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Determination of Structural Properties of Some Important Polymers Used as Interfacial Layer in Fabrication of Schottky Barrier Diodes (SBDs)

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ABSTRACT: In this study, structural, electronic and thermal properties of important polymers such as Perylene (PER), Polypyrrole (PPy) and Polyvinyl alcohol (PVA) commonly used in the production of metal-polymer-semiconductor (MPS) type Schottky Barrier Diodes (SBDs) were determined. Since the opto-electronic properties of the materials depend on the electronic band gap, the High Occupied Molecular Orbital (HOMO) and Low Unoccupied Molecular Orbital (LUMO) energies for the polymeric structures and the gap between of energy levels were calculated. In addition, entropy, heat capacity and total thermal energy values were calculated over a wide temperature range and it was determined how thermochemical properties of polymers were affected with temperature. The obtained results showed that while PER has a planar structure, PPy and PVA has a non-planar structure. PER also has the highest chemical reactivity among the polymers examined with large band gap calculated as 3.03 eV. In addition, thermochemical parameters of all polymers increase with increasing temperature almost as linearly.

Keywords: Schottky Barrier Diodes, Density Functional Theory (DFT), polymers, structural properties, HOMO-LUMO

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INTRODUCTION

Schottky barrier diodes (SBDs) with and without an interfacial layer are electronic devices formed by contacting metal and a semiconductor with one another at the lowest possible resistance (zero resistance in ideal case) at high temperature and low pressure. They are quite important in many semiconductor-based electronic devices manufacturing industries such as solar cells (SCs), photodetectors (PDs) and field effect transistors (FETs) [Bilkan, 2016]. While the interfacial layer is formed in the production of SBD, structural defects and impurities may occur that alter the energy band structure of the semiconductor and affect the device performance [Bilkan, 2016]. For this reason, recently various organic (polymer) layers such as rhodamine-101, poly(aniline), tetraamide-I, phenolsulfonphthalein, chitin, β-carotene, safranin T, PVA, P_2CIAn, PEDOT, polyindole, PER, and PPy are used to isolate metal and semiconductor from MS contacts, regulate charge transitions between them and reduce leakage current. If any of these polymers are placed at the metal/semiconductor interface, the MS type SBD converts to the MPS type SBD.

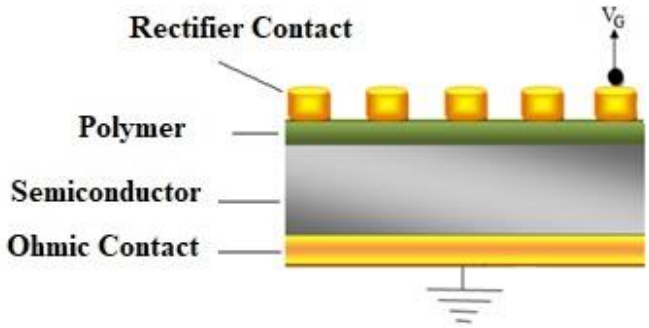

Figure 1. Schematic representation of SBD with polymer interfacial layer

Since the electrical properties of SBDs are often determined by their interface properties, determination of chemical and physical properties of the used polymers in SBDs is very important for scientific and industrial applications [Bilkan et al., 2016; Bilkan et al., 2017]. Unfortunately, in the literature, the number of studies in which the structural and electronic properties of polymers used in SBD fabrication are discussed in detail is quite limited. In order to fill this gap in the literature, the structural and electronic properties of the polymers have been investigated in detail in this paper.

Actually, since polymeric structures continue in the form of long chains, it is quite difficult to examine them theoretically. It is, therefore, more reasonable to consider a certain portion of the polymers for investigations. These type structures have been named as an oligomer [Jenkins et al., 1996]. For this study, octamer structures were taken into consideration in the investigation of PVA and PPy oligomers. Octamer modeling is a useful approach to understand the electronic and structural properties of polymeric systems and it has been used to investigate the structures of some polymers in the literature [Zgou et al., 2008]. To start with, the octamer structures of the oligomers have been optimized and the energies of the structures have been calculated. Later, HOMO and LUMO energies and thermochemical properties of the polymers have also been obtained from optimized octamer structures using the DFT method. The HOMO and LUMO are important parameters in determination of physical properties of chemical compounds. The energy gap between HOMO and LUMO energies is a considerable parameter in determining molecular electrical transport properties. The energy of the HOMO is directly related to the ionization potential, and LUMO energy is directly related to the electron affinity. This is also used by the frontier electron density for estimating the most reactive position in p-electron systems and also

