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An out of the box vision over oxidative chemical vapor deposition of PEDOT involving sublimed iron trichloride

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Oxidative chemical vapor deposition (oCVD) is an efficient technique to produce highly conductive films of Poly(3,4-ethylenedioxythiophene) (PEDOT). Despite numerous studies on the oCVD of PEDOT films, there is limited information on the stability of the sublimation of solid oxidants and on their impact on the polymerization reactions. In this work, we use an *in situ* Quartz Crystal Microbalance to monitor film formation over time. Through a series of deposition experiments between 20 °C and 100 °C and for FeCl₃/EDOT molar gas ratios between 17.3 and 75.3, we analyze in detail the correlations between process parameters and film morphology, composition, surface topography and electrical conductivity on 10 cm silicon wafers. By using multiple substrates at different positions into the reactor, we demonstrate that the formation of PEDOT occurs uniformly through purely surface reactions, following step growth polymerization principles. These results pave the way towards highly conductive oCVD PEDOT films processed from convenient solid oxidants.

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most significant conductive polymers used in the growing field of organic devices. It is widely used in organic solar cells [1], organic light-emitting diodes (OLEDs) [2], and supercapacitors [3], thanks to its mechanical stability, optical transparency and high electrical conductivity in comparison to other conductive polymers [4]. Its high electrical conductivity (up to 8797 S/cm for single-crystal nanowires [5]) comes from a conjugated bond structure that permits π -orbital overlap along with the alternating double- and single-bonds in the polymer backbone [6].

Since 1990, the main route of PEDOT production has been synthesizing in liquid solution through a series of oxidation and deprotonation steps [7–9]. Vapor phase processes, mainly vapor phase polymerization (VPP) [10] and oxidative chemical vapor deposition (oCVD) [9] have been developed more recently to provide conformal coatings on complex porous substrates and to avoid the substrate-solvent incompatibility in liquid deposition processes. While the VPP process still involves a liquid step, the oCVD is a one-step purely gas phase process where the oxidant serves both to promote monomer polymerization and to subsequently oxidize the neutral polymer to form the conductive, doped polymer. Another advantage of the oCVD is better control over film thickness by varying the deposition time. In the VPP, the

polymerization stops when there is no oxidant even if EDOT is still present [11]. By sending oxidant in a controlled manner, oCVD can control the film properties with more precision. Since the introduction of oCVD PEDOT by Gleason and coworkers [9], several solid oxidants have been used to produce films of PEDOT from EDOT monomer. Among them, iron trichloride (FeCl₃) is the most studied one [9,12–14], because of its availability and relatively low toxicity [15,16]. Solid oxidants are commonly placed on a crucible in the reactor and are sublimated at a temperature between 170 °C and 350 °C. Despite the wealth of the literature on oCVD PEDOT via FeCl₃, the sublimation rate and stability over time have never been reported [9,12–14,17–24]. These two parameters are important since the sublimation rate of the oxidant allows controlling the gas phase composition and, subsequently, the film's characteristics. The unreacted excess oxidant is often found in as processed PEDOT films, requiring an additional step of post deposition rinsing to improve the electrical conductivity [25]. On the other hand, the control of the stability of the sublimation rate over time is a prerequisite for process implementation. In order to circumvent such sublimation drawbacks [26], solid oxidants have been replaced by more conveniently volatilized liquid ones, such as bromine (Br₂) [19] and later on sulfuric acid (H₂SO₄) [27], molybdenum(V) chloride (MoCl₅) [28], antimony pentachloride (SbCl₅) [29] and vanadium oxytrichloride (VOCl₃) [29–31].

Despite the advantages of liquid oxidants, there are other issues

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related to their use, such as safety, availability, oxidation efficiency, and subsequent equipment corrosion [32]. Consequently, the oCVD of PEDOT from EDOT and solid oxidants, especially FeCl_3 , remains a promising process, provided sublimation issues are settled [15,16]. This condition comes together with the need to get a better insight into the gas-phase or surface reactions involved between the oxidant and the monomer. Indeed, deposition parameters such as the FeCl_3 /EDOT ratio in the gas phase are not always detailed in the literature, and except for the substrate temperature (T_{sub}), the correlations between the deposition conditions and the film characteristics and properties are not clearly established [9,16,22,23,29,32,33]. As a result, the potential of scaling up the oCVD of PEDOT remains to be more deeply analyzed in terms of film uniformity over large areas. The first effort toward large-scale PEDOT film synthesis has been made by Kovacik et al. who developed a roll-to-roll process [23]. They obtained deposition of PEDOT on 21×33 cm pre-cleaned glass slides with a thickness deviation of 5.5 % and a conductivity variation of 10 % after a post deposition rinsing in methanol. However, they did not correlate process parameters and film uniformity. Except for one study about PEDOT synthesis by oxidative Molecular Layer Deposition [28], no *in situ* measurements of the deposited mass were published, although they could bring new insights about stability and the gas phase and surface mechanisms involved.

The objective of the present work is to extend the knowledge on the oCVD process yielding PEDOT films from EDOT and FeCl_3 by getting insight into the involved mechanisms. We *in-situ* monitor the deposition of PEDOT using a Quartz Crystal Microbalance (QCM). We analyze in detail the film uniformity over a large scale and establish correlations between key process parameters like precursors ratio and substrate temperature and film characteristics, namely thickness, roughness, morphology, chemical composition, and electrical conductivity, both in as-processed and after standard rinsing with methanol.

2. Experimental

2.1. Materials and methods

oCVD experiments were performed in a custom-built stainless steel reactor (Neyco) schematically represented in Fig. 1a. The optimal reactor geometry is reported to be a substrate-holder placed above the oxidant crucible [34]. Our reactor design is close to those reported in the literature for the oCVD of PEDOT [35], allowing qualitative comparison with reported results [36]. Over and above the conventional

design, a Quartz Crystal Microbalance (QCM) with an oscillator (INFICON STM-2) was used for the real-time monitoring of the film deposition to evaluate the mass gain on the substrate per unit time. The measurement time interval of the QCM was 0.1 s. The quartz probe was installed inside the vacuum chamber, adjacently to the substrate where the deposition is performed. AT-cut crystals with a nominal frequency of 6 MHz are used with gold electrodes as probes. The decrease in frequency is linearly correlated with the mass gain on the surface of the crystal, if the deposited layer is not viscoelastic [37]. As PEDOT is a polymeric material, this correlation may not be accurate for the present study. For this reason, we only consider QCM frequency changes for observing process stability without converting to the mass. Before each deposition experiment, it was verified that the QCM frequency remains constant under EDOT and N_2 flow. Then, the frequency change due to PEDOT deposition was monitored in real-time.

2.2. Synthesis of poly 3,4-ethylenedioxythiophene (PEDOT via oCVD

3,4-ethylenedioxythiophene (EDOT, 97 %, Sigma-Aldrich) and iron-III chloride (FeCl_3 , 97 %, Sigma-Aldrich) were used as received. PEDOT was deposited on as-received 500 μm thick Si (100) 10 cm wafers, fixed facing down at the top part of the reactor on a thermally regulated substrate holder, allowing depositions up to 150 $^\circ\text{C}$. The FeCl_3 powder was placed at the bottom of the reactor on a resistively heated open crucible (2 cm \times 2 cm \times 5 mm) and was sublimated at fixed temperatures. EDOT was placed in a glass jar whose temperature was regulated at 70 $^\circ\text{C}$ by immersion in a water bath. Nitrogen, N_2 (99.999 %, Air Liquide) flowing at 10 standard cubic centimeters (sccm) was sent just after the EDOT jar to be used as the carrier gas for the monomer. The operating pressure was fixed at 100 mTorr and was regulated by a gate valve placed at the exit of the reactor, just before a turbo molecular pump (Edwards EXT 250). The leak rate of the reactor was systematically checked before each experiment and was lower than 1 Pa/min. The duration of a deposition experiment was correlated with the exposure time, initiated by simultaneously feeding the reactor with EDOT vapors and heating the FeCl_3 crucible at a constant temperature (T_{FeCl_3}). The consumption of FeCl_3 and EDOT was systematically determined for each experiment by weighting the crucible and the jar, respectively, before and after each experiment, with a KERN ABS 320-4N balance with a precision of 0.1 mg.

