the deposition substrate. On one hand, the non-orthogonal angle of incidence of the light inherent to the attenuated total reflectance sampling mode allows for the detection of longitudinal vibrational components. When both the thin film and the deposition substrate have a similar refractive index (no light reflection), monitoring thin film organization can be performed at various stages of its deposition, from substrate/film to film/air interfaces. This was demonstrated when we investigated SiO\textsubscript{x}H\textsubscript{y} layers (n = 1.46) on polypropylene substrate (n = 1.49). Data recorded from this system clearly indicate that chemical functionalities giving rise to LO vibrational features were more present near the substrate/film interface than in the bulk film. This analysis was more difficult when SiO\textsubscript{x}H\textsubscript{y} layers were deposited on silicon (n = 3.4), as the TO vibrational modes were slightly extinguished with a concomitant exaltation of the LO mode intensity, due to both the partial withdrawing between the incident and reflected electric fields components of the infrared light lying in the sample plane and the addition of those perpendicular to this sample plane. This resulted in an overestimation of the molecular disorder at the substrate/film interface up to film thicknesses of 100-150 nm, according to our data. The usefulness of FTIR-ATR to study molecular film disorder was highlighted when SiO\textsubscript{x}H\textsubscript{y} thin layers were deposited on polypropylene in either homogeneous or filamentary discharge conditions. These latter data confirm previous observations of homogeneously deposited coatings, which were more ordered than were those made under a filamentary regime. Indeed, FTIR-ATR spectra reveal that chemical moieties giving rise to LO vibrational features were more present when films were deposited in a filamentary rather than homogeneous plasma discharge.
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