explains several types of reaction in conjugated system [Al-Saadi et al., 2015; Bilkan, 2019]. The HOMO-LUMO energies and the gap between HOMO and LUMO levels are also used to the description characteristic electronic properties of the semiconductor. Charge transport relates to the ability of charge carriers to move from one molecule to another; this depends on the energy gap between HOMO and LUMO. The conduction band and the valance band are usually replaced by LUMO and HOMO, respectively. [Yıldırım, 2017]. The results obtained were discussed and many structural and electronic properties of the polymers were elucidated in detail.

MATERIAL AND METHOD

Three-dimensional geometries of the investigated polymers were drawn using Gaussview visualization program [Dennington et al., 2008]. Initially, the polymeric structures were optimized with a calculation level of DFT/6-311G(d,p). Using the optimized structures, HOMO-LUMO energies were calculated and the contour maps were drawn. The time-dependent DFT method (TD-DFT) was used for calculation of the electronic absorption spectra. Entropy and heat capacities of the structures were calculated with the same calculation level in a wide temperature range. All calculations were performed on a high-capacity computer by using Gaussian program [Frisch et al., 2004].

RESULT AND DISCUSSIONS

Structural properties

In order to determine the structural parameters and the electronic properties, at first, it is necessary to determine the optimized structures. In this study, three-dimensional structures of PER, PVA, and PPy were optimized by using DFT/B3LYP method and resulting structures were given in Figure 2.

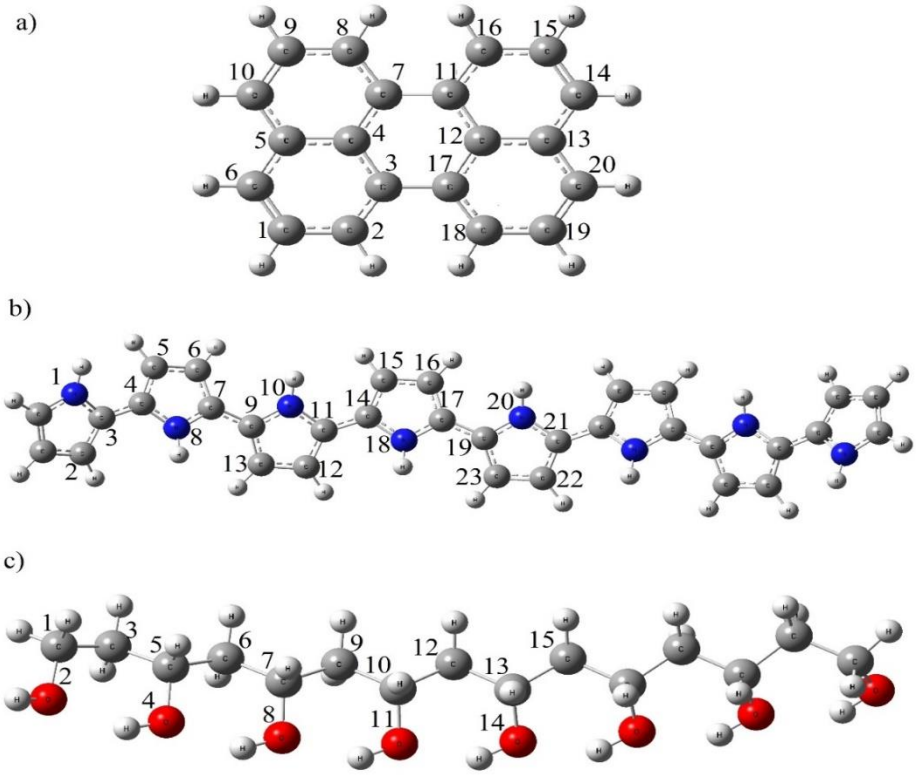

Figure 2. The optimized polymeric structures of a) PER b) PPy and c) PVA

In this part of the study, dihedral angles are examined to determine the structure of polymers because dihedral angles represent the angle between the two planes and provide important information