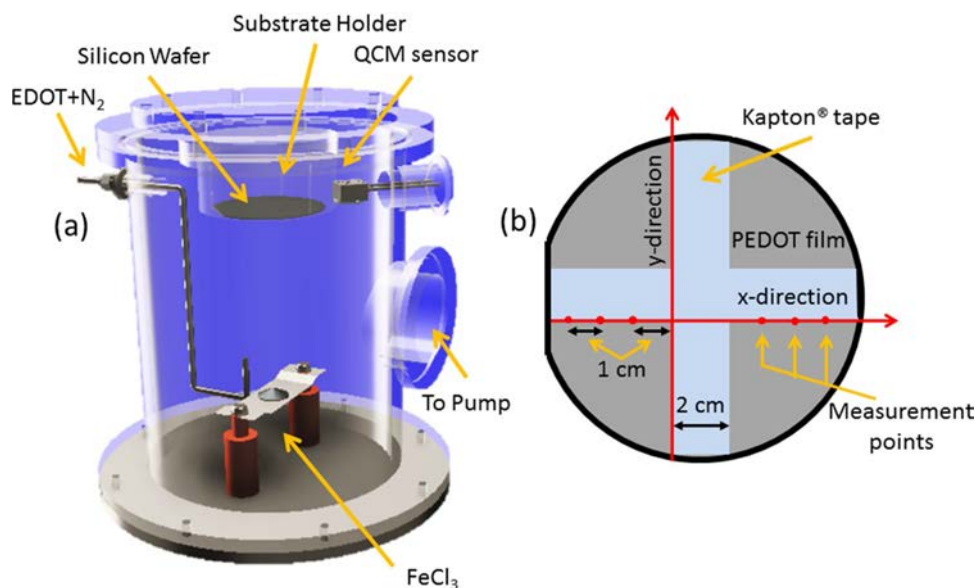


Fig. 1. Schematic illustration of (a) the oCVD reactor, (b) the substrate, depicting the areas covered by the Kapton[®] tape, and the thickness measurement points.

2.3. Film characterization techniques

The PEDOT film mass was evaluated by weighting the Si wafers, using a Sartorius R180D balance with a precision of 0.01 mg. For some experiments, immediately after the deposition, substrates were rinsed in methanol (MeOH 99.99 %, Sigma-Aldrich) for 15 min and then dried under N₂. Although MeOH is not the most efficient solvent for the present case [25], it is the most commonly used one; it is convenient, presents limited interaction with the PEDOT film and in such a way it facilitates the investigation of the process. Experiments corresponding to each set of deposition conditions were reproduced twice.

Film thickness was measured with a stylus profilometer (DektakXT) equipped with a 2 μm stylus tip radius operating under 3 mg load. Measurements were performed on consecutive 1 cm distant points, shown in Fig. 1b along both x and y-axes. Step heights were made on purpose by covering prior deposition a 2 cm large cross-zone of the substrates with a Kapton tape and then removing it. At each position, the average value of three measurements was considered revealing repeatability within ± 7 %. Optical images of film surfaces were obtained with a BX Olympus microscope. The film thickness was analyzed on cross-sections of selected samples by scanning electron microscopy (SEM) (Helios NanoLab 600i), which was also used to investigate the surface morphology from top view micrographs. The topography of the surfaces of the films was investigated by atomic force microscopy (AFM) using an Agilent Technologies AFM/STM 5500 (PicoPlus) instrument.

The film composition was analyzed using transmission Fourier transform infrared spectrometry (FTIR), performed with a PerkinElmer Spotlight 400 with 16 scans at 4 cm⁻¹ resolution. As the analyzed surface is centimetric, the spectra were acquired at the center of each quadrant formed after Kapton removal from the substrate.

Film sheet resistance, R_s [Ω/\square], was measured with a Signatone S-302-4 four-point probe station on 2.5×2.5 cm² coupons cut from the wafer substrates. A constant current of 200 nA was applied with a Keithley 6220 instrument, and the corresponding voltage was read on a Keithley 2182A one. A correction factor of 4.4516 was used in calculating the sheet resistance, as shown in Eq. (1) for cleaved samples [38], where V is the measured voltage, and I is the applied current. Untreated Si wafers systematically showed a sheet resistance of 35 ± 5 k Ω/\square , being significantly high to a void sheet resistance correction due to parallel conduction of the substrate. The conductivity (σ) of the films was evaluated from the R_s values using Eq. (2), where t is the local thickness on the film close to each resistivity measurement point. The four-point probe was systematically placed all over the films gathering sheet resistance data. Fifteen sheet resistance measurements were done on each sample. Thickness and sheet resistance profiles were overlaid to estimate the average electrical conductivity of each film.

$$R_s = 4.4516 \frac{V}{I} \quad (1)$$

$$\sigma = \frac{1}{R_s t} \quad (2)$$

3. Results and discussion

3.1. In-situ monitoring of film deposition

First, three experiments were performed in the same conditions at T_{FeCl_3} and T_{sub} equal to 175 °C and 20 °C, respectively, for three different exposure times equal to 3 min, 10 min, and 30 min, with the aim to monitor the stability of the process and the resulting characteristics and properties of the produced PEDOT films.

Table 1 presents the EDOT and FeCl₃ evaporated masses, and deposition mass, average thickness and average conductivity for the three experiments. The EDOT consumption per unit time for each deposition

experiment is constant, equal to 1.5 mg/min, expectedly, meaning a constant flow rate of the monomer. In contrast, the evaporated mass of FeCl₃ equals 87 mg for the three experiments despite the tenfold difference of the exposure times. We conclude that the oxidant mass does not change with sublimation time and the deposition might occur only during the first 3 min of each experiment. In line with these results, the mass gain of the substrates is ca. 0.1 mg, the same for the three experiments. Similarly, the measured thickness and the resulting electrical conductivity are also the same for all experiments, approximately 36 nm and 370 S/cm, respectively. During these experiments, the evolution of the QCM frequency as a function of time was also monitored. The results presented in Fig. 2a. Fig. 2b will be described in the following sections. For the three experiments, the frequency decreases during the first 3 min, revealing the film formation. Then, for the 10 min and 30 min experiments, it slowly and continuously increases.

The mass difference of both the crucible and the substrate for these three experiments concomitantly indicate a discontinuous sublimation of FeCl₃, taking place only in the first 3 min of operation. After each experiment, we observed that the FeCl₃ powder in the crucible was partly sintered and that its colour changed from dark grey to red, revealing at least partial superficial transformation [39,40]. We attribute this behavior to the high sensitivity of the FeCl₃ powder to moisture contaminations.

Despite the low leak rate of the reactor, traces of humidity contamination can be enough to superficially hydrolyze FeCl₃ at the applied sublimation temperatures, thus blocking its evaporation after a few minutes. As a result, the deposition of the film only occurs during the first 3 min, independently of the exposure time, in agreement with the mass gain of the substrate and the continuous decrease of the frequency of QCM only during the first 3 min of exposure time for the three experiments. Application of various protocol modifications with the aim to reduce the contact with air of the FeCl₃ powder during its introduction into the reactor, such as suppressing the weighing step, mixing the powder with dried silica powder, introducing it into the reactor under nitrogen flow, did not yield any improvement. The inability of a solid sublimator to deliver at a controlled rate a reproducible and stable flow of vaporized solid precursor is due to several factors such as inefficient heat and mass transfer and, as in the present case, changing specific surface area and alteration of the powdered precursor. Solutions to overcome this commonly met problem have been compiled by Vahlas et al. [41].

The increase of the QCM frequency after 3 min for runs #2 and #3 indicates a continuous mass loss during the last 7 min and 27 min, respectively with, however a smaller slope than that of the frequency decrease during the first 3 min of exposure time. Considering the presence of excess FeCl₃ on the PEDOT films as it will be presented hereafter, this desorption phenomenon could be attributed to the conversion of FeCl₃ to FeCl₂ [21,35] and to the release of gaseous by-products such as HCl or Cl₂ formed during the PEDOT polymerization in the films [28].

