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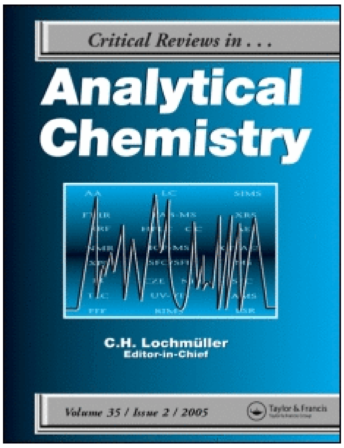

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Chemical Gas Sensors Based on Organic Semiconductor Polypyrrole

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ABSTRACT: Polypyrrole (PPy) is one of the most studied conducting polymers. It is well known that the mechanical, physical, and chemical properties of PPy strongly depend on the nature of the dopant anion. In this context, on overwiev of the influence of small anions and metallomacrocycles, for example, metallophthalocyanines (MPcTS), on the chemical transducer behavior of the doped PPy layer studied by the Kelvin Probe method is given. The gas-polymer interaction changes the work function of the polymer, which can be explained by a secondary doping of the polymer by the adsorbed gas molecule. Studies have revealed that the central metal ion in MPcTS plays an important role in the chemical sensing properties toward NO_2, chlorinated hydrocarbons, and organophosphorous compounds in the low ppm concentration range. Furthermore, the competitive doping method of PPy with a mixture of small anions and MPcTS strongly enhances the selectivity and reduces the response time of the conducting polymer, which are general problems in the use of conducting organic polymers for gas and vapor detection.

Chemical sensitive PPy layers have been used to build chemical sensors in which the organic semiconductor works both as the active component in the electronic device structure and as the chemical sensing transducer element, for example, polymer field-effect transistors, PPy/Au-Schottky, and PPy/Si-heterojunction diodes. The junction parameters of the polymer-based diodes, as the ideality and the rectification factor, are strongly influenced by the dopant of the conducting polymer. In both forward bias and reverse bias, these junctions exhibit a significant, fast, and reversible response to NO_2 gas, which can be explained by changes in the barrier height and in the charge carrier concentration of the PPy layer due to NO_2 interaction.

KEY WORDS: chemical sensor, gas sensor, polyprrole, schottky barrier diode, polypyrrole composite, polymer based electronic devices.

I. INTRODUCTION

The organic semiconductor polypyrrole (PPy) is one of the most frequently used and studied conducting polymers owing to its attractive properties from the practical point of view, for example, its inherent flexibility of organics, good environmental stability and relative ease of processing, as well as easy tunability of electric properties.[1] It is well known that the electrical, mechanical, and chemical properties strongly depend on the preparation methods and the nature of the dopant incorporated into the polymer backbone to maintain electroneutrality. Furthermore, several studies have shown that the chemical sensitivity of PPy toward certain vapors and gases exhibiting electron donor or acceptor behavior, for example, alcohols, ammonia, chlorinated hydrocarbons, nitrogen oxide gases, and organophosphorous vapors, changes with the dopants. The combination of the properties make PPy particularly attractive for applications in intelligent gas sensors, in which the organic semiconductor PPy acts as both the active semiconductor and the chemical sensitive transducer element of the sensor structure.[2-6]

However, it brings about a self-limitation of their use. Due to its sensitivity to various gases and vapors the selectivity is low, which is the most serious problem in the use of PPy for gas or vapor detection. The environmental stability of PPy doped with commonly used anions is rela-

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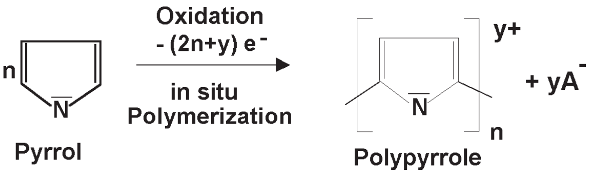
tively high compared with other conducting polymers. Nevertheless, the polymer is sensitive to electrochemical and chemical degradation and the conductivity exhibits a long-term irreversible decay presumably due to the irreversible attack of oxygen present in the ambient.

The following sections are focused on the chemical sensing behavior of PPy. A survey is given of the preparation of stable, sensitive PPy layers with reduced response time and enhanced selectivity to selected vapors and gases.

II. SYNTHESIS AND *IN SITU* DOPING PROCESS

PPy can be prepared in various forms, depending on the method used and on the preparation conditions. A general difficulty of the reproducible PPy preparation arises from its complexity. The structure and hence the properties of the resulting PPy are strongly influenced by a number of variables, for example, the applied potential, the monomer concentration,[7] and the preparation temperature.[8,9] Therefore, the results on PPy spread widely. Two basic methods are used for the preparation of PPy: chemical and electrochemical synthesis. The chemical synthesis of PPy produces easily arbitrary amounts of PPy in various forms, but its reproducibility is poor. An advantage of the electrochemical method is that the preparation process can be simply controlled through the current, the applied potential or the charge consumed. A disadvantage is that PPy can be prepared only in the form of a thin film deposited on the surface of a conducting material.[10]

The general mechanism, which is the same for both processes, is based on the oxidation of pyrrole monomer to form oligomeric intermediates, according to Eq. 1.[11]



(1)

When the polymerization propagates the polymer chain becames insoluble and is deposited on the working electrode to form a PPy film. In this first step, the ideal neutral polymer chain consists of PPy units consecutively rotated by 180°, prohibiting the formation of an extended π-electron system along the polymer backbone. The nonconducting or neutral state of PPy is considered to have the so-called benzoid structure, which exhibits a very low conductivity due to the large band gap of 3.2 eV (Figure 1).

In the second step, the neutral state is *in situ* oxidized and electrons are extracted from the polymer, which leads to a structural and electronic rearrangement of the pyrrole units in the polymer backbone. The former enables the formation of an extended conjugated π-electron system along the quinoid-like planar structure, the latter the formation of self-localized electronic states obeying the polaron (cation-radical) or bipolaron (dication) formalism (Figure 2). The charge injection into the macromolecular chain by oxidation is called doping. Besides this charge injection, doping of PPy implies also the insertion of anions present in the background electrolyte into the polymer backbone in order to maintain charge neutrality.

These anions are called dopants. The substantial difference between the doping of common inorganic semiconductors and doping of conducting polymers is the amount of dopants present in the bulk material, which is of 5 orders of magnitude higher with a charge carrier density up to 10^{22} cm^{-3}. The final structure resulting from the preparation is influenced by a number of parameters. The nature of the dopant and the solvent used for synthesis has the largest effect.

PPy doped with spherical anions, for example, ClO_4, BF_4 exhibits a generally isotropic structure.[12,13] On the other hand, the amphoteric, for example, *p*-toluenesulfonate, or planar aromatic anions for example, metallophthalocyanines tetrasulfonates, MPcTS (Figure 3) induce a measurable anisotropy in the PPy structure. It is known that the incorporation of electroactive MPcTS causes an increase in conductivity,[14,15] and crystallinity,[16-18] because of the layered structure and the high package density of the film.

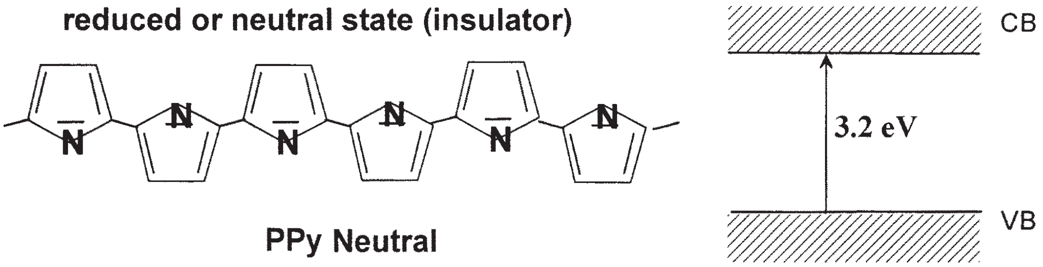


FIGURE 1. Neutral state of polypyrrole in the benzoid structure and its corresponding schematic electronic band diagram.

