

# PRAP-CVD: Up-scalable process for the deposition of PEDOT thin films

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## Abstract

Plasma radicals assisted polymerization via CVD (PRAP-CVD) is emerging as an efficient alternative to conventional vapour based techniques to synthesise and deposit conjugated polymers. PRAP-CVD process is based on the concomitant but physically separated injection of low-energy oxidative radical initiators and vaporized monomer species into a reactor where temperature and pressure are finely controlled. Gas phase oxidative radicals are generated by a remote plasma chamber from a pure or diluted initiator. The low deposition temperature, below 100 °C, allows polymers to be directly synthesised on a wide range of substrates, including fabric, paper and plastic, without any thermal degradation and keeping a high degree of surface conformality. Additionally, the PRAP-CVD does not require post-deposition rinsing procedure which allows a wider range of application. PRAP-CVD PEDOT depositions have been carried out on different substrates with a transparency higher than 80% in the visible range. Copyright © 2019 VBRI Press.

**Keywords:** Conjugated polymers, PEDOT, conductive polymers, PRAP-CVD.

## Introduction

The most of polymers have similar electrical and optical properties: they are insulators and colourless. It means that they do not possess mobile charges and the lowest electronic excitations are in the UV region. Nevertheless a peculiar class of polymers with quite different properties exist; it consists of polymers with conjugated double bonds in the main chain [1].

In 1977 Shirakawa, Heeger and McDiarmid obtained films of polyacetylene with a tremendously high conductivity comparable to metal value, when they were exposed to iodine vapour [2]. The advantages of conjugated polymers relies in their high flexibility compared to conventional electrically conductive inorganic materials [1]. Poly(3,4-ethylenedioxythiophene) (PEDOT) with its derivatives is one of the most successful conducting polymers because of excellent environmental stability, high electrical conductivity and transparency in thin oxidized films, and a low band gap (1.5-2.5 eV) [3, 4]. Currently PEDOT has good chemical and thermal stability but it difficult to process into thin-film form. This is only one of the issues related to the PEDOT, fixed by adding poly(styrene sulfonic acid) (PSS) [5]. Another problem, common to all wet processes, concerns the solvent-substrate incompatibility with subsequent damage of substrate beneath [6]. The solution to these drawbacks can come from vapour phase techniques as Vapour Phase Polymerization (VPP), where the solubility of the monomer is no longer required since injected as vapour.

VPP, is usually performed in two steps: deposition of the oxidant on the substrate, usually by means of a spin coater, and exposition of the pre-treated substrate to monomer vapours [7, 8]. The presence of liquid in the first step does not allow a full bypass of the drawbacks linked to the solvent-substrate incompatibility. Although the impact on the substrates is milder than in a conventional wet chemistry process, it is still present. Another process analogous to VPP, known as oxidative Chemical Vapour Deposition (oCVD) has been developed by Prof. K. K. Gleason at MIT. The main difference between the two techniques consists of the number of involved steps. OCVD is a single step process, where the oxidant and monomer are both delivered to the substrate through the vapour phase. Although the use of FeCl<sub>3</sub>, as oxidant, allows high conductivity (>1000 S.cm), post deposition rinsing step is still required to remove the residual oxidant molecules and formed derivatives. According to the authors, it is also rather difficult to provide a constant flow rate of oxidant owing to the solid nature of this product [9, 10].

So far halogens have been proposed as alternative dopants. In an attempt to make the process completely dry, bromine has been used as a replacement for FeCl<sub>3</sub> in the oCVD process. Despite first encouraging results, to the best of authors' knowledge, the literature concerning PEDOT deposition by vapour phase promoted by bromine is scarce [11].

Plasma Radicals Assisted Polymerization via CVD (PRAP-CVD) has been developed at Luxembourg Institute of Science and Technology (LIST) as an