These results indicate that the deposition of PEDOT requires the simultaneous presence of FeCl₃ and EDOT. This situation is similar to the VPP process, for which the substrate is first coated by an active film of dried FeCl₃ and vaporized EDOT can react and produce long chains as long as enough oxidant is available on the surface to produce radicals of EDOT [11]. Subsequent exposure to EDOT in the absence of oxidant to create monomer radicals, as is the case for the last 7 and 27 min for runs #2 and #3 does not yield further polymerization. This behavior is compatible with the step growth polymerization (SGP) mechanism [42], as firstly suggested by Gleason et al. [33]. During SGP, the very first functional, i.e., radical monomer, is produced by losing one electron in the presence of the oxidant. During several stepwise reactions, two functional monomers form intermediate components that can react with another monomer molecule or with another intermediate molecule, forming a larger intermediate. These steps continue until the high polymer is obtained. If the oxidant flow rate stops, the monomer can no

Table 1

EDOT and FeCl₃ evaporated mass, film deposition mass, average thickness and average conductivity for three experiments performed at T_{FeCl₃} and T_{sub} equal to 175 °C and 20 °C, respectively, for three different exposure times equal to 3 min, 10 min and 30 min.

Run #	Total exposure time (min)	Evaporated mass of EDOT (g)	Evaporated mass of FeCl ₃ (g)	Film mass (mg)	Average thickness (nm)	Average conductivity (S/cm)
1	3	0.0047 ± 0.0002	0.0873 ± 0.0002	0.09 ± 0.02	37 ± 3	372 ± 12
2	10	0.0148 ± 0.0002	0.0872 ± 0.0003	0.09 ± 0.01	35 ± 3	371 ± 8
3	30	0.0439 ± 0.0001	0.0871 ± 0.0001	0.10 ± 0.01	36 ± 5	365 ± 10

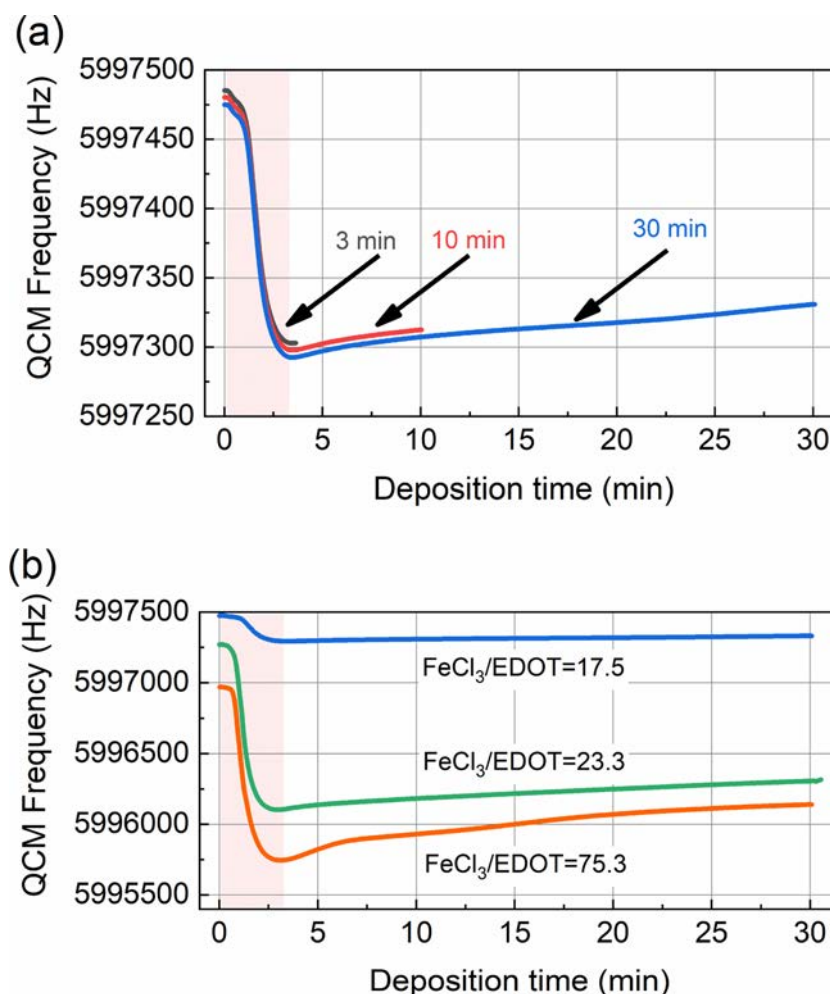


Fig. 2. (a) Evolution of the QCM frequency with the deposition time for runs #1, #2 and #3, (b) QCM response comparison for three oxidant/monomer ratios in runs #1 to #3 (T_{sub} = 20 °C).

longer transform into a functional form, and polymerization stops.

Considering an active deposition time of 3 min for runs #1, #2 and #3, the deposition rate is systematically close to 12 nm/min, much higher than that of VPP for the same exposure time [43]. The conductivity reaches 370 S/cm, in line with values reported in the literature for PEDOT oCVD from EDOT and FeCl₃ [16,21]. It is worth recalling that, in our experiments, the deposition conditions were optimized neither in terms of reactants ratio nor in terms of T_{sub} with the aim to increase the conductivity of the films.

3.2. Film uniformity and deposition mechanism

In order to get insight into the PEDOT deposition mechanisms, an experiment was conducted involving eleven 2 × 2 cm² Si coupons fixed vertically on a scaffold structure into the reactor, as illustrated in Fig. 3. One-third of each coupon was covered by Kapton tape in order to measure the deposition thickness by profilometry. A Si wafer and clean

quartz were also placed on the substrate holder and the microbalance, respectively, as usual in order to compare with the produced film on coupons. T_{FeCl₃} and T_{sub} were fixed at 175 °C and 20 °C, respectively. The average thickness measured on each coupon is also presented in Fig. 3. The eleven values vary between 35 ± 7 and 39 ± 6 nm, to be compared with 36 ± 6 nm on the Si wafer, indicating uniform deposition all over the reactor. On top of that, the thickness measurement over the quartz surface showed the same thickness of 36 ± 7 nm.

Considering that the total pressure is very low, the gaseous diffusivity is high, and the oxidant and EDOT concentrations are identical everywhere into the reactor, provided there is no gas phase reaction. No solid residues were found in the reactor witnessing gas phase reactions. Having similar thickness on eleven coupons means that the deposition rate is identical for all of them on the scaffold even if the residence time to reach each coupon is different. This could indicate that the deposition mechanisms of PEDOT on the surface of the substrates occurs through heterogeneous (surface) reactions and no intermediate species

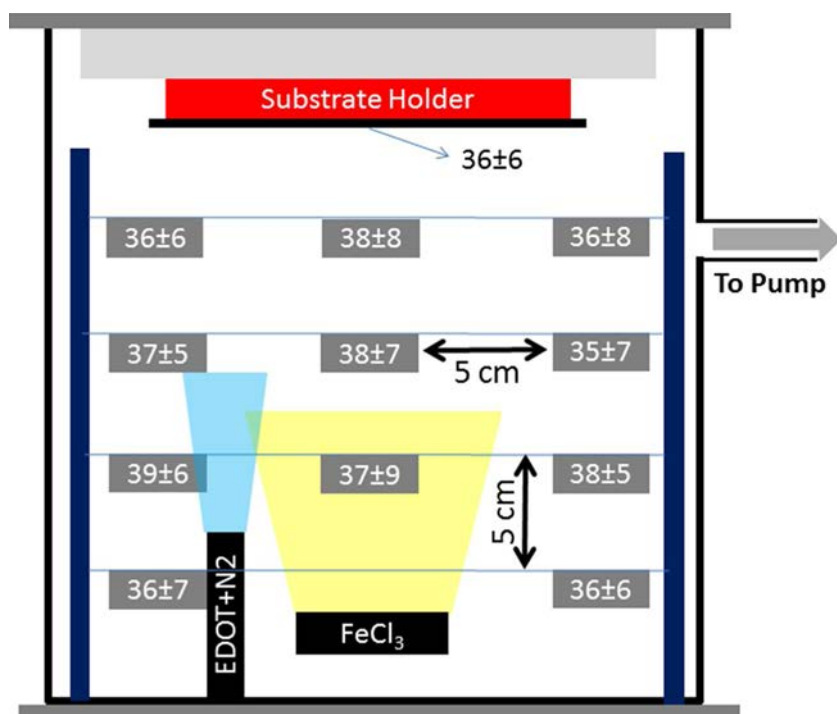


Fig. 3. Schematic view of the Si coupons placed on a scaffold into the oCVD reactor. The average thickness (in nm) of the deposited PEDOT on each sample is also reported.

are involved.

