

Oxidative Chemical Vapor Deposition of Conducting Polymer Films on Nanostructured Surfaces for Piezoresistive Sensor Applications

Fabian Muralter, Anna Maria Coclite,* and Kenneth K.S. Lau*

In this study, a novel, fully polymeric setup for piezoresistive sensing is prepared and tested. Monolayers of polystyrene (PS) nanospheres are assembled on flexible polyethylene naphthalate substrates. Subsequently, thin layers (≈ 50 – 100 nm) of poly(3,4-ethylenedioxythiophene) (PEDOT) are deposited conformally around the spheres by oxidative chemical vapor deposition (oCVD). Voltage–current characteristics and direct resistance measurements are performed to test the electrical properties of the samples in their unstrained state and their piezoresistive response during bending. Substrate deposition temperature (T_{sub}) and film thickness (t_{PEDOT}) are used as parameters to alter properties of the PEDOT thin films; increased T_{sub} and t_{PEDOT} lead to samples exhibiting lower intrinsic resistance. The electrical conductivity of the samples is estimated to range as high as tens of S cm^{-1} . Dopant exchange of the oCVD-PEDOT layer (intrinsically, chlorine-doped) is performed by putting the samples in 0.5 M sulfuric acid, which decreases their resistance by $\approx 1/3$. Regarding the piezoresistive properties of the devices, acid treatment, higher T_{sub} and t_{PEDOT} (thus, lower intrinsic resistance) yield samples with increased response. As a result, gauge factors as high as 11.4 are achieved. Due to their flexibility and low-cost, the proposed structures can be readily employed as skin-inspired or wearable electronic devices.

The piezoresistive effect is broadly used in various devices such as transducers, accelerometers, and piezo-field effect transistors (FETs), and most prominently in sensors.^[1] Recently, especially sensors for wearable electronics,^[2] skin-inspired electronic devices,^[3] and portable healthcare monitors^[4] have gained significant attention. Piezoresistive materials change their resistance as a function of bending, pressure, or stress acting on them (i.e., strain). In this work, the objective of strain sensing

with a novel, fully polymeric setup is proposed to serve as a basis, from which further possible applications can be derived. Up to now, materials for such applications are mostly silicon-based or involve other inorganic rigid solids. Their rigidity, however, is disadvantageous if large strains and/or small pressures are of interest (e.g., in the applications mentioned above). To overcome this limitation, hybrid setups of inorganic nanostructures and flexible polymers have been investigated. In the last decade, strain sensors based on solution-processed piezoresistive polymers (e.g., poly(3,4-ethylenedioxythiophene):polystyrene sulfonate – PEDOT:PSS) have also been developed.^[5–7] However, such setups exhibit lower sensitivity than their inorganic counterparts. Recently, the integration of (mostly inorganic) nanostructures into polymers was claimed to yield a new generation of strain sensors;^[1,7,8] it was reported to enhance the sensitivity by orders of magnitude. The nanostructures

used are in the order of tens to hundreds of nanometers in size; the present project aims at using polymeric nanostructures of similar sizes. Furthermore, the piezoresistivity of PEDOT:PSS is reported to depend on the sizes of PEDOT- and PSS-rich domains, which can change during mechanical deformation and thereby alter the conductive pathways.^[6,7] To investigate and use this fact, the conformal deposition of PEDOT thin films around polystyrene (PS) nanospheres assembled on the surface of a flexible substrate will be adopted.

In the first step, monolayers of PS nanospheres are deposited onto silicon wafers and flexible polyethylene naphthalate (PEN; 0.125 mm thick) substrates. An experimental routine similar to the one reported by Vogel et al.^[9,10] is adopted. Both types of substrates are coated readily and equally successfully via the assembly of a monolayer of PS spheres at an air–water interface and subsequent pick-up. Monolayers are assembled with little effort (no need for special equipment), with reasonable reproducibility over adequate areas ($\approx \text{cm}^2$), ensuring the potential scale up of the proposed methods. The structure of monolayers deposited onto a piece of silicon wafer is shown in the scanning electron microscopy (SEM) images in **Figure 1a,b**. Almost no spheres on top of the monolayer are observed. The beads form hexagonally close-packed (defect-free) arrays of $\approx 20 \times 20$ spheres.

Dr. F. Muralter, Prof. A. M. Coclite
Institute of Solid State Physics – Graz University of Technology
NAWI Graz – Petersgasse 16, Graz 8010, Austria
E-mail: anna.coclite@tugraz.at

Prof. K. K. S. Lau
Department of Chemical and Biological Engineering – Drexel University
3141 Chestnut Street – Philadelphia, Pennsylvania 19104, USA
E-mail: kkl27@drexel.edu

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aelm.202000871>.

