Piezoresponse in chemically synthesized polypyrrole thin films

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The resistance of chemically synthesized polypyrrole (PPy) thin films is investigated as a function of the pressure of various gases as well as of the film thickness. A physical, piezoresistive response is found to coexist with a chemical response if the gas is chemically active, like, e.g., oxygen. The piezoresponse is studied separately by exposing the films to the chemically inert gases such as nitrogen and argon. We observe that the character of the piezoresponse is a function not only of the film thickness, but also of the pressure. Films of a thickness of 70 nm show a decreasing resistance as pressure is applied, while for thicker films, the piezoresponse is positive. Moreover, in some films of thickness close to 70 nm, the piezoresponse changes from negative to positive as the gas pressure is increased above 500 mbars. This behavior is interpreted in terms of a total piezoresponse which is composed of a surface and a bulk component, each of which contributes in a characteristic way. These results suggest that in polypyrrole, chemical sensing and piezoresponse can coexist, which needs to be kept in mind when interpreting resistive responses of such sensors.

I. INTRODUCTION

One of the most intensely studied semiconductive polymers is polypyrrole (PPy) [1, 2, 3, 4, 5, 6, 7]. This material combines several advantages. It is stable under ambient conditions when highly doped and can be synthesized via both chemical and electrochemical polymerization [8, 9]. Moreover, since PPy is piezoresistive and reacts chemically with various gases, it has potential applications in gas and pressure sensors as well as in actuators. The detection of various gases with PPy has been demonstrated, for example H2 with a resolution limit of 0.06% [10], NH3 [11, 12, 13, 14] with a sensitivity of 8 ppm [15], O2 [16, 17], NO2 [11, 18] with a resolution limit of 40 ppm, CO2 [19] as well as more complicated molecules like trimethylamine [14] or sevofluorane [20]. Nonmonotonous evolution to gas exposure as a function of time has been observed in several experiments on PPy, see, e.g., Fig. 1 in Ref. [14], Fig. 4 in Ref. [11], Fig. 3 in Ref. [18], or Fig. 3 in Ref. [17]. While a quantitative understanding of the sensing mechanism is still absent, there are generally accepted suggestions of sensing mechanisms for some gases. For example, it is assumed that during NH3 sensing, an electron is transferred from the ammonia molecule to the polymer, thereby reducing the hole density and with it the conductivity, as observed experimentally [11, 13]. A similar explanation has been given for H2 sensing [10], while during NO2 or O2 sensing, the polymer is oxidized, resulting in an increased conductivity [11]. In some experiments, however, the response of PPy to the gas was ambiguous. In Ref. [18], it was observed that for low concentrations of NH3, the resistance R increases, while for larger concentrations, a decrease in R was observed, in contrast to the commonly accepted sensing mechanism. Furthermore, for some gases, the sensing mechanism is unclear at present, e.g. for CO2 [19] or trimethylamine [14].

On the other hand, it has been established that PPy is piezoresistive with a resolution of about 500 N/m² in PPy coated polyurethane foam [21]. This property has been used in various demonstrations of PPy based sensors and actuators, e.g. in wearable sensors [22], as drug delivery valves [23] or as artificial muscles [24]. It is therefore reasonable to assume that the response of PPy films to gas exposure may contain both chemical and physical (i.e., piezoresistive) components.

In the present manuscript, we shed some light on this interrelation by investigating the response of PPy thin films to exposure of various gases at different pressures. The studies are carried out with the inert gases nitrogen and argon, as well as with the chemically active oxygen. A recently reported technique based on chemical polymerization from the vapor phase [17] is used to prepare comparatively thin PPy films with low roughness. The sensing properties of PPy films prepared by this technique have not been investigated so far. Most importantly, we find that the piezoresistive response changes from negative to positive as the film thickness increases above 70 nm. Moreover, in some films with thicknesses close to 70 nm, we observe a change of the polarity of the piezoresponse (PR) as the pressure increases above 500 mbars. These findings indicate that the PR in PPy comprises a negative surface component and a positive bulk component. Furthermore, they offer a qualitative explanation for the ambiguous behavior observed in the earlier experiments by Ma et al. [14], Miasik et al. [11] or Hanawa et al. [18]. The character of the responses furthermore suggest that the piezoresponse surface effect is more suited for sensing applications than the bulk effect.

