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**Development of a robust oxidative Chemical Vapor
Deposition (oCVD) process to produce conductive polymer
thin films of poly(3,4-ethylenedioxythiophene) (PEDOT)**

DIPLOMA THESIS

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Abstract

Conductive polymers draw more and more attention these last years, because they are multifunctional organic materials combining optical transparency, lightness, electrical conductivity and additionally, they can be deposited on flexible substrates, like plastics or fabrics. Out of conducting polymers, poly (3,4-ethylenedioxythiophene) (PEDOT) is one of the most significant ones, mainly due to its high electrical conductivity, with values up to 6000 S/cm for PEDOT thin films. Its potential applications include innovative fields, such as organic solar cells, flexible electronic devices and organic light emitting diodes (OLEDs).

The present thesis focuses on the fabrication of conductive, thin polymer films of PEDOT through an innovative and reliable deposition process which is called oxidative Chemical Vapor Deposition (oCVD), by using SbCl_5 as an oxidant. This process allows the production of PEDOT films with controllable thickness at the nanometer scale, uniform on several tens of cm^2 , conformal on complex substrates with an electrical conductivity reaching 1000 S/cm and an optical transmittance of 95% at 550 nm. These characteristics appear promising for PEDOT films to be further integrated in various applications.

The work of this thesis was experimental and included the operation of a tubular, horizontal, hot-wall reactor in which the deposition of PEDOT on two kinds of substrates was conducted. The techniques used for the characterization of the films were Ultraviolet–Visible (UV-Vis) Spectroscopy and Four-Point Probe Measurement, through which conductivity and film thickness were calculated.

The initial part of this work concerns the establishment of reproducibility in the oCVD process, by changing experimental parameters and also technical parts of the equipment in order to increase the system's robustness. The second and most important part involves the optimization of the deposition process, in order to obtain PEDOT films with the highest physical properties, and mainly with high electrical conductivity values. The optimization included two parametric analysis: one by varying deposition time and another one by varying deposition temperature. After these experiments, correlations between conductivity, thickness, growth rate and deposition conditions were studied.

The analysis showed that these two deposition parameters affect significantly the properties of the PEDOT, which exhibited a consistent behavior while varying these parameters of the system. This indicates that the oCVD process to produce PEDOT films has great perspectives to be further investigated and optimized, with the aim to be industrialized and scaled up to larger surfaces.

Key Words: oxidative Chemical Vapor Deposition (oCVD), PEDOT, Conductive Polymers, UV-Vis, Four-Point Probe

Extensive Abstract (in Greek)

Εκτενής Περίληψη

Η συγκεκριμένη διπλωματική εργασία πραγματοποιήθηκε, εντός πρακτικής άσκησης μέσω του πλαισίου Erasmus+, σε συνεργασία με το Τμήμα Χημικών Μηχανικών του Εθνικού Μετσόβιου Πολυτεχνείου και του École Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques του Institut National Polytechnique de Toulouse το διάστημα μεταξύ Φεβρουαρίου και Ιουνίου 2022.

Τα αγώγιμα πολυμερή ελκύουν το ενδιαφέρον όλο και περισσότερο τα τελευταία χρόνια, καθώς είναι οργανικά υλικά που συνδυάζουν πληθώρα ιδιοτήτων, όπως οπτική διαπερατότητα, ελαφρότητα, ηλεκτρική αγωγιμότητα και επιπλέον, μπορούν να εναποτίθενται σε ελαστικά υποστρώματα, όπως πλαστικά ή υφάσματα. Ανάμεσα στα αγώγιμα πολυμερή, το πολύ (3,4-αιθυλενοδιοξυθειοφαίνιο) (PEDOT) αποτελεί ένα από τα πιο σημαντικά κυρίως λόγω της υψηλής αγωγιμότητάς του, με τιμές που ξεπερνούν τα 6000 S/cm για λεπτά υμένια PEDOT. Οι εφαρμογές του περιλαμβάνουν καινοτόμα πεδία, όπως οργανικές ηλιακές κυψελίδες, εύκαμπτες ηλεκτρονικές συσκευές και οργανικές δίοδοι εκπομπής φωτός (OLEDs).

Η εργασία επικεντρώνεται στη παραγωγή αγώγιμων, λεπτών υμενίων του πολυμερούς PEDOT, μέσω μιας καινοτόμης και αξιόπιστης διεργασίας εναπόθεσης, η οξειδωτική Χημική Εναπόθεση Ατμών (oCVD), χρησιμοποιώντας το πενταχλωριούχο αντιμόνιο (SbCl_5) ως οξειδωτικό. Η συγκεκριμένη διεργασία επιτρέπει την δημιουργία υμενίων PEDOT με ελεγχόμενο πάχος στη νανομετρική κλίμακα, ομοιόμορφων σε μερικά δέκατα εκατοστών, με τιμές ηλεκτρικής αγωγιμότητας που φτάνουν τα 1000 S/cm και οπτική διαπερατότητα 95% στα 550 nm, ενώ επιτρέπεται εναπόθεση σε σύνθετα υποστρώματα. Τα παραπάνω χαρακτηριστικά είναι πολλά υποσχόμενα για τα υμένια PEDOT καθώς τους προσφέρουν τη δυνατότητα να ενσωματωθούν σε ακόμα περισσότερες εφαρμογές.

Η διπλωματική εργασία ήταν πειραματική και περιλάμβανε το χειρισμό ενός κυλινδρικού, οριζόντιου αντιδραστήρα όπου πραγματοποιούνταν η εναπόθεση του PEDOT σε δύο είδη υποστρωμάτων: γυαλί και πυρίτιο. Στην αντίδραση εναπόθεσης συμμετείχαν δύο αντιδρώντα: το μονομερές EDOT και το οξειδωτικό SbCl_5 . Οι μέθοδοι που χρησιμοποιήθηκαν για τον χαρακτηρισμό των υμενίων περιλαμβάνουν Φασματοσκοπία Ορατού-Υπεριώδους (UV-Vis) και μέτρηση Four Point Probe, με την βοήθεια των οποίων υπολογίζονταν οι τιμές της αγωγιμότητας και του πάχους των φιλμ.

Το πρώτο μέρος αυτής της διπλωματικής εργασίας αφορά την εξασφάλιση της αναπαραγωγιμότητας της oCVD διεργασίας, διορθώνοντας παραμέτρους του συστήματος (όπως θερμοκρασία, ροή αντιδρώντων), καθώς επίσης και αλλάζοντας μέρη του εξοπλισμού από τεχνική πλευρά, προκειμένου να αυξηθεί η απόδοση του συστήματος.

Στην αρχή, παρατηρήθηκε πως η ροή του οξειδωτικού SbCl_5 ήταν μη συνεπής ή και μη υπαρκτή, οδηγώντας έτσι σε αποτυχημένες εναποθέσεις. Η συγκεκριμένη απόκλιση οφειλόταν στη μη ομοιόμορφη κατανομή θερμοκρασίας στο σωλήνα μεταφοράς του SbCl_5 . Στην περίπτωση που η θερμοκρασία μειωνόταν και προσέγγιζε εκείνη της συμπύκνωσης του SbCl_5 , τότε το οξειδωτικό συμπυκνωνόταν στα τοιχώματα του σωλήνα μεταφοράς, μπλοκάροντας έτσι τη ροή του και καταλήγοντας έτσι σε ανομοιόμορφη εναπόθεση PEDOT στα υποστρώματα. Για τον λόγο αυτό, προστέθηκε ταινία θέρμανσης κατά μήκος του σωλήνα για την αποφυγή του φαινομένου συμπύκνωσης, προκειμένου η θερμοκρασία να είναι σταθερή. Επιπλέον, στο πρωτόκολλο εναπόθεσης εντάχθηκε ο καθαρισμός του εξοπλισμού σε εβδομαδιαία βάση για την αφαίρεση τυχόν υπολειμμάτων SbCl_5 . Συνεπώς, γίνεται αντιληπτό πως οι συνθήκες ατμοποίησης και ροής του οξειδωτικού αποτελούν θέμα ύψιστης σημασίας για την επιτυχία της εναπόθεσης του PEDOT, λόγω της θερμικής ευαισθησίας του SbCl_5 .

Ακόμη, παρατηρήθηκε μεγαλύτερη ομοιομορφία στα αποτελέσματα των πειραμάτων τα οποία πραγματοποιούνταν διαδοχικά το ένα μετά το άλλο, αποφεύγοντας το άνοιγμα και το κλείσιμο του

εξοπλισμού, κάτι που θα επηρέαζε τη θερμική σταθερότητα του αντιδραστήρα και επομένως της διεργασίας, σε σύγκριση με τα αποτελέσματα από το πρώτο πείραμα μιας ημέρας. Επομένως, προτείνεται η πραγματοποίηση ενός τυφλού τεστ (blank test) στην αρχή κάθε πειραματικής διαδικασίας, το οποίο θα περιλαμβάνει μόνο την ροή των αντιδρώντων σε κανονικές πειραματικές συνθήκες, προκειμένου να προετοιμαστεί το σύστημα για την παραγωγή υμενίων με ομοιόμορφα χαρακτηριστικά στα επόμενα πειράματα. Πράγματι, η εφαρμογή αυτής της πρακτικής οδήγησε σε ενιαία αποτελέσματα που επιβεβαιώνουν την αναπαραγωγιμότητα της oCVD διεργασίας.

Παράλληλα, αναπτύχθηκε μια νέα μέθοδος προσδιορισμού του πάχους των υμενίων PEDOT η οποία συνδυάζει την Φασματοσκοπία Ορατού-Υπεριώδους (UV-Vis) και την Atomic Force Microscopy (AFM), η οποία παραδοσιακά χρησιμοποιείται για τη μέτρηση του πάχους φιλμ. Ωστόσο, σαν μέθοδος παρουσιάζει αρκετά μειονεκτήματα, επειδή είναι χρονοβόρα και περίπλοκη στον χειρισμό της, ενώ μπορεί να προκληθεί καταστροφή του δείγματος κατά τον χαρακτηρισμό. Για τον λόγο αυτό, δεδομένα διαπερατότητας μέσω της UV-Vis από δείγματα PEDOT προηγούμενων πειραμάτων, συσχετίστηκαν με δεδομένα πάχους των ίδιων δειγμάτων χρησιμοποιώντας την AFM ως μέθοδο χαρακτηρισμού. Έτσι, κατασκευάστηκε μια γραφική παράσταση και μέσω της μεθόδου της γραμμικής παλινδρόμησης, δημιουργήθηκε μια εξίσωση η οποία προβλέπει το πάχος των υμενίων PEDOT, d χρησιμοποιώντας την τιμή της διαπερατότητας, μετρούμενη μέσω UV-Vis.

$$d = \frac{96,78 - T}{0,27} \pm 3 \%$$

Όπου: d =Πάχος των υμενίων PEDOT (nm), T =Διαπερατότητα μετρούμενη μέσω UV-Vis (%)

Η παραπάνω εξίσωση αποτέλεσε ένα πολύ σημαντικό εργαλείο για το συγκεκριμένο project, καθώς εξοικονόμησε αρκετό χρόνο από τον υπολογισμό του πάχους των παραγόμενων υμενίων PEDOT, καθώς το τελευταίο χρησιμοποιείται στον υπολογισμό της ηλεκτρικής αγωγιμότητας, η οποία αποτελεί την ιδιότητα του PEDOT που μας ενδιαφέρει περισσότερο.

Το δεύτερο και πιο σημαντικό μέρος αυτής της διπλωματικής εργασίας αφιερώθηκε στην βελτιστοποίηση της διεργασίας oCVD, προκειμένου να παραχθούν υμένα PEDOT με τις υψηλότερες φυσικές ιδιότητες και κυρίως με υψηλές τιμές αγωγιμότητας. Η διαδικασία βελτιστοποίησης που ακολουθήθηκε περιλαμβάνει δυο παραμετρικές αναλύσεις: μία μεταβάλλοντας τον χρόνο εναπόθεσης και μια άλλη μεταβάλλοντας τη θερμοκρασία εναπόθεσης, δυο παράμετροι που επηρεάζουν σημαντικά τις ιδιότητες των παραγόμενων υμενίων PEDOT. Έπειτα, αξιοποιώντας τα παραπάνω πειραματικά δεδομένα, μελετήθηκαν συσχετίσεις ανάμεσα στην ηλεκτρική αγωγιμότητα, το πάχος, τον ρυθμό ανάπτυξης και τις συνθήκες της εναπόθεσης (θερμοκρασία, χρόνος), προκειμένου να αντληθούν συμπεράσματα σχετικά με τις παραμετρικές αναλύσεις.

Σχετικά με την επίδραση της διάρκειας εναπόθεσης, παρατηρήθηκε ότι κατά την αύξηση της, το πάχος των υμενίων PEDOT αυξάνεται γραμμικά, αποδεικνύοντας την ομοιόμορφη συμπεριφορά της oCVD. Η γραφική παράσταση που αντλήθηκε από τα παραπάνω δεδομένα, μπορεί να χρησιμοποιηθεί στο μέλλον για τη πρόβλεψη της διάρκειας εναπόθεσης με βάση ένα επιθυμητό πάχος υμενίου, ειδικότερα όταν πρόκειται να χρησιμοποιηθεί το τελευταίο σε κάποια εφαρμογή, όπου η ιδιότητα του πάχους επηρεάζει σημαντικά την απόδοση της εφαρμογής.

Η ηλεκτρική αγωγιμότητα αποδείχθηκε ανεξάρτητη του χρόνου εναπόθεσης, με μικρές αποκλίσεις, ενώ ο ρυθμός ανάπτυξης εξελισσόταν εκθετικά με την αύξηση του χρόνου. Σε μικρούς χρόνους εναπόθεσης (2,5 έως 5 λεπτά) τα χαρακτηριστικά των υμενίων ήταν ανομοιόμορφα ανάμεσα στα υποστρώματα, ενώ για μεγαλύτερους χρόνους (8 λεπτά και 15 λεπτά) η συμπεριφορά τους είχε μεγαλύτερη σταθερότητα. Αυτό υποδεικνύει πως στην αρχή της εναπόθεσης, η αντίδραση είναι σε μεταβατικό στάδιο, κατά το οποίο η ροή των αερίων αντιδρώντων δεν έχει σταθεροποιηθεί, ούτε η θερμοκρασία των υποστρωμάτων κοντά στην είσοδο

του αντιδραστήρα, λόγω της άφιξης ροής ψυχρότερου αερίου. Όμως, με την πάροδο του χρόνου, η αντίδραση εναπόθεσης γίνεται σταθερότερη και οι πολυμερικές αλυσίδες στοιβάζονται καλύτερα η μία με την άλλη, οδηγώντας σε ισχυρότερες ιδιότητες του PEDOT. Επομένως, οι μεγάλες διάρκειες εναπόθεσης οδηγούν σε συνθήκες μόνιμης κατάστασης, όπου το oCVD σύστημα παράγει υμένα PEDOT με υψηλά χαρακτηριστικά.

Αναφορικά με την επίδραση της θερμοκρασίας εναπόθεσης, παρατηρήθηκε ότι ο ρυθμός εναπόθεσης μειώνεται με την αύξηση της θερμοκρασίας, διατηρώντας τον ίδιο χρόνο εναπόθεσης, και συγκεκριμένα παρουσιάζουν εκθετική συμπεριφορά. Τα χαρακτηριστικά του PEDOT εμφανίζουν μεγαλύτερη ομοιομορφία σε υψηλές θερμοκρασίες, όπου ο ρυθμός της αντίδρασης είναι χαμηλός, οδηγώντας έτσι σε πιο αργή αντίδραση και άρα καλύτερες συνθήκες για τη δημιουργία των πολυμερικών αλυσίδων.

Εκθετική συμπεριφορά αποδεικνύεται και μεταξύ της ηλεκτρικής αγωγιμότητας και της θερμοκρασίας εναπόθεσης, εκτός από τη θερμοκρασία 190 °C, η οποία πλησιάζει τη θερμοκρασία αποσύνθεσης του οξειδωτικού $SbCl_5$, και που οδηγεί σε υμένα PEDOT με χαρακτηριστικά χαμηλής ποιότητας που δεν εντάσσονται στη συμπεριφορά των υμενίων των άλλων θερμοκρασιών. Λαμβάνοντας υπόψη αυτά τα αποτελέσματα, προτείνεται η αποφυγή εναπόθεσης στη συγκεκριμένη περιοχή θερμοκρασίας.

Τελικά, η συγκεκριμένη έρευνα απέδειξε πως τα χαρακτηριστικά των υμενίων PEDOT έχουν ενιαία συμπεριφορά που μπορεί να προβλεφθεί με τη χρήση μοντέλων. Επομένως, η διεργασία oCVD για την παραγωγή των υμενίων PEDOT έχει σημαντικές προοπτικές για περαιτέρω έρευνα και βελτιστοποίηση της, με απώτερο στόχο την βιομηχανοποίηση και την επέκτασή της σε μεγαλύτερες επιφάνειες.

Λέξεις Κλειδιά: Χημική Εναπόθεση Ατμών (CVD), PEDOT, Αγωγίμα Πολυμερή, Υμένα, Φασματομετρία UV-Vis, Four-Point Probe, OLED

Table of Contents

Acknowledgements	i
Abstract	iii
Extensive Abstract (in Greek)	iv
1 Introduction	1
1.1 Context of this Internship.....	1
1.2 Project POLEN.....	2
1.3 Project PhotoHyRem.....	4
1.4 Scope of this Work.....	6
2 Theoretical Part	8
2.1 Poly (3, 4-ethylenedioxythiophene) (PEDOT) Thin Films: Structure and Properties	8
2.2 PEDOT Film Forming Techniques	11
2.2.1 Common Coating and Printing Techniques for PEDOT-based Films (Wet coating) 11	
2.2.2 Oxidative Chemical Vapor Deposition (oCVD) (Dry coating)	12
2.3 Applications.....	15
3 Experimental Part	17
3.1 Experimental Set-Up	17
3.2 Materials.....	21
3.3 Characterization Methods	22
3.3.1 Four Point Probes.....	22
3.3.2 UV-Vis Spectroscopy	23
4 Results and Discussion	27
4.1 Correlation between Transmittance and Thickness	27
4.2 Establishing the reproducibility of the oCVD system	32
4.2.1 Study of the distribution of temperature in the system.....	32
4.2.2 Study of reactants (EDOT and SbCl ₅) Flux.....	33
4.3 Influence of Deposition Duration t_d (min).....	34
4.3.1 VarTime Tests	34
4.3.2 Repeating VarTime Tests.....	37
4.4 Influence of Temperature of Deposition T_d (°C)	41
4.4.1 Thermoprofiles of the oCVD reactor.....	41
4.4.2 VTemp Tests	43
5 Conclusions	47
6 Perspectives	49
7 Bibliography	51

1 Introduction

1.1 Context of this Internship

The present thesis was conducted as part of an internship performed from February to June 2022 at École Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques (ENSIACET) in Toulouse. This internship took place as part of research done at the Laboratoire de Génie Chimique (LGC) and at the Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT) for the Projects POLEN and PhotoHyRem funded by Région Occitanie. A more detailed description of the Projects will be presented in the following chapters.

ENSIACET is a state engineering graduate school with a three-year degree curriculum, overseen by the Ministry of Higher Education, Research and Innovation. In addition, it is one of three founding Graduate Schools, part of Institut National Polytechnique (INP) of Toulouse. At INP-ENSIACET there are four Research Centers (CIRIMAT, LCA, LCC, LGC) and two Centers for Innovation and Technology Transfer (CRITT Catar, CRITT Processes Engineering) which complement teaching activities. [1]

For the implementation of the POLEN Project, IRPI group from LGC, RTS group from CIRIMAT and Laboratoire Plasma et Conversion d'Énergie (LAPLACE) collaborated due to common research interests. Concerning PhotoHyRem Project, it was a joint project between IRPI group from LGC, RTS group from CIRIMAT, LAPLACE and DM3 group from Institut Européen des Membranes (IEM).

