■ RESEARCH ARTICLE

Effects of PCPDTBT:PCBM Ratio on the Electrical Analysis and the Prediction Of I-V Data Using Machine Learning Algorithms for Au/PCPDTBT:PCBM/n-Si MPS SBDs

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Abstract

In this study, Au/Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) : [6,6]-phenyl C61 butyric acid methyl ester (PCBM) /n-Si heterojunction Schottky barrier diodes (SBDs) with 1:1 and 2:1 PCPDTBT:PCBM doping ratios were produced, and the electrical analysis of metal-polimer-semiconductor (MPS) SBDs with different concentrations was investigated. Ideality factor (n), saturation current values (I_0) and barrier heights (F_0) of the materials were obtained based on the current-voltage (I-V) measurements performed. According to the results obtained, the PCBM concentration has significant effects on the electrical properties of the Au/PCPDTBT:PCBM/n-Si MPS SBD. To predict the electrical characterization of a system in detail, based on its doping concentration, the I-V data set consisting of 2 samples is typically split into a 70% training set and a 30% test set, which is used to train machine learning algorithms. Various methods, including Fine Tree, Cubic SVM, Fine KNN, Boosted Trees, Bagged Trees, Subspace KNN, RUSBoosted Trees, Wide Neural Network, Trilayered Neural Network, and Logistic Regression Kernel, have been analyzed. The obtained results indicate that certain algorithms can predict the I-V data of Au/PCPDTBT:PCBM/n-Si MPS SBD with full accuracy, i.e., 100%.

Keywords: Schottky barrier diode; PCPDTBT:PCBM ratio; electrical analysis; I-V data; machine learning

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1. Introduction

The vast majority of electronic devices used today are made of semiconductor materials. Semiconductor devices are commonly used in power-consuming devices, such as computers, televisions, mobile phones, and other electronic devices used in daily life [1]. Organic semiconductors have many advantages, such as easy production technologies,

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low production costs, and wide surface application areas [2]. Thanks to these advantages, electronic components such as organic field-effect transistors (OFET), organic light-emitting diodes (OLED), organic photodiodes (OPD), organic photovoltaic cells (OPV), and organic Schottky diodes are highly preferred using organic semiconductors [3]. Organic semiconductors are divided into two groups: carbon-based small molecules and polymers [4]. Since polymers are more often in solution, spin coating is the most commonly used organic growth method [5]. In contrast, small molecules are usually grown by methods such as vacuum evaporation or sublimation [6]. Metal-semiconductor (MY) Schottky contacts are widely used in optoelectronics and electronics due to their advantages such as easy conduction even at a voltage value of 0.25 V, low noise levels, and high efficiency [7]. In metal-semiconductor contacts, the performance, efficiency and electrical properties of the material can be directly changed by placing an interface material between the metal and the semiconductor. A Schottky barrier diode called metal-insulator-semiconductor (MIS) can be created by placing an insulating interface between the MY structure, and a Schottky barrier diode called metal-polymer-semiconductor (MPS) can be created by placing a polymer interface between the MY structure [9,10]. To improve the performance of MPS Schottky barrier diodes, it is important to understand and analyze their electrical properties in detail.

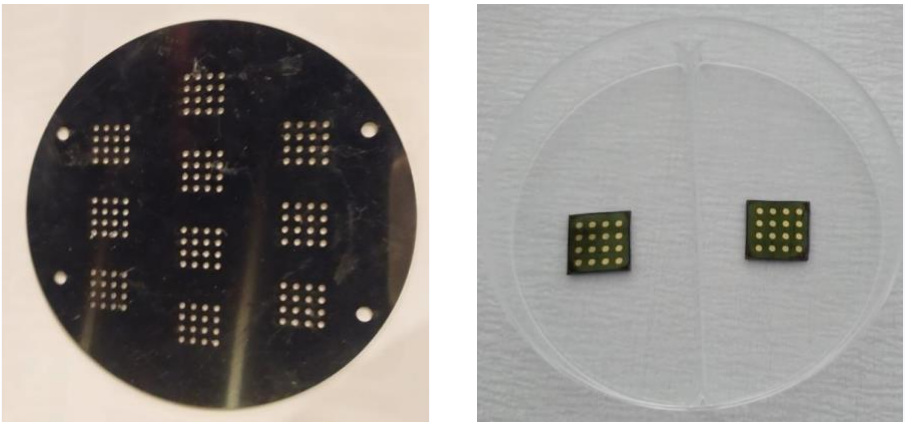
In this study, PCPDTBT{Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]}:PCBM{[6,6]-phenyl C61 butyric acid methyl ester} concentrations prepared with 1:1 and 2:1 doping ratios were used as an interface in MPS Schottky barrier diodes, and the electrical parameters obtained from the I-V measurements of these Au/PCPDTBT:PCBM/n-Si (MPS) Schottky barrier diodes in the dark, under vacuum, and at room temperature were investigated.