in predicting the shape of any chemical structure. For PER, 1C-2C-3C-17C, 2C-3C-4C-7C, 18C-17C-3C-4C, 15C-16C-11C-7C and 9C-8C-7C-11C dihedral angles were calculated as 180.0, -180.0, 180.0, 180.0 and -180.0° respectively, which indicates that the structure is planar. The C-C bonds for PER were calculated as 1.37 Å, C=C bonds as 1.43 Å. 7C-11C and 3C-17C bond lengths were calculated as 1.48 Å, all of which are consistent with the experimental data found in the literature [Donaldson et al., 1953]. For PPy, N-C bond lengths were calculated between 1.38 Å and C-C bond lengths were calculated between 1.38-1.45 Å. For PVA, C-C bond lengths were found to be 1.53-1.54 Å and C-O bond lengths were 1.43 Å. These values are quite similar to the results of previous calculations [Bala et al., 2015]. Furthermore, according to these results, PPy and PVA oligomers have a non-planar structure. Atomic charges are determinative in the formation of geometric parameters of a chemical compound. Whether the compound is in planar or nonplanar geometry is directly related to charges. In addition, whether the geometric structures are planar or not can trigger intermolecular interactions, which directly affect the electronic properties of the diode by reducing the gap between the HOMO-LUMO energy levels of the polymers used as the interfacial layer. The effect of planar geometric structure on electronic properties will be discussed in the following title electronic properties.

Electronic properties

In this paper, HOMO and LUMO energies for PER, PPy and PVA and the gap between of them were also calculated. Calculated parameters are given in Table 1. The band gap were calculated by $Eg = E_{LUMO}-E_{HOMO}$.

Table 1. Calculated HOMO, LUMO and LUMO-HOMO energies (eV) of the polymers

	HOMO	LUMO	HOMO-1	LUMO+1	Gap
PER	-5.21	-2.18	-6.81	-0.79	3.03
PPY	-4.31	-0.91	-4.71	-0.57	3.40
PVA	-6.36	0.05	-6.91	0.78	6.31

Determining HOMO-LUMO energies and gap between the two is important because these parameters provide the ability of electron-hole transport and a reasonable qualitative indication of excitation properties [Kaya, 2018]. The calculated band gaps were obtained as 3.03 eV for PER, 3.40 eV for PPy and 6.31 eV for PVA, respectively. The experimental band gap for PPy is around 2.83 eV [Chakrabarty, 2014]. The experimental band gap value of PVA is 6.18 eV [Abdullah et al., 2015]. As a result of our investigations, there are no experimental bandgap value of PER in the literature, but there are some studies in which the bandgap value was calculated for PER. One of these is the study conducted by Mohamad et al. [Mohamad et al., 2017], and the band gap value for PER was calculated to be approximately 2 eV. Although this value is close to the calculated value in our study, the reason why it cannot be the same is they used different calculation levels in their study.

For a chemical compound, the small energy gap means mostly high chemical reactivity and low kinetic stability because of narrow energy gaps in electronic transitions. This type compounds also termed as soft molecules [Fleming, 1976]. The computed band gaps of the oligomers were calculated very close to the experimental values in the literature. However, since the periodic boundary conditions are neglected in theoretical calculations, it is expected that there will be some difference between the calculated and the experimental values. In some studies made, it was seen that the obtained results were closer to the experimental values with increasing oligomer length. [Kaya, 2018].

For PER, PPy and PVA, HOMO and LUMO contour maps are shown in Figure 3.