Resistivity analysis of samples showed a similar electrical conductivity of 370 ± 15 S/cm for all samples. Both values of the electrical conductivity and the thickness are very close to the ones reported in Table 1 for the deposition on Si wafers, indicating the reproducibility of the deposition process.

3.3. $FeCl_3/EDOT$ ratio

Since the surface reactions leading to the formation of PEDOT involve both the oxidant and the monomer, it is important to analyze the influence of their ratio on the characteristics and properties of the films. We investigated this parameter by performing three experiments in nominal conditions at $T_{sub} = 20$ °C for 30 min, with T_{FeCl_3} equal 175 °C, 200 °C, and 240 °C. EDOT flow rate was kept at 1.5 mg/min. Fig. 2b presents the QCM frequency response for the three experiments. The frequency systematically decreases during the first 3 min indicating film deposition only during this period. The increase of T_{FeCl_3} has no effect on the duration of the sublimation of $FeCl_3$. In contrast, increasing the inlet $FeCl_3/EDOT$ ratio results in a stronger decrease of the QCM frequency, revealing higher deposition rates.

Again, after 3 min, the frequency increases, suggesting desorption of gaseous products from the surface. Desorption is higher when T_{FeCl_3} and consequently the $FeCl_3/EDOT$ ratio are higher, suggesting that a higher concentration of $FeCl_3$ in the gas phase provides the surface with a larger amount of iron unreacted compounds.

Table 2 presents the evaporated mass of the two reactants. Based on

the vaporization behavior of $FeCl_3$ observed in Fig. 2b, the reported $FeCl_3/EDOT$ molar ratio in the inlet gas was calculated by dividing by ten the mass of EDOT in order to consider the same vaporization time of 3 min for the monomer and the oxidant.

The film thickness profiles measured by profilometry locally in the x-direction along the wafer diameter on each substrate are presented in Fig. 4a as a function of the $FeCl_3/EDOT$ ratio. The effect of the rinsing step, often proposed in the literature to remove solid oxidant by-products from the film, is also presented. We observe that the average thickness of the as processed PEDOT films increases with the $FeCl_3/EDOT$ ratio from 36 nm to 261 nm for ratios of 17.5 and 75.3, respectively. After rinsing, the corresponding thicknesses slightly decrease to 33 nm and 248 nm, revealing a minor effect of rinsing. The same evolution is observed in the y-direction on the substrate. The thickness standard deviation on the substrate is 5 % for $FeCl_3/EDOT$ ratio of 17.5, indicating a satisfactory uniformity all over the surface of 10 cm wafers. It is moderately degraded by increasing the $FeCl_3/EDOT$ ratio to reach 14 % for the ratio of 75.3. The good uniformity observed on the 10 cm substrate for the lowest ratio confirms the results obtained in the previous section about the gas-phase concentration uniformity and surfacic deposition mechanisms.

Fig. 4b details the influence of the $FeCl_3/EDOT$ ratio on the average film thickness and mass on each substrate before and after rinsing. The film thickness increases from 36 nm to 265 nm, with the oxidant/monomer ratio. Similar behavior was observed in the literature for PEDOT films deposited at low substrate temperature [16]. The deposited mass also increases, but with decreasing slope at higher $FeCl_3/EDOT$

Table 2

Evaporated mass of EDOT and $FeCl_3$ during three deposition experiments performed during 30 min at $T_{sub} = 20$ °C. Each experiment was performed at different T_{FeCl_3} .

Run #	$FeCl_3$ temperature (°C)	Evaporated EDOT mass in 30 min (g)	Evaporated $FeCl_3$ mass in 30 min (g)	$FeCl_3/EDOT$ molar ratio
3	175	0.0439 ± 0.0001	0.0871 ± 0.0001	17.5
4	200	0.0442 ± 0.0002	0.1168 ± 0.0002	23.3
5	240	0.0441 ± 0.0001	0.3782 ± 0.0002	75.3

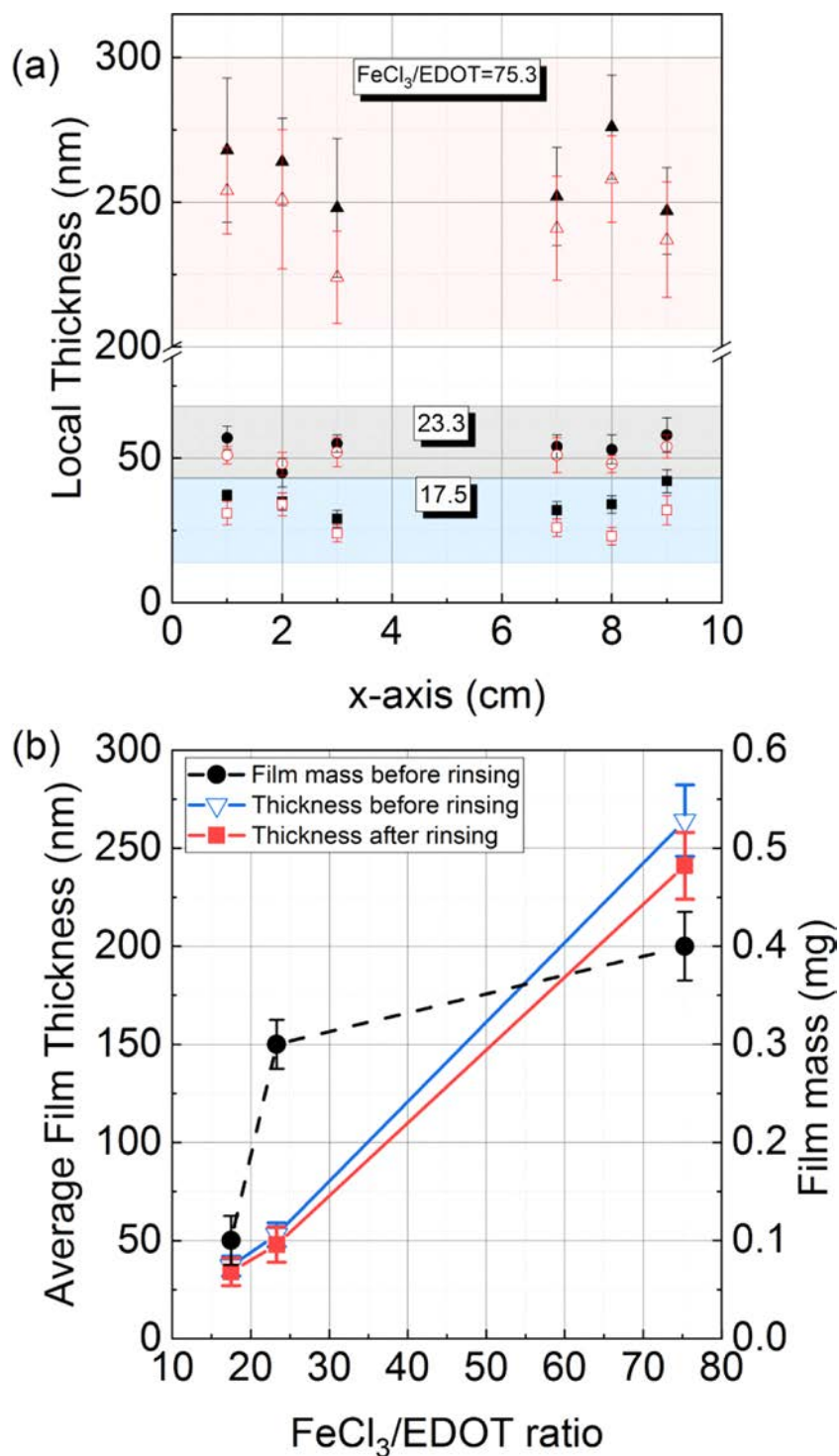


Fig. 4. (a) Thickness profiles measured on the substrates in the x-direction for the three FeCl₃/EDOT ratios before (full symbols) and after (empty symbols) rinsing. (b) Influence of the FeCl₃/EDOT ratio on deposition mass before rinsing and thickness evolution before (blue) and after (red) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

values. As a result, the apparent density decreases from approximately 850 kg/m³ for the FeCl₃/EDOT ratios of 17.5 and 23.3 to reach 250 kg/m³ for the ratio of 75.3. The former value is similar to reported ones for VPP PEDOT [11] and PEDOT:PSS [44]. These values are the first apparent densities determined for oCVD PEDOT. We attribute the decrease of the density with increasing the oxidant to monomer ratio to the evolution of the composition and/or to the increase of the porosity of the films. Indeed, due to its negligible vapor pressure at $T_{\text{sub}} = 20$ °C, gaseous FeCl₃ can be easily condensed on the surfaces since its partial

pressure in the adopted sublimation conditions largely exceeds its saturated vapor pressure near the substrate.