LGC is a National Center for Scientific Research (Centre National de la Recherche Scientifique, CNRS) Laboratory, operated jointly by the CNRS, the University Toulouse 3 – Paul Sabatier (UPS) and INP of Toulouse. Around 300 members of staff are involved at LGC. Its mission is to produce knowledge in the field of Chemical Engineering by focusing on industrial and societal constraints, while participating in the international competition for research. LGC is divided in six Research Departments, according to their research area [2]:

- Interface and Particle Interaction Engineering – GIMD
- Electrochemical Processes – PE
- Bioprocesses and Microbial Systems – BioSyM
- Innovative Multiphase Reactor Engineering – IRPI
- Process and System Engineering – PSI
- Science and Technology of Intensified Processes – STPI

CIRIMAT is a Mixed Research Unit (UMR, CNRS, INPT, UPS 5085) with about 240 people, including just over 100 permanent faculty and staff and about 90 doctoral students. It conducts collaborative research on all kinds of materials (metals, alloys, ceramics, polymers, composites, multi-materials) in the form of powders, thin films, coatings, massive pieces and also deals with current scientific questions in fields with strong industrial and societal impact, like Aeronautics, Space, Energy, Electronics, Health, Environment and Building. CIRIMAT is structured into 6 research teams since January 2021 [3]:

- Nanocomposites, Nanomatériaux Carbonés: Élaboration, Densification- NNCED
- Phosphates, Pharmacotechnics, Biomaterials- PPB

- Mixed valence oxides- OVM
- Coatings and surface treatments- RTS
- Mechanics, microstructure, oxidation, corrosion- MEMO
- P of Polymers- PhyPol

LAPLACE is a Mixed Research Unit of CNRS, INP of Toulouse and UPS. Its research focuses on the production, transportation, management, conversion and use of the electricity, while covering all the aspects right from the study of fundamental processes in solid and gas to the development of processes and systems. Within this widespread field, the major themes concern the plasma discharges, as well as plasma applications, the study of the dielectric materials (polymers, in particular) and their integration into systems, the study and design of the electrical systems, the optimization of the control and the power converters. Furthermore, it is the first French concentration of research in the field of Electrical Engineering and Plasma with 160 fulltime researchers and a similar number of PhD students and Post-Docs. [4]

IEM was founded in 1994 and consists of a reference laboratory in the field of membrane materials and processes. Main objectives of the laboratory include: the development and characterization of new membrane materials and so their application in membrane processes (effluent treatment, gas separation, biotechnologies related to food science and health). In agreement with the objectives and strategy of IEM, it is divided in 3 separate scientific departments based on 4 thematic axes, which are: membranes of the future, membranes for hydrogen and energy production, membranes for the treatment of water and membranes for the health.

The three departments of IEM are: [5]

- Design of membrane materials and multifunctional systems- DM3
- Interfaces, Physicochemistry, Polymers- IP2
- Membrane Process Engineering- GPM

1.2 Project POLEN

The goal of **POLEN Project** is to develop a new oxidative Chemical Vapor Deposition Process (oCVD) to produce PEDOT polymer films and integrate them into Organic Emitting Light Diodes (OLEDs) as a transport layer or as an electrode.

Due to the growing development of electronic and optoelectronic applications (like OLEDs and organic solar cells) that require the fabrication of thin, electrical conductive, flexible and optical transparent films, conducting polymers saw an increase of popularity in industry and academia in the last years. Conducting polymers show great advantages over common inorganic materials, such as lightweight structure, cost effectiveness and resource abundance. For these reasons, they have become “a new generation material” and have penetrated into industrial and commercial processes. [6] [7]

Out of conducting polymers, PEDOT is one of the most chemically and thermally stable ones. It is considered as a promising organic material for electronic devices with conductivities up to 8800 S/cm and large tunable work functions around 5.1–5.4 eV. [8] However, due to its poor solubility, PEDOT is seen in most applications as a mixture and most commonly as PEDOT:PSS. [9] The latter one is a polymer electrolyte consisting of positively charged conjugated PEDOT and negatively charged saturated PSS.

PEDOT:PSS has become one of the most successful conducting polymers in terms of practical applications, mainly including energy conversion and storage fields. [10] Yet, the PSS group has strong interactions with water and other possible solvents and most importantly, it possesses a strong acidic character. Therefore, due to these properties, premature degradation of devices is caused, in which PEDOT:PSS is integrated. [11] [12] These conclusions have led to the search for alternative processes that fabricate PEDOT in its pure state and eliminate the need of solvent, and which are called dry thin-film solvent-free deposition processes, with oCVD being one of them.

The oCVD process is a single-step method to convert vapor phase monomers, together with vapors of oxidant, into thin conductive polymer films. It consists of a versatile deposition method to produce conductive polymers, due to its unique combination of characteristics, such as formation of conformal coatings, handling at low temperatures, solvent free, uniformity of growth and industrial scale-up potential. Provided the vaporized oxidant flow rate is fully controlled, it yields films whose characteristics and properties can be finely tuned. [6] [7]

As mentioned, OLEDs are devices in which PEDOT is widely integrated. OLEDs are light sources used in displays of smartphones and TV screens as well as in panels for lighting applications. This device technology records a rapid evolution over the last 30 years in academia and industry. There are numerous structures of OLEDs, but in its simplest form it consists of a thin film of organic emitting material, sandwiched between two electrodes (anode and cathode) and at least one of the electrodes must be transparent. When a voltage is applied between the latter, charges are injected in the organic material, holes from the anode and electrons from the cathode. Next, the electrons and holes migrate through the electron and hole transport layers into the emissive layer (EML), where the recombination of the charge carriers and the formation of excitons takes place. The electroluminescence (EL) occurs as these excitons relax radiatively from the excited state to the ground state and release a photon. [13] A typical structure of an OLED can be seen in **Figure 1** below.

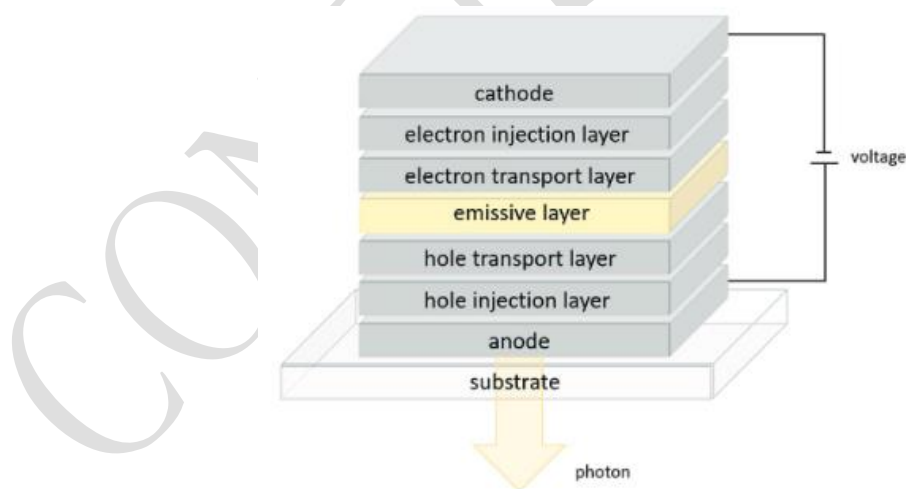


Figure 1: Schematic depiction of the structure of an Organic Light-Emitting Diode (OLED) [13]

ITO is the most widely used transparent anode for OLEDs due to its high optical transparency and electrical conductivity. The performance of OLEDs is highly affected by the hole injection ability of the ITO anode. In order to control that, hole injection layers, such as PEDOT:PSS, are inserted between the

anode and the emissive layer to improve the performance of OLEDs. In previous works [14] [15] [16] [17], it has been shown that PEDOT:PSS is a very good hole injection material, due to its high conductivity, good film-forming properties and environmental stability. However, as discussed above, it appears in OLEDs that when PEDOT:PSS is used as a hole injection material, destruction and limitation of stability of OLEDs occur, as a consequence of the acidic and hydrophilic nature of the PSS group. [12] Consequently, the replacement of PEDOT:PSS by oCVD PEDOT, as proposed by the POLEN project, enters in the idea to produce more efficient and stable OLEDs.

LGC, in collaboration with CIRIMAT, has been working since 2017 on the development of a new oCVD deposition process to fabricate thin films of PEDOT, free of PSS. Following this previous work, POLEN project aims to produce -through this oCVD process- thin PEDOT films, which are optimized in terms of conductivity and transparency, in order to replace PEDOT:PSS in the manufacturing of innovative OLEDs. The expected characteristics of the PEDOT films include: conductivity over 300 S/cm for 25 nm of thickness, a roughness (RMS) lower than 5 nm for thicknesses of 25 nm, optical transparency in the visible range greater than 80% and light performance equal to or better than PEDOT:PSS.

The PEDOT films were produced by oCVD process at the LGC and characterized at CIRIMAT, while the implementation of OLEDs was manufactured and studied at LAPLACE.

1.3 Project PhotoHyRem

The **PhotoHyRem Project** will contribute to the advancement of knowledge and technology in the field of Solar Water Splitting (SWS) for the production of green hydrogen through the development of a Photoelectrochemical Cell (PEC), in which innovative TiO₂ films coupled with polymer films of PEDOT will be used as photo anodes.

Hydrogen is regarded as a promising energy carrier because it possesses the highest energy density compared to any fuel (specifically three times that of gasoline and four times that of natural gas) and additionally no CO₂ emissions are produced during its combustion. An attractive approach to produce hydrogen is by collecting solar energy in chemical bonds. Photo-electrolysis of water achieves that by using semiconductors as both the light absorber and energy converter, to collect solar energy in the simplest chemical bonds. Splitting water into usable hydrogen has efficiently evolved into an innovative industrial photosynthesis process that could supply green fuel, with water being the only waste product during operation. In order to establish this new photo electrolysis process, an economically feasible water-splitting cell that consists of stable semiconductors designed to split water directly at the semiconductor surface has to be designed. In general, in a photoelectrode, whose structure can be seen in **Figure 2**, a semiconductor layer mainly acts as a light absorber to produce photogenerated electrons and holes; subsequently, these generated electrons and holes are separated and transferred to the electrode interface for surface redox reactions, as it can be seen in **Figure 3**. [18] [19]

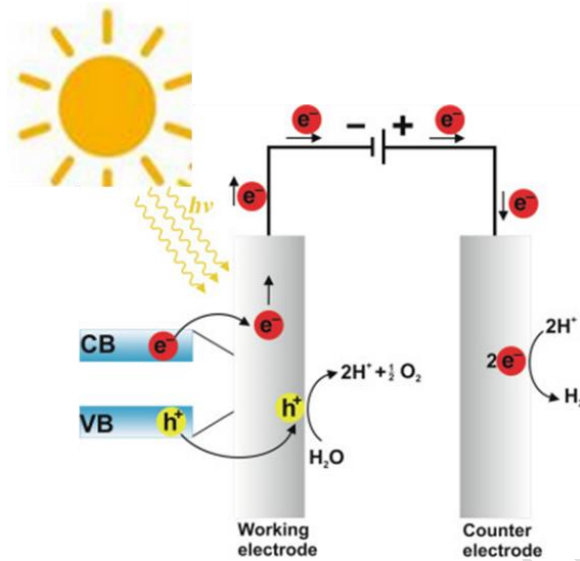


Figure 2: Scheme of a Photoelectrode. [20]

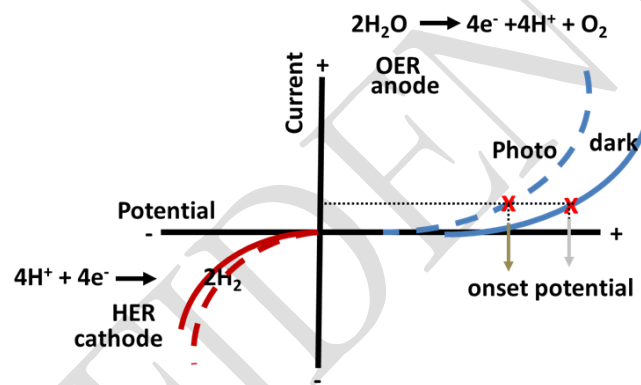


Figure 3: Surface Redox Reactions. [21]

A material to successfully catalyze Solar Water Splitting process is TiO_2 , according to literature. [18] [22] The reason to that is that it is non-toxic, chemically stable, abundant and affordable. It possesses high energy band-gap (3.2 eV) that makes it operational in the UV radiation domain. There are several methods to fabricate films of TiO_2 : sol-gel, anodization, reactive magnetron sputtering, atomic layer deposition (ALD) or metalorganic chemical vapor deposition (MOCVD). In particular, the latter one, MOCVD is a form of CVD that uses metalorganic compounds for one or more of the precursors. This process interestingly allows the production of various hierarchical morphologies that influence photocatalytic properties and consequently the performance of devices in which TiO_2 is used. [22] [23]

In spite of the wide range of data on TiO_2 material in literature, control and optimization of the TiO_2 films' properties is still necessary. [24] To shift the absorption edge of TiO_2 to the visible range, several processes have been carried out, such as:

- (i) conjugation with semiconductors that have small band gap [25],
- (ii) addition of transition metals [26],
- (iii) doping with nonmetal elements [27] and
- (iv) co-catalyst loading [28]

Except for the above, one of the new approaches is to modify it with conducting polymers in order to form composites. This is attributed to conducting polymers' unique capability to conduct electricity, their large absorption coefficient, and the excellent mobility of their photo-generated charges. As mentioned before, out of conducting polymers, PEDOT is one of the most optimal materials in energy storage devices, solar cells, electrochemical sensors and electrochromic display, due to its superior conductivity, good flexibility and large surface. [29] It has been used in organic light emitting diodes and in solar-to-chemical energy conversion, due to its excellent conductivity, stability and fast charge transfer, as referred above.

So far there has been work done in literature which shows the promising results of pairing TiO_2 with PEDOT. In study of Abdelnasser et al [18], it has been found that the photoelectrodes of TiO_2 nanotubes combined with PEDOT, showed a remarkable increase in the photocurrent response and lower charge transfer resistance, compared to pure TiO_2 . Tong et al. [30], produced PEDOT on TiO_2 fibers, achieving the highest capacitance values ever obtained with this composite of 87,9 F/g.

Therefore, TiO_2 with PEDOT as a photoanode increases the optical characteristics of the electrodes and in consequence the PEC activity. However, there still is a challenge to further improve TiO_2 paired with PEDOT in order to maximize the water decomposition reaction area, to achieve exciting bandgap (~ 2 eV), facile synthesis and high stability too.

PhotoHyRem Project aims to investigate the production of TiO_2 , paired with PEDOT, to be used as a photoanode for the SWS application in order to intensify the optical characteristics of the electrodes and the PEC performance. This will eventually lead to the development of a compact device that can be industrialized. Some of the specific goals of the project are explained below. In terms of the system, a primary goal is to achieve photoanode size of 1 m^2 active surface, while regarding energy supply, there is a target of an overall conversion efficiency and current density close to 10% and 10 mA/cm^2 , respectively, which will be suitable enough to produce hydrogen to supply a 100 W fuel cell.

1.4 Scope of this Work

The biggest part of this internship was devoted to the POLEN Project, which involved the study, operation and optimization of the oCVD reactor for the synthesis of PEDOT films, and simultaneously the characterization of the produced films through UV-Vis Spectroscopy and Four Points Probes Measurement. Regarding PhotoHyRem Project, I was responsible for the deposition of PEDOT on the TiO_2 substrates.

The first part of the internship included a familiarization with the theory and equipment of the oCVD system. In this stage of my work, I got acquainted with the operation of the oCVD reactor, while also I did deposition tests to ensure the reproducibility of the system and uniformity of the PEDOT films. At first, there were some inconsistencies in our results, which led to a few technical changes in the equipment that eventually improved the performance and quality of the produced PEDOT films.

Therefore, after altering the system and making it stable and robust enough to produce PEDOT films, optimization in order to meet the goals of the project was needed. In the second part of my internship, I performed two parametric analysis of the oCVD system in order to optimize the properties of the films regarding Conductivity, σ (S/cm) and Transmittance, T (%). The parameters of the system that I studied included Deposition Time, t_d (min) and Deposition Temperature, T_d ($^\circ\text{C}$).

Concerning the content of the current Thesis, the Theoretical Part will provide information regarding PEDOT and oCVD process, while the Experimental Part will explore the equipment and deposition method followed for the fabrication of the PEDOT films, in addition to the characterization techniques used. In the Results and Discussion sections, the findings of the above experimental work will be presented and analyzed, while in the end Conclusions and Perspectives of this work will be discussed.

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2 Theoretical Part

2.1 Poly (3, 4-ethylenedioxythiophene) (PEDOT) Thin Films: Structure and Properties

Over the last few years, **Conducting Polymers (CPs)** have gained attention in the global scientific community, thanks to a combination of unique properties and characteristics, such as: high and controllable electronic conductivity, optical transparency, and mechanical flexibility usually found in traditional polymers. For this reason, CPs have penetrated in the commercialization process and have substituted traditional materials used like metals, semiconductors and metal oxides. CPs can be found integrated in a wide range of applications, namely antistatic coatings, optical displays, energy storage and harvesting, electrocatalysis, tissue engineering, sensors and actuators, soft robotics etc. [7] [31]

In order to optimize the electrical properties of CPs, which are the ones mainly sought, an explanation of what makes them conductive should be done. First of all, CPs polymers are intrinsically amorphous and disordered materials with various chains lengths, non-uniformly dispersed within it. In their structure, **double conjugated chains** are found, which consist of alternating single sigma (σ) and double pi (π) bonds in the backbone (**Figure 4**).

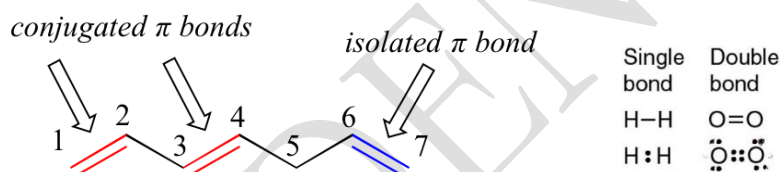


Figure 4: Simplified representation of CPs.

In general, when applying voltage, electric current is resulting due to the orderly movement of charges in the material as a response of forces that act on it. The positive charges flow in the direction of the electric field applied, whereas the negative charges move in the opposite direction. The constant movement of the double pi (π) bonds to stabilize the charge in the neighbor atoms causes, therefore, the movement of charge, which results to conductivity.

Secondly, **doping** contributes to the conductive nature of CPs, which is achieved either by removing electrons (oxidation) or by inserting them (reduction). The conductivity of a CP comes from the charge formed by the dopant and so, as the doping level increases, more charges are formed in the polymer and, thus, higher conductivity values are achieved. The conductivity of a CP also depends on the temperature, because as the temperature increases, molecules are distanced from one another. Therefore, the doping effect becomes more intense and, consequently, the amount of charges, which is the doping level of the polymer, is greater, leading to increased conductivity. For that reason, the higher the temperature, the higher the energy of the electrons is, and, therefore, the easier it is to excite the electrons to the conduction band. [32]

The best-known and most studied CPs are: Polyacetylene (PA), Polypyrrole (PPy), Polythiophene (PT), Poly(3, 4-ethylenedioxythiophene) (PEDOT), and Polyaniline (PANI) (**Figure 5**).