In the second part of the study, the main aim was to predict the effect of PCPDTBT:PCBM concentration on the electrical characterization of Au/PCPDTBT:PCBM/n-Si MPS SBD. To achieve this goal, 10 different machine learning methods were trained using feature engineering operations on the same data set and their performances were compared.

1. Material and Method

1.1. Fabrication And Characterization of Schottky Barrier Diodes

In this study, PCPDTBT:PCBM organic compounds were purchased from Sigma-Aldrich Company Ltd. The PCPDTBT and PCBM powders were dissolved separately in chloroform at a concentration of 25mg/ml at 30°C and stirred for 3 hours with magnetic stirrers to form a solution to create a polymer interface layer at different doping concentrations. Then, mixtures were prepared at 1:1 and 2:1 concentrations and left to stir overnight at 30°C. N-type (phosphorus-doped), single-crystal silicon (Si) wafer with <100> orientation and a thickness of 200±25μm and a resistivity of 4.8Ω.cm was used as a substrate to produce Au/PCPDTBT:PCBM/n-Si (MPS) Schottky barrier diodes with different PCPDTBT:PCBM doping ratios. The polished side of the Si wafer was chemically cleaned by the Radio Corporation of America (RCA) cleaning method is the basic procedure developed by Werner Kern in 1965 while working at the RCA [11]. The back surface of the cleaned Si wafer was coated with ~1500Å thick silver (Ag) metal without a mask, using a thermal evaporation system. Then, the Ag metal was annealed in a tube furnace under N_2 flow at 450°C for 30 minutes to create a good ohmic contact on the back surface of the n-Si wafer. After the formation of the ohmic contact, the front surface of the n-Si wafer was cleaned with 50% hydrofluoric (HF) acid to remove any thin oxide layer that might have formed. Following this oxide cleaning process, organic compounds with 1:1 and 2:1 (PCPDTBT:PCBM) doping ratios were spin-coated onto the front surface of the samples. The samples were heated at 45ºC on a hot plate for 15 minutes to evaporate the solvent in the organic film. To fabricate Au/PCPDTBT:PCBM/n-Si (MPS) Schottky barrier diodes, circular-shaped gold (Au) rectifying contacts with a thickness of ~1500Å were formed on the PCPDTBT:PCBM organic film using a mask containing 1mm diameter circles (Figure 1). The Au coating process also used thermal evaporation system, and the evaporation process was carried out at a pressure of ~1x10^{-6} Torr. At the same time, the thickness of the circular-shaped Au contacts was monitored using a digital thickness measurement monitor in the thermal evaporation system. The schematic representations of the produced MPS SBDs are shown in Figure 2.



a b

Figure 1. (a) The mask used for the rectifier contacts (b) Top view after coating the rectifier contacts.

Figure 2. Schematic representation of SBD.

The electrical characterization of Au/PCPDTBT:PCBM/n-Si (MPS) Schottky barrier diodes produced using 1:1 and 2:1 PCPDTBT:PCBM doping ratios were analyzed by I-V measurements performed under vacuum and in the dark at room temperature.

1.2. Machine Learning Algorithms

In essence, machine learning provides computers with the ability to "learn from experience", a capability naturally found in humans. Unlike relying on a pre-determined equation as a model, machine learning algorithms utilize computational methods to extract information directly from data. As the number of available samples for learning increases, these algorithms can adaptively improve their performance [12]. With the ability to make effective and error-free estimations, machine learning algorithms can be used for various purposes such as classification, estimation, and forecasting [13]. Essentially, machine learning aims to predict future outcomes based on past experiences [14]. This is achieved through the use of software design that can learn rules from data, adapt to changes, and improve its performance with experience. The field of machine learning is focused on developing computer programs that can automatically improve their performance using sample data or past experience [15,16].

In this study, different classifier models with varying structures were developed using MATLAB's machine learning toolbox. The objective was to estimate the impact of PCPDTBT:PCBM concentration on the electrical characteristics of Au/PCPDTBT:PCBM/n-Si MPS SBD. The models employed in this study included multi-layered neural networks, NB classifiers, KNN algorithms, DT algorithms, and SVM. All numerical results were obtained using MATLAB R2020 on an Intel processor running Windows 10.