The surface morphology of the films before rinsing is shown in Fig. 5 from SEM images at two different magnifications.

It can be seen that the surface morphology of PEDOT films is highly dependent on the FeCl₃/EDOT ratio. For the lowest ratio tested, at low magnification (Fig. 5a), two distinct regions can be observed: a continuous dark zone on which brighter micronic nodules are present. Fig. 5b shows that these bright zones exhibit a needle-like structure,

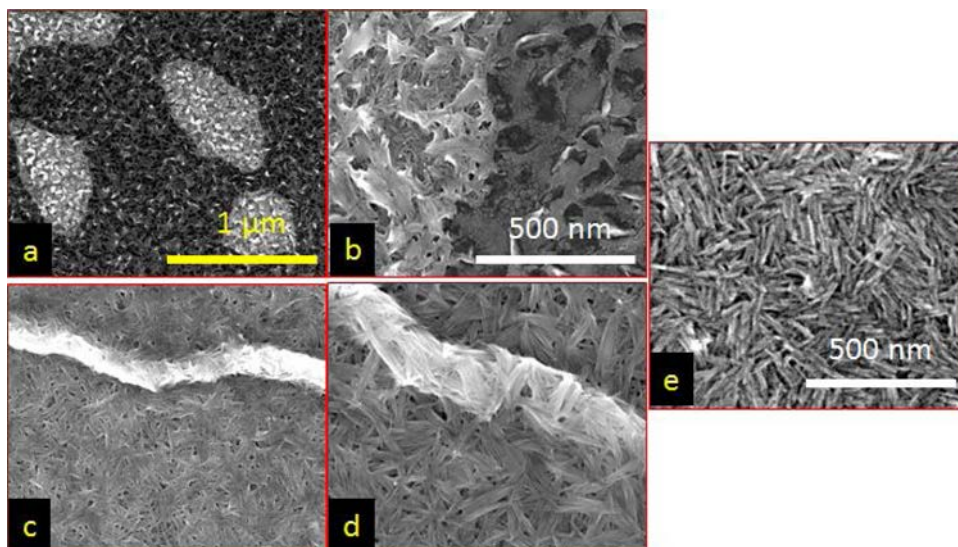


Fig. 5. SEM surface micrographs of as processed PEDOT films deposited at $T_{\text{sub}} = 20\text{ }^{\circ}\text{C}$ at $\text{FeCl}_3/\text{EDOT}$ ratios 17.5 (a, b) and 75.3 (c, d). A surface micrograph of a FeCl_3 film condensed on the Si wafer in absence of EDOT is shown for comparison (e). The scale for (a and c) is $1\text{ }\mu\text{m}$ while it is 500 nm for (b, d and e).

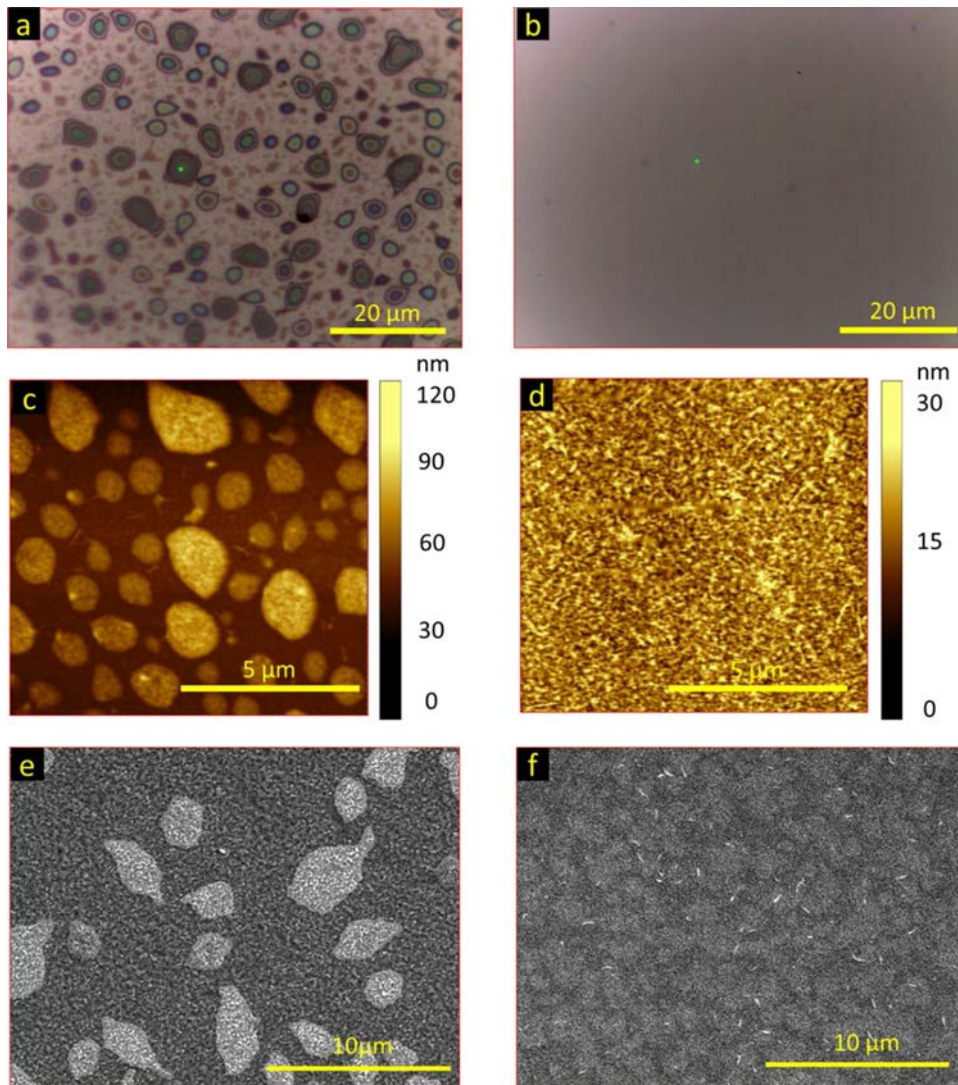


Fig. 6. Optical microscopy images (a, b), AFM surface micrographs (c, d) and SEM surface micrographs (e, f) of PEDOT films processed at $T_{\text{sub}} = 20\text{ }^{\circ}\text{C}$ and $\text{FeCl}_3/\text{EDOT}$ ratio of 17.5 (run #3). The left and right columns correspond to as processed and to rinsed samples, respectively.