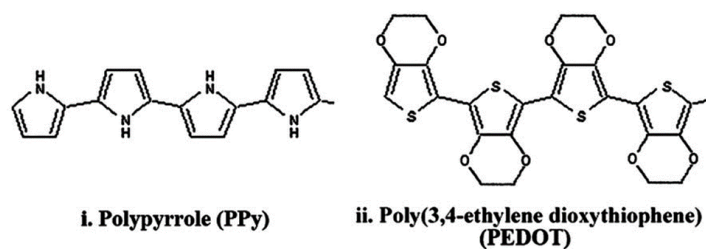


Figure 5: Simplified representation of CPs.

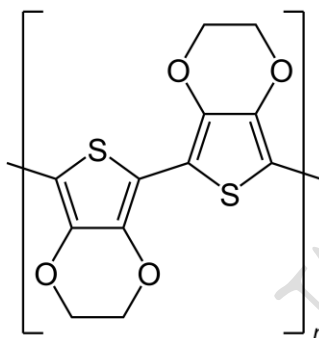


Figure 6: Chemical Structure of EDOT Monomer.

Out of CPs, **PEDOT** is regarded as the most promising one, as it shows both a high conductivity, good film forming ability, excellent optical transparency in the visible range and good chemical stability. Therefore, huge attention has been aroused regarding PEDOT both in the academic and industrial areas. [32] [33]

The main property of PEDOT that ensures its unique place among conducting polymers is its high and stable **electrical conductivity**. The latter has been raised up to 6259 S/cm for thin films and 8797 S/cm for single crystals. These conductivity values are outstanding, because they are very close to the ones of the most conductive metals, like silver and copper. This indicates that remarkable advancement on the conductivity enhancement has been performed, but simultaneously there always is the possibility for a better insight of that material, based on data found in literature. Fabrication process, crystallinity of the material and choice of the counter-anions are a few of the parameters that affect the growth of the electrical conductivity. [32]

Additionally, the **optical properties** of PEDOT-based materials make PEDOT remarkable, since values of Transmittance (%) of 80% in the visible range have been achieved, and so it can be found integrated in interesting applications of electrochromic devices and transparent electrodes. In the latter ones, the good electrochromic properties are regulated electrochemically by modifying the doping level, in which the thickness of the film plays an important role. More specifically, the thinner the film, the more transparent it becomes. [32]

Lastly, **mechanical stability** is an important feature that PEDOT films possess, especially for implantable devices, those designed for long-term use on tissue surfaces, or in vitro platforms, consisting of intricate fluid environment that require long-lasting stability. [34]

These above properties fully rely on the chemical structure of the polymer, the conditions used during fabrication process, and as well as additives, such as surfactants or secondary dopants. [34] Techniques to fabricate PEDOT films will be discussed in a later chapter.

Apart from these properties, PEDOT by itself has poor solubility in water and for that reason, a soluble macromolecular dopant is added to eliminate the insoluble nature of PEDOT. As mentioned in the Introduction Part of this Thesis, by oxidizing EDOT with persulfates and polymerizing it in the presence of PSS in water, an aqueous dispersion is created by positively charged PEDOT stabilized with PSS⁻, as a counter-anion, and more accurately, a polymer electrolyte **PEDOT:PSS** is obtained (**Figure 7**) PSS⁻ is a polymer surfactant, negatively charged, which helps disperse and stabilize PEDOT in water and as well as in other solvents. PSS⁻ serves two main roles in this polymeric complex; firstly, it acts as a counteranion to stabilize the doped PEDOT and secondly it provides a matrix to PEDOT in order to form an aqueous dispersion. [7] [32] [35]

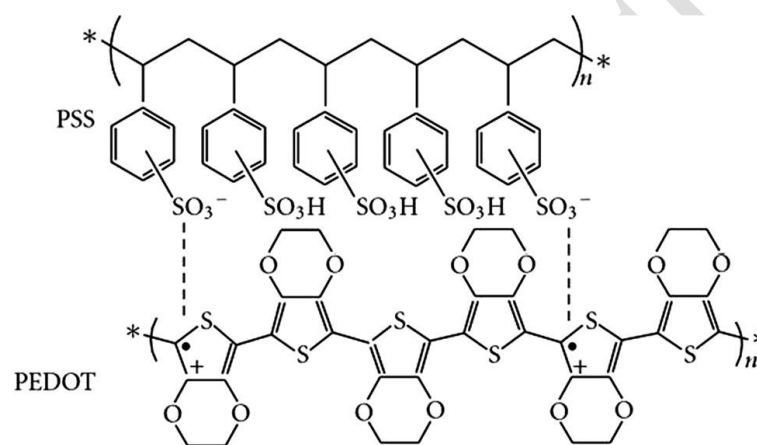


Figure 7: Chemical Structure of PEDOT and PSS.

In general, PEDOT:PSS is considered as the most successful conducting polymer in terms of practical applications, including energy conversion and storage fields. This huge success of PEDOT:PSS can be attributed to its outstanding properties. The PEDOT:PSS film is smooth and has a surface roughness generally less than 5 nm. In the visible light range, PEDOT:PSS thin film can achieve Transmittance, T(%) values over 90% at a wavelength of 550 nm for a 100 nm layer. Regarding conductivity, it exhibits electrical conductivities, σ (S/cm) that range from 10⁻² S/cm to 10³ S/cm, which can be enhanced by various methods mentioned in literature, for example thermal treatment and pre- or post-treatment with organic solvents or salts. [10] [32] [36]

However, it appears that when PEDOT:PSS is integrated in electronic applications, corrosion and degradation occur on air exposure or under the high humidity circumstances, a fortiori in the watery environments, which can lead to alterations in properties. One main reason is that the PEDOT:PSS film is extremely hydrophilic due to the excessive water-soluble PSS group, which has a tendency to swell or decompose in aqueous environment. The second reason is that the PSS group possesses an acidic nature, that also impacts negatively the devices in which PEDOT:PSS is integrated. For an example, when PEDOT:PSS is used as a hole transport material, degradation is caused due to the acidity of the film. Lastly, PSS is a non-conductive polymer and therefore it can reduce the already high performance of PEDOT films when integrated in applications. [11] [12] [37]

Therefore, there is a need to fabricate PEDOT films, **free of PSS**, in order to exploit the exceptional properties of PEDOT but also to eliminate its insolubility.

2.2 PEDOT Film Forming Techniques

2.2.1 Common Coating and Printing Techniques for PEDOT-based Films (Wet coating)

Since the properties and structure of PEDOT films highly depend on the fabrication technique and conditions applied, some of the main methods to produce PEDOT and PEDOT-based films will be discussed in this Chapter. The techniques will be described in short, so their advantages and disadvantages and how specific factors can affect the characteristics of the fabricated films. These techniques mainly refer to the production of PEDOT:PSS films, due to the wetting behavior of PSS dopant, that gives the solvable complex PEDOT:PSS. [7] [37]

With the increasing need of film production, versatile forming techniques have progressively been generated, that mainly include common coating and printing film techniques. In theory, all film-forming techniques are independent of the field of application in which the films will be used to, but in reality, numerous of these techniques were restricted to just one or several fields, because of the specific requirements in practical application. In **printing**, through the reversal action, a layer of ink is transferred from a stamp to a substrate, that is, in general, a physical contact between the stamp and the substrate, whereas in **coating** a layer of ink is transferred to the substrate by essentially pouring, painting, spraying, casting or smearing it over the surface. [37] [38]

The main coating and printing techniques used to fabricate PEDOT:PSS films include:

- 1) Dip Coating
- 2) Drop Coating
- 3) Spin Coating
- 4) Spray Coating
- 5) Screen Printing
- 6) Inkjet-Printing

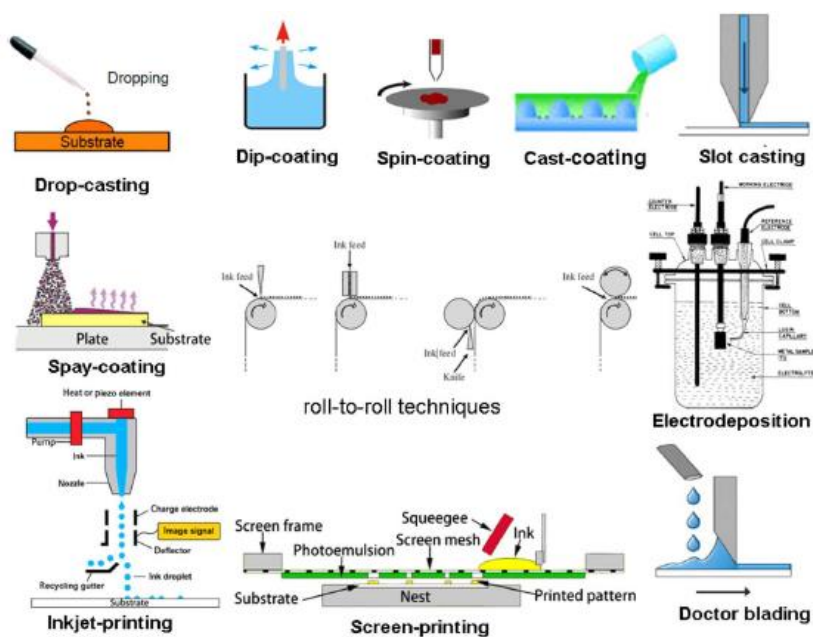


Figure 8: Scheme of Main Coating and Printing Techniques. [37]

By coating or printing PEDOT:PSS dispersion, highly stable, conductive, transparent, flexible, stretchable, durable and insoluble films can be formed, whose properties can be controlled by adding diversified formulation components or adjusting conditions. Additionally, these techniques have been introduced into several PEDOT:PSS devices such as electrodes, sensors, PLEDs, PFETs, batteries, capacitors and others. [37] [38]

However, the above film-forming techniques, due to their wet nature, have a potential for residual solvent in the films, which is crucial, since lack of biocompatibility often is present in small molecules trapped within the polymer coating in contrast to the macromolecules of the film itself. Additionally, the existence of solvent leads to dewetting phenomena, which then form pinhole defects. [7] These reasons make the solution processing of PEDOT films quite challenging and the investigation of new **dry –solvent free-** fabrication techniques critical.

2.2.2 Oxidative Chemical Vapor Deposition (oCVD) (Dry coating)

The expansion of the commercialization process of conducting polymers, and more specifically of PEDOT, is of great significance due to its unique properties and characteristics. In order to achieve this objective, **oxidative Chemical Vapor Deposition (oCVD)**, along with other Vapor Deposition methods, seem the promising approaches.

As mentioned, the conventional method to produce PEDOT mainly includes solution-based processing, yet, these solvents frequently damage the device in which the polymer complex is integrated in (as explained above for PEDOT:PSS). The need for solvent is eliminated by using Vapor Phase Polymerization (VPP) and oxidative Chemical Vapor Deposition (oCVD) as thin film formation techniques. oCVD was initially introduced in 2006 by the group of Prof. Gleason in MIT and showed promising results, since PEDOT films with conductivities of 105 S/cm and transmittance of 84% to visible light were produced. [39] Since then, this method has been drastically developing and it provides

conformal coatings on complex porous substrates, by avoiding substrate-solvent incompatibility, which is usually found in liquid solution techniques. [7] [6] [40]

In general, PEDOT follows a Step Growth Polymerization mechanism, which requires the monomer and oxidant present at the same time for constant polymerization. VPP and oCVD methods differ in the oxidant delivery method. VPP process includes a first liquid deposition step, to deposit the oxidant layer and as a second step EDOT vapors are introduced. When the oxidant is no more available, polymerization terminates, even though EDOT might still be present. Contrary to VPP, which requires a solution containing the oxidizing agent, oCVD is a one-step purely gas phase technique, in which the oxidant has two main functions: i) to boost the monomer polymerization and ii) to oxidize the neutral polymer to produce conductive, doped polymer. [6] [41]

In CVD processes, the reactants are in vapor phase and undergo similar polymerization mechanisms to those of solution-phase processing methods. In oCVD the step-growth polymerization takes place in three steps:

- a) oxidation of monomer to form a cation radical,
- b) dimerization of cation radical and
- c) deprotonation of dimer to form conjugation.

These steps are repeated and so a growing polymer chain is formed. [7]

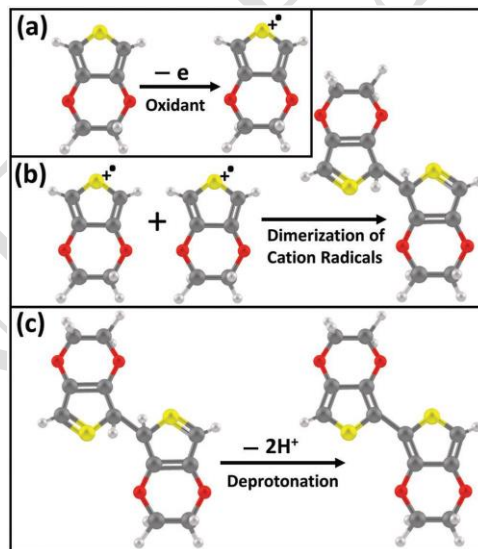


Figure 9: Scheme of Polymerization Mechanism in the oCVD Process. [7]

Subsequently, the PEDOT⁺ oCVD method was developed due to its ability to mimic the step-growth polymerization, to control properties of polymer films and to obtain highly desirable characteristics so that optoelectronic and energy storage devices can be fabricated. The oCVD method is a solvent-free method that promotes the deposition of conjugated polymer films, independently of the substrate, and which successfully produces films with coherent characteristics over large areas. The elimination of the solvent, which could be toxic or aggressive, leads the way to deposit PEDOT films on more complex substrates such as: plastic, paper, fabric, or polymeric membranes. By varying deposition time, film thickness is

controlled and consequently properties and characteristics can be finely tuned. Other advantages of oCVD over other techniques include: processing at low temperatures, uniformity of growth, mechanical flexible films and industrial scale up. [6] [7] [40]

The characteristics of oCVD PEDOT films are highly affected by the oxidant used in the process. Oxidants generally consist of ionic compounds, which contain halogenic atoms, and are used for their oxidation potential. In literature, there are several oxidants, which have been selected to fabricate PEDOT films from EDOT monomer, such as: FeCl₃, VOCl₃, SbCl₅, MoCl₅, Br₂, with the most common one being iron chloride (FeCl₃). FeCl₃ is widely available and has low toxicity, but often unreacted FeCl₃, its oxidation derivatives and residues are found in the films. This can degrade the latter's structure and characteristics, like electrical conductivity and film durability, and so post-deposition rinsing steps are required. [6]

Therefore, in order to make the oCVD process more viable, a new liquid oxidant is introduced, antimony pentachloride (SbCl₅), which is less costly and has low toxicity compared with other alternatives. Additionally, it is used in a liquid form, which shows better stability during evaporation compared to a solid one and therefore it can be easier to control during deposition. [6] [7]. M. Mirabedin et al [6], have done work using SbCl₅ as an oxidant, which showed good performance, since high conductivity values of PEDOT films were achieved (over 700 S/cm) and provided the possibility to control the oCVD process, due to its stable behavior.

In order to optimize the oCVD process and to obtain PEDOT films with desired characteristics, parameters of the system should be investigated. In previous work [7], it has been mentioned that **Deposition Temperature** T_d (°C) plays an important role to the electrical conductivity (σ) of the films. In particular, electrical conductivity and deposition temperature are linked through the Arrhenius equation:

$$\sigma \propto \exp\left(-\frac{A}{T}\right) \quad [\text{Eq. 1}]$$

It has been reported that by increasing deposition temperature PEDOT, crystallite size significantly increases too which leads to enhanced interdomain charge transport and so to higher conductivity values. The positive impact of increasing deposition temperature, has been verified by Mirabedin et. al [6], who also used SbCl₅ as an oxidant and conductivity values increased from 571 S/cm to 770 S/cm.

Another parameter for the optimization of the oCVD system that should be studied is the **Deposition Time**, t_d (min). Mirabedin et al. [6], using SbCl₅ as an oxidant, found that by increasing the duration of deposition, film thickness linearly increases which confirms the stability of the process. Regarding conductivity, it was found being independent of the duration of deposition, while in regards to Transmittance, T (%), it showed a small decrease by increasing time of deposition.

Finally, it has been found [6] that the **SbCl₅/EDOT molar ratio** influences the produced films, since by increasing the ratio, an overall decrease of electrical conductivity, but simultaneously an increase in film thickness, is observed. Mirabedin et al. discovered that PEDOT films are the most uniform and smoothest ones, with high conductivity values, when deposited with the lowest SbCl₅ (0,35 sccm¹) and the highest EDOT (2 sccm) flow rate.

¹ sccm: standard cubic centimeters per minute- a unit used to quantify the flow rate of a fluid

2.3 Applications

It has been made clear that PEDOT film is an innovative material with unique properties and consequently the applications of this conducting polymer are extensive. Here, the most important ones and those who came to fruition in the commercial world will be reported. In general, PEDOT films' use is seen in a long list of applications, which counts stretchable integrated circuits, active matrix displays, stretchable solar cells, light emitting diodes etc. Characteristics, such as high electronic conductivity and tunable mechanical properties of the active material, are sought for the integration of PEDOT in the above applications. [34] [42]. The main applications of PEDOT films that will be described in detail are: A) OLEDs, B) Organic Solar Cells and C) Sensors, due to their expanding growth and rich study in literature. Other applications will be summarized at the end with literature references.

A) PEDOT Grades for OLEDs

As mentioned in the Introduction Part for the POLEN Project, a significant application of PEDOT based thin film is **Organic Light Emitting Diodes (OLEDs)**. The latter have drawn large attention over the last 20 years in both academia and industry as thin and efficient light emitting devices. In OLEDs, PEDOT layers are linked with the transport/injection of holes into the device.

In this aspect, they are mainly used as holes injection layer (HIL) in devices. A HIL helps to transfer the holes from the anode into the emissive layer or the transport layer. When used on top of ITO, the most common anode in OLED, PEDOT also has the role to reduce the roughness of ITO and therefore to facilitate the deposition of the future layer. It is also used to adjust the energy level of the anode so it matches with the energy level of the organic material on top. [43]

B) PEDOT layers in Organic Solar Cells

Organic Solar Cells is an attractive field because they offer roll-to-roll printing, low cost, flexibility and transparency for solar cells. In the specific case of a bulk heterojunction, solar cells donor and acceptor materials are put together and compose a functional layer, where the charge separation happens while irradiation with light. Holes are extracted into a hole transport layer and electrons into an electron transport layer and then transferred to the respective electrodes. Like in OLEDs, PEDOT film layers can act as a hole transport mean in organic solar cells and/or as mean collect the current. It is crucial that the PEDOT dispersions disperse well on the underlying layer and that it provides the necessary transport characteristics. [43]

C) PEDOT:PSS film electrode for sensing application

Conducting polymers consist one of the most important categories of sensing materials and have been integrated into **Sensory Systems** with superior performance because of their unique properties. Accordingly, due to their self-advantages, PEDOT and its composites, mainly PEDOT:PSS, have been used for the development of efficient chemo/bio-sensors and have facilitated their architecture in environmental monitoring, food and drug analysis and health care. Examples of such sensors include: electrochemical sensors, optical sensors, photoelectric sensors, transistor sensors, capacitive sensors, piezoelectric sensors, resistive sensors. [37] [44]

D) Other Applications for PEDOT derivatives

Apart from the above-mentioned applications, PEDOT-based polymers are currently, and will in the future be, integrated in many **Other Applications**. A few of these applications are listed: through-hole plating of printed circuit boards, antistatic coatings for cathode ray tubes to prevent dust attraction, primers for electrostatic spray coating of plastics, rechargeable batteries, cathode radiation tubes (CRTs), photodiodes, electrochromic windows, corrosion protection, membranes for the preparation of ^{40}K beta radioactive sources and photovoltaic devices. [42]

Consequently, these above examples show that PEDOT is one of the few organic conducting polymers that has successfully found its way from laboratory research to numerous technical applications.