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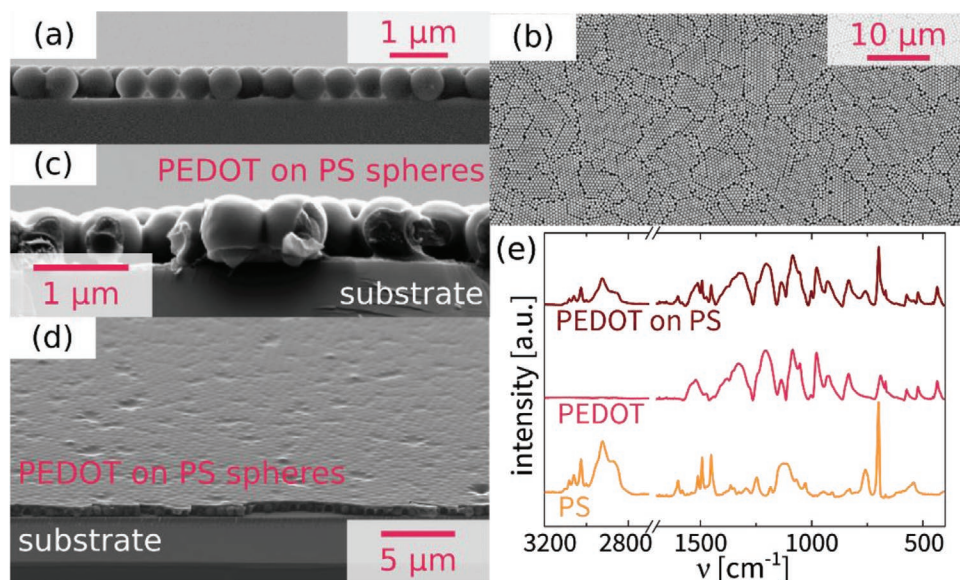


Figure 1. Scanning electron microscopy (SEM) images of regions on a silicon wafer covered by monolayers of polystyrene (PS) spheres (diameter ≈ 580 nm) via pick-up after assembly at the air–water interface in side a) and top view b); side c) and top view d) SEM images of a corresponding sample subsequently coated with ≈ 50 nm of poly(3,4-ethylenedioxythiophene) (PEDOT) by oxidative chemical vapor deposition (oCVD). e) Absorption spectra recorded by Fourier-transform infrared spectroscopy (FTIR) on a monolayer of PS nanospheres, a PEDOT thin film and the PEDOT-PS structure described above (on silicon substrates).

In the second step, depositions of PEDOT films by oxidative chemical vapor deposition (oCVD) are performed. Conformal depositions around 3D-nanostructures are achieved with VOCl_3 as the oxidant (high volatility, thus, low sticking coefficient).^[11] Besides a few recent (2019) publications^[12,13] on oCVD of PEDOT films with liquid oxidants, the present contribution is one of the first reporting on the successful deposition of PEDOT thin films with VOCl_3 as the (liquid) oxidant.

By SEM imaging of cross-sections exposed by cleavage of PEDOT-coated silicon substrates, the thickness of the oCVD-PEDOT films (t_{PEDOT}) is estimated to be 50–200 nm. All depositions on substrates pre-covered by a monolayer of PS nanospheres (with the conditions reported herein) yield thin film samples with excellent uniformity (Figure 1d). Conformality (Figure 1c) appears to be excellent on the top parts of the spheres. The voids between the lower hemispheres are likely to be filled, e.g., due to capillary condensation. However, no appreciable defects are observed. To the authors' knowledge, this contribution is among the first to report on such conformal and uniform oCVD of conducting polymer thin films completely around nanospheres.

Fourier-transform infrared spectroscopy (FTIR) spectra (Figure 2e) recorded on different PEDOT samples compare well to data on PEDOT thin films deposited by oCVD with the same oxidant in the literature,^[12] confirming the successful polymerization of EDOT for all the reaction conditions applied. Furthermore, the successful deposition of oCVD-PEDOT thin films onto/around PS nanospheres is confirmed by the FTIR spectra recorded on samples with only PEDOT, and only PS, explaining all the peaks in the absorption spectrum of the combined PEDOT-PS structure (Figure 2e).