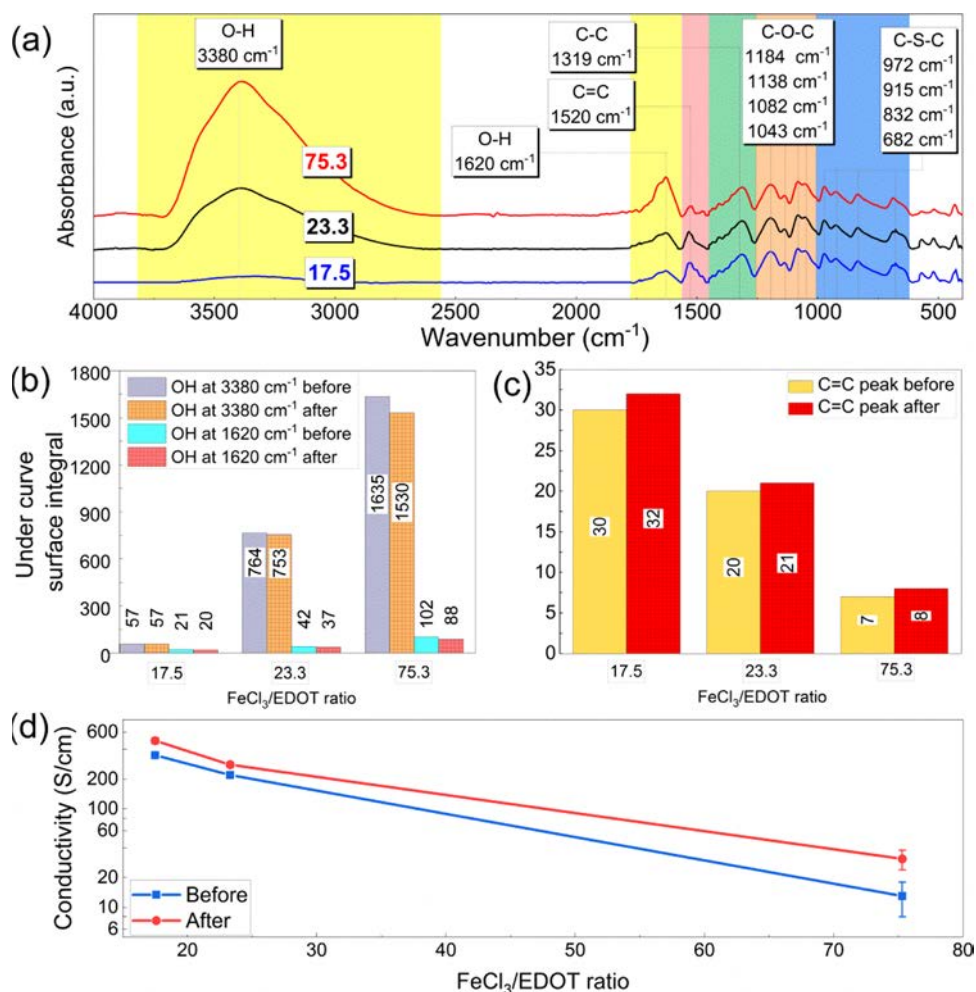


Fig. 7. For the three investigated FeCl₃/EDOT ratios, (a) FTIR spectra of PEDOT films after rinsing. (b) Under curve surfaces of OH peaks at 1620 and 3380 cm⁻¹ before and after rinsing. (c) Under curve surfaces of the C = C peak at 1520 cm⁻¹ before and after rinsing. (d) Evolution of the electrical conductivity before and after rinsing.

whereas dark zones are more continuous with some pores. The morphology of films processed at the intermediate FeCl₃/EDOT ratio is similar, with smaller and more numerous bright islands (not presented). At the highest ratio, (Fig. 5c and d), the morphology is different, more uniform with a localized presence of bright lines which seems to be cracks or creases (fold). For comparison, Fig. 5e presents the surface of a FeCl₃ film condensed on the Si surface upon sublimation in the same conditions as in run #5 ($T_{\text{FeCl}_3} = 240$ °C) without EDOT flux. This morphology, made of tangles of needles, is close to that of Fig. 5c and d, and to the bright zones in Fig. 5a and b. This similarity indicates the systematic presence of unreacted FeCl₃ or derivatives on the surface of PEDOT films. Zuber et al. found that in the PEDOT VPP process from Fe (III) tosylate, the oxidant reacting with water could form crystallites which are non active for polymerization [45]. In the presence of EDOT, the needles seem more significant, as if PEDOT coated the needles or grew from or around them. Fig. 6 presents optical, AFM, and SEM surface micrographs, before and after rinsing, of a film obtained for the lowest FeCl₃/EDOT ratio (17.5). The bright nodules observed by SEM are also shown on the optical micrographs (Fig. 6a) and AFM topography images (Fig. 6c). On optical micrographs, they exhibit various colors in contrast to the continuous background phase (dark zone on SEM), with shimmer effects on the edges of the domains, characteristic of thickness variations of thin films. The thickness difference between the continuous dark phase and micronic nodules is confirmed by the AFM topography image, where the height of the nodules above the continuous phase is approximately 80 nm. It is interesting to note that

these nodules are removed during the rinsing step (Fig. 6b and d), leading to a flatter surface with more uniform morphology, as shown in SEM images in Fig. 6e and f. These nodules were not detected during thickness determination by profilometry experiments operating in contact mode, probably due to the non-cohesive or viscous behavior of the matter in these domains. Indeed, during profilometry measurements, the stylus passed through these iron-containing islands and the reported values for the thickness only concern the continuous film of PEDOT. In contrast, AFM operating in tapping mode does not deform the surface topography of such samples and allows measuring the thickness over such Fe-rich islands without any deposition modification.

As the saturated vapor pressure of FeCl₃ at 20 °C is very low [46], the excess FeCl₃; i.e., not participating in the formation of PEDOT, could condensate on the film during its deposition and partly decompose into sub-chlorides which, in turn, could be hydrolyzed to iron hydroxides upon exposure to air. These results indicate that the investigated FeCl₃/EDOT ratios are systematically larger than the optimum one resulting in films with the highest electrical conductivity and lowest impurities.

Fig. 7a shows the FTIR spectra of the PEDOT films after rinsing, normalized to the C–O–C peak at 1082 cm⁻¹. Vibrations are observed at 1520, 1319, 1184, 1138, 1082, 1043, 972, 915, 832 and 682 cm⁻¹. Those at 1520 and 1319 cm⁻¹ are assigned to the asymmetric stretching mode of C=C and intra-ring stretching mode of C–C in the thiophene ring, respectively. The ones at 1184, 1138, 1082, and 1043

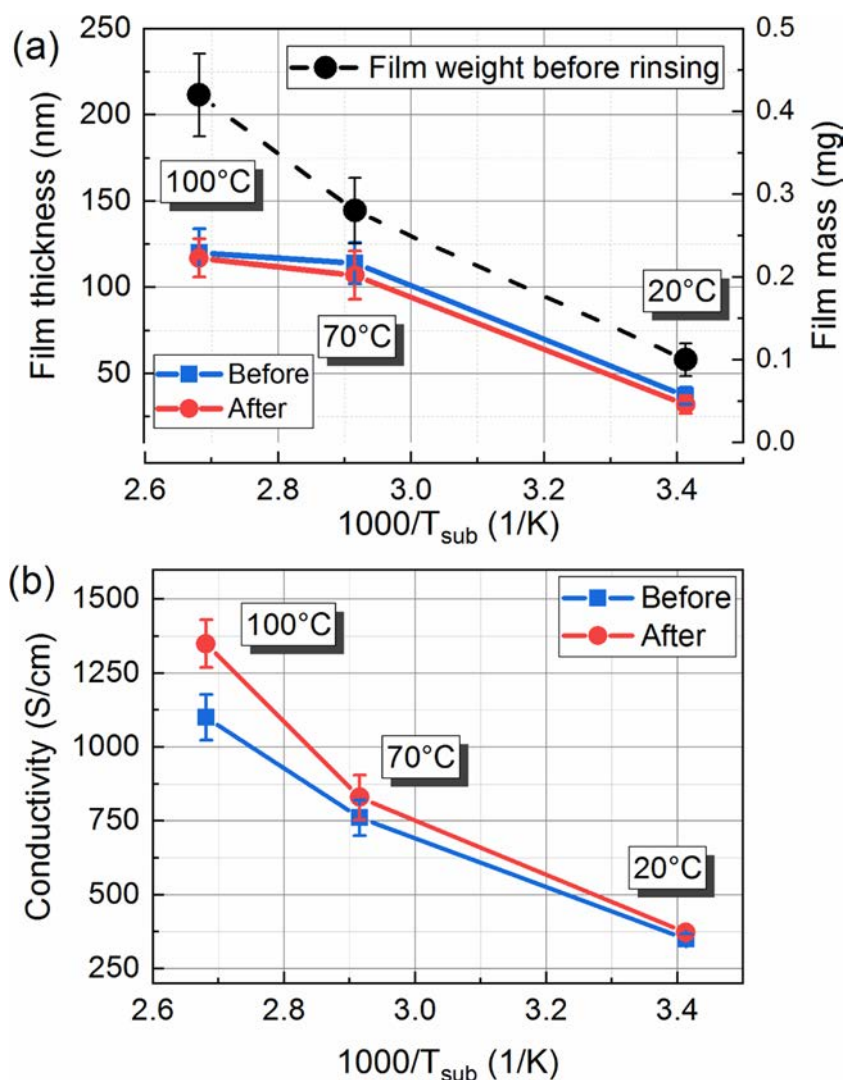


Fig. 8. Evolution of the deposition rate (a) and the electrical conductivity (b) as a function of T_{sub} .

cm^{-1} are attributed to the C–O–C bending vibration in ethylenedioxy group, while those at 972, 915, 832, and 674 cm^{-1} are characteristic peaks of stretching vibrations of the C–S bond in thiophene ring, which confirms the successful formation of PEDOT [47–49]. The C–H vibration at 3100 cm^{-1} reported in the monomer spectrum disappears in the spectra of the polymer, confirming the successful polymerization of the EDOT molecules. Vibrations at 3380 and 1620 cm^{-1} are commonly associated with OH bonds in the film [50]. The observed peaks correspond to previously published data for PEDOT [13] and confirm the formation of PEDOT for all investigated conditions.