CONFIDENTIAL

3 Experimental Part

3.1 Experimental Set-Up

The experimental set-up used to produce the PEDOT films by the oCVD process, can be divided into three main parts:

1) **Before** the Reactor

The initial part of our system consists of the **Oven**, in which the SbCl_5 and EDOT reservoirs are held and heated at a specific temperature ($90\text{ }^\circ\text{C}$) (**Figure 10**). The temperature of the oven affects the vapor pressure of the SbCl_5 and EDOT reservoirs and subsequently the amount of vapor that will enter the reactor. Its value should be that so there is an equilibrium of vapor and liquid inside the reservoir, since, in order to control the reaction, the flow rates of the gas reactants should be low. In that case, the deposition is slower and the produced films have robust characteristics, such as high conductivity values. For that reason, after multiple tests, it has been found that the ideal temperature to keep the reactants is at $90\text{ }^\circ\text{C}$. Additionally, a fan is available inside the oven, so that the air heating is evenly dispersed inside. At the exit of the oven, the tubes of the reactants have micro valves that control the flow. For EDOT and SbCl_5 the micro valve values vary from 0 to 10 turns.



Figure 10: The SbCl_5 and EDOT reservoirs inside the oven.

2) The **Reactor**, in which deposition occurs.

The entrance of the reactor is connected with three tubes carrying flowing gases, two of which are the ones from the oven containing the SbCl_5 and EDOT reactants. A crucial part of the experimental set-up is to transfer the reactants from the exit of the oven to the reactor and to maintain them at temperature over the one of the oven's (around 110°C) to avoid condensation on the tubes, which can lead to blocking of the flow. In addition, there are two extra two ways valves, one on each tube, to control the flow of the reactants. The third tube connected with the entrance of the reactor carries Nitrogen Gas (99,999%),

Messer), at a stable flow of 16,9 sccm and is set at temperature similar to the one of the reactants, so that it doesn't affect the deposition temperature. Nitrogen is an inert gas and so it doesn't participate in the deposition mechanism. Its main role is to help the reactants disperse uniformly along the reactor and to clean the inside from any traces of oxidant or monomer at the end of the deposition. It is also used to dilute the reactant thus reducing again the deposition rate.

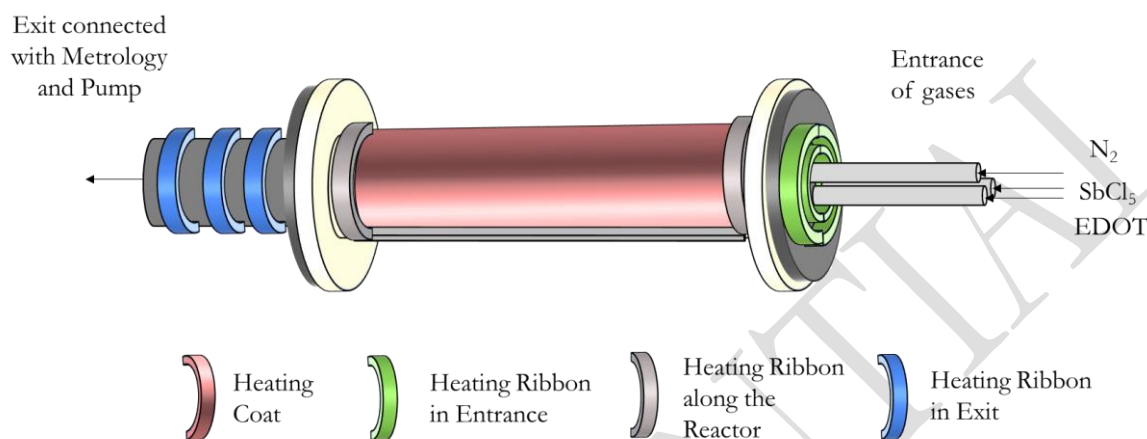


Figure 11: Schematic of the oCVD reactor.

The deposition takes place inside a horizontal, tubular, hot-wall reactor, (**Figure 11**) consisted of fused silica material with an inner diameter of 5 cm and a length of 32 cm. It is essential to maintain the temperature along its extent, so that there are similar conditions of temperature during deposition and to obtain films with coherent characteristics. A heating coat and three heating ribbons serve this purpose. The exit of the reactor is connected with a tube, which leads the unreacted gases to the liquid nitrogen trap. In **Figure 12** below, the thermopprofile of the reactor can be seen, which includes the temperature distribution along its length in detail.

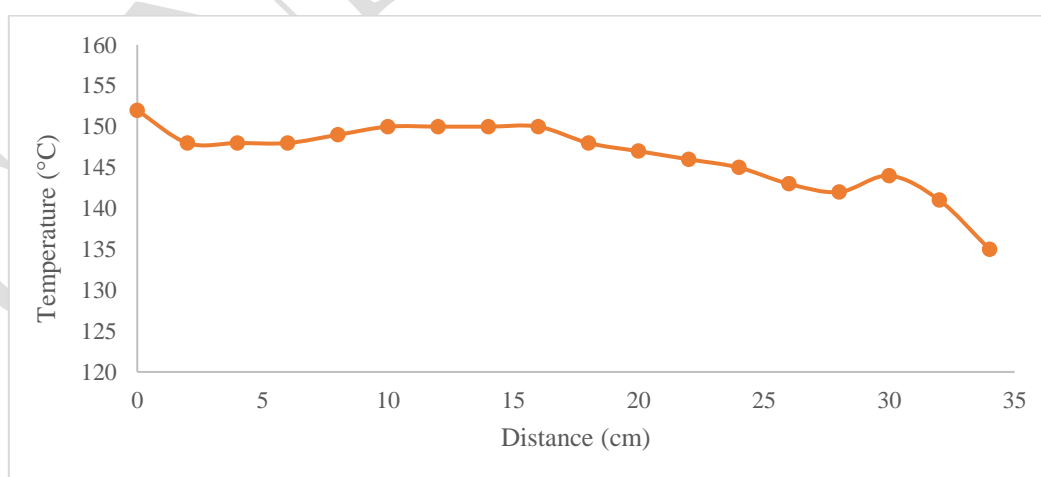


Figure 12: Thermopprofile of Reactor at Temperature $T=150$ °C. Distance of 0 cm corresponds to the entrance of the reactor.

3) After the Reactor

The part of the system after the reactor contains the Metrology, which measures constantly the conditions of the system, and the Pump Edwards XDS10, which sets the reactor to vacuum state.

The metrology of the system includes:

- Thermo-controllers, to set the temperature values (**Figure 13** and **Figure 14** accordingly),
- Tylan General Mass Flow Controller, to set the Nitrogen Gas flow value (**Figure 15**),
- MKS Type 651C Pressure Controller, to read the pressure value (**Figure 16**),
- Baratron Pressure Gauge, to record the pressure value
- Butterfly Valve, to adjust the pressure of the reactor



Figure 13: Thermoprofile of Reactor at Temperature $T=150\text{ }^{\circ}\text{C}$. Distance of 0 cm corresponds to the entrance of the reactor.

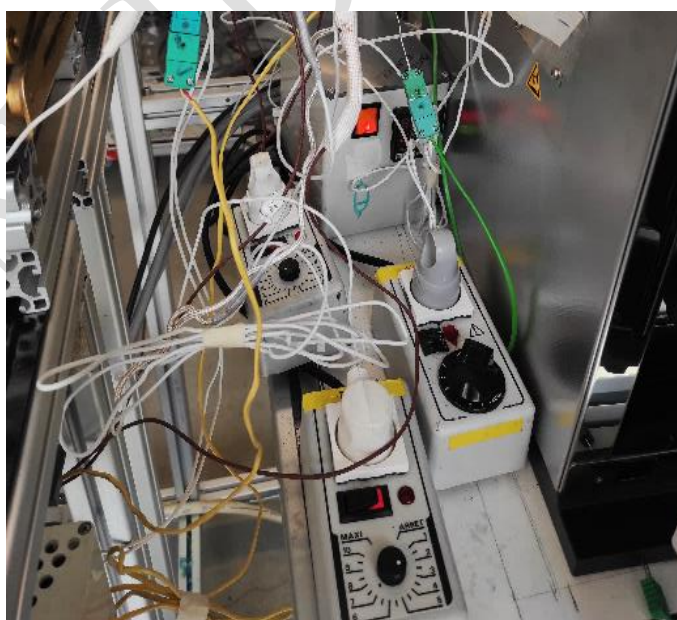


Figure 14: Thermo-controllers used for the heating purposes of the tubes containing the reactants.



Figure 15: Tylan General Mass Flow Controller.



Figure 16: MSK Type 651C Pressure Controller.

Figure 17 below, contains a flowchart which describes where each component stands in the total experimental set-up.

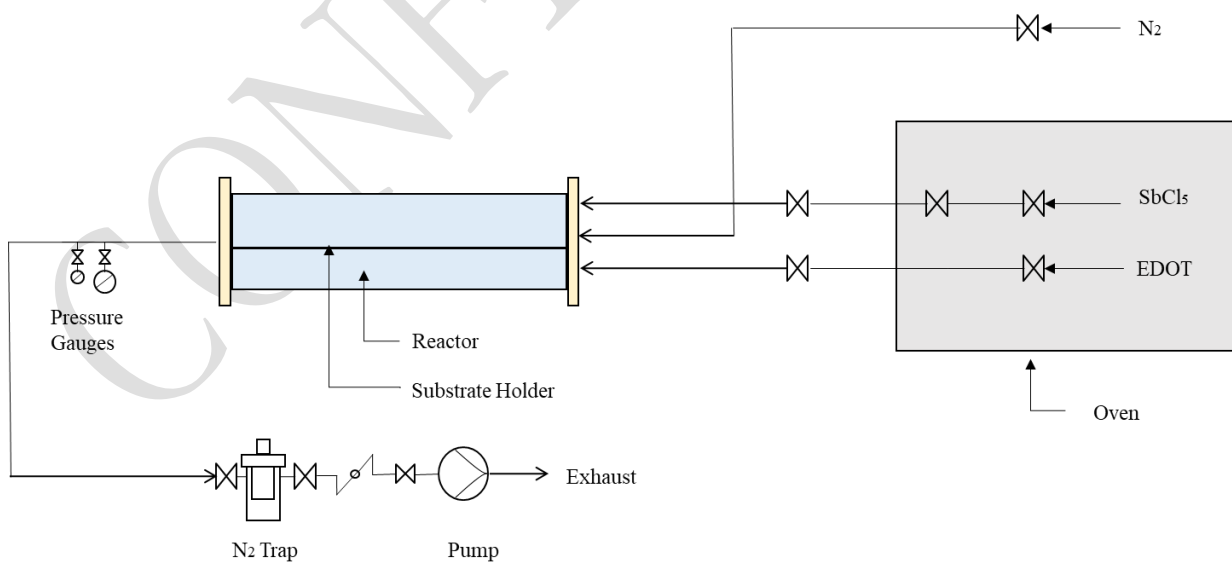


Figure 17: Flowchart of the Experimental Setup.

3.2 Materials

The PEDOT films of the present work were fabricated from monomeric 3,4-ethylenedioxythiophene (EDOT, 97%, Sigma-Aldrich) and oxidant SbCl_5 (99%, Acros Organic). The SbCl_5 reactant was filled in the reservoir in a glove box under argon atmosphere, due to the formation of HCl gas when in contact with air. The EDOT reactant was inserted in the reservoir under fume hood in air atmosphere. The amount of SbCl_5 and EDOT usually used was around 3-4 grams.

The PEDOT films were deposited in two types of substrates: **Glass Slide** (2,5 cm x 3,5 cm) and parts of **Silicon (1 0 0) Wafer (Neyco)** (**Figure 18**).

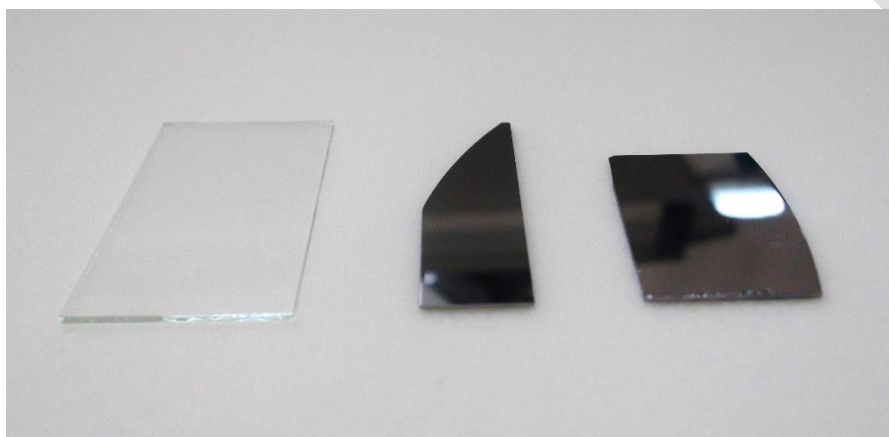


Figure 18: Glass Slide (left) and Silicon Wafer (center and right) substrates (post deposition).

Pretreatment of both substrates was done to clean them from any particles or traces. The cleaning process includes: ultrasonic bath in distilled water to remove dust, in acetone to remove organic material, in isopropanol (IPA) to remove organic and acetone remains, then drying under gas argon flow and finally plasma cleaning.

In order to place the substrates inside the cylindrical reactor, a glass substrate holder (30 cm x 4,2 cm x 2 mm) was used (**Figure 19**).

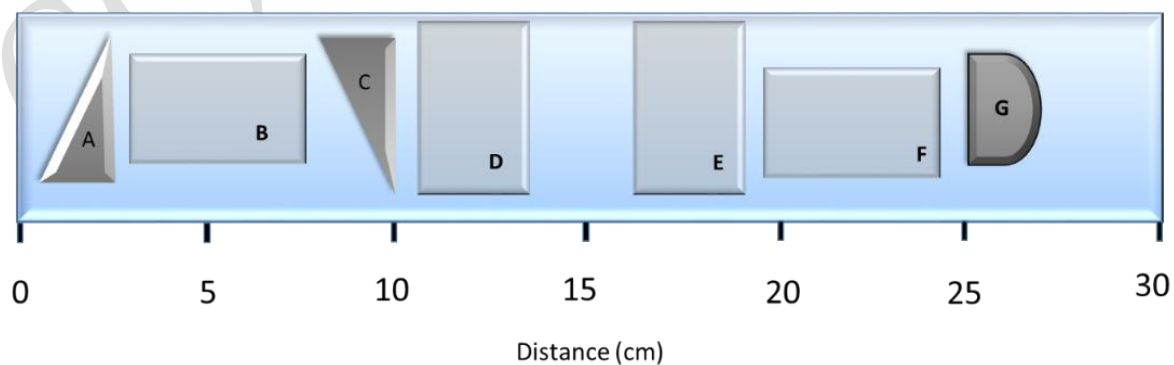


Figure 19: Schematic Illustration of the substrate holder containing the Glass Slide (B, D, E, F) and Silicon Wafer (A, C, G) substrates.

3.3 Characterization Methods

3.3.1 Four Point Probes

Four Point Probes is a tool used to measure the resistivity value of the PEDOT layers. A SIGNATONE Point Probe was used to make the measurements (**Figure 20**). The device is connected with software DASYLab9 and is coupled with two Keithley Sourcemeters; the one reads the applied current and the other one the resulting voltage.

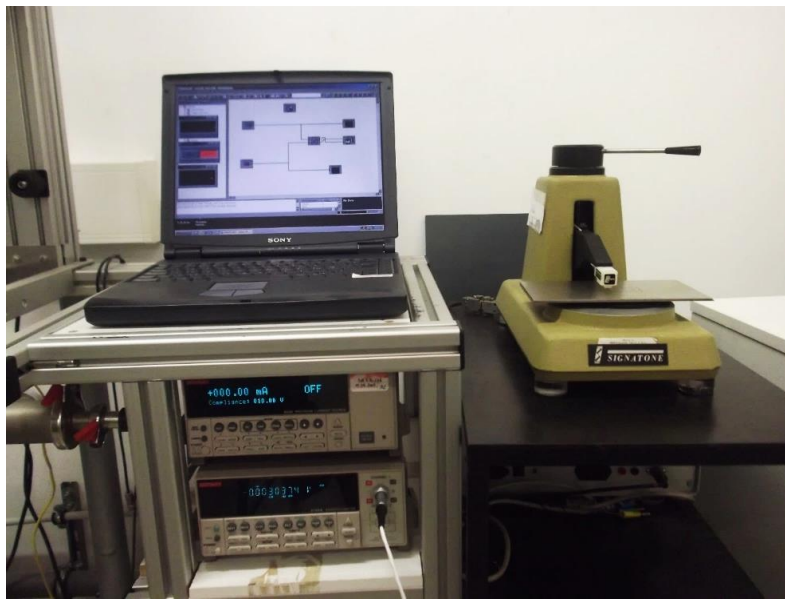


Figure 20: The total experimental setup of the Four Point Probe Measurement (SIGNATONE). On the right there is the measurer and on the left the two Keithley Sourcemeters (bottom part) and the computer connected with the measurer (upper part).

The measurer of this technique, like its name, consists of four probes, as shown in the **Figure 21** below. DC current is applied in the external two probes (1 and 4) and a voltage drop is measured between the inner two probes (2 and 3). They are made in a straight line and are arranged in a way so that they have the same distance between one another.

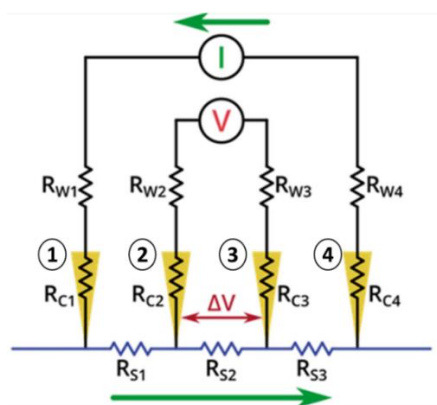


Figure 21: Circuit Diagram of a Four-Point Probe Measurer, showing the Wire Resistances (R_w), Contact Resistances (R_c) and Sample Resistances (R_s). The green arrow represents the current flow. [45]

As described, no current is flowing through the inner two probes (2 and 3), and therefore the wire resistances R_{W2} and R_{W3} , and the contact resistances of R_{C2} and R_{C3} do not influence the voltage measurement at the voltmeter. Only R_{S2} is involved in the measurement of voltage decrease ΔV between the inner probes. Consequently, the calculated ΔV is valid to be used along with the applied current in the equation to calculate the value of resistivity (ρ). More specifically, the resistivity equation is:

$$\rho = \frac{\Delta V}{I} \cdot c \cdot d, \quad [\Omega \cdot cm] \quad [\text{Eq. 2}]$$

where: V = Change in voltage measured between the inner probes (2, 3), I = Current applied between the outer probes (1,4), d =thickness of the film, c =4,532 correction factor.

Then, conductivity (σ) is calculated by reversing resistivity:

$$\sigma = \frac{1}{\rho}, \quad \left[\frac{S}{cm} \right] \quad [\text{Eq. 3}]$$

In the current measurements, three different currents were applied (10^{-6} A, 10^{-5} A and 10^{-4} A) in order to obtain an accurate value of resistivity. The control of the current is computer assisted. In each applied current, voltage drop in six different points on the PEDOT films was measured to estimate the variability of the resistivity (or conductivity) on the film, as shown in **Figure 22**. Similar values of resistivity (or conductivity) along the film show that oCVD process is reliable and produces PEDOT films with consistent characteristics, which is a factor of success of our project.