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II. SAMPLE PREPARATION AND EXPERIMENTAL SETUP

The films are prepared by chemical polymerization of Py monomers from the gas phase. This technique is described in detail in Ref. [17]. The films are formed on a glass substrate with Pt electrodes on top which allow 4-terminal measurements. They were patterned by optical lithography on top of the glass substrate and have a thickness of 100 nm. The separation between the electrodes is 2 μm. The patterned substrate is inserted into the polymerization chamber filled with Ar gas at pressure of 1 atm. A droplet of H₂O₂ : HCl (1000:3 volume fraction) is deposited on the surface of the patterned substrate. The H₂O₂ serves as oxidizing agent and the HCl provides the Cl⁻ ions which not only are necessary for charge neutrality, but also act as dopants. The substrate was kept at room temperature during the polymerization. The pyrrole monomers were evaporated from a boat by heating it to 100°C. The surface of typical PPy films are shown in the lower part of Fig. 1 while the roughness and the conductivity as a function of the film thickness, prepared in one run of sample fabrication, are reproduced in the main figure. A characteristic, egg-like surface morphology is observed, with a roughness of approximately 10% of the film thickness. Such flat films are characteristic for our chemically grown films, [6, 17] provided the substrate has a low roughness of the order of 1 nm. The conductivity increases almost three orders of magnitude as the film thickness increases from 6 nm to 78 nm, and continues to increase weakly as the thickness is further increased. This behavior presumably indicates that highly localized surface or interface effects dominate the transport in the thin films and that bulk conductivity begins to evolve only at thicknesses above 80 nm.

Immediately after growth, the samples are transferred to a vacuum chamber and vacuum dried at room temperature for at least one day. The vacuum chamber is equipped with a hand valve and a pressure sensor (Ionvac Transmitters ITR 90 from Leybold Vakuun) which allows adjustment and control of the gas pressure with an accuracy of ≈ 0.5 mbars for pressures between 50 mbars and 900 mbars. Temperature dependent transport measurements [6] have revealed that the films are p-doped and strongly disordered. The transport is dominated by thermally activated hopping for temperatures above ≈ 30 K, which transforms to Efros-Shklovskii - type hopping at lower temperatures [8], a typical behavior for strongly disordered semiconductors.

III. RESULTS

In Fig. 2 the response of a PPy film of 50 nm thickness to the exposure of oxygen (a) and argon (b) is shown as a function of time. Prior to gas exposure, the films are kept in vacuum, and a drop of the resistivity over time is observed which saturates after about 1 day. We attribute this to vacuum drying of the film, which removes residues from the polymerization solution. As the film is exposed to 150 mbars of oxygen, see Fig. 2(a), its resistivity increases with the increase slowing down after about 12 h, but does not show saturation even after 2 days. This response is only partly reversible when the vacuum is reestablished. Such a behavior is well known from PPy films of larger thickness made by other techniques and is attributed to overoxidation [20, 24, 27, 28]. Fig. 2(b) shows how this film responds to argon exposure. No chemical reaction is expected due to the inertness of the noble gas. However, application of 150 mbars of Ar causes the film resistance to drop and saturate within a few minutes. Since this response should have a purely physical origin, we attribute it to a negative piezoresistance, dR/dp < 0. We note that the resistance dip observed immediately after exposure to Ar originates from the pressure equilibration over time in the vacuum chamber. This is clearly demonstrated in (c), where the film response is compared to that one of a commercial pressure sensor. Apparently, the opening of the gas valve in our setup generates a pressure burst which relaxes to the preset value within ≈ 30 s. This comparison furthermore shows that the response time of the PPy film is in the range of a few seconds.