1.2.1. Artificial Neural Networks (ANN)

The artificial neural network (ANN) structure, which is used for classification processes, was designed to include 1, 2, and 3 hidden layers and modelled as a single output and feedback structure.

1.2.2. Support Vector Machine (SVM)

The SVM classification approach is a two-step process. In the first step, the classifier's high-dimensional input is non-linearly mapped to another attribute space. In the second step, a new linear hyperplane is created from this attribute space to maximize the separation between the samples' parts [16].

1.2.3. Decision Tree Classifier Algorithm

One of the most widely used machine learning algorithms is tree-based learning, which falls under the category of data mining classification algorithms. In this approach, a set of multiple decision trees is created to train a model. The decision tree structure resembles a flowchart that tests attributes to determine the sample corresponding to each internal node. Each branch represents a test result, and each node represents a class. Each decision tree is built using randomly selected input data values.

1.2.4. k-Nearest Neighbor Algorithm (KNN)

The fundamental principle of the k-nearest neighbor algorithm in classification problems is that a chosen value of K can identify the nearest neighbor of a given data point. The data point is then assigned to the class with the highest frequency among its K nearest neighbors. The K value refers to the number of neighboring data points considered in the classification process.

1.2.5. Naive Bayes

The Naive Bayes classifier is a statistical classification model that is based on Bayes' theorem. It assumes that the effect of a particular attribute on a class is independent of other attributes, even if they are correlated. This simplifying assumption makes the calculations easier and is referred to as "naive".

2. Results and Discussions

In this study, measurements of Au/PCPDTBT:PCBM/n-Si heterojunction SBDs with 1:1 and 2:1 PCPDTBT:PCBM doping ratios were performed in a closed circuit cryostat at approximately 1x10^{-4} mbar pressure, at 300K room temperature in the dark, within the voltage range of -3V to +3V. Figures 3 and 4 show the I-V curves of the diodes fabricated using 1:1 and 2:1 PCPDTBT:PCBM doping ratios, respectively.

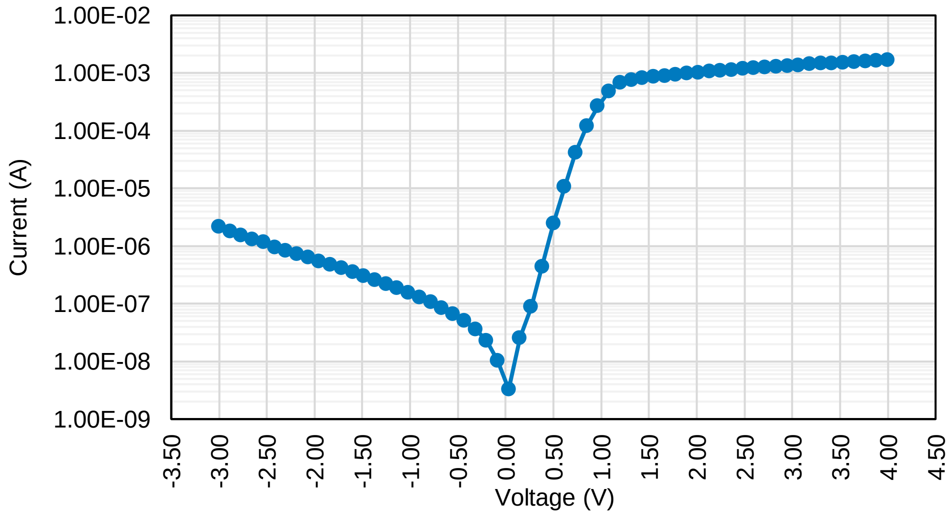


Figure 3. I-V characterization of 1:1 PCPDTBT:PCBM used Au/PCPDTBT:PCBM/n-Si MPS SBDs.