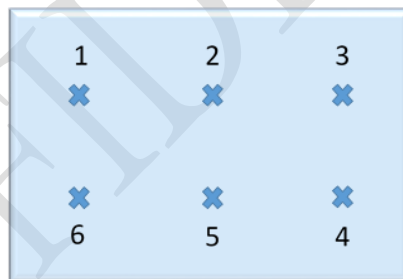


Figure 22: The six different points on the PEDOT films in which resistivity was measured.

3.3.2 UV-Vis Spectroscopy

UV-Vis Spectroscopy method was used to obtain Transmittance, T (%) data for the produced PEDOT films on glass substrates. UV-Vis Spectroscopy is an important characterization method for this work, since it is fast and provides us information regarding transmittance of the PEDOT films. A Cary 5000 UV-Vis-NIR Spectrophotometer (Agilent) was used for the characterization, which was operated at 900-250 nm wavelength range (**Figure 23**).



Figure 23: The Cary 5000 UV-Vis-NIR Spectrophotometer (Agilent).

UV-visible spectroscopy is a fast, inexpensive, non-destructive analytical technique that measures the absorbance or transmittance of light as a function of the wavelength. Its theory relies on electronic transitions of organic molecules, which happen when absorbing light and electrons excite from a lower energy orbital (highest occupied molecular orbital- HOMO) to a higher energy unoccupied orbital (lowest unoccupied molecular orbital- LUMO). The energy of the light wavelength absorbed should be equal to ΔE of the HOMO-LUMO energy gap and corresponds to a specific frequency which generates a variation in the distribution of the electronic density (electronic spectroscopy). [46] [47]

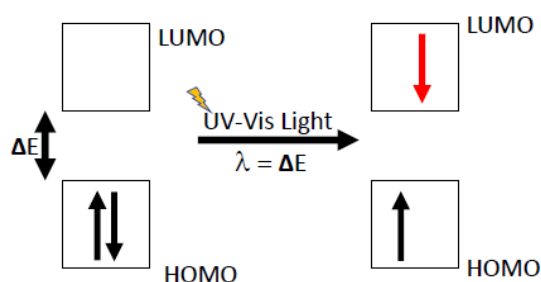


Figure 24: Molecular orbitals and energy gap needed to excite the electro energy state. [46]

The Bohr model can represent this impact:

$$\Delta E = E_2 - E_1 = h\nu \rightarrow h\nu = hc\bar{\nu} = \frac{hc}{\lambda} \quad [\text{Eq. 4}]$$

where E_1 and E_2 are the initial and final energies, respectively; h = Planck's constant (6.62×10^{-34} Js); c = light velocity in vacuum (2.99×10^8 m/s); ν = frequency; λ = wavelength; $\bar{\nu}$ = wavenumber. [47]

In addition, Lambert and Beer built a relation that connects the intensity of an absorption with the concentration and thickness of the absorbing species:

$$A = \varepsilon b c = -\log(T) = \log\left(\frac{1}{T}\right) \quad [\text{Eq. 5}]$$

where A = absorbance; ε = molar absorptivity or molar absorption coefficient; b = thickness of the sample; c = concentration; T = transmittance. [47]

The basic structure of a UV-Vis Spectrometer consists of one or more polychromatic light sources, one or two wavelength selectors to separate the radiation into its different wavelengths, and finally one or more detectors which measure the radiation coming in contact with the sample. [46] [47] In the current spectrometer, an internal sample holder was also included (**Figure 25**).



Figure 25: Sample Holder of the Cary 5000 UV-Vis-NIR Spectrophotometer.

Software «Scan Cary Win UV» connected with the spectrometer is used to select desired conditions for the characterization and to retrieve the results. The latter ones include graphs, which report Transmittance (%) on the y-axis and Wavelength in nanometers (nm) on the x-axis. Before characterization of samples, a baseline test is required to calibrate the machine in case of contamination or disturbance in the system. The baseline line can be seen in the graph. In order to execute the characterization, a glass with no deposited film is placed in the first holder and sample with deposited film to be characterized in the second holder. It should be mentioned that the Wavelength, λ (nm) that interest us due to the OLED application, is $\lambda=562$ nm. Therefore, the value of transmittance corresponding to wavelength $\lambda=562$ nm is the one that determines the transparency of the PEDOT film.

As mentioned, resistivity is measured through Four Points Probe Method and in order to calculate conductivity, thickness data are needed. During POLEN Project, thickness was measured by Atomic Force Microscopy (AFM) and was performed by another individual. However, AFM method shows some disadvantages during operation such as: slow rate of scanning and destruction of sample. This led to the search of a more viable method to calculate thickness of PEDOT films. For that reason, correlation

between Transmittance (%) by UV-Vis and Thickness (nm) by AFM is studied in the current work, to obtain thickness data from transmittance of the PEDOT films. This analysis will be further discussed in the Results and Discuss Section of the present Thesis.

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4 Results and Discussion

4.1 Correlation between Transmittance and Thickness

As mentioned in the Experimental Part, in order to estimate the Conductivity, σ (S/cm) of the produced PEDOT films, their Thickness, d (nm) has to be measured. For that reason, in the past work of POLEN project, Atomic Force Microscopy (AFM) was employed. However, this method shows some disadvantages, such as slow rate of scanning and destruction of sample, and a new way to calculate PEDOT film thickness had to be established. Contrarily to AFM, UV-Vis Spectroscopy is a fast and non-destructive characterization technique. In order to take advantage of these benefits, correlation between Transmittance, T (%) by UV-Vis and Thickness, d (nm) measured by AFM is studied, using data from 13 substrates (from past depositions done in the frame of this project), which were collected and combined in the graph seen below (**Figure 26**). Thus, an equation of T (%) = $f[d(\text{nm})]$ is obtained, which calculates directly the thickness of the films by using transmittance data. It is important to highlight, that the transmittance values correspond to the wavelength λ of 562 nm, as it is the dominant wavelength of the OLED made as part of this project.

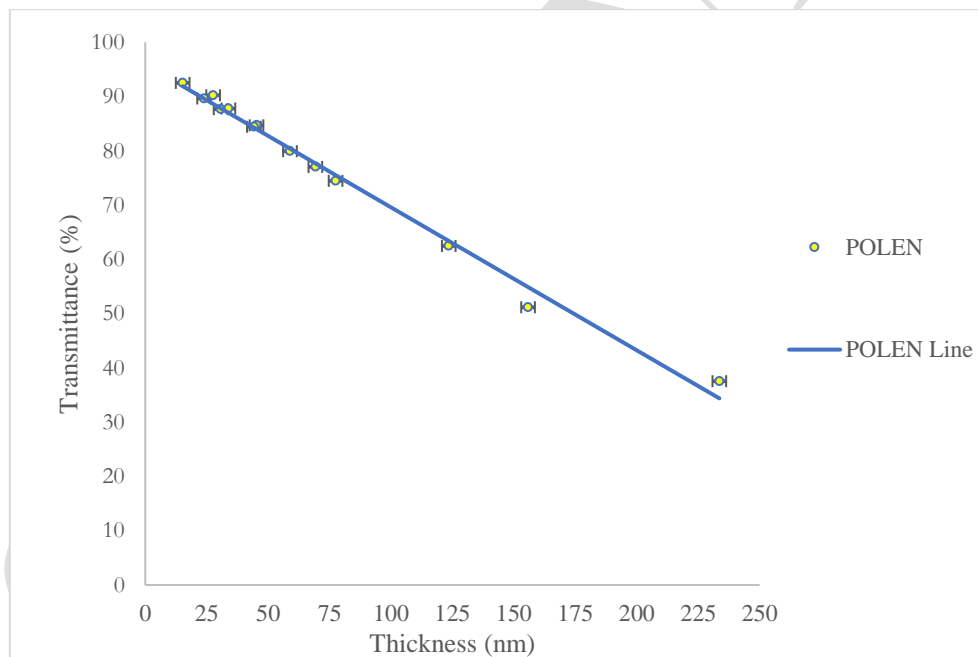


Figure 26: Correlation between Transmittance (%) determined by UV-Vis and Thickness (nm) determined by AFM of PEDOT films. The straight line is a trendline indicating the linear correlation between Transmittance and Thickness of PEDOT films.

A linear correlation between the two parameters can be observed with a coefficient of determination of $R^2=0,991$, which is showing a good adaptation of the line to the data. The equation obtained is as follows:

$$T = -0,26 \cdot d + 95,93, \quad R^2 = 0,991 \quad [\text{Eq. 6}]$$

Error bars are added to the graph too. The error of transmittance is equivalent to the error of the UV-Vis machine and is calculated by repeating four measurements on the same sample; results of these tests can be seen in the **Table 1** below. From these values of transmittance, the standard error is **0,16%**.

Table 1: Results of Transmittance and Thickness for the calculation of the machine error of UV-Vis.

No. of Test	Transmittance (%)	Thickness (nm)
1	76	78
2	76	78
3	76	77
4	76	77

Regarding the error thickness measured by AFM it is equivalent to the standard deviation of the measurements, which, after gathering results of thickness by AFM, it has been found to be around **2,7 nm**. (More specifically, the AFM method measures thickness on multiple points on the film, and the final thickness corresponds to the average of these values. Therefore, this deviation of the measurement data on a single film corresponds to the error thickness measured by AFM.)

In order to increase the accuracy of **Eq.6** each time after a deposition, data of transmittance and thickness regarding PEDOT films were added to the graph of **Figure 26**. Therefore, 15 more sets of data are included. The transmittance of a clean glass slide (substrate used in this study for the PEDOT deposition) without any deposition was also measured and added to the graph as the intersection at X=0. The new version of **Figure 26**, including the new data points, is seen in **Figure 27**, below.

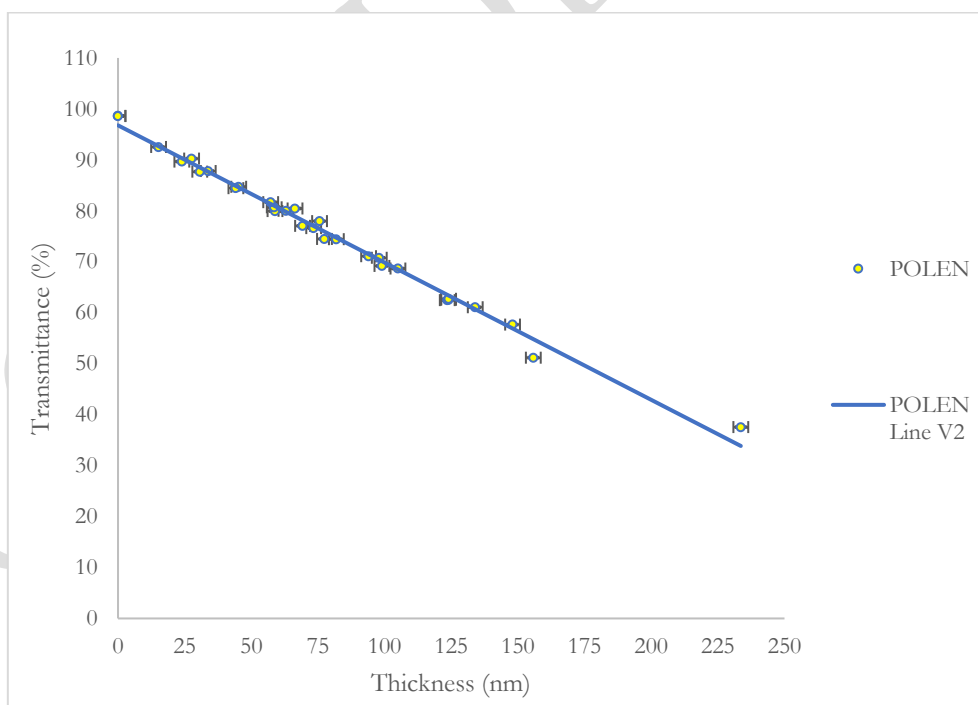


Figure 27: Correlation between Transmittance (%) determined by UV-Vis and Thickness (nm) determined by AFM of PEDOT films, using data from 30 samples, 2 of which refer to pure glass slide with no deposited material. The straight line is a trendline indicating the linear correlation between Transmittance and Thickness of PEDOT films.

The new equation obtained with 30 data points is shown below:

$$T = -0,27 \cdot d + 96,78, \quad R^2 = 0,991 \quad [\text{Eq. 7}]$$

Comparing **Eq.6** and **Eq.7**, it is apparent that they have the same coefficient of determination, R^2 . Taking into account that **Eq.7** includes more sets of data, in addition to the values of pure glass slide, it seems as a more viable route to calculate the thickness of the PEDOT films through transmittance.

As a next step to evaluate the performance of **Eq.7**, the results of thickness from this equation with the ones from measurement by AFM should be compared. For that reason, in a set of 13 deposited substrates, two values of thickness are measured for each sample: one by using AFM and one by UV-Vis Method using **Eq.7**.

Table 2: Data of Thickness (nm) of 13 PEDOT films calculated by AFM and UV-Vis (**Eq.7**). A percentage of the absolute difference of these two values is also added.

Substrate	AFM (nm)	UV (nm)	abs(AFM-UV) (%)
1	57	58	1%
2	59	58	0%
3	63	61	3%
4	66	59	11%
5	73	74	1%
6	76	69	9%
7	82	82	1%
8	94	95	1%
9	98	96	2%

The average deviation of **Eq.7** to AFM, which corresponds to the real thickness, is equal to **3%**, based on the results of **Table 2**. It is not considered as a high value and for that reason, **Eq.7** can be valid for the calculation of thickness, even though there might be a small inclination from the real value.

Lastly, data from literature regarding Transmittance and Thickness of PEDOT were retrieved and were compared with the results of **Eq.7**, which are seen on **Table 3**. The literature on oCVD is relatively limited, since it is a recent CVD method, and most do not mention transmittance data of PEDOT, as it is not relevant for their applications. Therefore, the data used for this comparison are of PEDOT films fabricated with FeCl_3 as oxidant and not with SbCl_5 which is used in the current project. To this day, there are no studies proving that the oxidant may have an influence on the transmittance values and therefore these are the only data available to our knowledge that can be used for the comparison with the results of **Eq.7**.

Table 3: Data of Transmittance (%) and Thickness (nm) of PEDOT films from Literature.

Literature	Transmittance (%)	Thickness (nm)
Sunghwan Lee et al. [48]	80	55
Rachel M. Howden et al. [49]	80	15
	90	27
Peter Kovacik et al. [50]	88	46
	75	88
Commercial ITO [51]	84	100

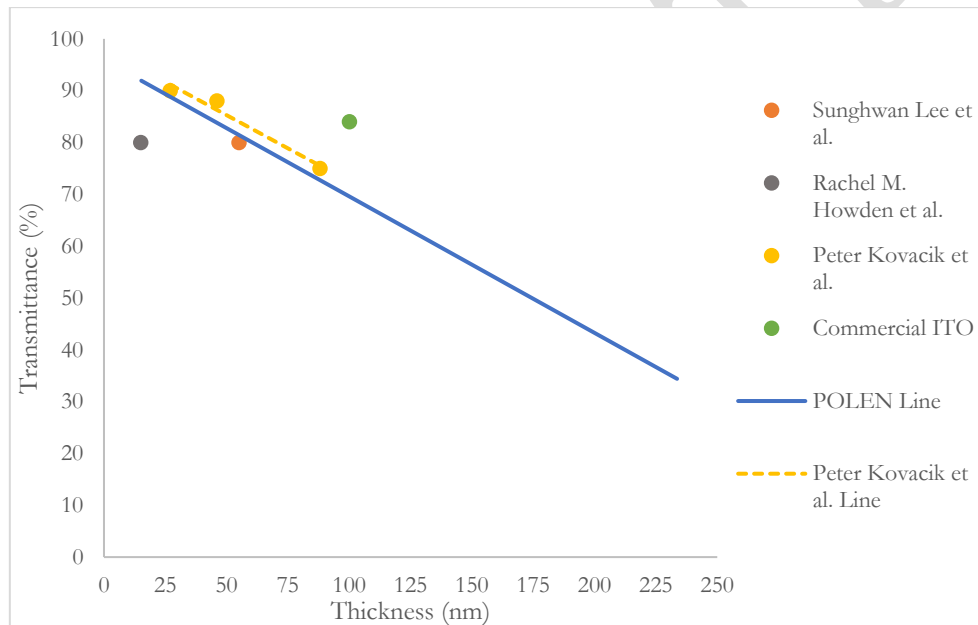


Figure 28: Correlation between Transmittance (%) determined by UV-Vis and Thickness (nm) determined by AFM of PEDOT films, using data from 30 samples, 2 of which refer to pure glass slide with no deposited material. Literature data regarding PEDOT films and ITO are also included for comparison with the POLEN data. The straight lines are trendlines indicating the linear correlation between Transmittance and Thickness of PEDOT films.

Peter Kovacik et al. provide three experimental points and so an equation can be determined:

$$T = 0,26 \cdot d + 98,09, \quad R^2 = 0,96 \quad [\text{Eq. 8}]$$

It can be concluded, that **Eq.8** is in good agreement with **Eq.7** and with the data point given by Sunghwan et al. Rachel M. Howden et al. shown a transmittance of 80% for a 20 nm PEDOT film and therefore, our film demonstrated higher performance and it is more adapted to the OLED application.

As mentioned previously, one goal of POLEN Project is to use PEDOT films produced by oCVD to replace ITO in the OLED application. Therefore, it is important to compare the PEDOT films fabricated by POLEN to commercial ITO. For that reason, commercial ITO's values of transmittance and thickness are added in **Figure 28** too, in order to compare the two materials. As seen in **Figure 28**, it is evident that ITO still has an advantage on PEDOT for now. Therefore, one future object of research for the development of PEDOT by oCVD lays in the understanding of the factor which influences the PEDOT film transmittance and therefore the further optimization of the oCVD process.

In summary, a good correlation between transmittance and thickness was determined and the following equation was developed:

$$d = \frac{96,78 - T}{0,27} \pm 3 \% \quad [\text{Eq. 9}]$$

Where, d=Thickness of PEDOT films(nm), T=Transmittance measured by UV-Vis Spectroscopy (%)

In the following sub-chapters, when presenting thickness of PEDOT films, it corresponds to the one calculated using **Eq.9**. Some limitations of this method that should be taken into account prior to using it, are the following:

- i) Deposition should occur on only one side of the glass slide substrate, since double-sided layer of PEDOT would lead to decreased value of transmittance compared to a single layer and therefore that would correspond to false PEDOT thickness by using **Eq.9**. It is important to clean the undeposited side of the sample to make sure that no PEDOT has been deposited there.
- ii) There should be uniform deposition of PEDOT along the substrate, because UV-Vis method characterizes a small part of the substrate and the results of transmittance are generalized for the whole sample.
- iii) The core characteristics of PEDOT films should remain the same, so that transmittance values are not affected. **Eq.9** refers to PEDOT fabricated under specific conditions, as mentioned in the Experimental Part and these should be maintained that same in order to use this equation to calculate thickness. Otherwise, a new version of **Eq.9** should be created if PEDOT has a different chemical composition.
- iv) The thickness of very thin or thick PEDOT films still needs to be further checked by AFM to increase the validity of **Eq.9**.

Despite the above restrictions, the route of calculation of PEDOT film thickness through UV-Vis still is reliable and quicker compared to AFM, making it a strong tool for the characterization of PEDOT films in this project. AFM method can still be used in the case of a two-sided deposition on glass slide sample and on very thin or thick PEDOT films in order to further verify the results calculated using **Eq.9**.

4.2 Establishing the reproducibility of the oCVD system

Reproducibility is a crucial parameter in the development of any new process. In the case of oCVD of PEDOT, this applies to the strict control of temperature of the system and also the control of the reactants flux. In the following sub-chapters, the practices applied in the current oCVD to improve its reproducibility will be discussed.