In Fig. 3 the response of a PPy film with thickness 30 nm is compared to that one of a commercial pressure sensor. Apparently, the opening of the gas valve in our setup generates a pressure burst which relaxes to the preset value within ≈ 30 s. This comparison furthermore shows that the response time of the PPy film is in the range of a few seconds.

In Fig. 4 the response of a PPy film with thickness 30 nm is compared to that one of a film with thickness 150 nm. While the PR is negative for the thin film, it is positive for the thicker film. After the pressure is applied, the resistance in the thin film drops by ≈ 5% and saturates quickly. The resistance of the thicker film increases by ≈ 1.5% within one minute after pressurization, i.e., a significantly weaker response than the negative PR. It keeps increasing slowly over a long period of time afterwards, with no clear signature of saturation even after 20 minutes. Note also that in the thicker film, a sharp spike towards lower resistance, i.e., a short term negative piezoresistive response, is observed immediately after the pressure is applied. This behavior, however, is quickly overcompensated by the positive PR just described.

The piezoresistivity studies were performed on films of thicknesses 30 nm, 50 nm, 70 nm, 100 nm, 120 nm and 150 nm. An overview of the evolution of the dependence of the PR on film thickness, pressure and type of gas is given in Fig. 5. The negative (positive) PR is typical for all films of thicknesses well below (above) ≈ 70 nm at all pressures. At this critical thickness, a transition between the two responses takes place.

The films were exposed to a pressure which was step-wise increased between 50 mbars and 900 mbars; in between the steps, vacuum was reestablished. The films were exposed to Ar and N₂ as well as to O₂ for comparison. The thin film (thickness 30 nm) responded approximately identically to Ar and N₂ pressure, and a pronounced negative PR is observed, with an approximately constant amplitude which does not show a monotonous behavior as a function of the pressure. This effect is also
observed in oxygen atmosphere. Here, however, we see also a slow but strong increase of the resistance which is persistent and most likely reflects the chemical response of the PPy film. This nicely demonstrates that the total response of the PPy films is a superposition of a physical and a chemical component. The thick film (thickness 150 nm) shows a positive PR for all pressures, with the characteristic time dependence as discussed in Fig. 3. At an intermediate film thickness of \( \approx 70 \text{ nm} \), the positive and the negative piezoresistive components are of approximately equal strengths, which moreover depend slightly on the pressure. In the run with Ar-exposure, we observe that the time dependence of the resistance after the pressure exposure is different in comparison to the thin film. After the resistance drop, we no longer observe an approximately constant resistance; rather, it increases with a time dependence as observed in the thicker films with a positive PR, but does not exceed the resistance value under vacuum within our hold time of 25 minutes. This behavior gets more pronounced as the pressure is increased, which is in tune with the fact that the positive PR component has a stronger pressure dependence. In a second run, the same film was exposed to \( N_2 \). Here, we observe a pressure-induced transition from negative to positive PR as the pressure is increased above 500 mbars. Since the positive PR increases more strongly than the negative one as the pressure is increased, an overall switch of the PR polarity can be observed here. Note that a similar transition can be also seen in the experiment with oxygen. We remark that in our opinion, the differences observed between Ar and \( N_2 \) exposure are not due to gas selectivity, but rather reflect the slowly changing properties of the film over time which are briefly discussed below.

Apparently, our PPy films do show a piezoresistive response to inert gas atmospheres, which comprises two parts, namely a negative PR component that dominates in films of thicknesses below 70 nm, saturates quickly and depends only weakly on the pressure level, and a positive PR component which dominates in films of thicknesses above 70 nm, shows a stronger dependence on the pressure and saturates only on very long time scales of the order of hours. Furthermore, the negative PR component is also present in thicker films where the positive PR component dominates, as manifested in a sharp dip in the resistance as a function of time directly after pressurization. In contrast to this, the positive PR component is absent in the films which show a negative PR.