As deposition conditions influence the resulting thin films (e.g., electrical, piezoresistive properties), deposition

time (30/60 min) and substrate deposition temperature T_{sub} (60/80 °C) are varied. Temperatures below 100 °C are chosen to not damage the PS spheres thermally (glass transition temperature of PS at ≈ 100 – 107 °C).^[14]

Various samples are acid-treated by placing them in a 0.5 M H_2SO_4 solution for 10 min to achieve a dopant exchange process in the PEDOT layer^[15] and a sulfonation of the surfaces of the PS spheres^[16] as described in the literature. SEM and FTIR analysis performed before and after this treatment do not indicate significant changes.

For the electrical investigation of the samples, two nickel top-contacts with a separation of 0.5 mm are deposited onto the PEN-PS-PEDOT structure. The final device setup, as assembled (a) and when strained via bending (b), is sketched in Figure 2. Nickel is chosen due to its work function (4.9–5.2 eV in films)^[17] matching the estimated work function of PEDOT (5.1–5.2 eV in oCVD films).^[18] This ensures Ohmic behavior, which is confirmed by all the samples exhibiting linear voltage–current characteristics (also during bending; see Figure 2c).

For the sake of usability, further resistance values are reported from direct measurements with a multimeter. The values on the unstrained devices (as-deposited and H_2SO_4 -treated) are given in Table 1. In accordance with literature, the resistance decreases with T_{sub} and t_{PEDOT} due to altered crystallinity and conduction pathways.^[12] Furthermore, H_2SO_4 -treatment decreases the resistance by $\approx 1/3$. In the literature (oCVD-PEDOT with iron chloride as the oxidant), even larger increases in conductivity were reported (more than 100%), possibly due to different species and levels of doping.^[15] However, the present work is among or even the first to report on a dopant exchange in sulfuric acid significantly enhancing the conductivity of oCVD-PEDOT films deposited with VOCl_3 as the oxidant.

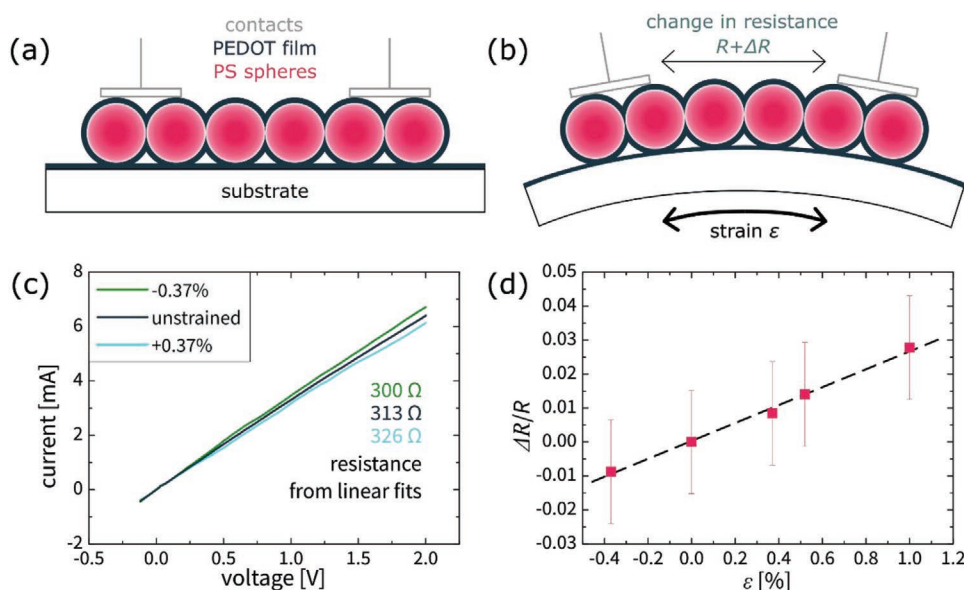


Figure 2. Sketch of the device structure proposed and tested for strain sensing (electrode separation 0.5 mm, dimensions not to scale), with resistance R in unstrained conditions a), and changing by ΔR when strained via bending b); c) voltage–current characteristics as measured on a device ($T_{\text{sub}} = 80\text{ }^{\circ}\text{C}$; 60 min; H_2SO_4 -treated) when unstrained and under $\pm 0.37\%$ of strain ϵ (tensile and compressive); d) $\Delta R/R$ measured on a device ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$; 60 min; H_2SO_4 -treated) as a function of different levels of ϵ (bending radii down to ≈ 6 mm); linear fit as a guide for the eye.