Most of the PEDOT peaks do not demonstrate any change in relative intensity with the $\text{FeCl}_3/\text{EDOT}$ ratio, except for the ones at 3380, 1620 cm^{-1} corresponding to OH bonds and at 1520 cm^{-1} corresponding to the asymmetric stretching mode of C=C. We found no significant difference in the FTIR spectra after rinsing. Fig. 7b and Fig. 7c highlight the areas under the peaks at 3380 and 1620 cm^{-1} (left) and 1520 cm^{-1} (right) for non-rinsed samples. The under peak area of the C=C stretching mode at 1520 cm^{-1} decreases from 30 to 7 with increasing the $\text{FeCl}_3/\text{EDOT}$ ratio from 17.5 to 75.3. For the 3380 and 1620 cm^{-1} peaks, these areas increase with increasing the $\text{FeCl}_3/\text{EDOT}$ ratio before and after rinsing while the area decreases for the stretch peak at 1520 cm^{-1} . Together, they suggest less iron oxide products for the sample with the ratio of 17.5 and the presence of more C=C bonds in the back chain, respectively.

The OH bond peaks may be attributed to the hygroscopic nature of iron (sub-)chlorides, resulting in the formation of, e.g., $\text{Fe}(\text{OH})_2$ or Fe_2O_3 , which have already been observed in such films [51]. Indeed, unreacted FeCl_3 may be present on the surface of the films for the highest $\text{FeCl}_3/\text{EDOT}$ ratios tested, which leads to the formation of larger amounts of iron oxides. This confirms the interpretation of the AFM results for run #3, where iron-containing islands were formed over the PEDOT film. Interestingly, the corresponding two peaks at 3380 and 1620 cm^{-1} present slightly lower intensities after rinsing in MeOH, suggesting that iron-containing species are not wiped out entirely and can still absorb humidity. This result confirms that MeOH is not optimal in removing these undesired products, in agreement with the dedicated work by Howden et al. [25]. It also shows that it is necessary to optimize the deposition conditions in order to minimize the condensation of excess FeCl_3 and, consequently, to avoid the post deposition rinsing step.

Fig. 7d presents the evolution of the electrical conductivity of the films as a function of the $\text{FeCl}_3/\text{EDOT}$ ratio, before and after rinsing. A small improvement of conductivity is observed after rinsing, in agreement with previously reported results [9,22,25]. It is correlated to a small increase in the under peak area of the C=C bond after rinsing. This improvement of the conductivity could also be due to the partial removal of iron byproducts. Increasing the $\text{FeCl}_3/\text{EDOT}$ ratio from 17.5 to 75.3 results in a decrease of the conductivity from 500 to 12 S/cm

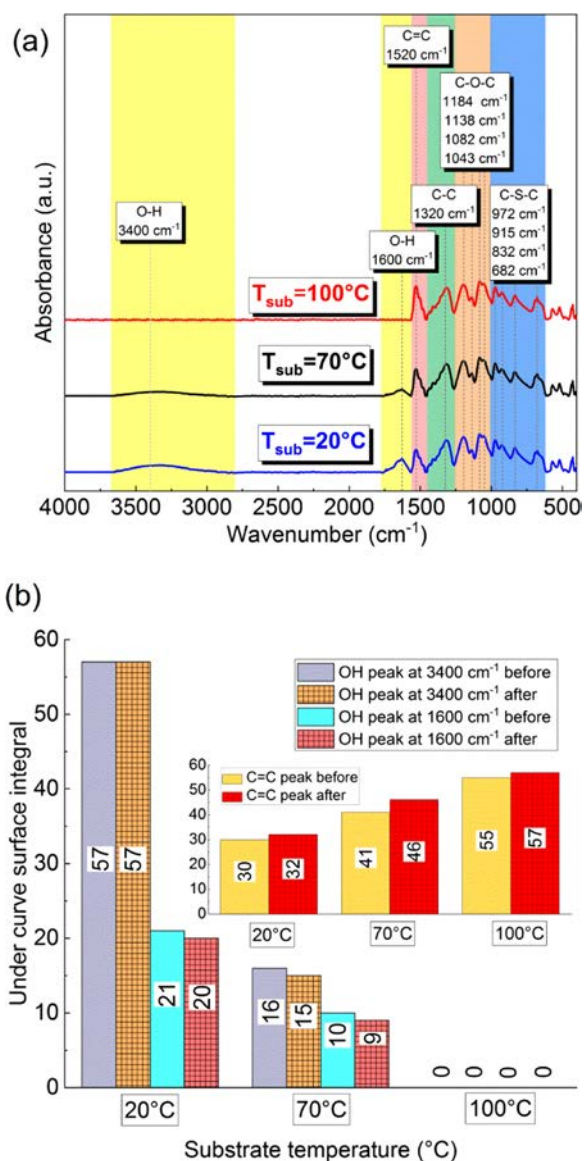


Fig. 9. (a) FTIR spectra of PEDOT films as a function of T_{sub} after rinsing, (b) Comparison of under curve surfaces of OH and C = C peaks before and after rinsing.

after rinsing. This demonstrates that the $\text{FeCl}_3/\text{EDOT}$ ratio is a key parameter to optimize the film conductivity.

Fig. 7c shows that the intensity of the C=C peak at 1520 cm^{-1} decreases by increasing the $\text{FeCl}_3/\text{EDOT}$ ratio. The charge transfer in conductive polymers can be a function of several parameters, including polymer chain length, crystallinity, polymer conjugation length and impurities [4]. It has been reported that the intensity of the C=C peak at 1520 cm^{-1} on the FTIR spectra increases with increasing the conjugation length of PEDOT [13] and that such an increase enhances the electrical conductivity of conductive polymers [52]. Our conductivity measurements are in agreement with the conjugation length decrease. Zhao et al. reported a similar trend using direct polymerization of PEDOT, namely an increase of the conjugation length by reducing the $\text{FeCl}_3/\text{EDOT}$ ratio [53]. For the same T_{sub} and total pressure, sending 3 sccm of EDOT and sublimating the oxidant at $320\text{ }^\circ\text{C}$, Im and Gleason reported a conductivity of 0.05 S/cm after rinsing in methanol [13]. This lower value, in comparison with the present results, is indeed attributed to the larger excess of FeCl_3 in their case.

It should be pointed out that the conductivity variations observed in our study are limited within one decade, to be compared with reported

results on PEDOT films spanning within five decades. This might be due to the small range of the investigated $\text{FeCl}_3/\text{EDOT}$ ratio. Taking into account the previously presented uncertainties of the thickness measurements, this relative stability highlights the robustness of the oCVD process for the production of conductive PEDOT films.

3.4. Substrate temperature

The parametric investigation of the oCVD of PEDOT films is mainly focused on the variation of T_{sub} [9,16,22,23,29,32,33]. For example, Im et al. [14] reported that increasing T_{sub} from $15\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$ allows increasing the electrical conductivity of the film from 1 S/cm to 350 S/cm . They associated this improvement to the longer conjugation length and the higher doping level of the films processed at high T_{sub} [13,14]. Drewelow et al. recently observed the same trend reaching conductivities at $T_{\text{sub}} = 100\text{ }^\circ\text{C}$ as high as 2440 S/cm when applying a multi-step post deposition rinsing and drying protocol [16].