For a qualitative interpretation, we recall (Fig. 4) that the film conductivity increases very strongly up to thicknesses of about 80 nm and depends only weakly on the film thickness for larger thicknesses. It appears plausible that for thicknesses below \( \approx 80 \text{ nm} \), the current-carrying states do not have bulk character but rather are localized surface or interface states with a two-dimensional character and a localization length that depends on the film thickness. Since the hopping conductivity depends exponentially on the localization length, a strong thickness dependence of the conductivity would result from this scenario. As the film thickness is increased beyond 80 nm, the current is more and more carried by bulk states and the conductivity depends only weakly on the film thickness. Thus, it seems likely that the negative PR is related to a surface effect, while the positive PR originates from a bulk property of the film. Let us assume that the film is composed of a surface layer of \( \approx 70 \text{ nm} \), minus an unknown interface layer thickness due to the electronic structure of the film at the SiO\(_x\)/PPy interface, and a bulk layer in between the surface and the interface layer. Then, the surface-induced, negative PR would dominate for sufficiently thin films and also be present in thicker films, but would be of reduced relevance as the film thickness increases, due to the increasing weight of the positive bulk PR component. Suppose that the pressure just squeezes the surface layer somewhat. This would result in an increased overlap between the localized states responsible for the hopping transport, and hence in a reduced resistance. It can be expected that the squeezing occurs quickly and is stable once the pressure is applied. This is consistent with the observed fast and stable piezoresistive response.

We conclude this Section with a remark regarding the long-term behavior of our samples and the significance of a quantification of the film response in terms of characteristic sensor quantities, like the sensitivity or the gauge factor. As suggested by the data shown in Fig. 2, the resistance of the films vary over time by as much as 50% with typical time constants of hours. The origin of these changes are not completely clear. One mechanism is an initial drop of the resistance due to vacuum drying. Also, long-term memory effects are significant, like earlier exposure to oxygen or to inert gases of pressures above \( \approx 500 \text{ mbars} \). Another factor may be current- or voltage-induced conformational changes, well known from cyclic voltammetry performed on comparable films. The net effect of such mechanisms is a slowly varying time dependence of the resistance that is influenced by the history of the sample and is not well understood. The piezoresistive sensitivity is defined as \( s(p) \equiv \frac{R(p)-R(0)}{R(0)} \), where \( R(p) \) denotes the resistance at a pressure \( p \), and thus depends on the history of the sample. Consequently, this is also the case for the gauge factor, defined as \( G \equiv ds(p)/dp \). Therefore, the values obtained for these quantities have
to be considered with caution, and comparability is not given, not even for experiments performed on the same film at different times. Moreover, the resistance changes are not stable over time, in particular for the positive PR where saturation in reasonable periods of time is not observed, which means that the sensitivity depends strongly on the hold time after the application of the pressure. As served, which means that the sensitivity depends strongly in reasonable periods of time is not observed, which means that the sensitivity depends strongly on the hold time after the application of the pressure. As a consequence, the absolute values are of little meaning and we therefore refrain from a quantitative discussion in terms of $s$ or $G$. Rather, these considerations ask for a better understanding of the long-term behavior of the resistance as a prerequisite for a more quantitative analysis. Ultimately, applications of such films for accurate quantitative pressure or gas sensing will require an elimination of such drift effects.

IV. SUMMARY AND CONCLUSIONS

We have studied the response of the electronic transport in chemically synthesized PPy films to exposure of different gases at various pressures. A pronounced piezoresistance is found which is composed of a negative and a positive component. In thin films with thicknesses below 70 nm, only the negative PR component is present. It is characterized by a quick saturation in combination with a weak pressure dependence. In films of thicknesses $> 70$ nm, a positive piezoresistance is dominant, while the negative contribution is also visible. This response does not show a clear saturation but rather evolves over many hours. However, its pressure dependence is stronger than the negative PR effect. Due to the different pressure dependencies of the two contributions, a pressure-induced transition from negative to positive PR is possible in films of $\approx 70$ nm thickness. Attribution of the negative PR to a surface effect and the positive PR to a bulk effect is consistent with the observations. Moreover, measurements in oxygen atmospheres reveal that the chemical response used in sensing applications coexists with both kinds of piezoresistivities. At present, we have no indication that chemical sensitivity and the PR are interdependent.