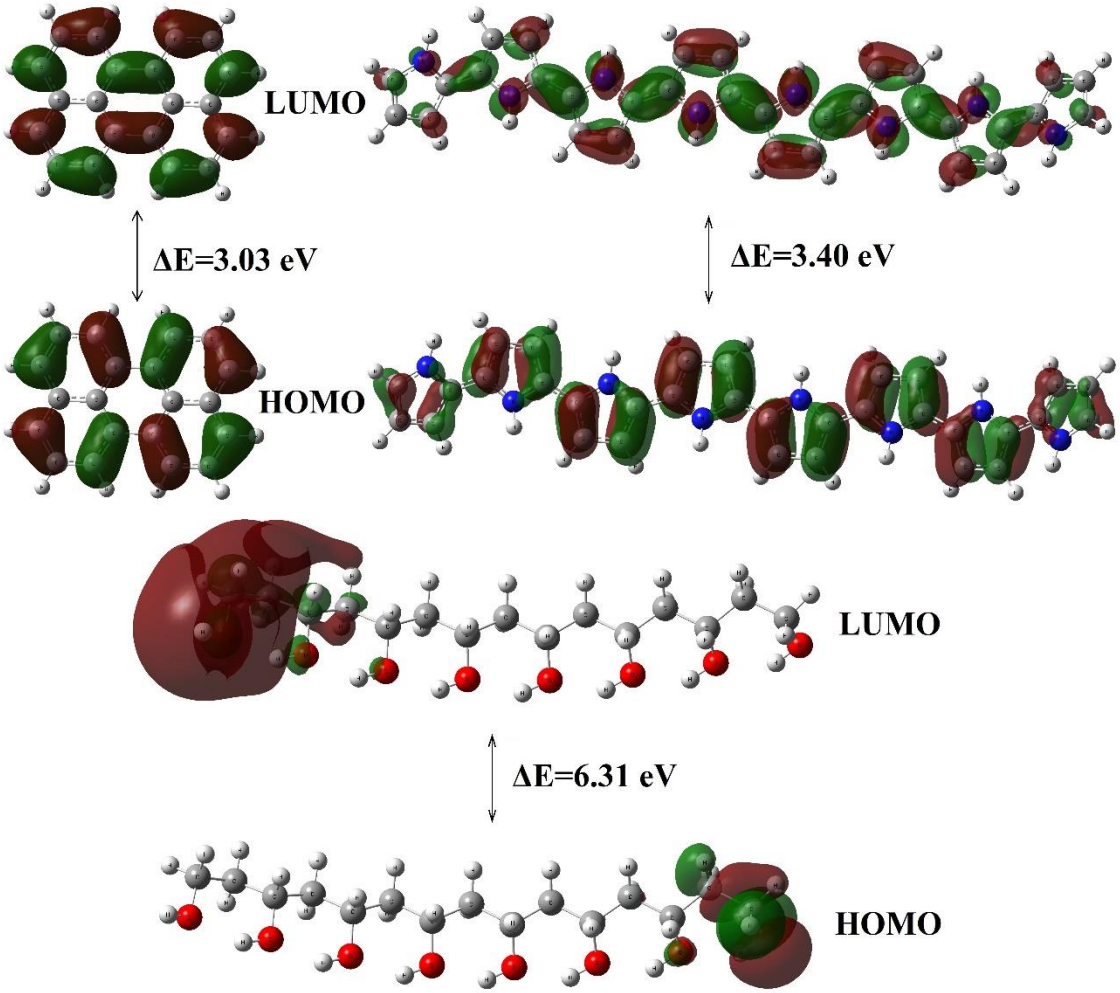

Figure 3. HOMO-LUMO contour maps and energy gap of PER, PPy and PVA

The absorption wavelengths, oscillator strength and excitation energies of the polymers were calculated and they were given in Table 2.

Table 2. The absorption wavelengths (λ_{max}), Oscillator strength and excitation energies of PER, PPy and PVA

	PER	PPy	PVA
*λ_{max} (nm)	435.22 (418.70)	414.97 (446.00)	198.27 (200.00)
Oscillator strength	0.3509	2.2902	0.0000
Excitation energy (eV)	2.8488	2.9878	6.2534

*The experimental values of λ_{max} were given in brackets.

If molecular structures absorb light, the energy excites structure to a higher energy level. The wavelength of the light determines the type of excitation. If UV or visible light is emitted on the structure, electrons rise to the higher energy levels. The absorption spectrum of the compounds is the absorption of incoming light as a function of wavelength. The spectrum depends on its energy level structure and it is useful for identifying compounds. For the PER, absorption band was calculated at 435.22 nm with an oscillator strength of 0.3509 and calculated excitation energy is 2.8488 eV. In the literature, for PER, the experimental value of λ_{max} is 418.70 nm [Joblin et al., 1999]. Furthermore, the calculated λ_{max} of PPy

oligomer is 414.97 nm. Chougule et al. observed to λ_{max} of PPy thin films at 446.00 nm in their experimental studies [Chougule et al., 2011]. Finally, λ_{max} of PVA were obtained at 198.77 nm in this study. The experimental value of λ_{max} was measured at 200.00 nm for PVA nanocomposite material [Nakhaei et al., 2012]. The results calculated in this study are very close to the experimental values in the literature.