With the samples' geometry, their conductivity can be estimated to range in values of up to tens of S cm^{-1} . This is in the range of conductivities reported in other studies on oCVD-PEDOT,^[19] especially when deposited at relatively low T_{sub} .^[12] For depositions carried out at higher T_{sub} (e.g., $145\text{ }^{\circ}\text{C}$), conductivity values of up to several thousands of S cm^{-1} have been reported.^[12,13]

Piezoresistive properties of the samples are confirmed and investigated by measuring changes in the samples' resistance (ΔR) as a function of straining (varying the bending radius). A few percent in ΔR for applied strains of below 1% (cf. Figure 2d) are observed. Compressive and tensile strains yield shifts in the opposite directions, but comparable in magnitude. The response of different samples to 0.37% of tensile strain is given in Table 1. It is higher for samples prepared at higher T_{sub} (i.e., more conductive) and longer deposition time (i.e., greater t_{PEDOT}). Furthermore, acid treatment increases the response by a factor of ≈ 2 , indicating an influence of the dopant species on the piezoresistive behavior. Howden et al.^[15] hypothesize that acid rinsing aids in removing residual oxidant, solvating the

Table 1. Resistance (unstrained) and response to 0.37% of tensile strain (change of resistance measured upon bending in percent compared to the unstrained state) on device structures as-deposited and H_2SO_4 -treated for different deposition conditions.

Deposition conditions	Resistance [Ω]		Response [%]	
	As-deposited	H_2SO_4 -treated	As-deposited	H_2SO_4 -treated
60 $^{\circ}\text{C}$; 30 min	1711 ± 16	1056 ± 11	0.2	0.4
60 $^{\circ}\text{C}$; 60 min	448 ± 6	320 ± 5	0.5	0.9
80 $^{\circ}\text{C}$; 30 min	1059 ± 11	717 ± 7	0.8	1.6
80 $^{\circ}\text{C}$; 60 min	397 ± 6	298 ± 5	2.3	4.2

structure to allow for optimized morphology and lowering the film's roughness; it also allows for the incorporation of further dopant ions (higher doping level), observable in a higher conductivity.^[15] A contribution of the sulfonated PEDOT-PSS interfaces (doped aromatic units on the surfaces of the PS spheres) to the conduction mechanisms in the material is assumed, also enhancing the piezoresistive response, as reported and hypothesized in the literature.^[6,7,20] Overall, the data presented above elucidates a correlation between an increase in conductivity and an increase in piezoresistive response.

By applying different levels of strain (cf. Figure 2d), the relation between a change in resistance and the applied strain is studied. A linear relationship between these two parameters is found (in the range of strains investigated). Such behavior is widely reported in the literature^[5,6] and is used to assess the quality of piezoresistive devices by extracting a quantity termed gauge factor k ; k relates the measured resistance change normalized by the resistance of the unstrained device ($\Delta R/R$) to the applied strain ϵ :

$$k = \frac{\Delta R}{R} / \epsilon \quad (1)$$

With the values from Table 1, the gauge factors can be calculated, yielding values as high as 11.4. The Poisson's ratio of the polymer (ν ; transverse change in length resulting from longitudinal straining) is estimated to be ≈ 0.35 .^[5] This can be used to subtract the factor merely resulting from the geometrical change upon straining the device as follows:^[1]

$$k = 1 + 2\nu + \frac{1}{\epsilon} \frac{\Delta \rho}{\rho} = 1 + 2\nu + k_p \quad (2)$$

Thus, the "true" gauge factor (k_p), resulting (only) from the change in conductivity ($\Delta \rho$) of the polymeric structure, is

estimated to be ≈ 9.7 . Still, this value lies well above gauge factors of conventional metal strain gauges ($k < 5$).^[1] Considering other polymer-based materials, the extracted k compares well to values determined on PEDOT:PSS-based structures measured in similar configurations (e.g., 0.48,^[5] 17.8^[6]). In conventional semiconductors (e.g., silicon, germanium), gauge factors of >100 have been reported.^[21] However, these materials bear the disadvantage of a trade-off between their rigidity (inability to sense large strains and/or small pressures) and high k . Furthermore, in more sophisticated sandwich geometries (top-bottom contacting), very large responses to pressure (changes of the resistance of up to ≈ 3 orders of magnitude) were reported for PEDOT:PSS films containing gold nanoparticles.^[7] However, such devices exhibit a very large intrinsic resistance in their unstrained state ($\approx 10^{11} \Omega$). Moreover, very high gauge factors (55–396), depending on the range of strains applied, were reported for an electrospun PEDOT:PSS-PVA nanofiber material; also for this material, low conductivities were reported (10^{-5} – $10^{-8} \text{ S cm}^{-1}$).^[8]

Conclusively, in this work, a novel, fully polymeric composite material for piezoresistive devices is proposed, prepared, and tested in a simple approach. A composite layer of PS nanospheres conformally coated with a thin film of PEDOT is reported to exhibit promising piezoresistive properties, with the possibility of tuning its intrinsic resistance and, thus, the piezoresistive response via processing parameters (e.g., T_{sub} , t_{PEDOT} , H_2SO_4 -treatment). Gauge factors as high as 11.4 are extracted.