Three T_{sub} of $20\text{ }^\circ\text{C}$, $70\text{ }^\circ\text{C}$ and $100\text{ }^\circ\text{C}$ were studied for T_{FeCl_3} equal to $175\text{ }^\circ\text{C}$. Fig. 8a presents the obtained average film thickness and mass both film thickness and mass increase with T_{sub} . This trend is somehow contrary to the overall observation by Drewelow et al., who operated at 8 mTorr [16]. The authors attributed the observed behavior to the higher vapor pressure of FeCl_3 near the substrate at higher T_{sub} , which became higher than their FeCl_3 partial pressure, with subsequent limited surface adsorption. In our case, the total pressure is higher (100 mTorr), leading to partial pressures of FeCl_3 near the substrate high enough to exceed the saturated vapor pressure of FeCl_3 even at $100\text{ }^\circ\text{C}$, thus suppressing any limitation of surface adsorption. The deposition rate is seemingly reaction-rate limited between 20 and $70\text{ }^\circ\text{C}$, as T_{sub} controls it. Again, a slight decrease in thickness is observed after rinsing. The film's apparent density increases from 850 kg/m^3 at $20\text{ }^\circ\text{C}$ to 910 kg/m^3 and 1000 kg/m^3 by heating the substrate respectively at $70\text{ }^\circ\text{C}$ and $100\text{ }^\circ\text{C}$. This could indicate that the porosity of the films decreases when T_{sub} is increased. Fig. 8b shows the evolution of the electrical conductivity of the PEDOT films as a function of T_{sub} . In agreement with reported results [54], the conductivity of the as-processed films increases from 360 S/cm at $20\text{ }^\circ\text{C}$ to 1100 S/cm at $100\text{ }^\circ\text{C}$. A minor improvement of the conductivity is observed for all T_{sub} after methanol rinsing. The highest electrical conductivity obtained is 1350 S/cm at $100\text{ }^\circ\text{C}$ after rinsing.

Fig. 9a shows the FTIR spectra of the films deposited at the three T_{sub} . The spectra are comparable, with minor differences concerning the intensity of the peak of the C=C conjugation peak at 1520 cm^{-1} , which increases with T_{sub} , similarly to the literature [13,14]. Also, the films deposited at high T_{sub} present weaker peaks relative to OH groups containing species, namely those at 3400 cm^{-1} and 1600 cm^{-1} . The histograms of Fig. 9b quantify these trends. Heating the substrate from $20\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$ increases the under curve area for the C=C peak at 1520 cm^{-1} from 30 to 55 while it reduces the under curve area of OH peaks from 57 to almost zero. It can be concluded that the rearrangement of the conjugated bonds is in agreement with the increase of electrical conductivity for films processed at higher T_{sub} . Moreover, heating the substrate reduces the condensation of the excess FeCl_3 during deposition, which also contributes to the improvement of the conductivity.

Fig. 10 presents surface SEM micrographs of the films deposited at the three investigated T_{sub} . The film morphology clearly depends on the substrate temperature. A two-phase morphology prevails at $T_{\text{sub}} = 20\text{ }^\circ\text{C}$, depicted by isolated bright areas surrounded by a dark grey continuum. The entire morphology of the films is characterized by an acicular microstructure, characteristic of condensed, unreacted FeCl_3 . Increasing T_{sub} to $70\text{ }^\circ\text{C}$ results in a sharp decrease of the bright areas and, at the same time, in morphological coarsening of the continuous grey one. The bright zones disappear at $100\text{ }^\circ\text{C}$ (Fig. 10c). At this T_{sub} , the acicular microstructure disappears, in agreement with the FTIR results, where less OH bonds were visible for higher substrate

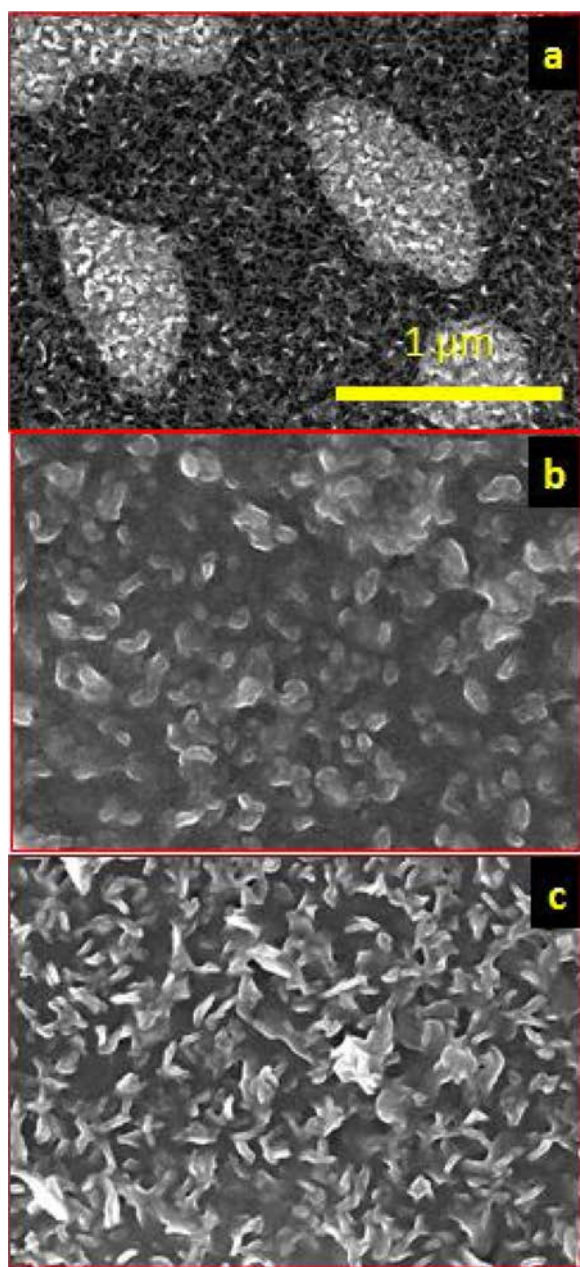


Fig. 10. Surface SEM micrographs of PEDOT films deposited at (a) $T_{\text{sub}} = 20$ °C, (b) $T_{\text{sub}} = 70$ °C and (c) $T_{\text{sub}} = 100$ °C. The scale is 1 μm .

temperatures. The film seems more homogeneous and continuous at 100 °C. However, it is difficult to conclude from these micrographs about a possible decrease in the film porosity with increasing T_{sub} .

4. Conclusions

In this work, we revisit the oCVD process for the deposition of PEDOT films from EDOT and FeCl_3 in standard process conditions, including 100 mTorr and 20–100 °C operating pressure and substrate temperature, respectively. The combination of an *in situ* Quartz Crystal Microbalance and the determination of the EDOT and the FeCl_3 consumption for each experiment revealed a discontinuous FeCl_3 evaporation rate in a standard sublimation hardware architecture often reported in the literature. Simultaneous deposition on 10 cm silicon wafers and coupons positioned on a large-scale scaffold demonstrates that film thickness and electrical conductivity are uniform, independently of the location in the reactor. It also illustrated the absence

of gas-phase reactions and intermediate species in the polymerization of PEDOT. The enhanced gas diffusivity prevailing in the adopted process conditions favors a purely surface PEDOT deposition mechanism occurring through step growth polymerization. Such a mechanism, based on heterogeneous reactions, allows in turn deposition of uniform PEDOT films over large and/or complex substrates.

Detailed correlations between the deposition conditions and the film thickness, weight, chemical composition, morphology, and electrical conductivity were established for various FeCl_3 /EDOT inlet ratios and substrate temperatures.

This work brings an out of the box vision of the oCVD of PEDOT films from sublimed solid oxidants. It reveals the hard points of the process, and in such, it paves the way towards highly conductive oCVD PEDOT films processed from convenient solid oxidants. New studies are in progress to develop a setup ensuring a constant flow rate of oxidant and to optimize the oxidant/monomer ratio to reduce contaminations in PEDOT and suppressing the rinsing step.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author statement

As the corresponding author, I state that all co-authors have contributed equally to the work

described in the publication entitled “An out of the box vision over oxidative chemical vapor deposition of PEDOT involving sublimed iron trichloride”.

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