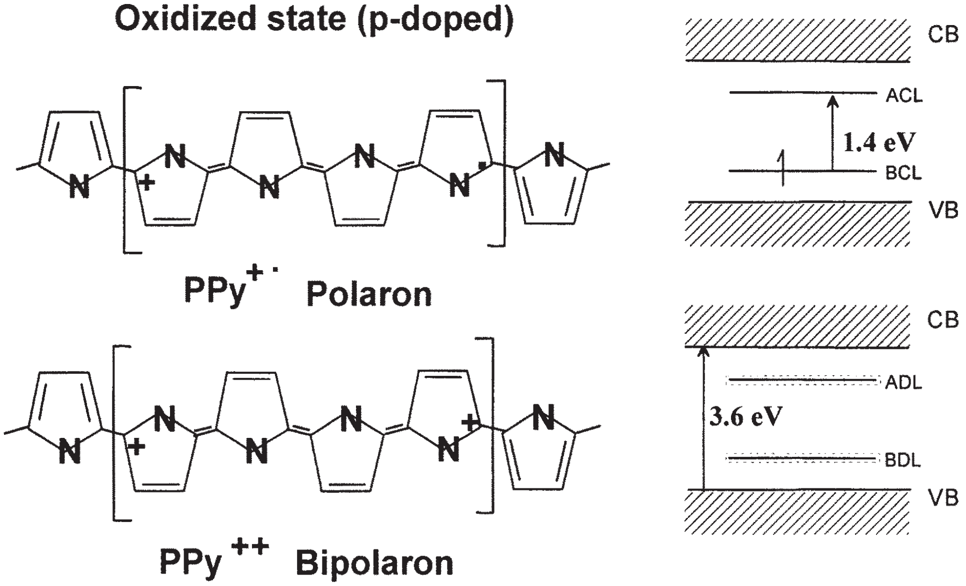


FIGURE 2. Quinoid polaron and bipolaron structure for light and heavily doped polypyrrole with their corresponding schematical electronic band diagram.

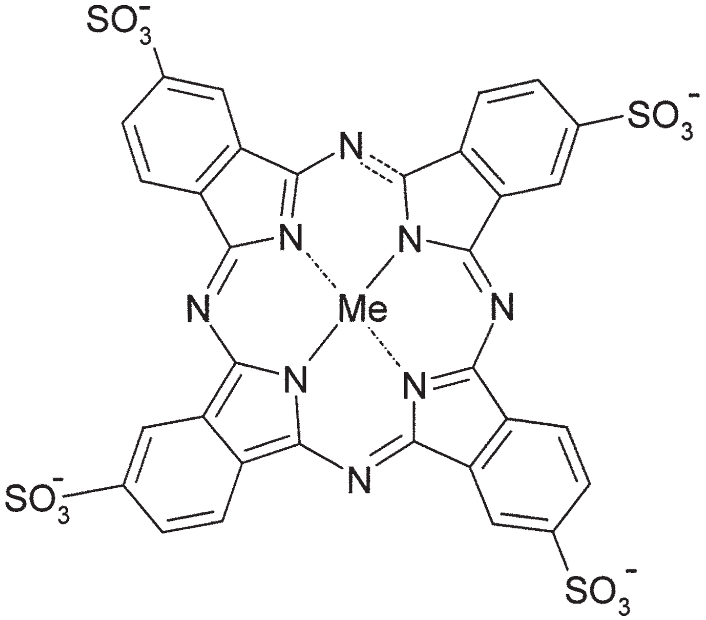


FIGURE 3. Chemical structure of metallophthalocyanine tetrasulfonate anion, MPcTS.

III. SENSITIVITY

The chemical sensing behavior of PPy is based on the interaction between the polymer layer and the ab- or adsorbed gas molecules. The interaction leads to a heterogeneous charge transfer reaction[19] and hence to a chemical modulation of the polymer doping level, which is directly related to the Fermi level of the organic semiconductor.[20] This type of interaction is often described as a secondary doping of the sensitive polymer layer. The effect results in a change in the electronic conductivity or the work function, Φ, of the organic layer. In case of Φ, the polarity of the response depends on the ability of the entering gas molecule to exchange charge density with the polymer matrix either by oxidation ($\Delta\Phi > 0$) or reduction ($\Delta\Phi < 0$). The gas molecule behaves as an electron acceptor and donor, respectively.

A. Chemical Sensing Properties of Doped PPy Layers

Several studies deal with the influence of the nature of the dopants on the morphology and the chemical sensing behavior of PPy to selected vapors and gases, which is presented in more detail.[21-23]

Anions commonly used for the electropolymerization of PPy, such as ClO_4, BF_4, and TOS, were chosen for comparison with PPy layers doped with the metallophthalocyanines (MPcTS, M = Cu, Pb, Al, Fe, and Ni).[21,23] Pure MPcTS layers show good sensitivity toward nitrogen oxide gases[24-27] and organophosphorous vapors.[28] The majority of these investigations has been focused on measuring the changes in electrical conductivity at elevated temperatures. Furthermore, several studies revealed that the incorporation of metallomacrocycles, such as metallophthalocyanine or metalloporphyrin complexes, drastically changes the properties of PPy.[16-18, 29-32] Their use as dopants causes an increase of crystallinity,[17,18] conductivity, and stability in air.[14,15]

The instability of PPy in air is related to its slow and irreversible degradation due to overoxidation of the polymer backbone. Oxygen, present in the air, can act as an irreversible dopant of the neutral form of PPy,[31] which is always present in a small amount in even highly oxidized PPy used as a chemical sensitive layer. The degradation process can be the reason for the slow irreversible drift of the work function of PPy often observed in long-term gas measurements. However, the signal remained constant (a drift of ca. 0.1 mV h^{-1}) when PPy doped with CuPcTS was investigated in air over a long period of time.

It was assumed that the incorporated electroactive MPcTS anion itself interact with oxygen and therefore prevent the overoxidation of doped PPy.[21]

The sensitivities of PPy films doped with various anions to DMMP, PER, and NO_2 are compared in Figure 4.

The interaction of these gases or vapors with PPy lead to both a positive and negative change in the work function. PPy doped with NiPcTS, PbPcTS, Fe(II)PcTs, and AlPcTS yielded negative changes in the work function for all the examined substances. This differs from CuPcTS, TOS, BF_4, and ClO_4 doped PPy, where the work function shows positive changes for NO_2 and negative changes for PER and DMMP. The measured signals were found to be comparable with those published.[28]

The difference and the opposite direction of $\Delta\Phi$ for PPy/CuPcTS and the other PPy/MPcTS layers after exposure to NO_2 indicates that the central metal ion of the phthalocyanine anions plays an important role, which is as yet not understood.[33] Furthermore, it indicates that the intrinsic electronic state of doped PPy, which can be described by the intrinsic work function, is strongly dependent on the nature of the dopant anion. This observation was confirmed recently by the determination of the built-in voltages of Au-PPy-Schottky diodes, comprising different doped anions as dopants, which are discussed later.[34]

A strong irreversible interaction of NO_2 with PPy/Fe(II)PcTS could be observed.[23] After several exposures to NO_2, the polymer layer shows only very small signal changes during further gas measurements. Owing to this strong irreversible interaction, PPy is practically insensitive towards all gases and vapors investigated thereafter, for example, DMMP. After a thermal treatment at elevated temperature (60°C) and reduced pressure, the layer can be reactivated and a work function change in the presence of DMMP is obtained. This clearly indicates that NO_2 is blocking the gas/polymer interaction sites of the PPy layer, which are strongly related to the nature of the dopant.

Cabala et al. assumed that the reason for the high and positive signals of PPy/ClO_4 and PPy/BF_4 in the presence of NO_2 could be caused by a

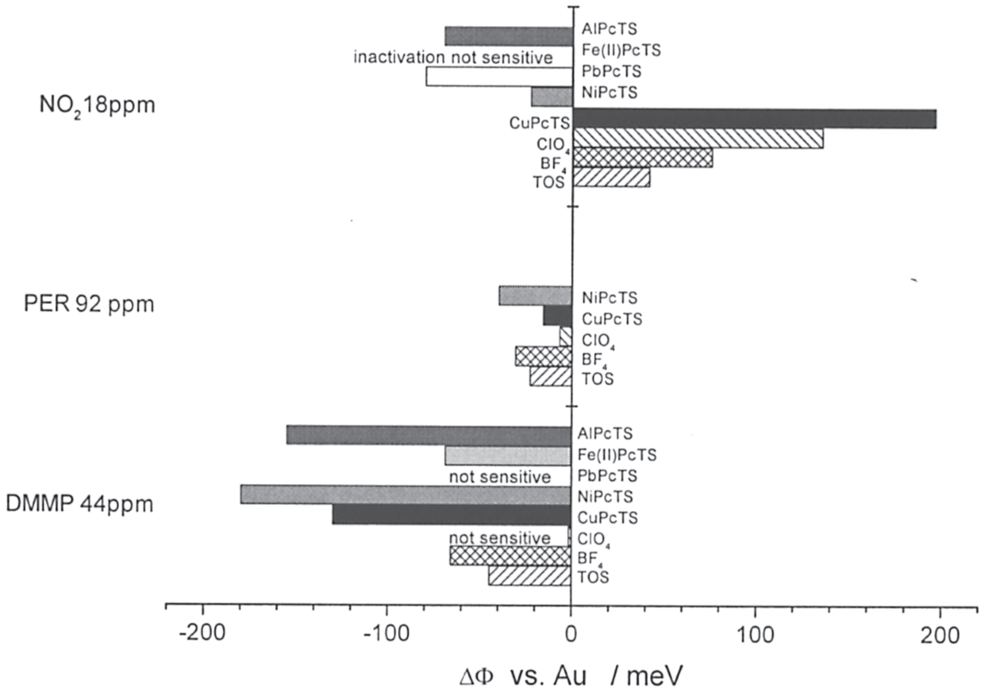


FIGURE 4. Comparison of the work function change, $\Delta\Phi$, of PP layers doped with various anions in the presence of NO_2, PER and DMMP in ambient air, measured with the Kelvin probe.

reaction of NO_2 with the water present in the polymer, yielding the strong acid HNO_3.[21] *In situ* impedance analysis of PPy samples doped with various anions has shown that ClO_4 and BF_4 anions transport a high amount of water into the bulk of the PPy film during electrochemical deposition, whereas in the case of TOS, CuPcTS and NiPcTS the amounts of water is negligible.[21] The responses of all the examined samples to PER are comparable and low.

The results presented above show that PPy doped with suitable anions, such as CuPcTS, ClO_4, NiPcTS, or AlPcTS, exhibits a high sensitivity toward NO_2 and DMMP, respectively, and can be used as a chemical transducer for gas and vapor sensors. However, the selectivity of such layers is not sufficient for practical applications.

Another important drawback in the application of PPy/MPcTS as sensitive film is the long response time (t_{90}), which is in the range between 10 to 16 min (NO_2) and 20 to 100 min (DMMP). It is assumed that, due to the highly ordered layered structure and the relatively high packing density of MPcTS-doped PPy, the vapor diffusion in and out of the layer is very slow, resulting in a long response time. In contrast, PPy samples doped with smaller inorganic anions such as ClO_4 and BF_4 exhibit an amorphous structure and a lower density. They show faster response times in the range of 1 to 3 min.

Several attempts can be made to address this problem. A general approach is to reduce the packing density or to increase the porosity of the conducting polymer by the introduction of an additional component into the polymer layer. Recently, Cabala et al. have shown that this can be done by the additional incorporation of a small spherical dopant besides the anion determining the sensitivity of PPy.[21] Another approach consists of grafting or copolymerization of PPy with chemical inert, nonconducting polymer forming a polymer blend or polymer composite, which is discussed later in Section III.B.

The simultaneous incorporation of various anions in PPy is called competitive doping[35-38] and is carried out in solution that contains a predetermined mixture of anions. The ambient air stability of competitively doped PPy samples is comparable to samples doped with a single anion. In order to obtain the highest sensitivities of the PPy layers toward DMMP and $NO_{2,}$ NiPcTS was combined with BF_4, and CuPcTS with ClO_4 as dopants for PPy, because they yielded the highest changes in the work function for the respective gases (see Figure 4). The work function changes of PPy doped with various molar ratios of ClO_4 in CuPcTS are presented in Figure 5. The results obtained for PPy doped with mixtures of NiPcTS and BF_4 are shown in Figure 6.

The data presented in Figures 5 and 6 indicate that the sensitivity of PPy layers to any examined gas is not enhanced with either pair of anions. The competitive doping of PPy decreases the work function change of about 30% after exposure to DMMP and NO_2, respectively, but the sensitivities are still high enough for sensing purposes. The change in the work function does not depend linearly on the composition of the background electrolyte. On the other hand, the responses of PPy/CuPcTS+ClO_4 to DMMP and PER, and of PPy/NiPcTS+BF_4 to NO_2 and PER decrease in such a way that the detection is practically impossible. This decay has the advantage of enhancing the selectivity of PPy. Transients in the work function response of PPy/CuPcTS+ClO_4 layers to NO_2 can be seen in Figure 7.

The dependence of work function of the PPy layers on the logarithm of the NO_2 concentration is shown in Figure 8. The sensitivity of PPy/CuPcTS+ClO_4 (0.5) obtained by the slope of a straight line in the signal vs. log (concentration) representation is 69 mV (ppm decade)$^{-1}$.

The work function signals of all PPy/CuPcTs+ClO_4 layers show no tendency to level off in the ppm concentration range indicating the high sensitivity of these layer with a relatively low detection limit ranging from 0.02 to 0.06 ppm. For concentrations above 40 ppm, the films become saturated reaching the upper detection limit. The sensitivity of the PPy/CuPcTs+ClO_4 films is found to be comparable with that of pure metallophthalocyanine films and higher than that of conducting polymer films in the published works.[26,27,39,40]

The time constant of the work function signal, $t_{90\%}$, to NO_2 decreases strongly from 16 min for PPy/CuPcTS to 1 to 3 min for the PPy/CuPcTS+ClO_4 layers indicating a faster diffusion

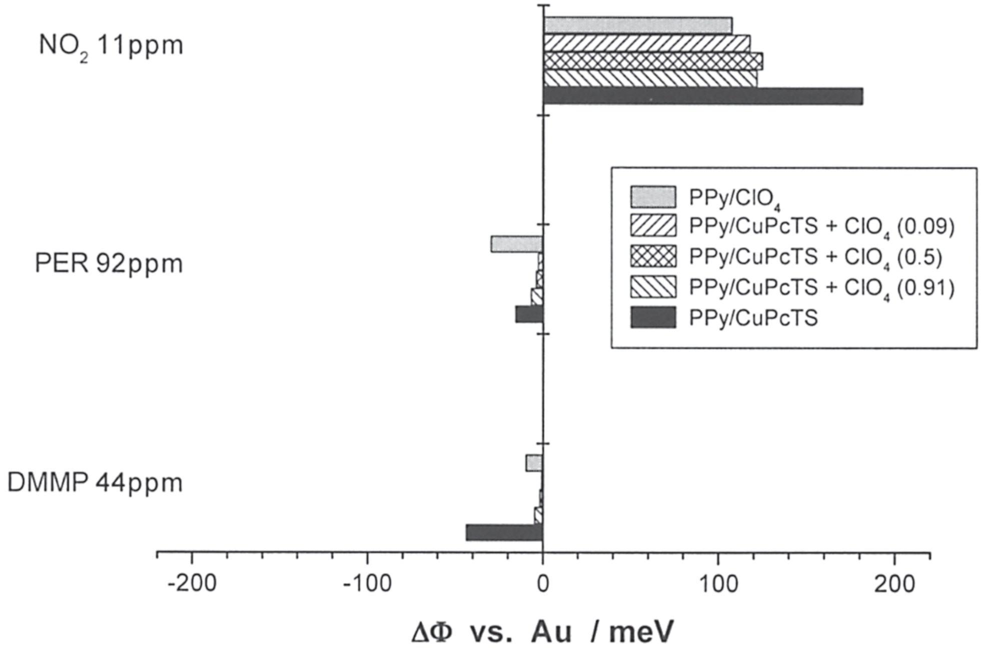


FIGURE 5. Work function changes, $\Delta\Phi$, of PPy doped with ClO_4 ,CuPcTS, and CuPcTS+ClO_4 of different molar ratios (given in the parentheses) upon exposure to various concentrations of NO_2, PER and DMMP as indicated. Ambient air was used as carrier gas.

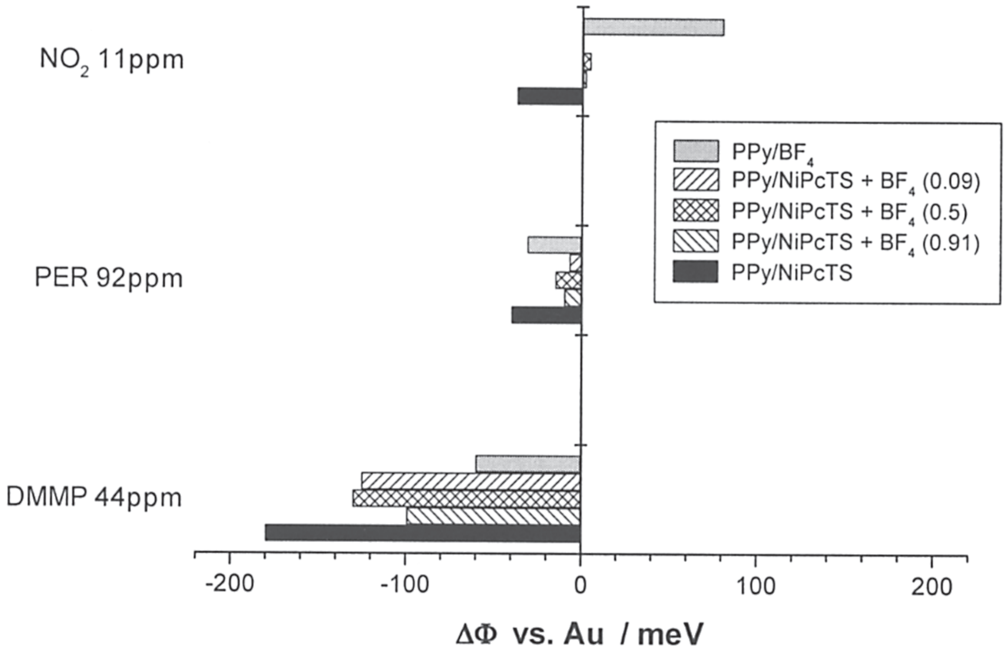


FIGURE 6. Work function changes, $\Delta\Phi$, of PPy doped with BF_4 , NiPcTS, and NiPcTS+BF_4 of different molar ratios (given in the parentheses) upon exposure to various concentrations of NO_2, PER and DMMP as indicated. Ambient air was used as carrier gas.

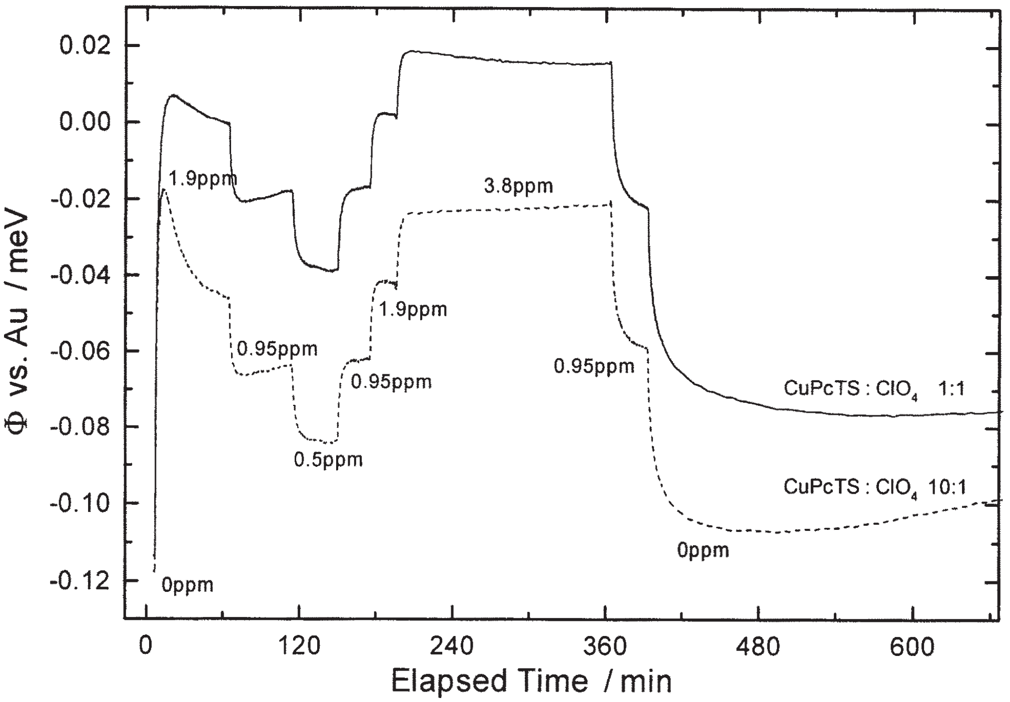


FIGURE 7. Transient responses of PPy layers doped with CuPcTS+ClO_4 of different molar ratios to various concentrations of NO_2 measured with the Kelvin probe. Ambient air of 38 to 42% r.h. was used as carrier gas.

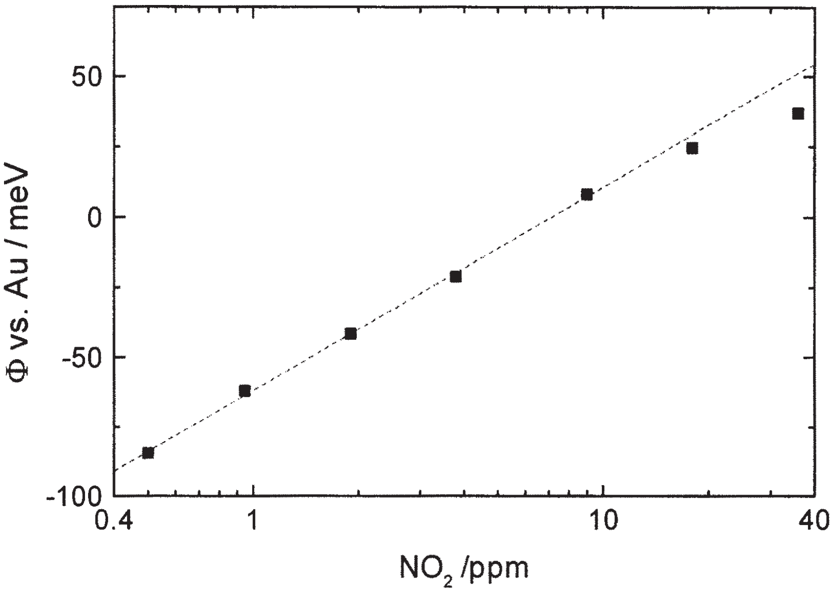


FIGURE 8. Dependence of work function, Φ, of PPy/CuPcTs+ClO_4 layer on the concentration of NO_2 measured with Kelvin Probe. The carrier gas was ambient air.

of the gas molecules into the bulk of the polymer. The additional incorporation of the non-planar anion ClO_4 probably disturbs the parallel orientation of CuPcTS in the polymer and simultaneously decreases the density. Similar behavior can be obtained for PPy layers doped with NiPcTS+BF_4. The $t_{90\%}$ value of the signal decreases from 100 min for PPy/NiPcTS to 3 to 5 min for PPy/NiPcTS+BF_4, owing to the large size of the DMMP molecule, the diffusion coefficient is lower than that for NO_2.

B. Chemical Sensing Behavior of PPy Composites

Recently Aguilar et al. published a new approach to increase the porosity and manipulate the sensing properties of the chemically sensitive PPy films.[22] It is based on the incorporation of an inert polymer matrix into PPy by an *in situ* electrochemical polymerization process. They used polyoxyphenylene (POP) as matrix to form a PPy composite and investigated the chemical sensing properties, that is, the transient response toward DMMP and NO_2. The sensitivities of the PPy-POP copolymer films are -79 mV (ppm decade)$^{-1}$ and 23 mV (ppm decade)$^{-1}$ for DMMP and NO_2, respectively, which indicate a better sensitivity for DMMP than for NO_2 in about a factor of three. The work function changes agree with the relative resistance changes, which are lower for the NO_2 interaction than for the DMMP interaction.[41] Figure 9 shows the $t_{90\,\%}$, values and the sensitivities toward DMMP obtained for PPy and PPy-POP films doped with 4-hydroxybenzene sulfonate (4HBS) and MPcTS. An improvement in the time constant can be achieved by using the POP as an insulating polymer matrix for PPy. It decreases from a maximum value of 101 min (PPy/CuPcTS) to approximately 4 to 7 min for all PPy-POP copolymer films. The main reason for this faster response may be due to the disturbance of the parallel orientation of the large and planar dopants in the polymer layer, which causes a decrease in density from 1.4 to 1.5 g cm^{-3} (PPy) to 1.27 g cm^{-3} (PPy-POP), leading to faster diffusion of the vapor molecules into and out of the bulk of the polymer film.

The sensitivities of the PPy/MPcTS+POP films (aside from PPy/Fe(II)PcTS+POP) to DMMP lie in the range 66 to 76 mV (ppm decade)$^{-1}$, which corresponds to a decrease of 22 to 40% compared with the respective commonly prepared PPy films. Nevertheless, these values are still high enough for sensing purposes. Fe(II)PcTS-doped PPy provides the lowest sensitivity to DMMP and the largest decrease in work function signal after the incorporation of POP, which may be due to the stronger inactivation of the central metal ion located in the macrocycle ring by the inert polymer matrix. However, PPy/Fe(II)PcTS+POP shows the fastest work function change after exposure to DMMP with a time constant of 3 min.

IV. CHEMICAL SENSORS MODIFIED WITH DOPED PPY

In terms of electronic devices conjugated polymers have been studied most extensively in the form of unipolar structures. Typical examples of unipolar devices are heterojunction and Schottky diodes, MIS diodes, as well as MIS field effect transistors, all of which have been demonstrated with conjugated polymer semiconductors. Good device characteristics have been obtained for both diodes and MISFETs, but these devices cannot compete with inorganic semiconductor devices if high speed operation is required because the carrier mobilities that are found are very low, of the order of 10^{-4} to 10^{-6} cm^2 V^{-1}s^{-1}.[42]

Nevertheless, MIS field effect transistors, Schottky, and heterojunction diodes can be used as chemical sensors, in which the conducting polymer acts as both the active semiconductor and the chemical-sensitive transducer element of the sensor structure.[2-6]

A. Polymer Oxide Silicon Field-Effect Transistor

A large number of gas sensors based on field-effect devices were developed in the last few years.[43-48] For the devices chemical-sensitive organic layers can been used either as gate[49-51] or as bulk material.[52,53] With both types good results

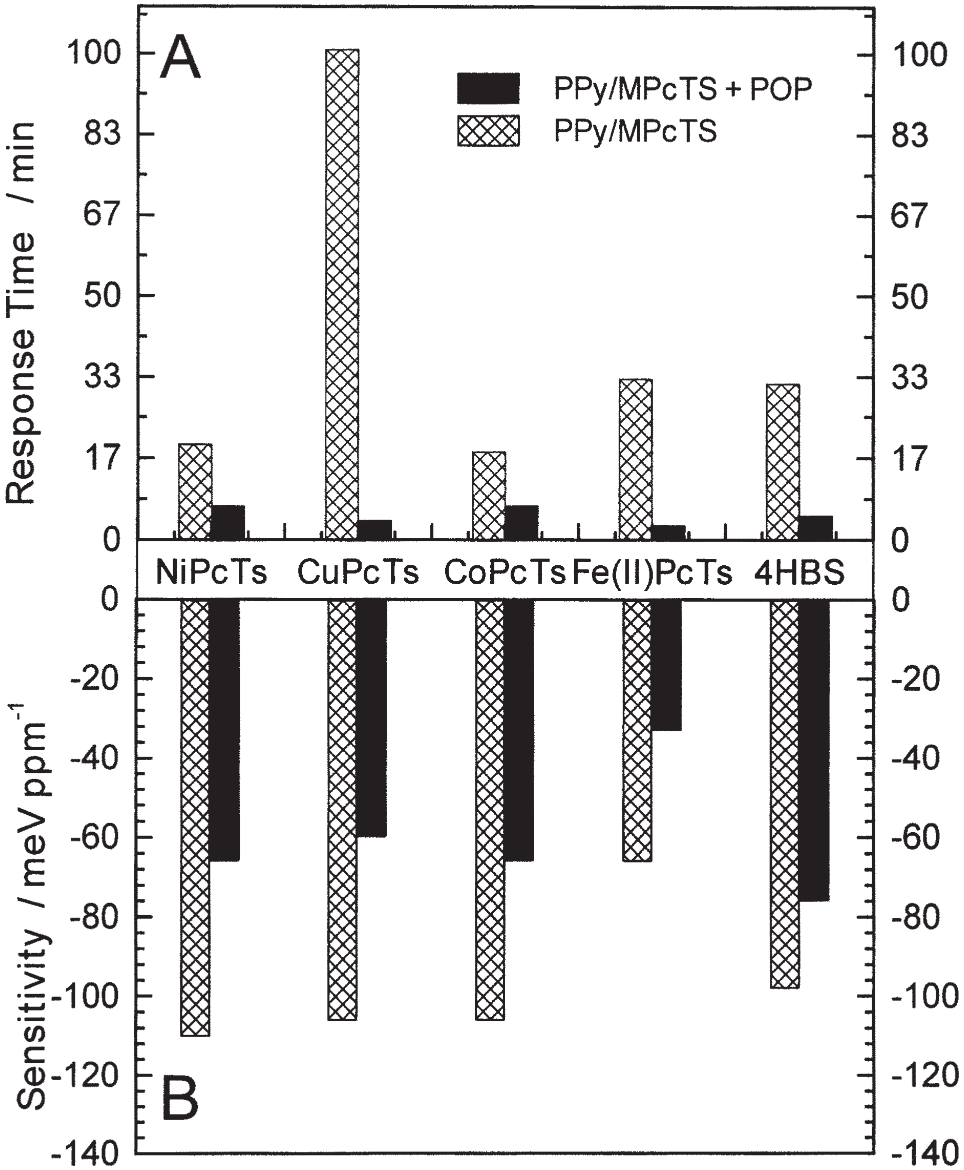


FIGURE 9. Comparison of (A) time constants, $t_{90\%}$, and (B) sensitivities toward DMMP obtained for PPy and PPy-POP films doped with 4HBS and McPcTS (M = Ni^{+2}, Cu^{+2}, Co^{+2}, Fe^{+2}).

have been achieved for the detection of reducing and oxidizing gases. The sensor signal is dependent on the change of the work function of the sensitive layer.

The polymer oxide silicon field-effect transistor (POSFET) is a modification of the classic MOSFET (metal oxide silicon FET), where the metal gate is replaced by a chemical sensitive semiconducting polymer layer (e.g., PPy) to achieve a sensitivity toward gases and vapors. The structure of a POSFET is shown in Figure 10. An electropolymeriztion process can be used for the deposition of the PPy gate, which allows the variation of the sensing properties in a wide range.[21] Due to the direct contact between polymer and insulator the number of surface effects at this interface decreases, resulting in a higher stability and lower noise of the sensor.

A change of the work function of the sensitive polymer by a chemical modulation of its work function during gas or vapor interaction will influence the current-voltage characteristic of the POSFET and is directly reflected in the change of the threshold voltage in same order and direction.

Figure 11 shows the response of PPy/CuPcTS+ClO_4 gate to various concentrations of NO_2 in ambient air measured at room temperature. The POSFET shows a signal shift of 100 mV for 18 ppm NO_2. NO_2 acts as an electron acceptor, leading to an increase of the work function of the gate polymer. The plot displays the response over a period of about 18 h with a slightly change in the ambient temperature leading to a small baseline drift of the signal.

B. Polymer Bipolar Devices

The rectifying behavior of polymer Schottky diodes and heterodiodes relates directly to the Fermi level of the polymer layer and can be influenced not only by the structure, the dopant type, and the doping level,[21] but also by interaction of the polymer with gases or vapors. By exposing the polymers to certain gaseous species exhibiting electron donor or acceptor behavior, the Fermi level position is changed[54-56] by either lowering or enhancing the doping level. In this case, a gas-induced change in the current-voltage characteristics can be observed, which can be exploited for gas-sensing measurements.

1. Heterojunction Diode comprising p-Doped PPy as Sensitive Layer

The deposition of the organic semiconductor can be carried out either by chemical and electrochemical polymerization or by spin coating, depending on the properties of the polymer layer. Polypyrrole can be grown on n-type semiconductors by a photoassisted electroxidation.[4] A recti-

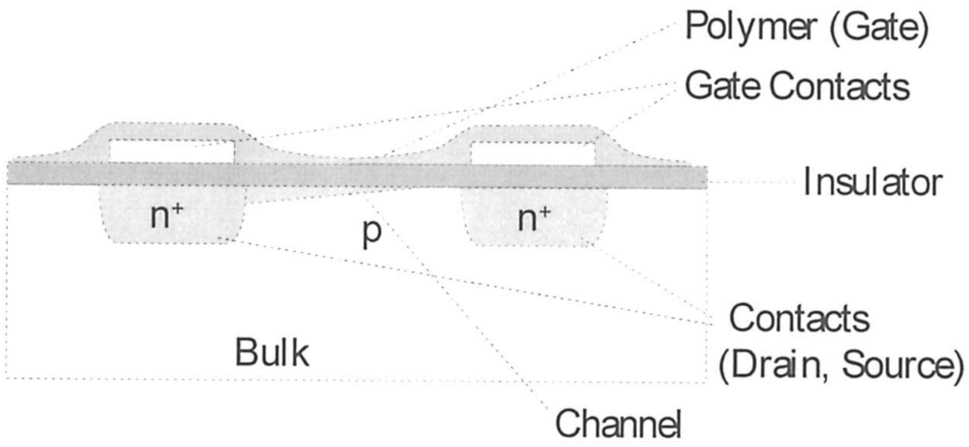


FIGURE 10. Schematic diagram of a POSFET. The chemical sensitive layer is a conducting polymer.

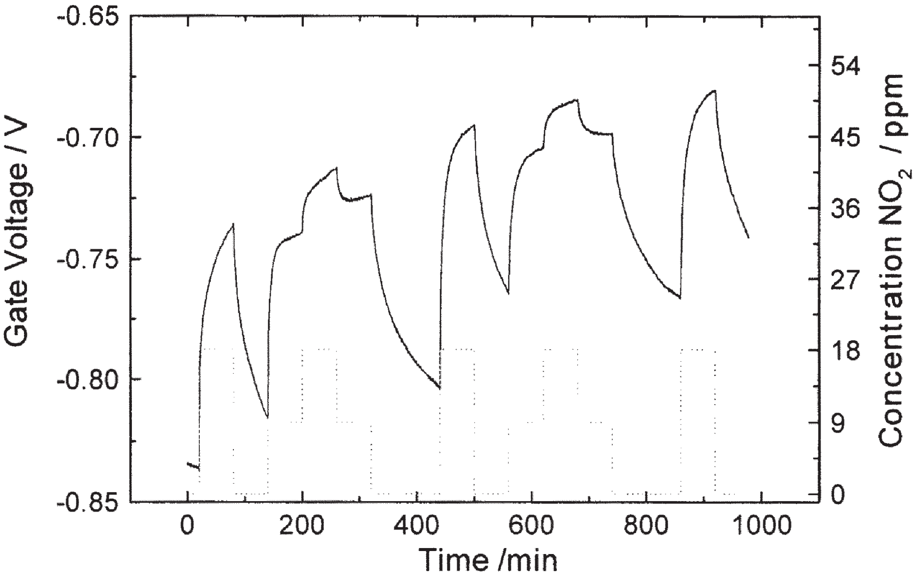


FIGURE 11. Transient response of a POSFET modified with a PPy/CuPcTS + ClO_4 gate toward various concentrations of NO_2 according to the profile shown at the bottom. The carrier gas was ambient air.

fying semiconductor/electrolyte contact is formed between n-type silicon and an electrolyte containing pyrrole. Minority charge carriers (holes) for polymerizing pyrrole monomer onto the n-type Si substrate can be created by illumination. Light-induced electron-hole pairs are dissociated by the depletion layer field, and the holes are consumed during polymerization of PPy.

A typical dark-current density vs. applied voltage (*J*-*V*) curve of a PPy-Si sandwich structure measured at room temperature is shown in Figure 12. In general, the *J*-*V* characteristics of the PPy-Si heterojunction contact is asymetrical and show a nonohmic or rectifying behavior. When applying positive bias to the PPy film, the diode is forward biased.

The rectifying behavior of the bipolar device is controlled by the space charge region located on both sides of the heterojunction. The potential drop over this junction, which is generally called barrier height, is dependent on the work function difference of the materials used and their charge carrier density, *N*. Therefore, during gas or vapor interaction any change in *N* leads to shift in the work function and the barrier height. The forward biased current decreases with increasing carrier density.

In the case of the PPy-Si heterojunction diode, the charge carrier density of PPy is of about five orders of magnitude larger than that of Si. The width of the space charge region is dependent on $1/\sqrt{N}$. Therefore, the potential drop or the partial barrier height located on the side of PPy is very small compared with to that on the Si side. Thus, any change in the barrier height is reflected only in a very small change of the diode current in forward bias, and the influence of the conductivity change in the bulk of PPy is strongly enhanced. The bulk resistance or series resistance is dominant relative to depletion or space charge region resistance, and the forward current increases with increasing carrier density due to change in conductivity of PPy.

These compensatory effects of the gas/polymer interaction on the diode characteristics can be realized by the incorporation of different type of dopants. PPy/TOS comprises a high charge carrier concentration and the respective junction diode shows an almost ideal diode characteristics (Figure 13 left).

The interaction with NO_2 causes a decrease of the forward current or a negative voltage shift at constant current (Figure 13 right). The sensor response is bulk resistance controlled. The charge carrier density of PPy/CuPcTS is of two orders of magnitude lower than that of PPy/TOS. In this case, the sensor response is junction controlled and shows a positive voltage shift (Figure 14).

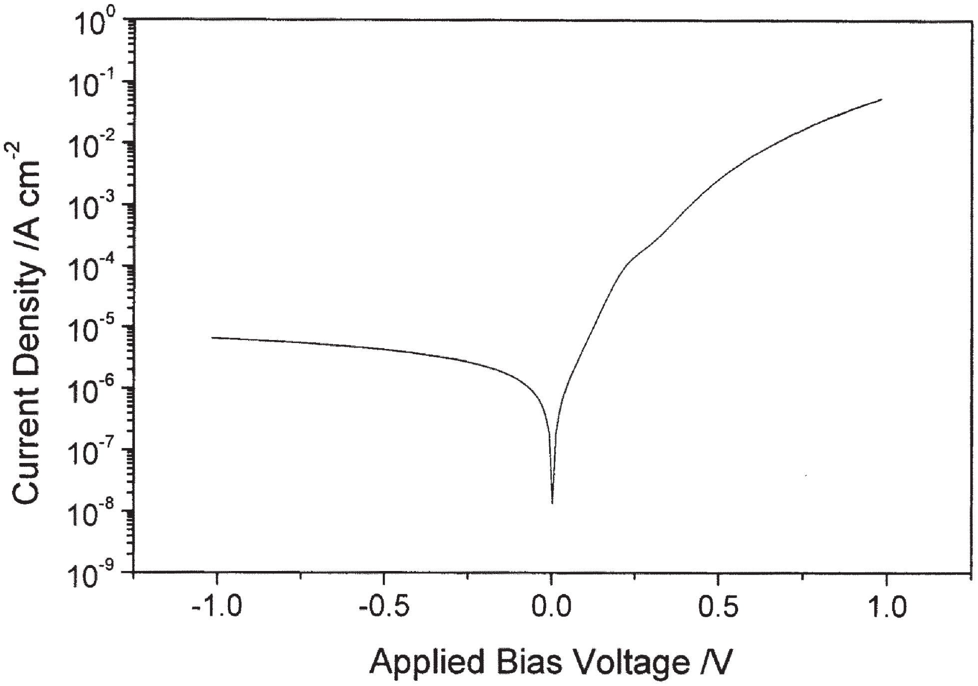


FIGURE 12. *J-V* characteristics of a n-Si-PPy/TOS heterojunction diode measured in ambient air.

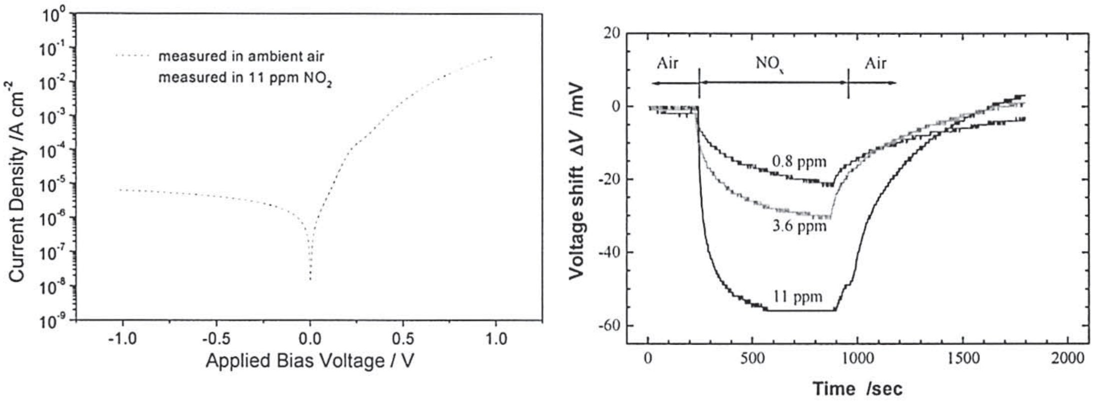


FIGURE 13. (left) *J-V* characteristics of PPy/TOS-Si heterojunction diodes and (right) transient characteristics of the gas-induced voltage shift at a constant current of 9×10^{-3} A cm^{-3} after exposure to NO$_2$.

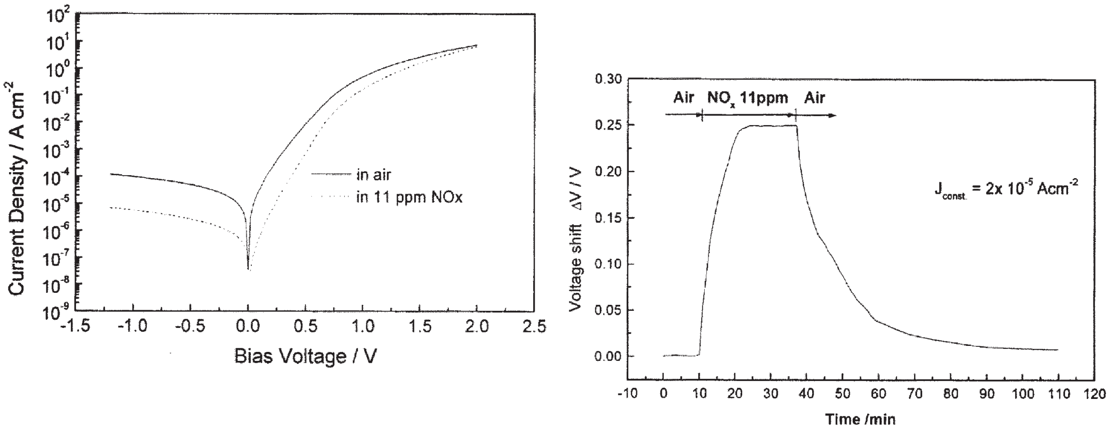


FIGURE 14. (left) *J-V* characteristics of PPy/CuPcTS-Si heterojunction diodes and (right) transient characteristics of the gas-induced voltage shift at a constant current of 2×10^{-5} A cm^{-3} after exposure to NO$_2$.

2. Schottky Barrier Diode Comprising p-Doped PPy as Sensitive Layer

One approach to increase the influence of the gas-induced work function shift on the junction-controlled or junction resistance-limited sensor response can be achieved by the replacement of n-doped Si by a metal. The junction between a low work function metal and a high work function semiconductor is called Schottky barrier.[20] The depletion or space charge region is now completely located on the semiconductor side.