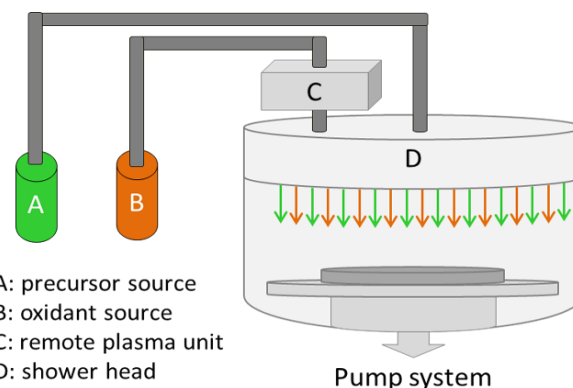
efficient alternative to conventional vapour-based processes of conductive thin films [12]. In PRAP-CVD, gas phase oxidative radicals are generated by a remote plasma chamber from a selected initiator, pure or diluted with an inert carrier gas. PRAP-CVD has been developed in the Polymer Vapour Phase Deposition reactor (PVPD) set up by AIXTRON SE (Herzogenrath, Germany). This process is based on the concomitant but physically separated injection of low-energy oxidative radical initiators and vaporized monomer species into a reactor where temperature and pressure are finely controlled. Reagents are uniformly introduced through the showerhead surface over the entire area of deposition as depicted in Fig. 1. According to the distribution of species generated in the remote plasma chamber, the density of radicals is usually at least two orders of magnitude larger than the one of ions. Their longer lifetime, up to a few milliseconds, promotes a natural selection in favour of the arrival of oxidative radicals in the reaction chamber. The density of radicals depends on the remote plasma parameters, inert gas flow rate, etc., while the concentration of organic monomer is finely controlled by a dedicated vaporiser and distributed all over the substrate surface through the showerhead. The transport of oxidative radicals into the reaction chamber via the complex geometry of multi-channel showerhead and the growth of PEDOT thin-films with the PRAP-CVD have been already demonstrated [4]. A few advantages of making the process completely dry include the possibility of processing solvent-sensitive substrates such as paper. In essence, PRAP-CVD could be scaled up to process large substrate and be integrated into clusters tool. This technique also assures quite unique capabilities in terms of conformality [13]. PEDOT has been chosen as a case study to demonstrate the effectiveness of PRAP-CVD. In the current work, a completely dry process, utilizing bromine as oxidant as well as dopant, is investigated to efficiently deposit conductive PEDOT films with high stability over the time [4].

## Experimental

### Materials/ chemicals details

PRAP-CVD of PEDOT films was carried out on 8-inch silicon wafer with a resistivity of 0.5-100  $\Omega$  cm (SIEGERT WAFER GmbH, Germany) and glass (15 x 15 cm). In order to avoid any influence on the conductivity measurement, an insulator layer of 50 nm SiO<sub>2</sub> was grown by Rapid Thermal-CVD (RT-CVD) on the wafer prior to deposit PEDOT. 3,4-Ethylenedioxythiophene (EDOT, 97%) and bromine (puriss. p.a.,  $\geq 99.0\%$ ), Sigma-Aldrich (Belgium), were used as received. The deposition took place in the PRODOS-200 PVPD™ R&D System- $\beta$  version (AIXTRON SE, Herzogenrath, Germany). EDOT monomer vapour was delivered into the reactor by a TriJet® ( $\varphi_{\text{EDOT}} = 1.4 \times 10^{-3}$  mol/min) and bromine by a bubbler system ( $\varphi_{\text{Br}_2} = 1.9 \times 10^{-3}$  mol/min). The different pathways allowed a well-separated injection of

monomer and oxidant. Any mix occurred whilst mingling the respective jet in the reactor close to the surface of the substrate. The substrate temperature was fixed at 80 °C while the reactor pressure was kept constant at 390 mTorr by a throttle valve.



**Fig. 1.** Process flow in PVPD equipment for PRAP-CVD. Process monomer is introduced into the showerhead through run line (green). Oxidant passes before through the remote plasma unit and then it reaches the process chamber through run line (orange).

### Characterizations

**Raman spectroscopy.** The Raman spectra were recorded by a Renishaw inVia micro-Raman spectrometer, with an incident wavelength of 633 nm and a laser power below 10 mW.

**UV-vis-NIR spectroscopy.** Transmittance and reflectance were recorded with a Perkin Elmer Lambda 950 UV-Visible-Near IR spectrometer. The wide wavelength spectrum was covered by a Deuterium (UV)/ Tungsten (Vis) lamp and a photomultiplier (UV-Vis)/InGaAs (NIR) detector. The set-up used an integrating sphere in order to collect the diffuse light transmittance and reflectance from the sample. Films of 100 nm thick were deposited on 15x15 scm BOROFLAT® 33 glass (Schott, Louisville, KY, USA) and the spectra were normalised.