4.2.1 Study of the distribution of temperature in the system

As mentioned in the Theoretical Part, temperature is crucial for the deposition reaction and for that reason, an investigation of the distribution of temperature along the reactor was done, by creating a thermoprofile. The latter is a graph, which depicts temperature values measured in specific points in the reactor. Temperature was measured with the help of a thermocouple every 1 cm from the beginning of the reactor, corresponding to 0 cm, until 33 cm, which is the end of the reactor.

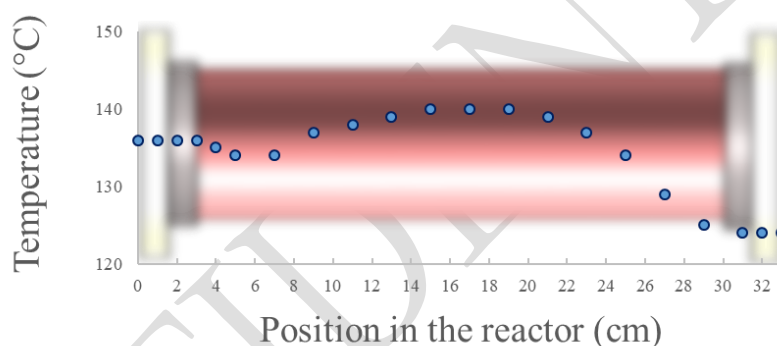


Figure 29: Thermoprofile of oCVD Reactor. Values of the thermocontrollers: Entrance:150 °C, Heating Coat: 150 °C, Exit: 150 °C.

As it can be seen in **Figure 29**, the temperature after 20 cm, from the beginning of the reactor, drops quickly by 10°C. Therefore, the value of the thermocontroller corresponding to the exit of the reactor is increased, to stabilize this variation of temperature. The new distribution of temperature can be seen in the next thermoprofile in **Figure 30** below.

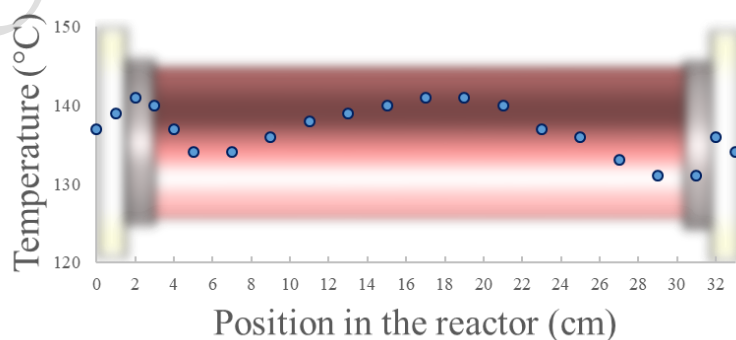


Figure 30: Thermoprofile of oCVD Reactor. Values of the thermocontrollers: Entrance:150 °C, Heating Coat: 150 °C, Exit: 165 °C.

As it can be seen, the temperature tends to be more uniform compared to the previous heating state of the reactor (**Figure 29**). Therefore, this study provides us that the deposition temperature is stable enough along the reactor to produce PEDOT film with coherent characteristics.

4.2.2 Study of reactants (EDOT and SbCl₅) Flux

Later, it was important to study the reproducibility of the reactants, EDOT and SbCl₅ flow rates, to ensure the success of the deposition in the later experiments. For that reason, their flux had to be calculated.

Before and after each deposition, the mass difference of the SbCl₅ and EDOT reservoirs was determined using a KERN ABS 320-4 N balance with a precision of 0,1 mg. By this method, flow rates of the vaporized SbCl₅ and EDOT can be calculated through **Eq.10** below.

$$Flow\ Rate_i = \frac{m_{evaporated}}{t \cdot M_i} \cdot 22400 , \quad [sccm] \quad [Eq. 10]$$

Where: i=EDOT, SbCl₅, $m_{evaporated}$ =evaporated mass (g), t=time of evaporation (min), M_{EDOT} =142,17 g/mol, M_{SbCl_5} =299 g/mol

Firstly, four tests of EDOT's flow were performed to ensure the monomer's reproducibility, preserving the same conditions at each time EDOT valve turn was set at 3 and time of EDOT flow was 10 minutes). In the **Table 4** below, the data obtained from these four tests can be seen.

Table 4: Results of EDOT Fluxes from different Tests.

No. of Test	EDOT Flux (sccm)
1	2,7
2	2,7
3	2,5
4	2,4

The results from **Table 4** reveal that the tests show a great similarity and that is a good outcome, since it can be verified that EDOT has a stable behavior in the current oCVD system, leading to uniform results.

Next step is to ensure the same conclusions regarding the reproducibility for the oxidant; **SbCl₅**. At first some explanations related to technical changes in the deposition protocol done in order to improve the consistency of the SbCl₅ flux will be presented. Later, results of flux after these amendments will be shown.

At the beginning of this work, it was noticed that at some deposition tests, the tube of the oxidant was blocked due to condensed material on the walls. This happened, due to unstable values of temperature along the tube carrying the oxidant inside the oven, since condensing temperature of SbCl₅ is below 100 °C. Therefore, it was crucial to ensure a stable distribution of temperature along the length of the SbCl₅ tube in order to avoid deposited material which would block the flow of the oxidant and consequently the

deposition reaction. To solve this problem, a heating ribbon around the SbCl_5 tube was inserted and adjusted at $110\text{ }^\circ\text{C}$. This amendment to the system brought a positive impact on the SbCl_5 flow, since after a few deposition tests, less or no deposited oxidant was seen on the tube's components and most importantly the SbCl_5 flux had stable values on each deposition.

Results of SbCl_5 flux from deposition tests after these improvements (SbCl_5 valve turn set at 2), are presented below in **Table 5**.

Table 5: Results of SbCl_5 Fluxes (sccm) from different deposition tests.

No. of Test	SbCl_5 Flux (sccm)
1	2,4
2	2,9
3	2,8

Based on these values of flux, it can be concluded, that SbCl_5 flux is stable enough to lead to a reproducible deposition.

4.3 Influence of Deposition Duration t_d (min)

4.3.1 VarTime Tests

As mentioned in the Theoretical Part, time of deposition plays an important role in the characteristics of the PEDOT films, since it is known that by increasing deposition time film thickness linearly increases too. Therefore, it is essential to see if this fact applies to the oCVD process as well and also to see how the conductivity of the PEDOT films will be influenced by this change, as it could modify the packing of the polymer chains, a crucial parameter to conductivity. It should be mentioned that the PEDOT film characteristics are measured for each glass slide substrate (named as B, D, E, F) used. The exact placement of each substrate on the substrate holder and therefore its position along the reactor can be seen in detail by **Figure 19**: Schematic Illustration of the substrate holder containing the Glass Slide (B, D, E, F) and Silicon Wafer (A, C, G) substrates.

In the previous work of POLEN, the standard duration of deposition was 5 min. Thus, it is important to understand how the properties of PEDOT films evolve by higher and lower durations. Especially, the lower ones consist of an object of interest, since they are close to the starting point of the deposition and it is intriguing to see if deposition is instant, or if it is a slow reaction, with constant rate independent of duration of deposition. For that reason, growth rate of deposition, r_d (nm/min) is also calculated.

$$r_d = \frac{d}{t_d}, \quad \left[\frac{\text{nm}}{\text{min}} \right] \quad \text{[Eq. 11]}$$

Where: d = thickness of PEDOT films (nm), t_d = duration of deposition (min)

For the study of influence of time to the oCVD system, six tests (VarTime) were performed by varying deposition time, with conditions seen in the **Table 6** below. The rest of the conditions, except for deposition time, were kept the same for all the experiments.

Table 6: Deposition conditions for VarTime tests.

Test	Deposition Time, t_d (min)	Deposition Temperature, T_d (°C)	Pressure, P (Torr)	SbCl ₅ Flow Rate (sccm)	EDOT Flow Rate (sccm)
VarTime2	2	150	0,33	2,7	2,1
VarTime2,5	2,5	150	0,33	2,7	2,1
VarTime5	5	150	0,33	2,7	2,1
VarTime8	8	150	0,33	2,7	2,1
VarTime15	15	150	0,33	2,7	2,1

It should be reported that the tests were performed in random order and not by starting from the lowest t_d to the highest.

The results of the above runs are presented in the graphs, which are seen below. These graphs include effect of deposition time to film thickness (**Figure 31**), conductivity (**Figure 32**) and growth rate (**Figure 33**), measured on the four glass slide substrates (B, D, E, F) as presented in the Experimental Part.

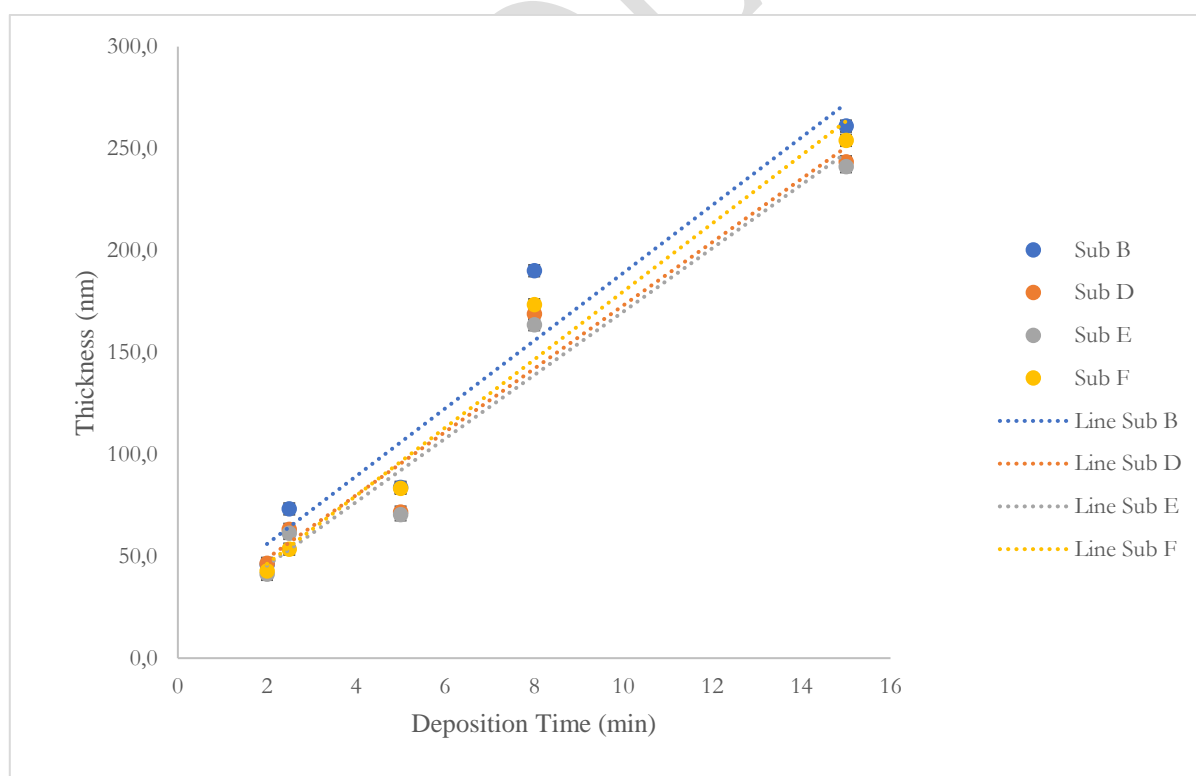


Figure 31: Effect of Deposition Time to the Thickness of PEDOT films.

Observing the graph above (**Figure 31**), it can be seen that there is a linear trend between thickness and deposition time, as expected. More specifically the regression line for each substrate is:

$$\text{Sub B} \quad d = 16,62 \cdot t_d + 22,75, \quad R^2 = 0,94 \quad [\text{Eq. 12}]$$

$$\text{Sub D} \quad d = 15,52 \cdot t_d + 17,86, \quad R^2 = 0,95 \quad [\text{Eq. 13}]$$

$$\text{Sub E} \quad d = 15,57 \cdot t_d + 14,27, \quad R^2 = 0,96 \quad [\text{Eq. 14}]$$

$$\text{Sub F} \quad d = 16,71 \cdot t_d + 12,81, \quad R^2 = 0,97 \quad [\text{Eq. 15}]$$

A comment that can be made is that the substrates at the end of the reactor (E and F) show a more linear behavior than the other ones (higher coefficient of determination). A reason for this could be that the substrates in the entrance of the reactor are more impacted by the flow of the reactants and nitrogen, leading to inconsistent product of PEDOT. For that reason, the deposition of PEDOT in the first part of the reactor (between 0 and 15 cm) is not so effective.

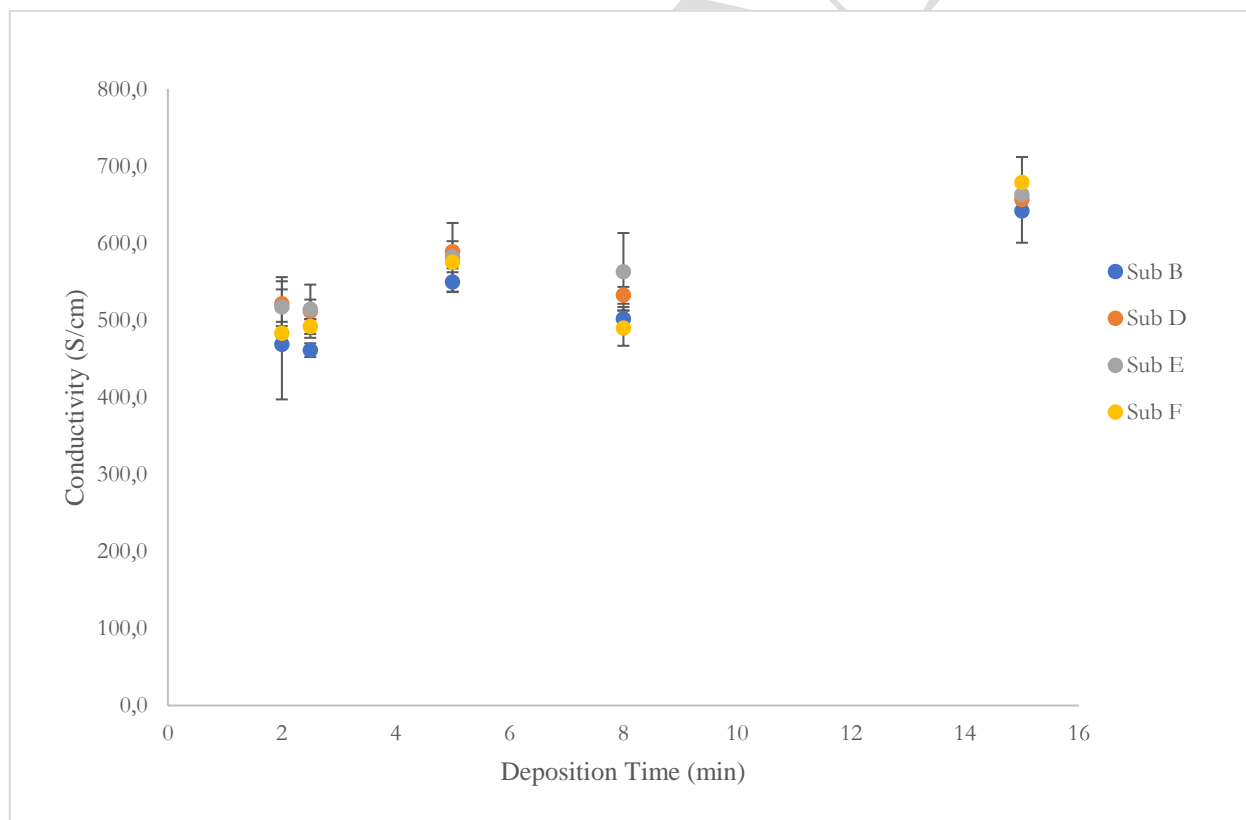


Figure 32: Effect of Deposition Time to the Conductivity of PEDOT films.

Studying the above graph (**Figure 32**), conductivity values are around 500-600 S/cm, with a maximum one of 678 S/cm achieved at deposition time $t_d=15$ min, corresponding to film thickness around 250 nm. A small increase of conductivity by increasing deposition time can be seen. This could be justified by the fact that in very thin films there is a bigger error of measurement compared to the thicker ones, leading to varied results. Taking into account that the variation is small, this event is considered insignificant. In

general, it is expected for conductivity to be independent of the film thickness, and of deposition time as well; therefore, this type of behavior depicted in the graph is valid.

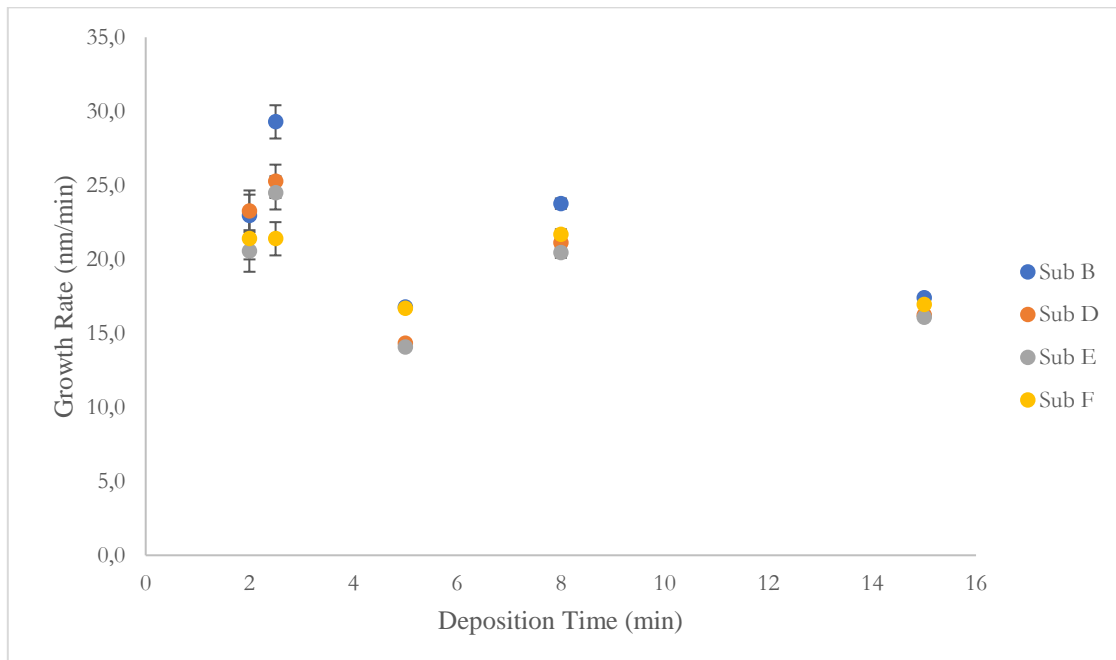


Figure 33: Effect of Deposition Time to the Growth Rate of oCVD reaction.

Regarding deposition growth rate, it is observed in **Figure 33**, that in small deposition times it tends to have larger error bars compared to the bigger deposition times, showing that deposition in the first minutes varies, while at some point a few minutes later, it is getting steadier among the substrates. In addition, at t_d of 15 min, the biggest duration of deposition tested, all four substrates show similar growth rate (16-18 nm/min and 15-16 nm/min accordingly for substrates B, D, E, F) which confirms that deposition is more reliable in bigger deposition times.

4.3.2 Repeating VarTime Tests

In order to verify the previous results, a second run of the above experiments at the same five different durations of deposition was done, preserving the same conditions as well. An extra experiment of deposition time of 3 minutes is also added to the study. It should be noted, that in this run too, the tests were done in random order and not by increasing time of deposition.

Table 7: Deposition conditions for VTime tests.

Test	Deposition Time, t_d (min)	Deposition Temperature, T_d (°C)	Pressure, P (Torr)	SbCl5 Flow Rate (sccm)	EDOT Flow Rate (sccm)
VTime2	2	150	0,30	2,7	2,1
VTime2,5	2,5	150	0,32	2,7	2,1
VTime3	3	150	0,31	2,7	2,1
VTime5	5	150	0,30	2,7	2,1
VTime8	8	150	0,31	2,7	2,1
VTime15	15	150	0,31	2,7	2,1

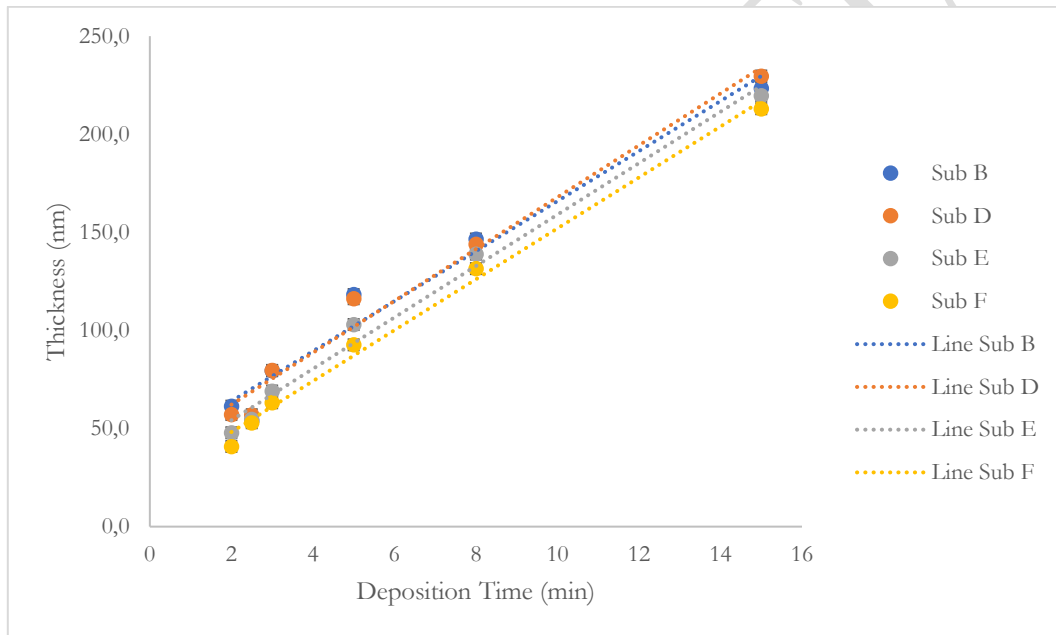


Figure 34: Effect of Deposition Time to the Thickness of PEDOT films.

The new equations correlating Thickness and Deposition time are:

$$\text{Sub B} \quad d = 12,75 \cdot t_d + 38,42, \quad R^2 = 0,97 \quad [\text{Eq. 16}]$$

$$\text{Sub D} \quad d = 13,22 \cdot t_d + 35,72, \quad R^2 = 0,98 \quad [\text{Eq. 17}]$$

$$\text{Sub E} \quad d = 13,11 \cdot t_d + 27,99, \quad R^2 = 0,99 \quad [\text{Eq. 18}]$$

$$\text{Sub F} \quad d = 12,98 \cdot t_d + 22,25, \quad R^2 = 0,99 \quad [\text{Eq. 19}]$$

From the above equations, it can be observed that the PEDOT film thickness in this set of experiments showed better uniformity and consistency among the substrates. The adaptation of the thickness data to the linear line is very good (R^2 coefficient very close and equal to 0,99) which validates the linear relation between thickness of PEDOT films and the deposition time, stated before. Comparing these equations (Eq.16 to Eq.19) with the ones obtained from the previous run (Eq.12 to Eq.15), it can be seen that the current ones show better behavior. This can be attributed to the fact that the experiments were performed close to each other, without turning off the equipment and without cooling down the two reactants. $SbCl_5$ and EDOT were able to produce in that way PEDOT films with consistent characteristics, due to their robust conditions of reaction. This information is very important for the following part of the project to increase the robustness of the process.

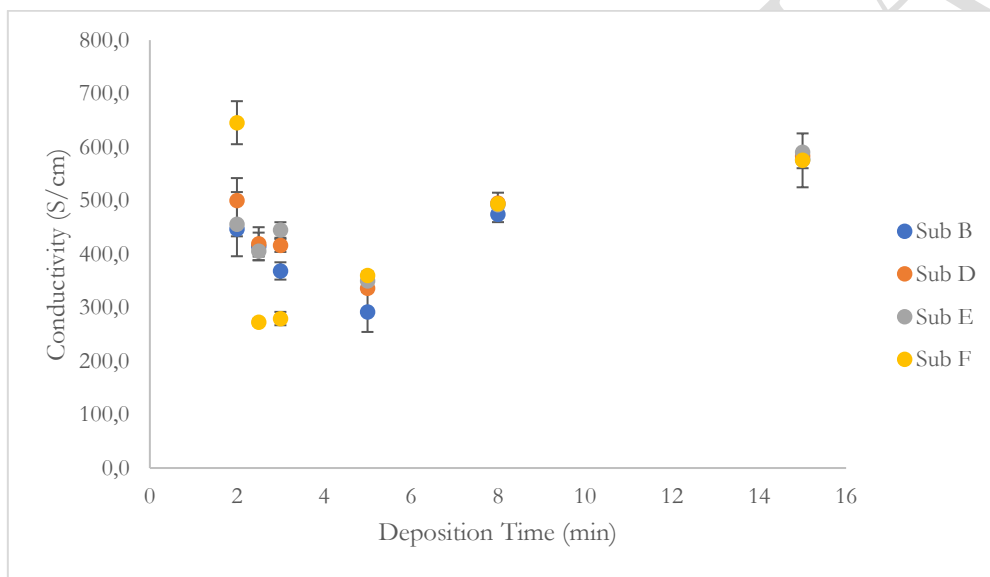


Figure 35: Effect of Deposition Time to the Conductivity of PEDOT films.

Conductivity values of the produced PEDOT films in this run of experiments are around 350 S/cm to 600 S/cm, with a maximum value of 645 S/cm at $t_d=2$ min of a 40 nm film. In the low deposition durations, the conductivity values show a trend of decrease compared to the previous set of experiments. This can be explained by the fact that in low deposition times, the reaction corresponds to the transient behavior of the process that can't be easily predicted. PEDOT films fabricated in higher deposition times (15 min and 8 min) show better performance regarding conductivity and uniformity among the substrates, like shown in the previous run. Therefore, it can be concluded, that the properties of the PEDOT films at low deposition times can be unpredictable and these deposition durations are not reliable, due to the transient nature of the reaction. However, it should be mentioned that the protocol at the beginning of the deposition is crucial, since when it is executed precisely on each deposition, then results will be similar with one another. This is a reason of probably why the PEDOT film characteristics vary among the low deposition times tests.

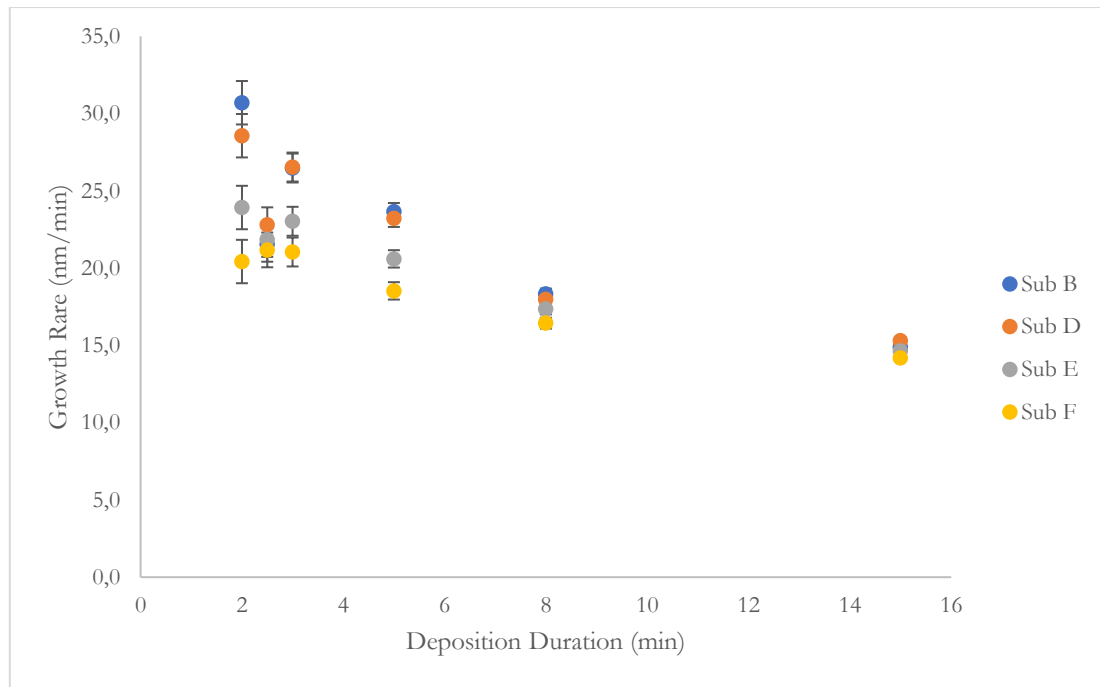


Figure 36: Effect of Deposition Time to the Growth Rate of oCVD reaction.

Studying **Figure 36** above, the exponential relation between growth rate and deposition duration can be seen. As time of deposition increases, growth rate decreases, as well as the deviation among the substrates. Especially, for $t_d=15$ min, the growth rate is much more consistent among the four substrates, indicating the steady and uniform deposition at that time, as proven before. On the other hand, at low deposition times, the range of growth rate is larger, which confirms the transient behavior of the process for short deposition times.

4.4 Influence of Temperature of Deposition T_d (°C)

4.4.1 Thermoprofiles of the oCVD reactor

As mentioned in the Theoretical Part, temperature of deposition plays an important role in the characteristics of the produced PEDOT films and especially in their conductivity, a property that is essential to be enhanced according to this work's goals. According to the literature [52], $SbCl_5$ decomposes at temperatures around 150 °C, and for that reason, the standard temperature of deposition in the previous experiments of this work was 150 °C. However, the phenomenon of decomposition is not clear and could be beneficial to a certain point, as it could produce free radicals of chloride, which promote perfect PEDOT polymerization [4]. Furthermore, in post work found in literature [7], it has been found that increased deposition temperature leads to higher doping effect, resulting to improved conductivity of PEDOT films. Therefore, it is interesting to see the effect of a range of deposition temperatures to the oCVD process. For these above reasons, temperatures with a difference of 20 °C, lower and higher than 150 °C were explored and the total strategy of this study can be seen in **Figure 37** below.



Figure 37: Deposition Temperatures, T_d (°C) that are investigated in this set of experiments.

Therefore, in order to make this study, temperature of the whole oCVD reactor had to be changed and adapted to each of these values. As shown in the Experimental Part, for the heating purposes of the oCVD reactor, three thermocontrollers are used and for that reason it is complex to achieve uniform temperature along the length of it. In order to understand the temperature distribution and to see how it evolves in the different parts of the reactor, **Thermoprofiles** at these five different temperatures (by changing appropriately the temperature values of the thermocontrollers) had to be done in advance, before performing the deposition test at each temperature.

In total five thermoprofiles were done, with each one corresponding to one of the desired T_d , and the results can be seen in the **Figure 38** to **Figure 42** below. The temperature was measured with the help of a thermocouple every 2 centimeters from the beginning of the reactor, corresponding to 0 cm, until 30 cm, which is the end of the substrate holder when inserted in the reactor. In this way, the temperature along the substrate holder (and therefore of each substrate) was measured, which is the aim of this analysis.

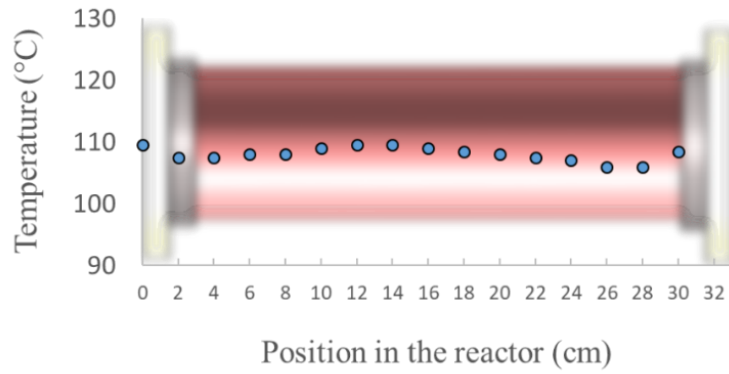


Figure 38: Thermopprofile of oCVD Reactor for deposition temperature $T_d=110$ °C. Values of the thermocontrollers: Entrance:110 °C, Heating Coat: 110 °C, Exit: 125 °C

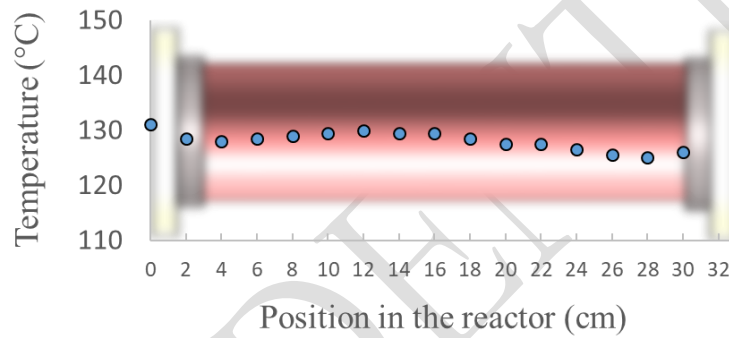


Figure 39: Thermopprofile of oCVD Reactor for deposition temperature $T_d=130$ °C. Values of the thermocontrollers: Entrance:130 °C, Heating Coat: 130 °C, Exit: 145 °C

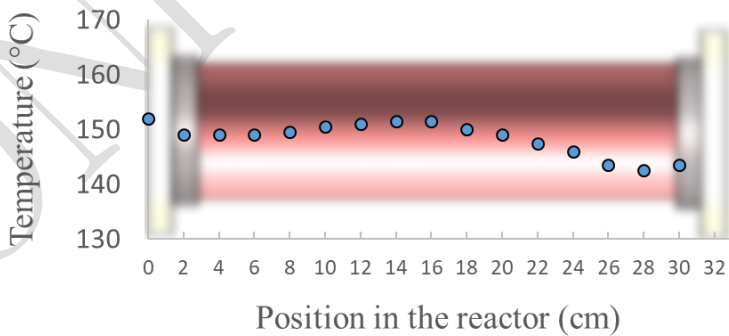


Figure 40: Thermopprofile of oCVD Reactor for deposition temperature $T_d=150$ °C. Values of the thermocontrollers: Entrance:150 °C, Heating Coat: 150 °C, Exit: 165 °C

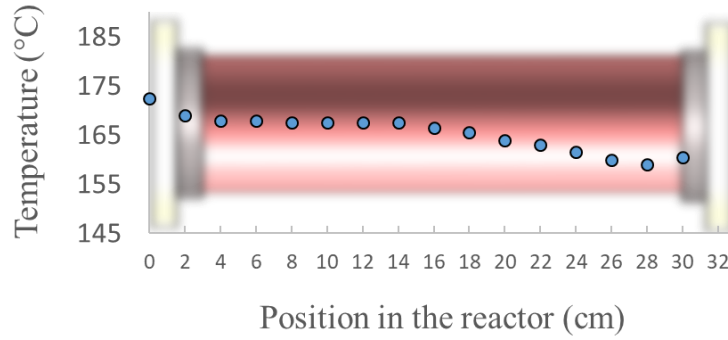


Figure 41: Thermopprofile of oCVD Reactor for deposition temperature $T_d=170$ °C. Values of the thermocontrollers: Entrance:170 °C, Heating Coat: 170 °C, Exit: 195 °C

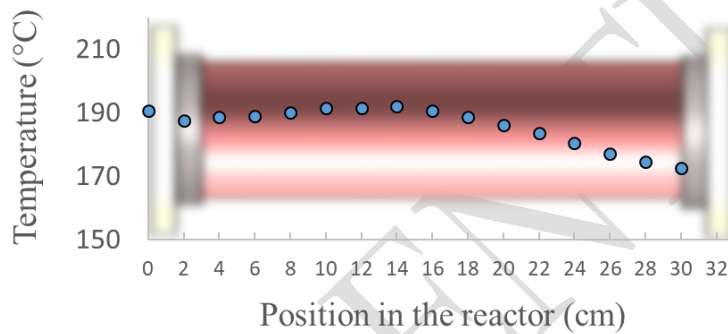


Figure 42: Thermopprofile of oCVD Reactor for deposition temperature $T_d=190$ °C. Values of the thermocontrollers: Entrance:190 °C, Heating Coat: 190 °C, Exit: 192 °C

As it can be seen, the thermopfiles show a rather constant temperature along the length of the reactor, a crucial factor for the deposition process. Only the last thermopfile (**Figure 42**) depicts a drop of temperature in the end of the reactor, due to a technical problem of the equipment used in the current experimental set up (limited temperature of a thermocontroller equal to 192 °C).

Consequently, later, the properties of the PEDOT films, deposited in each different T_d temperature, can be correlated with the values of temperatures based on these thermopfiles.

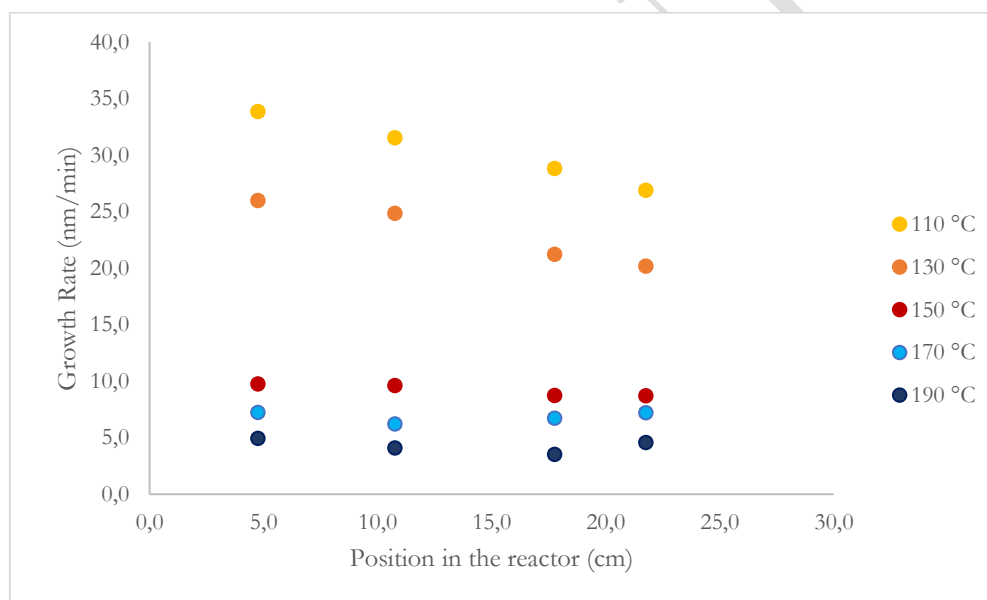
4.4.2 VTemp Tests

In order to study the influence of temperature on the PEDOT film characteristics, five deposition tests (VTemp Tests) were performed. All the conditions of deposition were kept the same, except for the deposition temperature, and they can be seen in the **Table 8** below. It should be noted that the deposition time was selected to be 8 min, as in the previous study (VTime Tests) this duration showed good performance on the uniformity and consistency of PEDOT films at $T_d=150$ °C and should provide thick enough PEDOT films, even at temperatures of 170 °C or 190 °C.