The set of materials and structures used and the measurement geometry employed serve as a promising basis for the optimization and further development of this system for its application in piezoresistive devices. Furthermore, the read-out geometry (e.g., sandwich), the size of the nanospheres and, overall, the oCVD process yield great potential for tailoring and tuning material properties and, thus the piezoresistive response of the devices. For instance, as an increased conductivity was found to correlate with an increased gauge factor, a very promising outlook are the remarkably high conductivity values (thousands of S cm^{-1}) reported on oCVD PEDOT in the literature;^[12,13] while the use of other more robust nanosphere materials would overcome thermal instability issues of PS. In addition, there are reports that indicate synergistic properties can be derived when oCVD polymers are integrated with nanostructures, so potentially synergies can also be derivable from the nanoarchitecture in our study here.^[22] Additionally, compared to regular PEDOT:PSS-based structures, the methods applied in the present work open up a vast number of tunable parameters, potentially enabling the structures to outperform conventional architectures. As gauge factor is not the only parameter relevant for piezoresistive devices, properties such as the mechanical flexibility, elasticity, compatibility with biological systems, and low-cost of fully polymeric setups like the one proposed herein make it particularly interesting for various applications such as in biosystems and wearable electronics.

Experimental Section

Sample Preparation: Silicon wafers (University Wafer) were used as test substrates for the deposition of PS nanospheres and PEDOT thin films, and PEN films (thickness 0.125 mm, Goodfellow) were used as substrates for the final test devices.

Various PEDOT thin films were synthesized by oCVD in a custom-built reactor described by Smolin et al.^[23,24] EDOT (97%) and VOCl_3 (99%) were the liquid monomer and oxidant sources, respectively (Sigma-Aldrich). The glass jar of EDOT was heated to 90 °C while VOCl_3 was kept at room temperature. Both flow rates were set to 1 sccm (standard cubic centimeters per min); equal flow rates were adopted to avoid overoxidation.^[12] Nitrogen was used as an inert carrier gas for both gas lines (1 sccm each). The reaction pressure was kept constant at 200 mTorr. T_{sub} was held at 60/80 °C. Deposition times of 30/60 min were adopted to achieve samples of different film thickness.

Monolayers of PS nanospheres were assembled at an air–water interface with subsequent pick-up onto the respective substrates. A H_2O dispersion of PS beads (580 nm; 5 wt%) was kindly provided by Prof. Vogel's group in Erlangen, Germany. These were suspended 1:1 in volume ratio with EtOH (200 Proof, Decon Laboratories, Inc; purity 99.2%) and used as described by Vogel et al.^[9] All the substrates were plasma-cleaned under an air-atmosphere in a Harrick PDS-001 plasma cleaner for 10 min at 30 W.

Acid treatment was performed by placing the samples (PEDOT-PS-PEN) in 0.5 M H_2SO_4 solution. For this purpose, concentrated H_2SO_4 (Sigma-Aldrich) was diluted with Milli-Q water.

Nickel top-contacts were deposited in a Thermoionics VE 90 thermal evaporator with a contact mask creating a spacing of 0.5 mm between the two contacts. A quartz crystal microbalance was used to monitor the Ni growth rate to achieve a target film thickness of $(50 \pm 2) \text{ nm}$.

Investigation: FTIR measurements were performed on a Thermo Nicolet 6700 spectrometer in transmission mode. The spectra were collected in the wavenumber range 400–4000 cm^{-1} at a resolution of 4 cm^{-1} using a DTGS detector.

SEM was performed on a Zeiss Supra 50VP with an accelerating voltage of 5 kV. All the presented images were recorded at a working distance of $\approx 11 \text{ mm}$. The samples were sputtered with Pt for 40 s before SEM analysis.

Voltage–current characteristics were measured on a Gamry Reference 600 system in the linear sweep voltammetry mode. Direct resistance measurements were performed on a Fluke 112 multimeter. A piece of aluminum foil between the probe contacts and the electrodes was used to prevent the ultrathin nickel film from being scratched. Strain was exerted on the devices via bending (longitudinal to the separation of the contacts). The electrical characterizations were performed at constant temperature (22 °C) and relative humidity (40%).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

nanospheres, oCVD, PEDOT, piezoresistive sensors

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