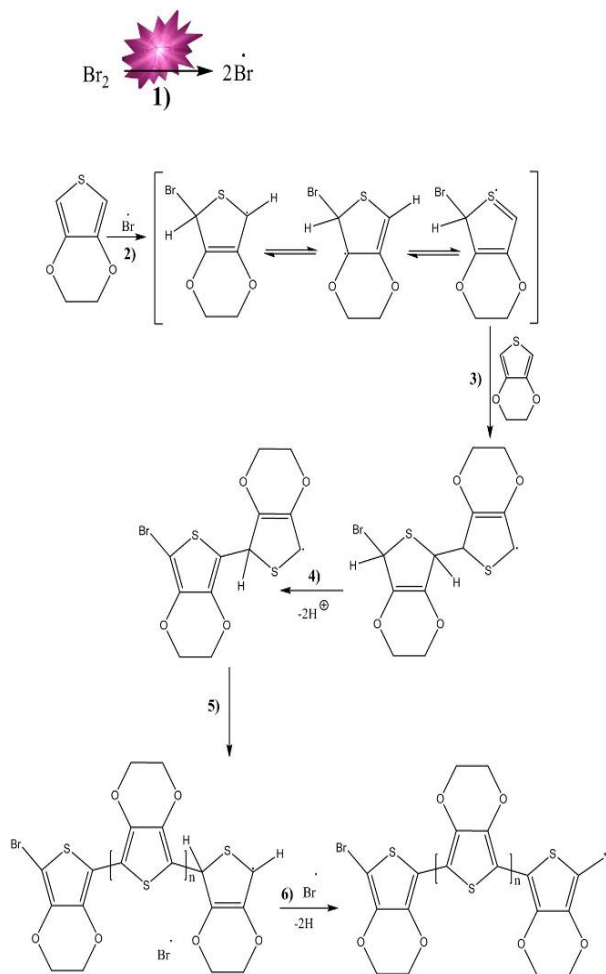
**Scanning electron microscopy.** Helios NanoLab™ 650 (FEI, Eindhoven, Netherland) was used to measure the thickness of PEDOT films deposited on the SiO<sub>2</sub> layer and to investigate the morphology of films, with the following parameters: acceleration voltage (2kV), current (25 pA), working distance (4 mm). Image resolution did not need to be improved with any sputter coated metal layer.

**Electrical measurements.** The electrical measurements, temperature dependent, have been performed in a liquid nitrogen flow cryostat with the sample placed in the nitrogen flow. The measurement presented here have been performed on a PEDOT film 50 nm thick deposited on glass, on a square sample of 1x1 scm. Four contacts were deposited on the corners by using silver paste, and the sheet resistance of the film was determined by using the van der Pauw method. The conductivity was calculated considering the film thickness of 50 nm.

## Results and discussion

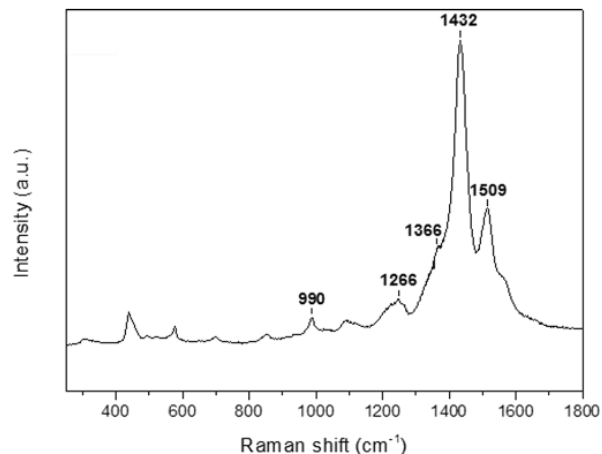
In the current work, a completely single step dry process, to deposit conductive PEDOT films, by using of bromine radicals, generated by remote plasma, is presented. The polymerization mechanism of EDOT to form PEDOT via PRAP-CVD is depicted in **Fig. 2**.

(1) A preliminary step to produce bromine radicals took place into cylindrical inductive plasma source chamber. Radicals reached the reaction chamber where EDOT monomer molecules were simultaneously injected [14]. (2) Bromination of EDOT molecules occurred. According to the presence of resonance structures, the bromination took place in  $\alpha$  position, on the most stable resonance form [15]. (3, 4, 5) Free radical polymerization followed the formation of dimer, trimer, etc. (6) The polymerization stopped when also  $\alpha'$  position was brominated [4].



**Fig. 2.** Polymerization mechanism of EDOT via PRAP-CVD.

Raman spectroscopy investigation was carried out to prove PEDOT polymerization by determining the vibration modes of spectra. Raman spectrum of doped PEDOT film in the wavenumber range from 250 to 1800  $\text{cm}^{-1}$ , is reported in **Fig. 3** and relative assignments are reported in **Table 1**.