Our results show that the response of polypyrrole films to gas exposure is more complicated than presently anticipated in the literature, and that piezoresistivity must be expected to be always present in addition to a chemical sensing mechanism. Thus, piezoresistivity may explain the ambiguous and nonmonotonous responses to gas exposures observed in earlier experiments, even though the PPy films were prepared by a different technology. Films with thicknesses below 70 nm respond unambiguously to the pressurization and the response saturates within seconds. Therefore, such thin PPy films appear better candidates for pressure sensors than thicker films where the bulk PR component becomes detectable as well.

Gas sensing applications typically require detection levels in the ppm regime and below. State of the art PPy films have shown resolution limits around 40 ppm for gas sensing and of about 500 N/m² in pressure sensing. It remains to be seen in future studies how this interplay between chemical and piezoresistive response scales into this regime. However, if we assume that the unusual behavior observed by Hanawa et al. [18] on a 40 ppm level in NO₂ - detection can be explained by piezoresistivity, the properties reported here will in fact be relevant in the interesting regime of detection levels. Moreover, we note that oxygen sensing is important for pressure levels up to 1 atmosphere, where the results presented here are directly relevant. For example, a resistance measurement on a PPy thin film would not be able to distinguish between a pressure fluctuation and a change of the oxygen contents on a time scale of seconds. Finally, we note that the observed behavior also offers a potential solution to this ambiguity, for example by constructing resistance bridges with PPy arms of different thickness which nullify the piezoresistive signal.

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Dr. Carlos Cesar Bof Bufon received his PhD in 2007 at the Heinrich-Heine University Düsseldorf, where he investigated the transport properties of Polypyrrole films and devices. He is presently working as a postdoctoral researcher at the Institute for Integrative Nanosciences in Dresden (Germany) where he works on mechanoelectric silicon devices.

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Figure captions:

Figure 1:
Top: roughness and conductivity of the PPy films as a function of the film thickness. Bottom: scanning probe microscope image of the morphology of the film with 78 nm thickness used for this study (left). The roughness, i.e., the variance of the height fluctuations, of this film is 8.5 nm. For comparison, the morphology of a film with a thickness of 7.4 nm is shown to the right.

Figure 2:
Resistance of a 50 nm thick PPy film as a function of time when exposed to oxygen (a) and argon (b). In (c), the time-resolved response of the film is shown in comparison to the commercial pressure sensor used in the experiments.

Figure 3:
The normalized response of the film resistance to exposure of 150 mbars Ar for PPy films of thickness 30 nm with a negative piezoresistance in (a) and of 150 nm thickness with a positive piezoresistance in (b).

Figure 4:
Piezoresistive response of films with thicknesses 30 nm (top), 70 nm (middle) and 150 nm (bottom), to exposure of Ar (left), N2 (center), and O2 (right) gas at various pressures, which are labeled as 1 to 4 for pressures from 50 mbars to 200 mbars in steps of 50 mbars, and from 5 to 11 for pressures from 300 mbars to 900 mbars in steps of 100 mbars, respectively. The dashed vertical lines from the measurement traces to the top and to the bottom indicate the points of opening the gas inlet valve and its closing with simultaneous begin of pumping to establish vacuum, respectively.
FIG. 1:
FIG. 2:

(a) Graph showing resistance ($R$) over time ($t$) with markers for vacuum, $O_2, 110$ mbar, and vacuum.

(b) Graph showing resistance ($R$) over time ($t$) with markers for vacuum and $Ar, 110$ mbar.

(c) Graph showing pressure ($p$) and resistance ($R$) over time ($t$) with markers for vacuum, $Ar, 110$ mbar, pressure sensor, and PPy film.

FIG. 3:

Graph showing change in resistance ($R(t)/R(0)$) over time ($t$) with markers for $Ar, 150$ mbar, film thickness 150 nm, film thickness 30 nm, film thickness 70 nm.
FIG. 4: