ZnO-doped PFPAMA: a novel transparent conducting polymer for fast photodiodes

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ABSTRACT

In this article, a new Schottky diode based on a transparent conducting polymer 2-(4-fluorophenyl)-2-oxoethyl-2-methylprop-2-enoate (PFPAMA) that is doped up to 5% with ZnO is presented. PFPAMA is a promising transparent polymer that is inclined towards n-type behavior with the potential to be used as an electron transport layer. Each device had the Al/p-Si:(PFPAMA:ZnO)/Al structure. The diode ideality factor was found to depend on bias and illumination but the calculated interface state density is lower by 3 orders of magnitude than for most reported Al/p-Si diodes, suggesting that the presence of the polymer suppresses interface states. The measured electrical and photoresponse characteristics confirm that the resulting diodes are suitable for fast photodiodes over the intensity range of dark to 100 mW/cm² whose performance can be optimized by ZnO doping. The application of functionalized polymers on p-silicon for sensing applications is an emerging field.

1 Introduction

Electronic conduction in some polymers is intermediate between hopping and energy band-type transport. Although conjugated electrically conducting polymers (ECPs) are today more widely studied, conjugation is not requisite for conduction [1–3]. Certain important issues remain in the study of ECPs. For a start, the exact mechanisms of redox and anionic/cationic doping, while assuring transparency for optical applications [3], are not yet fully understood. Also, polymer doping to n-type is considerably harder to achieve than to p-type [4]. In the last few years, polymers have been shown to have the
potential to be host frameworks that better disperse dopants and improve the mechanical and electrical attributes of the final device [5–8]. The questions of environmental safety, thermal and electrochemical stability, ease of processing, continue to be just as important for industrial application [9–12]. Much research is being carried out in the search for suitable deposition precursors and methods for functional materials that pose challenges due to their peculiar chemical properties such as geometry, reactivity and solubility, etc. [7, 13–22]. There is growing interest in special-group functionalized polymers, which ample literature evidence suggests are strong candidates for opto-electronics applications [23–26]. It is thought that the added group encourages electron-donor exchange of photogenerated carriers by virtue of the polarons that arise from the unique molecular charge states of the group [27–29]. The design thinking behind n-type conducting polymers, which is also followed in this article, is to functionalize them with an electron-donating comonomer that withdraws electrons, such as by introducing fluorine or nitrogen atoms into the polymer backbone. This improves electron injection by deepening the lowest-unoccupied molecular orbital (LUMO), reduces the π–π stacking in conjugated polymers. This improves device planarity and device stability in air. However, the persistent challenge in determining the charge transport properties of organic semiconductors (OSCs) arises since OSCs deviate from idealized theoretical models that were developed for highly ordered lattices [30–32]. OSCs have substantially different architecture and operating conditions such as bias, the presence of other charged components and densities [33, 34]. At present, there are no direct measurements that indicate whether PFPAMA is n- or p-type, apart from the expectation that it is n-due to its fluoroarylketone functionalization. However, C–V measurements at 0% ZnO doping show that Al/p-Si:(PFPAMA:ZnO)/Al diodes behave like Al/p-Si:ZnO/Al, which are well reported in the literature. n-type materials, such as ZnO [35], produce a specific plots of 1/C²–V plots since they involve donor-type interactions. Furthermore, one notes that doping PFPAMA with ZnO the polymer’s electron-donating ability. However, a definitive answer requires the determination of the highest-occupied and lowest-unoccupied molecular orbitals (HUMO/LUMO) of PFPAMA. In this article, a new solution processed fluoroarylketone functionalized methacrylate polymer, poly-2-(4-fluorophenyl)-2-oxoethyl-2-methylprop-2-enoate (PFPAMA), is investigated both as a host framework, and as a conducting polymer. It is doped up to 5% with ZnO and used in aluminized p-Si Schottky diodes. PFPAMA was recently devised by Erol and Güler [5, 36, 37], who also characterized its properties by scanning electron microscopy, Fourier transform infra-red spectroscopy, thermogravimetric analysis, and X-ray diffraction. The measurements showed that the functional group imparts to PFPAMA superior transparency, tensile strength, mechanical stability, high dielectric strength, and good morphological and structural properties. In this article, we show that PFPAMA has good interface compatibility with silicon, is inclined towards n-type behavior, and potentially passivates the p-Si surface thereby reducing the interface state density. This raises the novel possibility to use PFPAMA as an electron transporting layer to realize fast photodiodes. The passivation of p-Si by macromolecules such as PFPAMA is not widely reported. However, there is some evidence for the effectiveness of surface passivation by azide-group functionalized methacrylate polymers to seek and stabilize deposition surfaces [38–40]. The lowering of the interface state density demonstrates for the first time the passivation of p-Si using a macromolecule. This is a new and highly emergent area, with few comparable studies [41]. Hoex et al. [42] found that p-Si surfaces can be passivated effectively by a negatively charged dielectric such as Al₂O₃ as highly doped n-type surfaces. We suggest that the passivation of the p-Si occurs because PFPAMA presents an n-type dielectric with high surface compatibility at the interface. In a real device, this manifests as a lowered interface state density which, conversely, can be used to indicate the polarity of the polymer. The determined barrier properties, interface states, the electrical, photoelectronic behaviors of the constructed devices under illuminations of 0, 20, 40, 60, 80 and 100 mW/cm² confirm that the resultant devices are fast photodiodes.
2 Experimental

2.1 Synthesis of ZnO nanoparticles

First, zinc acetate (0.25 M) was dissolved in 80 ml of deionized water. Then, 0.25 M NaOH solution in 80 ml of deionized water was prepared. The pH of the zinc acetate solution was adjusted to about 9 with the help of the prepared NaOH solution. Finally, the solution was kept at 150 °C for 24 h. The resulting ZnO powders were filtered on paper and dried in a vacuum oven at 50 °C for 12 h.

2.2 Preparation of PFPAMA/ZnO nanocomposites

Composites containing 1.3% and 5% (w/w) ZnO nanoparticles were produced by the hydrothermal method. The following procedure was followed to obtain a composite containing 1% by weight of ZnO nanoparticles; 1 g of PFPAMA, 10 mg of ZnO, and 15 ml of water were added to a Teflon cup. The mixture was first stirred at room temperature for 15 min with a mechanical mixer. The mixture was then homogenized in a nitrogen atmosphere with an ultrasonic probe for 15 min. Finally, the homogenized mixture was placed in the Teflon container of the hydrothermal synthesis system from Fytronix Scientific Instruments [43]. The hydrothermal process was continued at 150 °C for 24 h. The resulting PFPAMA/ZnO nanocomposites were filtered and dried in a vacuum oven at 70 °C for 12 h. Fig. 1 shows the hydrothermal synthesis of PFPAMA.

The starting resistivity of the p-Si substrate was 10 Ωcm to assure Ohmic contact with Al. The Al electrodes were thermally evaporated onto the devices using a thermal evaporation system. Figure 2 shows the schematic operation of the Al/p-Si:(PFPAMA:ZnO)/Al diodes, without external bias. Incident illumination generates hole-electron pairs in the depletion region. The electrons and holes are swept away by the strong internal field and accumulate on p-Si, and produce a photocurrent in a biased external circuit. The electrical characteristics of the diode were analyzed using the LSS 9000 Solar Simulator [44] and an IV/CV analyzer [45], both sourced from Fytronix Scientific Instruments.

3 Results and discussion

3.1 Current–voltage characteristics

The Schottky junction current $I$ in thermionic emission theory (TE) is given by [46, 47]

$$I = AA^*T^2 \exp\left(\frac{-q\phi}{kT}\right) \exp\left(\frac{qV - IR_s}{nkT}\right) \left[1 - \exp\left(\frac{qV - IR_s}{kT}\right)\right].$$  \(1\)

where $V$ is the applied voltage, $R_s$ is the series resistance, $T$ is the absolute junction temperature, $\phi$ is the effective barrier height, $q$ is electron charge, $k$ is the Boltzmann constant, $A$ is the diode area, $A^*$ is the Richardson constant, and $n$ is the diode ideality factor. A recent work, termed the Ocaya-Yakuphanoglu method (OYM), rigorously proved that $R_s$ is the instantaneous derivative of $(V, I)$ data [48] such that the $R_s$ compensated bias at any measured point is $V_a = (V - IR_s)$, hence the reduced TE equation:

$$I = AA^*T^2 \exp\left(\frac{-q\phi}{kT}\right) \exp\left(\frac{qV_a}{nkT}\right) \left[1 - \exp\left(\frac{qV_a}{kT}\right)\right].$$  \(2\)

On the other hand, the Cheung-Cheung method (CCM) effectively averages $R_s$ and $n$ over a wide bias range using the following functions [49].

$$\frac{dV}{d\ln I} = R_s \left(\frac{nT}{q}\right), \quad H(I) = R_s I + n\Phi_b,$$

where

$$H(I) = \left[V - \left(\frac{nT}{q}\right) \ln\left(\frac{I}{AA^*T^2}\right)\right].$$  \(3\)

Figure 3 shows the I–V characteristics of the fabricated diode with varying ZnO doping. ZnO doping is seen to increase the dark photoconductive current in all cases by a factor of $\sim 10$. In photovoltaic mode, doping at above 1% ZnO increases the forward current by a similar factor. In both regions of bias this can be explained by a reduced $R_s$. Figure 4 shows the graphs of $R_s$ determined using the OYM and CCM using 5% ZnO doping in PFPAMA as an illustration. The straight lines in Fig. 4 are the estimated trends in $R_s$, with each straight line corresponding to an illumination and determined as follows: the CCM Eq. (3) is typically evaluated using straight lines in at least
two separate, narrow-bias regions since applied-bias impacts I–V curve linearity and, therefore, also $R_s$. We identified two ranges, 1.2 to 2.0 V and 2.1 to 4.5 V and hence two sets of $R_s$ and $n$. Each straight line in Fig. 4 was obtained by plotting the $R_s$ values at each bias end point (i.e., 2 V and 4.5 V) and extrapolating with dotted straight lines. The plots show strong agreement between CCM and OYM. However, the OYM employs a much wider-bias range. In this article $A^* = 32 \text{ A/K}^2 \text{ cm}^2$ and 2 mm diode diameter.

Figure 5 shows the effect of the ZnO content of PFPAMA on the forward and reverse characteristics of the diodes. Figure 5a shows that the dark current increases with doping but the forward current is largest for 3% ZnO. Figure 5b shows that the maximum reverse currents are comparable for both 3% and 5% ZnO below −2 V bias. The forward currents are nearly identical under both dark and 100 mW/cm² illumination. This suggests that the devices are not very responsive to illumination in the photovoltaic mode.

Figure 6 summarizes the $R_s$ values determined using the OYM as described above. The figure shows that ZnO doping lowers $R_s$, with the most lowering occurring at 3% ZnO in both forward and reverse bias. In reverse bias $R_s$ is also almost constant with bias for this doping. This suggests that 3% doping of PFPAMA is best for photoconductive applications. In forward bias, doping levels produced similar $R_s$ trends with illumination. The lowest $R_s$ for a given bias is also for 3% doping.

Table 1 lists and compares the calculated $R_s$ using the three different methods. The CCM averages $R_s$ in two regions and, like the C–V method, understates the true values of $R_s$, which may be closer to those of the OYM.

Figures 7 and 8 plot the calculated ideality factor in regions of low- and high-bias using OYM and CCM, respectively. Both methods show that $n$ strongly depends on bias and illumination. The lowest $n$ for 3% ZnO. At low illumination, the apparent trend using the OYM method shows that at low bias $n$ increases with doping from $n \sim 2$, peaks at medium bias with $n \sim 20$, then decreases and settles around $n \sim 10$ at high bias. At high illumination, the low bias value of $n$ is higher but the high bias trends are similar. In contrast, at low bias the CCM method reports higher $n$, between 8 and 15 at lower doping, but similar trends to OYM at high bias are seen.

Figure 9 plots and compares $\Phi$ obtained using three different methods, which give similar results regardless of the % ZnO doping. Figure 10 is a histogram plot of the barrier heights determined by C–V.
with % ZnO doping. There are no prior reports of PFPAMA-based diodes and hence no directly comparable literature data. However, some useful analogies can be drawn between Al/p-Si/ZnO/Al and Al/p-Si:(PFPAMA:ZnO)/Al under 0% ZnO doping. Several researchers have studied sputtered diodes of the former structure and reported an average barrier height and a built-in potential and an average donor density of 0.76 eV, 0.66 V, $10^{15}$ to $10^{16}$ /cm$^3$, respectively [50–52]. Other literature report typically 0.7 eV for p-Si/ZnO-doped Schottky diodes [53, 54]. In Table 2, the closest matches in $\Phi$ and $V_{bi}$ with those of Ocak [50] are from the OYM method. The interface state density of 0% ZnO diodes was calculated from low frequency C–V data to be $1.3 \times 10^9$/(eV cm$^2$). Benhaliliba [51] recently reported it at $3.5 \times 10^{12}$/(eV cm$^2$), while Benhaliliba et al. [52] reported $\sim 10^{12}$/(eV cm$^2$). Thus, the presence of PFPAMA at the interface reduces the interface state density by a factor of $\sim 10^3$. This provides further evidence of interface modification by PFPAMA.

### 3.2 Impedance characteristics

The interface state distributions of the devices were obtained by C–V–f and G–V–f measurements in the space charge region [55–58]. The series resistance is given by [55–57]

$$R_s = \frac{G_m}{G_m^2 + (\omega C_m)^2},$$

(4)
where \( C_m \) and \( G_m \) are the capacitance and conductance measured, respectively, at the angular frequency \( \omega \). Figure 11 shows the C–V–f method determined \( \ln(R_s) \) plots for 100 kHz and 1 MHz. It can be seen that doping beyond 3% ZnO increases the measured \( R_s \). \( R_s \) is seen to strongly depend on frequency, reaching a peak with low bias [59]. This can be attributed to the frequency dependence of the interface charges. Since an AC signal is used in C–V measurements, similar \( R_s \) are seen in both bias regions of the plots. However, \( R_s \) is lower than in both the CCM and OYM methods due to the inability of the interface states to follow the AC signal.

Figure 12 shows that in forward bias, the trends in the calculated \( R_s \) from the C–V–f method and the OYM are in good agreement. However, in reverse bias, the C–V–f method significantly underestimates \( R_s \).

The corrected capacitance \( C_c \) and conductance \( G_c \) are:

\[
C_c = \frac{G_m^2 + (\omega C_m)^2}{a^2 + (\omega C_m)^2} C_m
\] (5)

and

\[
G_c = \frac{G_m^2 + (\omega C_m)^2}{a^2 + (\omega C_m)^2} a,
\] (6)

where \( a = \frac{C_m - (\omega C_m G_m)^2 R_s}{C_m G_m} \).

Figures 13, 14 and 15 show the measured C–V data for various %ZnO doping. The highest junction capacitance is seen at 3% ZnO. The three distinct regions that are expected in metal oxide semiconductor (MOS) capacitors can be seen in each plot. These are accumulation (below –2 V), depletion (–2 V to about –1 V) and inversion (above –1 V). For a continuous interface state distribution the interface state density \( D_{it} \) (a.k.a \( NSS \)) can be estimated from the conductance peak by [56]

\[
D_{it} = \frac{(G/\omega)_{\text{max}}}{0.402 \mu A},
\] (7)

where \( A \) is the effective junction area. At temperature \( T \), the device capacitance (\( C \)) for a device of area \( A \) is related to applied bias (\( V \)) by [47, 55, 56, 60]

\[
\frac{1}{C^2} = \frac{2}{q \varepsilon_0 A^2 N_A} \left( V_{bi} - V - \frac{kT}{q} \right),
\] (8)

where \( \varepsilon_0 \) is the effective permittivity of the dielectric and \( N_A \) is the concentration of the nonionized acceptors in p-Si. Figure 16 plots both \( D_{it} \) and \( N_A \) calculated in the depletion region using Eqs. (7) and (8), respectively. Clearly, the \( D_{it} \) has a strong frequency dependence such that at high frequencies the interface states cannot adequately follow the AC signal.
signal and are, therefore, under-reported by the measurement. However, these values of $D_{it}$ are much lower than those typically reported for Al/p-Si diodes [57, 61–64]. This suggests that the Al/p-Si:(PFPAMA:ZnO)/Al diodes have fewer interface states. Apart from the interactions of the fluoroarylketone functional group with the interface states, another possible reason could be the interaction of the oxygen species with PFPAMA at the interface such as way to that reduces the impact of the interface states. A more detailed analysis is clearly needed in the scope of future work. Figure 16 shows that the interface states are fewest at 3% ZnO by some optimal interaction between ZnO and PFPAMA that limits the interface states in p-Si. Table 2 summarizes the results of the various

![Image of Figure 6](image)

**Table 1** Summary of $R_s$ (kΩ) calculated at dark and 100 mW/cm² using the three different methods in the text. The C–V measurements were under dark conditions.

| Method   | 0% ZnO | 1% ZnO | 3% ZnO | 5% ZnO |
|----------|--------|--------|--------|--------|
| OYM      |        |        |        |        |
|          | 11.64  | 17.85  | 6.58   | 4.02   |
| CCM      |        |        |        |        |
| H(I)     | 5.14   | 4.39   | 6.33   | 3.39   |
| H(I)     | 1.76   | 3.40   | 0.55   | 0.73   |
| dV/dln(I) | 5.14 | 4.74   | 5.17   | 2.76   |
| C–V (100 kHz) | 0.36 | –      | 5.15   | –      |

*The bias range is 0.5 V to 5.0 V

*Region A is the 1.2 V to 3.0 V bias range

*Region B is the 3.1 V to 3.8 V bias range
parameters and the methods used. The values of \( N_A \) correspond to a 300 K p-Si resistivity of 10.2 \( \Omega \) cm, which is in agreement with the starting substrate stated above.

The barrier height is given by

\[
\Phi = V_{bh} + V_{th} \left(1 + \frac{N_v}{N_A}\right),
\]

where \( N_v \approx 1.04 \times 10^{19} / \text{cm}^3 \) is the valence band hole density of states [65, 66].

### 3.3 Photoconductive sensing

Figure 17 plots the diode photo current at \(-2.0 \text{ V}\) for PFPAMA:ZnO. The plots follow the reported power law [57]:

\[
I_{ph} = aP^\gamma.
\]

Table 2 includes the calculated \( \gamma \), which indicates the dominant recombination mechanism in the diode [67, 68]. It is evident from Table 2 and Figs. 3, 6, 9, 10 and 17 that 1\% ZnO doping produced significantly
different I–V, C–V, and photoresponses such that comparable plots used for other doping levels could not be performed for 1% ZnO. For example, the dark current (see Fig. 3), for instance, is seen to fluctuate widely with reverse bias, and there is no consistent change in the photocurrent with illumination. For 3%...
ZnO, $0.5 < \gamma < 1$, indicating that the recombination mechanism is mostly monomolecular. For an exponential distribution of trap states which form the main recombination centers, $0.5 < \gamma < 1$. We see 'supralinearity' i.e., $\gamma > 1$ in 5% ZnO. This is due to the improvement in the population of recombination centers.
centers, which increases bimolecular recombination [67, 69, 70]. Evidently, the extent of ZnO doping impacts the recombination mechanism in the device, in support of the hypothesis of Rose [67]. In general, despite the higher light sensitivity with $c_1$, the interest may be to attain a predictable and wider-bias photoconductive response [48] to attain a continuous trap states distribution by careful doping, as with 3% ZnO.

### 3.4 Transient photoresponse

Photocapacitance and photoconductance responses are crucial parameters that highlight the suitability of a photodiode for high-speed sensing applications. A slow transient response points to the trapping of photogenerated carriers in deep sites, which gives an undesirable high capacitance. Figure 18 shows the responses to on/off illumination of 100 mW/cm$^2$ at 10 kHz, and 50% duty cycle. The device exhibits low photocapacitance and high photoconductance, implying fast recovery between dark/light conditions [71]. The ZnO doping therefore gives PFPAMA:ZnO photodiodes the potential for high-speed applications.

Figure 19 shows the transient current behavior of the fabricated diodes. It can be seen that the undoped
The diode has the best photo-current under these conditions. However, 3% ZnO doping achieves the best overall performance, many parameters considered i.e., photoconductive current linearity, $R_s$ and $D_{it}$ values.

It still remains to investigate the mechanism by which $D_{it}$ is reduced by doping PFPAMA with ZnO. The interplay between defect states and free charge carriers is not yet fully understood in the devices based on emergent technologies [72]. Carrier mobilities in conductive polymers, which are dielectric semiconductors, are also typically much lower than in ordered lattice semiconductors and cannot be measured using the same time-of-flight (TOF) methods [73, 74]. The carrier mobility depends on the film thickness, the maximum number possible of optical generated carrier, incident pulse width, the dielectric relaxation time. In the ZnO-doped PFPAMA, the carriers are generated within ZnO while PFPAMA is thought to provide the passivation through better interface compatibility.

4 Conclusions

We have reported on the construction and the electrical and photoresponse evaluations of Schottky diodes based on ZnO-doped poly-2-(4-Fluorophenyl)-2-oxoethyl-2-methylprop-2-enolate matrices are reported. The device structure is Al/p-Si:(PFPAMA:ZnO)/Al. Three different methods were
used to measure the characteristics and parameters of the diodes. The barrier height was found to be around 0.7 eV. The estimated interface state density in the devices are much lower than in comparable literature devices, suggesting that the surface chemistry of PFPAMA plays a significant role in suppressing the interface states. The results show that careful ZnO doping can yield lower series resistance and ideality factor, and good photoconductive response over a wider range of bias. Such diodes have been shown to be suitable for photoconductive applications. We have presented evidence that undoped PFPAMA did not directly participate as an n-type semiconductor but as a suitable host matrix for ZnO on p-Si. There is considerable scope for investigating the semiconducting properties of PFPAMA and its optimization as a host matrix for other inorganic semiconductors and understanding the physics of its surface passivation interaction, which reduces the number of interface states and improves device performance. There remains in the scope of future work to determine the HUMO/LUMO levels and other parameters such as the electron mobility using modified time-of-flight methods.

Acknowledgements

The authors acknowledge the support of King Khalid University for this research through Grant No. RCAMS/KKU/p002-21 under the Research Center for Advanced Materials Science at King Khalid University, Kingdom of Saudi Arabia.

Author contributions

All authors contributed equally to this work.

Funding

Funding was provided by Research Center for Advanced Materials Science, King Khalid University (SA) (Grant No. RCAMS/KKU/p002-21).

Data availability

All data generated or analysed during this study are included in this published article.

Declarations

Conflict of interest  The authors declare that there are no competing interests.

Research involving human and animal participants  This article neither contains any studies on human or animal subjects, nor involved the collection of such samples.

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