Thermochemical properties

Determination of the thermochemical properties of chemical compounds and identification of behaviors of them under the temperature is quite important because these properties play an important role in the examination of the energy and heat associated with chemical reactions and physical transformations. Because of this, in Table 3, the entropy and heat capacities of the polymers in the wide temperature range of 100-400 were calculated together with the thermal energies at 1.0 atm pressure.

Table 3. Calculated thermochemical properties of the polymers in the wide temperature range of 100-400K.

	Temp. (K)	Entropy	Heat Cap.	Thermal Energy
PER	100	75.620	16.982	159.797
	150	84.834	25.363	160.848
	200	94.033	35.293	162.359
	250	103.501	46.086	164.392
	298.15	112.875	56.672	166.866
	300	113.239	57.076	166.971
	350	123.151	67.729	170.094
	400	133.119	77.693	173.733
PPy	100	132.176	50.696	330.971
	150	156.707	68.071	333.926
	200	179.599	88.497	337.830
	250	202.144	110.559	342.803
	298.15	223.810	132.023	348.644
	300	224.639	132.837	348.889
	350	247.049	154.253	356.072
	400	269.227	174.128	364.289
PVA	100	109.588	42.232	307.520
	150	130.210	56.448	309.987
	200	148.966	70.740	313.165
	250	166.771	85.450	317.068
	298.15	183.416	100.082	321.533
	300	184.045	100.649	321.719
	350	201.020	115.865	327.133
	400	217.716	130.534	333.296

*(Entropy and heat capacity is in Cal $(Mol.K)^{-1}$, and thermal energy is in Kcal Mol^{-1}.

Heat capacity is one of the most important thermochemical parameters and is based on vibrational motions of molecular structures. Many other thermal parameters such as enthalpy, entropy and Gibbs free energy of a material can be calculated by utilizing heat capacity [Umesh Gaur and Bernhard Wunderlich, 1982]. Therefore, it is very important to determine the heat capacity for the polymers. As

seen from Table 3, heat capacity and other thermochemical parameters of polymers with increasing temperature showed a linear increase. Thermochemical parameters have a direct effect on the vibrational between the atoms of chemical compounds. Alters in the vibrational modes of atoms can change the electronic properties of compounds shortly (with the effect of polarization). This may affect the compound's ability to perform intra and intermolecular interactions as previously mentioned and the electronic properties of the diode used as the interface layer. It is seen from results of a detailed investigation of the literature [Moraki et al. 2016; Gümüş and Altındal, 2014, Bilkan et al. 2017] for SBDs with PER, PPy, PVA interfacial layers, with increasing temperature the value of barrier height (Φ_{bo}) increased whereas the value of ideality factor (n) decreased. This is due to the effects of the changing temperature on both the semiconductor structure and the polymer layers.

Applications of the polymers in SBDs

The most important physical parameters for SBDs are rectification ratio (RR), saturation current (I_0), n, series resistance (R_s) and short circuit resistance (R_{sh}). The conventional method for calculating these values is to interpret experimental current voltage (I-V) curves.