The rectifying behavior of the polymer Schottky diodes is directly related to the Fermi level of the polymer layer, which, for example, in case of PPy, can be influenced by the structure, the dopant type, the doping level,[21] and by interaction of the polymer with gases or vapors. Furthermore, the increase or decrease in the ideality factor during gas-polymer interactions, which is due to a generation or reduction of the interface state density, can influence the gas sensitivity of the junction as well.[2,3,6] Nevertheless, the current voltage characteristics are controlled by both the barrier height in the low forward bias region and the bulk conductivity of PPy in the high forward bias region.

The Schottky barrier diode structure allows to study the influence of the dopant on the diode characteristics. The Schottly barrier characteristics is dependent on the built-in voltage of the junction, which is the difference in work function of PPy and gold. Capacitance-voltage (*C-V)* measurements show that PPy/CuPcTS exhibits the highest charge carrier density of all layers studied and hence the most positive work function. Hence, PPy/CuPcTS leads to the highest built-in voltage of all polymer diode studied (Figure 15A). Furthermore, it has already discussed that the interaction of PPy/CuPcTS with NO$_2$ causes the highest change in work function (see Figure 4), which is related to the highest change in the charge carrier concentration as *C-V* measurements have shown (Figure 15B). Both effects are enhancing the sensor signal of the Schottky barrier diode when compared with work function measurements using Kelvin Probe or POSFET. The Schottky barrier diode shows a NO$_2$-induced junction voltage shift of 260 mV (Figure 15C), whereas a work function of 182 mV is obtained when a POSFET comprising a PPy/CuPcTS layer was used for the same measurement.

The charge carrier concentration of the PPy layer decreases from PbPcTS to TOS as dopants. The junction between PPy/TOS and Au shows a very low rectifying ratio due to the low built-in voltage and is practically quasi-ohmic. When the difference between the work function of metal and the Fermi level of the polymer layer is small, a low contact potential accompanied with a thin depletion layer is expected to form at the junction. In this case the bulk resistance of polymer cannot be neglected even in the low bias voltage range. The bias voltage range, in which the current density is exponentially dependent on applied voltage, becomes smaller when the contact potential decreases. The tendency of the NO$_2$-induced junction voltage shift to decrease when the built-in voltage of the

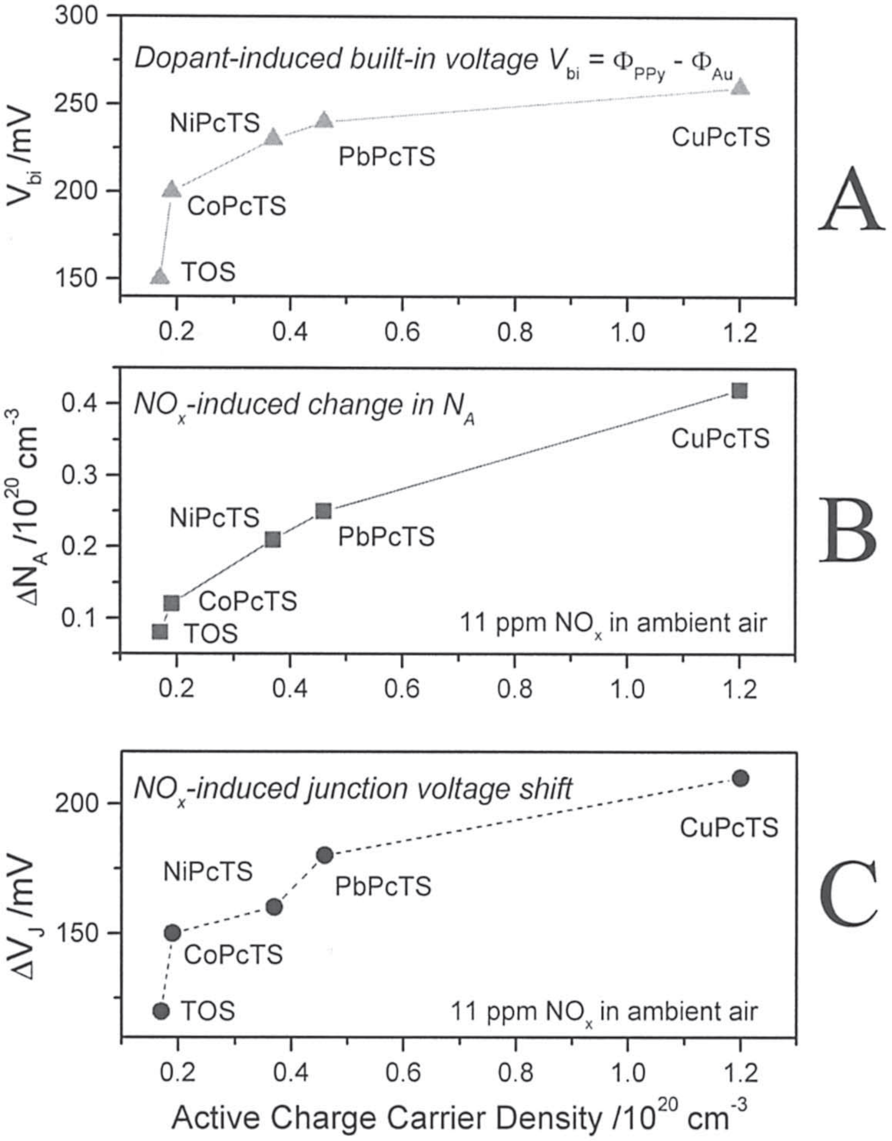


FIGURE 15. A–C: Dependence of electrical parameters and the sensor signal of PPy-CuPcTs/Au Schottky barrier diodes on the nature of the dopants.

diode decreases can be explained in terms of the enhancement of the compensatory effect in the PPy bulk. This can be seen in Figure 15 along the series PbPcTS, NiPcTS, CoPcTS, and TOS.

The PPy/Au diodes prepared at room temperature (22°C) show low rectification ratios.[2] This may be due to a very thin barrier formed at PPy/Au junctions and an effect of the tunnelling current.[2,57] Due to the acceptor concentration of the order of 10^{19} cm^{-3} and assuming the depletion width to scale as the square root of the acceptor density,[20] a depletion width of about 1 to 10 nm is expected for these devices. An increase in the depletion width may be reached either by increasing the built-in potential or by decreasing the charge carrier concentration. It was found that the charge carrier concentration calculated from $1/C^2$ vs. V curves is far different from that estimated from the doping level obtained from EQCM measurements (~10^{21}, assuming that all dopant charges give rise to one hole polaron, or half a bipolaron[58]). This may be due to the existence of a large concentration of defects in amorphous semiconductor materials.

PPy has an amorphous structure with a certain degree of crystallinity in between 5 to 10% depending on the structure of the dopant. Therefore, a large amount of structural defects exists caused, for example, by branching or overoxidation, introduced during the preparation of the polymer. The concentration of structural defects increases with increasing preparation temperature, because the polymerization rate rises up simultaneously. Due to these structural defects, the majority (about 80 to 90%) of the self-localized electronic defects (polarons or bipolarons) are trapped in that way, that they cannot contribute anymore to the current transport through the polymer layer. Therefore, the concentration of the active charge carriers is dependent on the preparation temperature and decreases with increasing preparation temperature (Figure 16A). Simultaneously, the size of the space charge region increases and therefore the junction resistance is enhanced with respect to the bulk resistance. Hence, the NO_2-induced voltage shift increases for the same concentration (Figure 16D) enhancing the sensitivity of the Schottky barrier diode.

Furthermore, with increasing temperature the crystallinity decreases and is zero when reaching the glass transition temperature (which is between 42 or 55°C for PPy/CuPcTS). The gas or vapor can only be absorbed by the amorphous part of the polymer, which increases with the preparation temperature. Hence, NO_2 interacts stronger with layers prepared at higher temperatures leading to a higher relative change in the active charge carrier concentration (Figure 16B) and a higher change in built-in voltage for the same NO_2 concentration (Figure 16C). Both effects cause a further increase of the gas-induced junction voltage shift with the preparation temperature.

The diffusion of the gas or vapor in conducting polymers and their adsorption on polymer surfaces are the fundamental processes that control the chemical sensing response. It is supposed that diffusion processes at the crystalline polymer phase are much slower compared with that at the amorphous phase.[59] Hence, the polymerization temperature is an important parameter influencing the diffusion processes of polymeric sensor transducers. Figure 17 shows the response curves of diodes with PPy films exposed to 11 ppm NO_2. The PPy layers were electrochemically prepared at different temperatures.

The diode based on the PPy film prepared at 50°C exhibits the response time and the recovery time being much faster than that of diodes based on PPy films prepared at 10 and 30°C. The decrease in response and recovery time can be explained by an increase in the amount of the amorphous phase compared with that of the crystalline phase in PPy when the preparation temperature increases.

V. SUMMARY

The nature of the anion used as dopant for PPy exhibits the major influence on the sensing properties of PPy. The various anions are responsible for the subtle differences in the electronic structure of particular PPy samples. Their electronic structure, or, in other words, the content of polarons and bipolarons, is responsible for the quality of the interactions between the polymer and the species of interest. The use of MPcTS as a dopant for PPy preparation enhances the stability of PPy compared with PPy doped with small anions and makes PPy practically insensitive to ambient air. The central metal ion in MPcTS plays an important role in the sensing properties of PPy, but this effect is not yet understood.