**Fig. 3.** Raman spectrum of PRAP-CVD PEDOT film as-deposited, principal bands are highlighted.

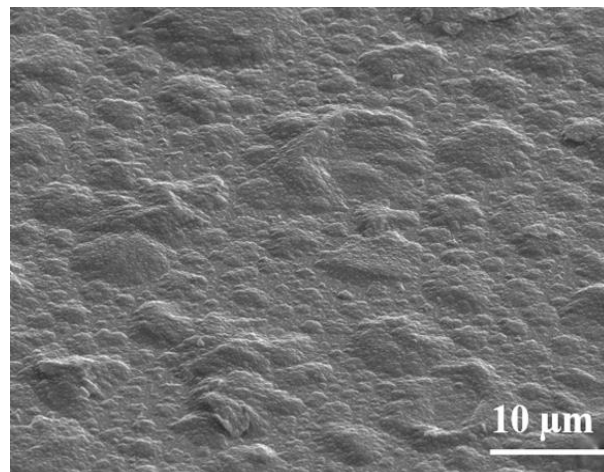
**Table 1.** Observed frequencies of doped Poly(3,4-ethylenedioxythiophene) with assignment of the principal bands.

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
1509	asymmetric $\nu$ $\text{C}\alpha=\text{C}\beta$
1432	symmetric $\nu$ $\text{C}\alpha=\text{C}\beta$ (-O)
1366	$\nu$ $\text{C}\beta-\text{C}\beta$
1266	inter-ring $\nu$ $\text{C}\alpha-\text{C}\alpha$
1096	$\nu$ $\text{C}-\text{O}-\text{C}$
990, 573	oxyethylene ring deformation
699	$\nu$ symmetric $\text{C}-\text{S}-\text{C}$
439	$\delta$ $\text{SO}_2$

The observed band positions and their assignment were all in good agreement with literature, confirming the obtained successfully polymerization [16-19].

Furthermore, the authors did not observe any band at 1705  $\text{cm}^{-1}$ , this absence supported the hypothesis that the polymerization took place without ring opening in favour of PEDOT film formation [19].

The morphology of film was investigated by SEM. A top view picture is reported in **Fig. 4**.



**Fig. 4.** SEM images top view, 52 °C tilted.

The deposition experiments were carried out for 30 minutes and the thicknesses of polymer film measured all around the wafer was  $(113 \pm 15)$  nm. The resulting deposition rate was calculated as  $(3.8 \pm 0.2)$  nm/min, revealing that PRAP-CVD can compete in terms of the deposition rate with the other process nowadays investigated as VPP and oCVD [11, 20].

An example of PRAP-CVD PEDOT film deposited on sheet of glass is reported in Fig. 5.

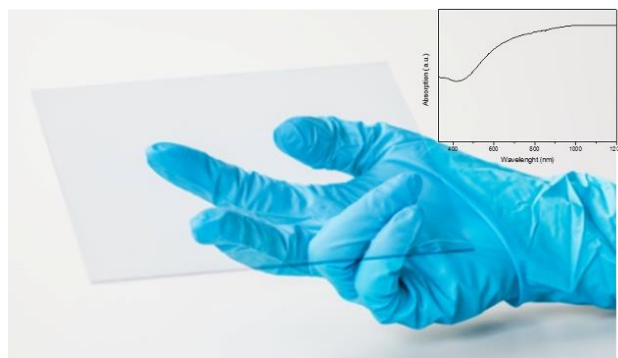


Fig. 5. BOROFLAT® 33 square glass covered with PRAP-CVD PEDOT film, as inset the relative UV-vis-NIR absorption spectrum.

The UV-vis-NIR absorption spectrum of PEDOT film, reported as inset, attested the high transparency degree of PRAP-CVD PEDOT films. The spectrum presented a broad absorption band in the vis-NIR, starting at approximately 500 nm and extending into mid IR region. This response corresponds to a polymer having a long conjugation length and probably attributed to polar and/or bipolaron bands [21].

Performances of films have been investigated also in terms of conductivity as function of temperature. Fig. 6a shows the conductivity as a function temperature in the range 130 to 350 K, both when cooling-down and warming-up the sample. The good reproducibility showed that there was no structural changes in the film, and that the temperature-dependence of the conductivity was owing to the intrinsic carrier transport mechanism in the film. The observed decreasing in conductivity, while the temperature decreases, is typical for an organic conductor, where carrier transport usually occurs by hopping conduction. In order to further investigate the carrier transport mechanism, in Fig. 6b the natural logarithm of the conductivity as a function of the inverse temperature,  $1/T$  have been reported. It was observed a good fit with a power, implying the following dependence for the conductivity:

$$\sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^\alpha \right] \quad \text{eq. 1}$$

The best fit was obtained with  $\alpha = 0.63 \pm 0.07$ . This value is far from  $1/4$ , already reported for 3D variable range hopping (VRH), far from 1, as reported for nearest neighbor hopping, and far from  $1/3$ , as reported for 2D variable range hopping [22-26]. The value is closer to  $1/2$ , already reported for PEDOT:PSS and which corresponds to 1D VRH or hopping in a granular material [27-29].

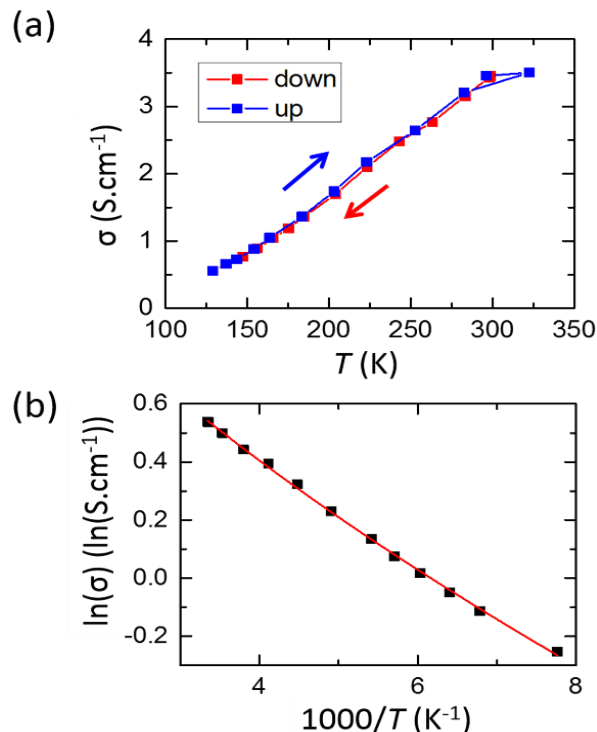


Fig. 6. (a) Conductivity of the 50 nm thick PEDOT film deposited on BOROFLAT® 33 as a function of the sample temperature. The measurements were performed both during cooling-down (red) and warming-up (blue) the sample. (b) Natural logarithm of the conductivity plotted as a function of  $1000/T$  (black points) for the data measured during the cooling-down. The red curve is a fit of the data by eq. 1, with the power  $\alpha = 0.63 \pm 0.07$

## Conclusion

In conclusion, PRAP-CVD has been successfully demonstrated to be a novel promising technique to deposit conjugated polymers. In particular, PRAP-CVD of EDOT leading to the formation of uniform conducting doped PEDOT film, by using bromine as oxidant, has been proved. The use of bromine, as oxidant, avoids any supplementary rinsing process, making the process completely dry. PEDOT deposited by PRAP-CVD does not require the use of PSS, so as consequence all issues related to the corrosion, owing to the acidic behaviour of PSS, are removed. The use of bromine and the absence of PSS allows the use of PRAP-CVD on a wide range of substrates which could be damaged by a wet step like papers, plastics, etc. Raman spectroscopy confirmed the chemical composition of PEDOT films. Dopant segregation was not observed, creating an enormous potential benefit for producing organic device with superior interfaces. PRAP-CVD was developed in a  $\beta$ -side machine version and 8-inch silicon wafer as well as  $15 \times 15$  scm BOROFLAT® 33 glass were used as substrates for the deposition demonstrating the industrial maturity of the technique and the easily scaling up of this process featuring highly competitive growth rate compared to other vapour phase growth of PEDOT thin-films. In the future, other characteristics of PRAP-CVD PEDOT films, as the electrochromism, will be investigated. The main achievement of this study is the



effectiveness of the PRAP-CVD as novel alternative CVD technique and the possibility of depositing other conjugated polymers.

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### Author's contributions

Conceived the plan: BRP, KM, DL; Performed the experiments: BRP, KM; Data analysis: BRP, DA, RL. Wrote the paper: BRP, RL, DA. Authors have no competing financial interests.

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