Table 8: Deposition conditions for VTemp tests.

Test	Deposition Time, t_d (min)	Deposition Temperature, T_d (°C)	Pressure, P (Torr)	SbCl ₅ Flow Rate (sccm)	EDOT Flow Rate (sccm)
VTemp110	8	110	0,32	2,7	2,1
VTemp130	8	130	0,32	2,7	2,1
VTemp150	8	150	0,32	2,7	2,1
VTemp170	8	170	0,32	2,7	2,1
VTemp190	8	190	0,32	2,7	2,1

As in the study of time of deposition previously, film thickness, conductivity and growth rate were calculated for all the samples of the tests. The results and the correlations between these three parameters are presented below (**Figure 43**, **Figure 44**, **Figure 45**, **Figure 46**).

**Figure 43:** Evolution of Growth Rate (nm/min) of PEDOT films along the oCVD reactor for different deposition Temperatures (°C).

To begin with, by studying **Figure 43**, it can be seen that by increasing deposition Temperature T_d (°C), growth rate (nm/min) decreases. This means that at low deposition temperatures, the reaction of deposition is faster. The adsorption of the reactants on the substrate surface is decreased when deposition temperature is increased and therefore it can be concluded that at low temperatures, the mechanisms of polymerization seem to be enhanced. Additionally, regarding the uniformity of the growth rate along the different substrates, it is clear by increasing deposition temperature, the growth rate is more uniform along the reactor length. That could be explained by the fact that the growth rate at these temperatures is low and the deposition reaction is slower, leading to more consistent and homogenous PEDOT films, while at low temperatures where the deposition is faster, the produced PEDOT films are not so uniform with one another. In addition, SbCl₅ and at a lesser extent EDOT concentrations decrease along the length of

the reactor, leading to a decrease of the deposition rate and therefore larger thickness gradients at positions in the end of the reactor.

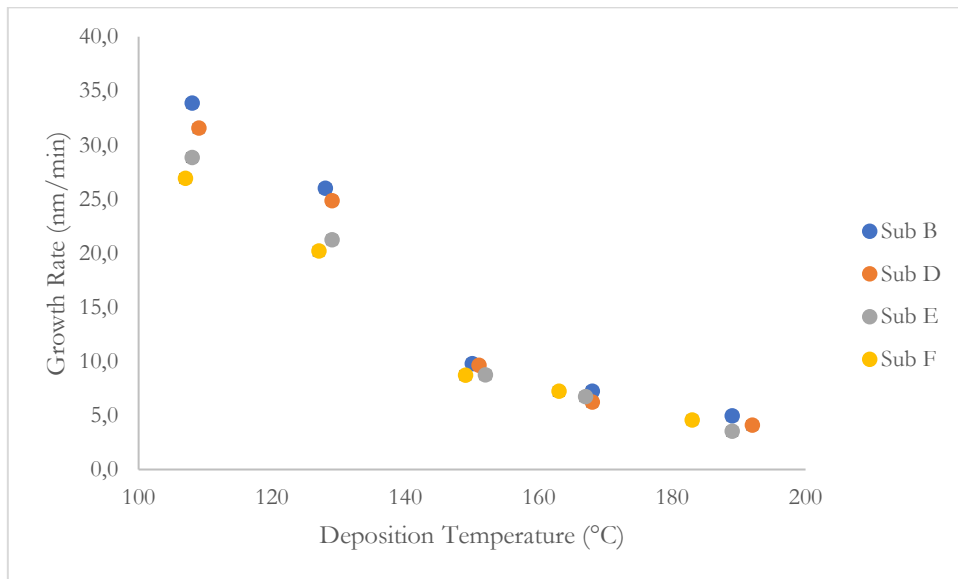


Figure 44: Effect of Deposition Temperature (°C) to the Growth Rate (nm/min) of the different substrates (B, D, E, F).

Studying **Figure 44** above, there is an exponential correlation between growth rate (nm/min) and deposition Temperature (°C). As seen earlier in **Figure 43**, at high deposition Temperatures (°C), the growth rate (nm/min) decreases. Furthermore, at low temperatures, it can be seen that the values of growth rate are not so uniform among the substrates of the same temperature. This behavior is explained as before in **Figure 43**, that the deposition is slower at high temperatures, leading consistent PEDOT films, while at low temperatures, where the rate is higher, the resulted PEDOT films are built in a more unsteady and inconsistent way.

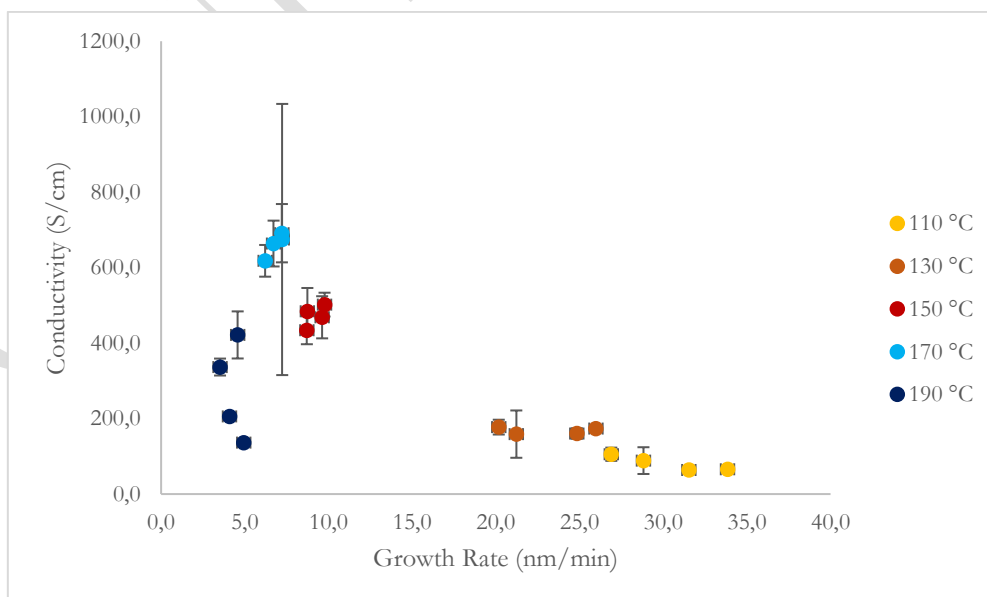


Figure 45: Evolution of Conductivity (S/cm) by Growth Rate (nm/min) for different deposition Temperatures (°C).

It can be seen in **Figure 45**, that by decreasing growth rate, conductivity values increase, except for those ones at deposition temperature $T_d=190$ °C. The low conductivity values there could be explained by the decomposition and degradation of $SbCl_5$ at this temperature. These results explain that the limits where the decomposition of oxidant $SbCl_5$ and the increase of deposition temperature are beneficial to the oCVD process have been reached. It can be concluded that deposition at temperature equal and over 190 °C doesn't lead to successful results and should be avoided in future depositions.

In addition, low conductivity values are seen at low deposition temperatures too, which is explained by the poor quality of PEDOT polymerization at high deposition rates. The highest conductivity values in this study are obtained at deposition temperature of 170 °C, which vary from 618 s/cm to 691 S/cm. These high conductivity values can be attributed to the low growth rate at this temperature, which leads to better structure of PEDOT films and therefore stronger film characteristics.

This graph is important for the project, since it can create an exponential model that will predict the conductivity values by varying the growth rate.

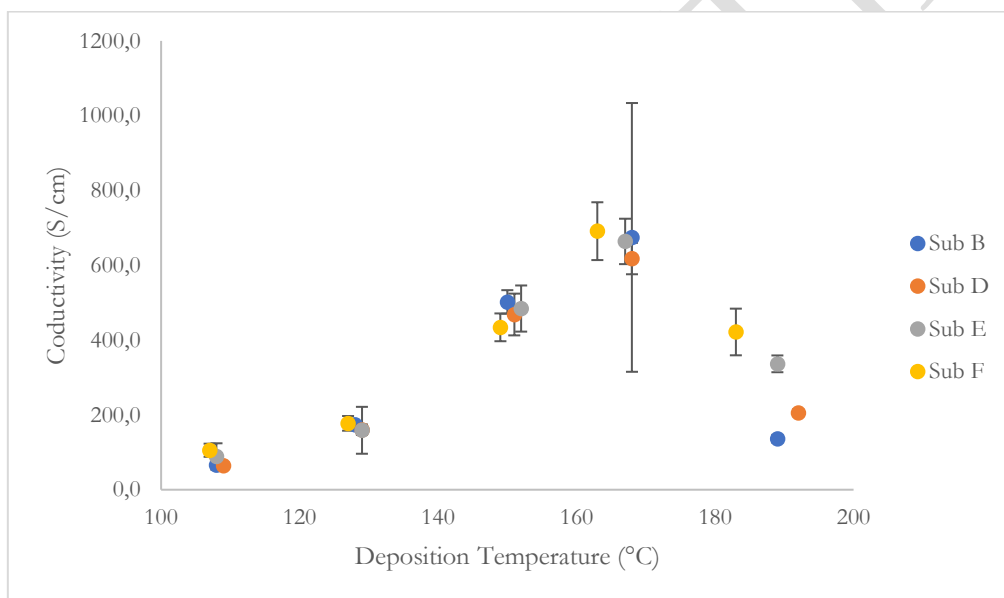


Figure 46: Effect of deposition Temperature (°C) to Conductivity (S/cm) for the different substrates (B, D, E, F).

Just as before, so in this graph too, conductivity values increase when increasing deposition temperature. However, the deposition time for all the experiments is the same, leading to different film thicknesses (since growth rate is affected by temperature) and therefore thicker films are obtained at lower temperatures, where the growth rate is higher. As a consequence, the conductivity values are lower in the thicker films. Additionally, it can be seen that at lower deposition temperatures, the films show more uniform values of conductivity among the substrates, while when increasing deposition temperature, the range of conductivity increases. The latter is associated with the increase of measurement error due to the decreased film thickness in high temperatures, leading to a decrease of accuracy in the results. The degradation of $SbCl_5$ at 190 °C, as mentioned before, is verified with this graph, and it can be clearly seen that at this temperature coating of the substrates is not conformal and effective.

5 Conclusions

In this work a new, robust, full dry oCVD process was established, using EDOT as a monomer and SbCl_5 as an oxidant, with the aim to produce PEDOT polymer thin films. Based on previous work by Mirabedin et al., who also used SbCl_5 as an oxidant, a tubular reactor was developed, which was modified in the frame of this internship in order to improve its reproducibility. Then, correlations between key process parameters (such as duration of deposition, temperature of deposition) and the PEDOT film characteristics and properties were for the first time investigated, leading the way to further understand the behavior of the oCVD system.

UV-vis Spectroscopy and Four Point Probe Measurement were the two characterization methods which were employed for the determination of the properties of the produced PEDOT films, by measuring Transmittance (%) and Resistivity (Ω/cm) respectively. In previous works, the film thickness of the PEDOT films was mainly measured using Atomic Force Microscopy (AFM), a complex and time-consuming method. Transmittance data by UV-vis were correlated with the film thickness data measured by AFM (which was performed by another individual) in order to establish a new equation which would determine the thickness of the PEDOT films and would eliminate the need of AFM. The new, developed correlation equation showed an error of 3%, which is considered small and therefore insignificant, since it is a quick method to measure the thickness, compared to AFM. To ensure its reliability, comparison of the equation's results with three sources of literature data of PEDOT films regarding their transmittance and thickness was done too and which showed close results, making it then dependable. Therefore, this equation was a smart tool in this project to measure easily and quickly the PEDOT film thickness, which is inserted in the calculation formula of conductivity, the latter one being the property of PEDOT films that mainly interests us.

A crucial factor for the deposition experiments has been the SbCl_5 oxidant flow stability, which was inconsistent in the beginning of this work. This irregularity appeared due to the non-uniform temperature along the tube carrying SbCl_5 , which resulted to condensation of material on the tube's walls, leading to blocked flow of oxidant and therefore to unsuccessful deposition. For that reason, modifications on the deposition protocol were done in order to avoid such phenomenon. These include an installation of an extra heating ribbon around the SbCl_5 tube to preserve its temperature and secondly a frequent check of the temperature prior to deposition along the length of the tube, to ensure that it is heated properly. Additionally, a weekly clean of the components of the equipment is also integrated in the protocol to ensure that reactants flow regularly along the system and that no deposited material block their flux. As a conclusion, the conditions of the oxidant vaporization and flow are of great importance to the success of the deposition reaction, since it is sensitive to temperature change.

In addition, it was noticed that for depositions conducted at the beginning of an experiment day, (when the system had not fully reached a steady state behavior), the produced PEDOT films were slightly not uniform with one another. Along the substrate holder, the different glass slide substrates presented varying thicknesses and conductivities, a non-desired trait of the deposition process. However, it was observed that when performing successive depositions throughout an experiment day, by avoiding to turn on and off the equipment, which would influence the thermal stability of the process, it showed great deposition robustness and consistency of results. This is evidence that in order to achieve reliable results, a blank deposition test should be done in advance to properly prepare the system and to produce films with uniform characteristics in the following experiments. It could be also suggested to maintain the oCVD reactor continuously turned on in order to preserve its robustness. Indeed, these practices improved the reliability of the deposition process, leading to coherent results when repeating experiments.

Regarding the study of influence of duration of deposition, as expected, it was seen that when increasing the deposition duration, film thickness linearly increases too, showing great uniformity among the different substrates. The obtained graph correlating film thickness to duration of deposition, is of great importance, since it can be used to predict deposition duration based on a desired film thickness of PEDOT, especially when PEDOT films are about to be used in a particular application (such as OLEDs) where their thickness significantly influences the application's efficiency.

In short times of deposition (2,5 min to 5 min) conductivity values were inconsistent among the substrates, while for longer durations (8 min and 15 min) they were more uniform, since they showed very small standard deviation, thanks to the higher thickness. This can also be confirmed by the results of growth rate calculated in each duration of deposition, presenting an exponential correlation. There is a variation among the substrates in low deposition durations, while there is better consistency among the substrates in higher durations. This indicates that at the beginning of a deposition, the reaction is at transient regime, during which the flow of gases is not stabilized, nor the temperature of the substrates closer to the entrance of the reactor, since it could be influenced by the arrival of the colder gas flow. On the other hand, while as time passes by the deposition reaction is stabler and the polymer chains are better stacked up with one another.

Consequently, it is important to provide to the oCVD system long durations of deposition in order to be in steady state conditions and therefore robust enough. Thus, an optimization between low film thickness and high conductivity has to be done in order to obtain PEDOT films with strong characteristics. This can be accomplished by studying the influence of the reactants' molar flows to the PEDOT films' properties. More specifically, by reducing the flux of the two reactants (by adjusting their valves' turns accordingly) less amount of gas would enter the reactor, and therefore the deposition reaction would be slower, with low deposition rates, leading to thin PEDOT films but simultaneously large PEDOT chains, since there is enough time for EDOT and SbCl_5 to react.

Concerning the influence of temperature on the oCVD system, it was observed that by increasing temperature, the deposition rate decreases for the same duration of coating, as expected. Therefore, better uniformity among the PEDOT films' characteristics is observed by increasing temperature, since this leads to low deposition rates and so to lower reactant consumption along the length of the reactor, achieving uniform deposition rates. Deposition rate and temperature show an exponential correlation, with values of growth rate at high temperatures showing better uniformity as explained before due to slower reaction. The graph correlating deposition rate to temperature is important for future work, since a desired deposition rate can be predicted by choosing a specific temperature.

There is an exponential correlation between conductivity and temperature of deposition too, except for deposition temperature at 190 °C, which is close to the decomposition temperature of SbCl_5 , leading to low performance of the PEDOT films. Initially, it was interesting to study deposition of PEDOT near such temperatures, since it hasn't been studied before and it would provide us valuable information regarding the behavior of the system at these conditions. However, taking into account the results of this investigation, it is suggested to avoid deposition in these temperatures and prefer the lower ones.

It is suggested that a two parametric analysis should be done in the future by varying deposition time for different deposition temperatures; a work that could be done in the frame of this project, but wasn't accomplished due to time restriction.

6 Perspectives

The oCVD process is an innovative and relatively recent thin film fabrication method and this project helped to further understand how this system behaves. Several ideas for further improvements to be applied in future work will be mentioned in the next paragraphs, so that there is a perspective of the oCVD process to be industrialized and scaled up into larger surfaces. The absence of water in the reaction can lead to the integration of pure PEDOT films to devices with increased durability, by avoiding the fabrication route of PEDOT:PSS, which can contribute to their degradation as mentioned in the Theoretical part.

This system might show some difficulties in its operation and handling, but it should be taken into account that the nature of this project was exploratory, and that its core task was to achieve reproducibility in the deposition process and also to investigate the influence of deposition conditions on the properties of the produced PEDOT films. The conclusions drawn from this study can be used in future work to aim to PEDOT films with strong characteristics, such as high conductivity values, over 1000 S/cm and low film thickness, near 20-30 nm.

Possible directions for further research in this oCVD system include the following:

- i) Extensive characterization of the PEDOT films

So far in this project, the characterization methods mainly focused on the physical properties of the PEDOT films, such as resistance and transmittance. What has not been done in this study is to identify the chemical composition and structure of the produced PEDOT films, and for that reason further characterization should be done, with characterization methods including: Fourier-transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). In this way, the chemical synthesis of the fabricated PEDOT films can be explored, which could also explain the trend of their properties when varying deposition conditions. In particular, it would be interesting to see what the PEDOT films fabricated in temperatures near the decomposition temperature of SbCl_5 are composed of. This direction of research has been already assigned to another individual who will continue the investigation of work in another master thesis.

- ii) Influence of Reactant's Flow and Molar Ratio

As mentioned in the Conclusions Part, slower deposition reaction leads to better PEDOT film structure due to better stacking of the polymer chains. Therefore, by decreasing the EDOT and SbCl_5 flux, the deposition rate would be lower. Therefore, it would be intriguing to see if there is an improvement in the PEDOT properties (such as high conductivity) by decreasing the flux of the reactants. Additionally, an important parameter to the oCVD process is the molar ratio of SbCl_5 and EDOT. It has been suggested that by increasing the EDOT flow compared to SbCl_5 PEDOT films with better characteristics are achieved. [7]

- iii) Improvement of UV-Vis and AFM Graph

In order to increase the reliability of the equation obtained from the graph correlating UV-Vis and AFM, more experimental and characterization data of PEDOT films have to be inserted in the graph. In addition,

different wavelengths which correspond to a different light color in the OLED application, could be explored such as: 420 nm (blue light) and 700 nm (red light) (while in this project the light color in the OLED application was green, 550 nm of wavelength).

iv) Oxidative Molecular Layer Deposition (oMLD) of PEDOT

Another route to fabricate conductive, conformal PEDOT films is oxidative Molecular Layer Deposition (oMLD). The oMLD method is a chemical extension of Atomic and Molecular Layer Deposition (AML), where self-limiting half reactions are occurring in a binary cycle to fabricate uniform thin films with sub-monolayer precision. In this process, monomer and oxidant vapors are introduced sequentially in a reactor chamber under viscous flow at reduced pressures (around 0,8 Torr), where reactant exposures are separated by an inert gas (N_2) purge step. In this way, excess monomer, oxidant, and any volatile polymerization byproducts are removed [53]. In literature [53], it has been found that high conductivity values can be achieved at moderate deposition temperatures (around 150 °C), by avoiding the use of additives or post polymerization processing. Therefore, it would be intriguing to see the results of PEDOT films produced through this method and to compare them with the ones by oCVD.

7 Bibliography

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