Cross-sensitivities can be effectively suppressed or modified by competitive doping with a suitable complementary anion. The most sensitive layer for DMMP detection was found to be PPy/NiPcTS, whereas PPy/CuPcTS shows the highest sensitivity to NO_2. With increasing content of small anions in mixtures with MPcTS, the response time of PPy samples decreases from hours to minutes. Competitive doping of PPy with a mixture of small anions and MPcTS slightly decreases the sensitivity but enhances the selectivity of the measurements.

The introduction of POP as inert matrix offers a general approach to reduce the packing density or to increase the porosity of the conducting polymer PPy in a definite way. Referring to the sensitivity and response time as measured by the Kelvin probe technique, an improved transient behavior was achieved due to the electro-

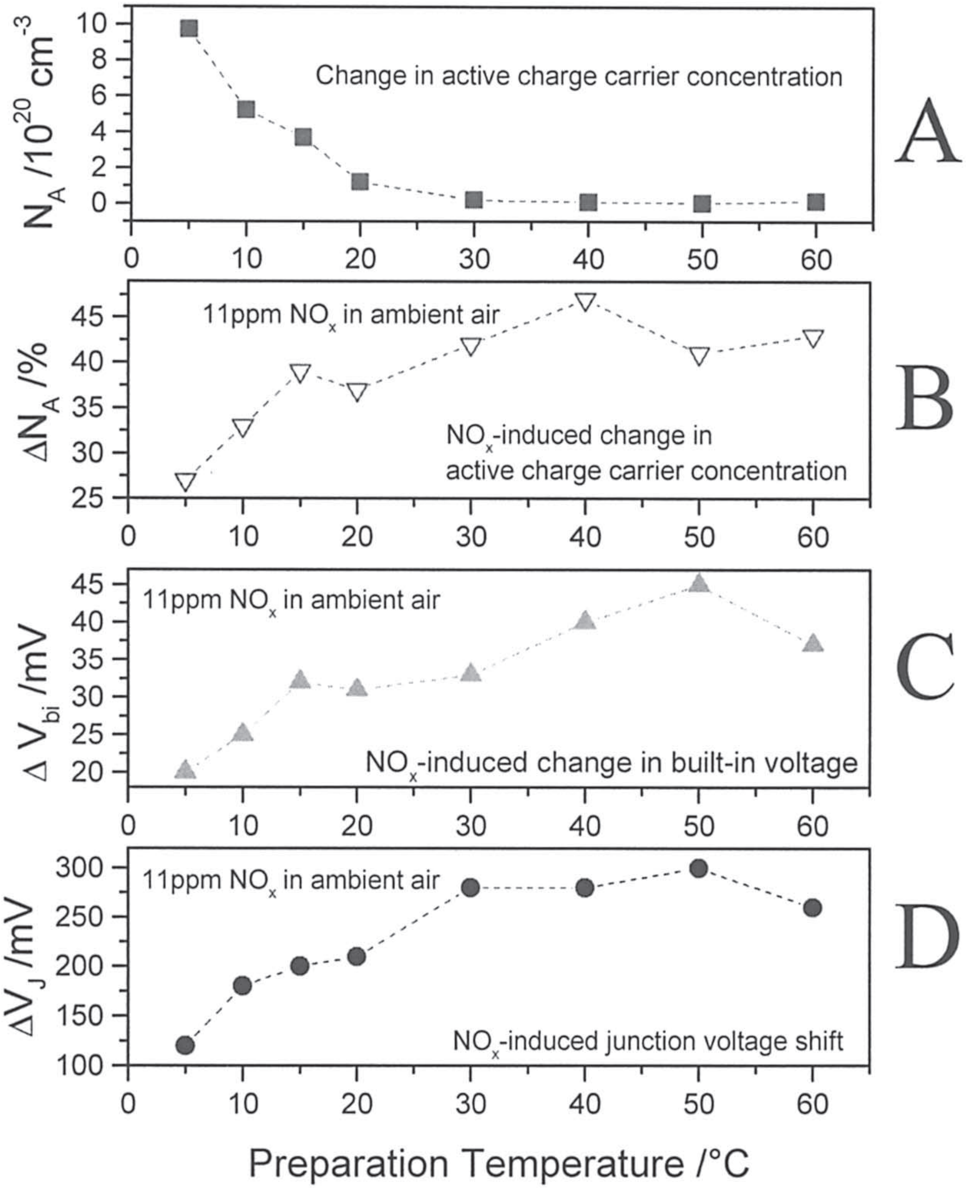


FIGURE 16. A–D: Dependence of electrical parameters and the sensor signal of PPy-CuPcTs/Au Schottky barrier diodes on the preparation temperature.

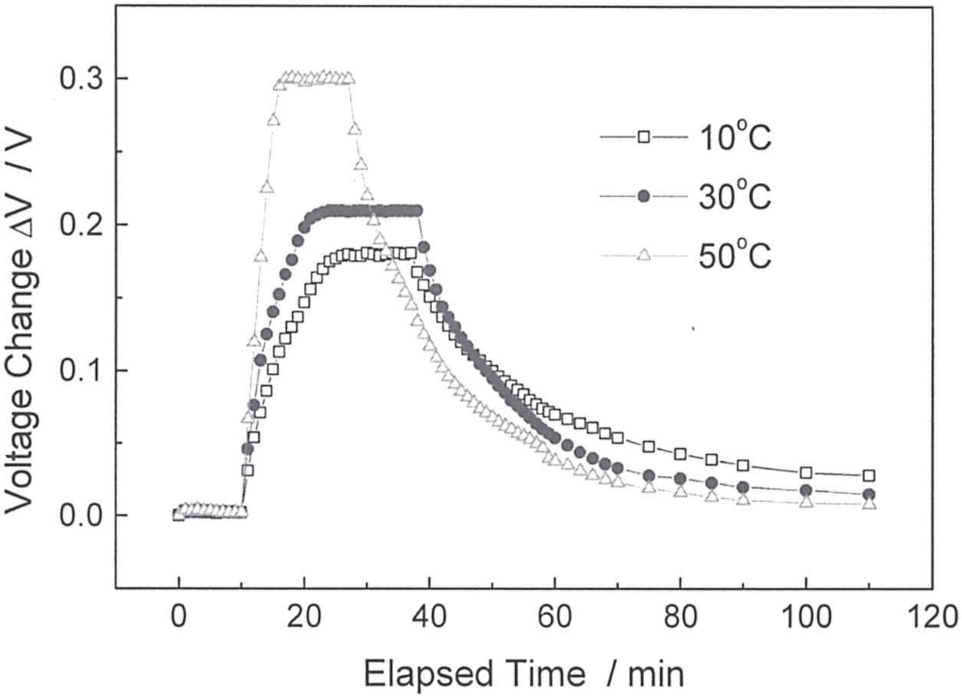


FIGURE 17. Transient response of Schottky barrier diodes comprising PPy-CuPcTS layers electrochemically prepared at different temperature, exposed to 11 ppm NO_2. The carrier gas was ambient air.

chemical incorporation of POP and the simultaneous decrease in density when compared with commonly doped PPy layers. Time response is reduced up to more than 70%.

For their potential application in electronic devices, PPy has been studied most extensively in the form of unipolar structures. Typical examples of unipolar devices are heterojunction and Schottky diodes and MIS field effect transistors.

Field-effect transistors comprising a doped PPy instead of a metal as the gate material show sensitivity toward a specific components (e.g., NO_2 or DMMP). Thus, it is possible to combine the stability of an integrated, silicon-based device with the variability of an organic layer. Due to the electrochemical deposition of the polymer directly on top of the gate insulator, the contact between the sensitive layer and the oxide is ensured. The noise level of the sensor is reduced.

In Schottky barrier and heterojunction diodes the conducting polymer PPy acts as both the active semiconductor and the chemical sensitive transducer element of the sensor structure. It has been shown that the sensitivity of the sensor device can be strongly influenced by nature of the dopant anion, doping level, and the preparation temperature of the PPy layer.

In summary, PPy is a new type of organic material exhibiting interesting properties, for example, low density, mechanical flexibility, semiconductivity, environmental stability, and solution processablity that offer enormous potential for applications within the field of microsensors. The macromolecular character and the high degree of flexibility in the preparation make various physical and chemical properties realizable. Individual modification of each sensor is possible in only one step. This allows for the inexpensive fabrication of small series of specific sensors. Additionally, the sensitivity and selectivity can be varied over a wide range by changing the anions, which are used as dopants. The use of thin layers decreases the response time and is associated with a higher sensitivity. Additional benefits are the low device prices, due to the use of standard processes for integrated circuits, the small dimensions, and low power consumption.

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