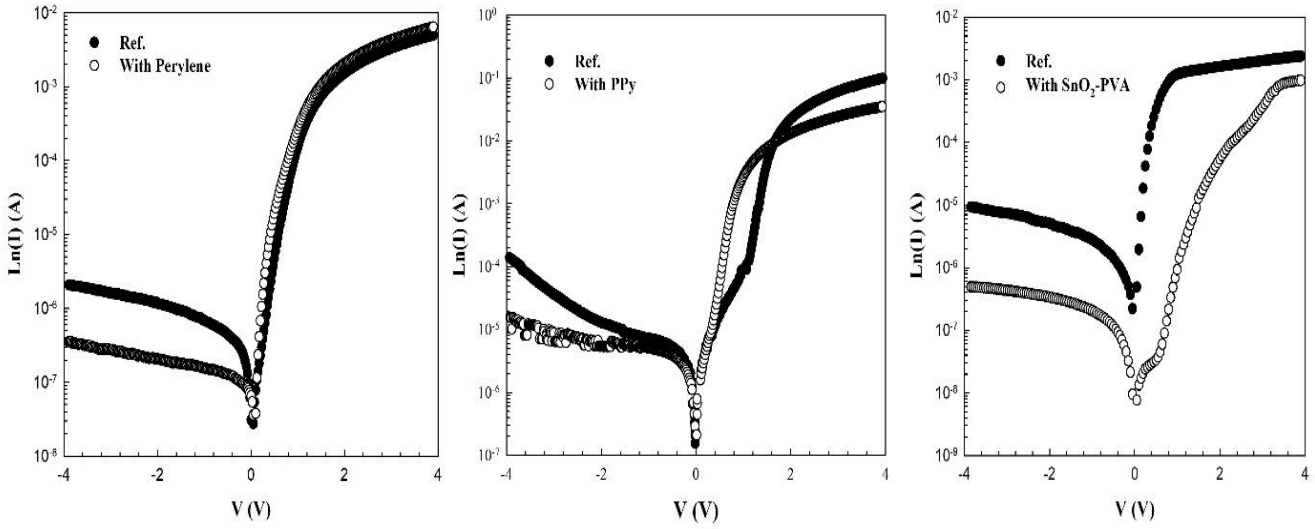

Figure 4. I-V characteristics of SBDs with and without PER, PPy and PVA interfacial layers.

Experimental I-V curves of SBD with PER, PPy, PVA interfacial layers were compared to ones without an interfacial layer, and they were given in Figure 4. The experimental data were taken from our previous studies [Bilkan, 2016; Bilkan et al. 2014 and Bilkan et al. 2019]. The characteristics of an ideal diode are: the diode must have a good rectification (RR high), be able to start early transmission (I_0 low), have an ideality factor close to 1 (ideally 1), low series resistance (ideally 0) and high short circuit resistance (ideally infinite). It is clear that the values of *n* for diodes are considerably larger than unity. The high values of *n* can be also attributed to the existence of interfacial layer, the particular density distribution of interface states (N_{ss}) at p-Si/PER interface and wide distribution of low SBH or patches at Al/p-Si interface.

Table 4. Comparison of some main diode parameters.

	PER		PPy		PVA	
	Without	With	Without	With	Without	With
RR	$2.06x10^{3}$	$15.7x10^{3}$	345	1730.7	249.5	249.5
I_R (A)	$1.61x10^{-6}$	$2.75x10^{-7}$	$2.32x10^{-6}$	$5.92x10^{-7}$	$2.46x10^{-7}$	$2.95x10^{-9}$
n	3.8	2.8	5.62	3.3	1.97	7.15
R_s (Ω)	544	716	50.5	124.5	1643	3995
R_{sh} (MΩ)	10.7	1.83	0.08	0.3	0.41	7.99

The values obtained from the graphs for diode parameters were compiled into Table 4. It can be clearly seen from the values in the table that the performance in MPS type SBDs are better than the MS type SBDs.

CONCLUSIONS

In this study, we have investigated structural, electronic and thermal properties of some important polymers such as Perylene, Polypyrrole and Polyvinyl alcohol used in the SBDs production. The reliability of the calculations was confirmed by comparing the results of the study with the experimental data in the literature. Since the conduction band, valance band and band gap, which are very important parameters for semiconductors, are the equivalents in the molecular structures, HOMO and LUMO energies and the gap between them are determined for each polymer. In addition, entropies, heat capacities and thermal energies of the polymers were calculated and their changes depend on temperature were investigated. As a result of the study, it is clearly seen that PER has a planar structure, PPy and PVA has a non-planar structure. Moreover HOMO-LUMO gap was calculated as 3.03 eV, 3.40 eV, 6.40 eV for PER and (n=8) oligomer structures of PPy and PVA, respectively. According to this result, PER exhibit higher chemical reactivity than other polymers investigated in this study. Furthermore, it is seen the increased temperature caused a linear increase in the heat capacity of the polymers.

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