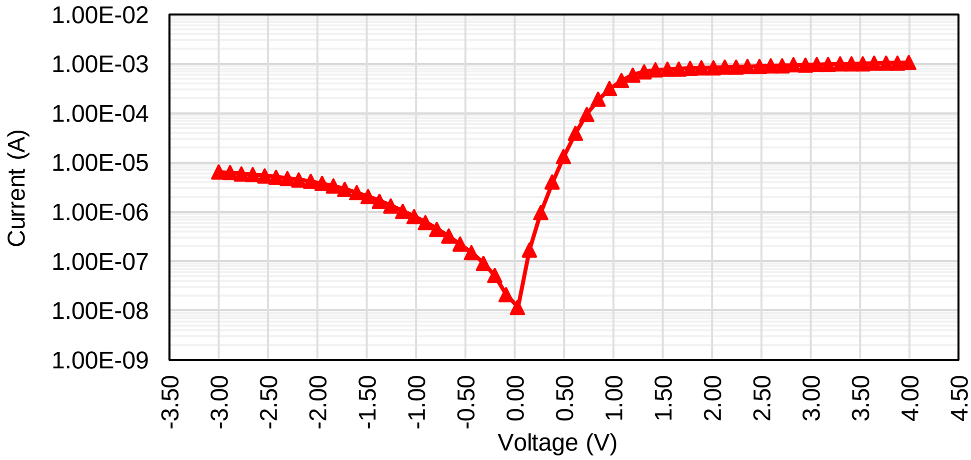


Figure 4. I-V characterization of 2:1 PCPDTBT:PCBM used Au/PCPDTBT:PCBM/n-Si MPS SBDs.

Ideality factors (n), barrier heights (ϕ_B) values, and saturation current values (I_o) values were calculated from the current-voltage (I-V) characteristics of the produced diodes. The ideality factors were obtained from the slope of the linear region of the obtained I-V graphs using the following equation [17].

$$n = q/kT tan\theta \quad [1]$$

According to equality [1], q:electron charge, k:boltzman constant and T:temprature(in ^oK). The ideality factors(n) obtained using the above expression are 2.97 for the diode with 1:1 PCPDTBT:PCBM ratio and 3.09 for the diode with 2:2 PCPDTBT:PCBM ratio.

The $\emptyset_B$ values are obtained using the following equation:

$$\emptyset_B = \frac{kT}{q} \ln \left(\frac{AA^*T^2}{I_0}\right) \quad [2]$$

In this equation, I_o is the saturation current value, which is obtained from the current values obtained from the I-V curve at the point where the voltage is zero. The saturation current value of the diode with a 1:1 PCPDTBT:PCBM ratio was obtained as $6.92x10^{-9}$ A in the dark. Using the saturation current, the $\emptyset_B$ value obtained using the Equation 2 was calculated as 0.88 eV.

When the same procedures were applied to the diode produced with 2:1 PCPDTBT:PCBM ratio, the saturation current value was calculated as $1.22x10^{-8}$ A and the $\emptyset_B$ value was calculated as 0.87 eV. All the obtained values are given in Table 1.

Table 1. Comparison of characteristic features of SBDs.

PCPDTBT:PCBM Ratio	***n***	***I_o(A)***	$\emptyset_B$(eV)
1:1	2.97	6.92×10^{-9}	0.88
2:1	3.09	1.22×10^{-8}	0.87

The comparison of the I-V curves obtained in the dark at 300K for Au/PCPDTBT:PCBM/n-Si heterojunction SBDs with 1:1 and 2:1 PCPDTBT:PCBM doping ratios is given in Figure 5.

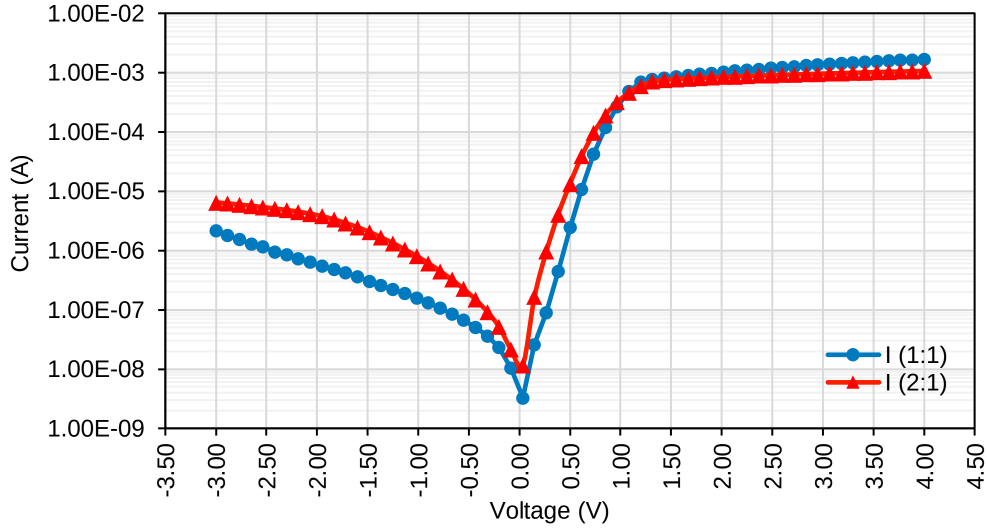


Figure 5. Comparison I-V characterization of 1:1 and 2:1 PCPDTBT:PCBM based SBD.

As shown in Figure 5, the diode produced using a 1:1 PCPDTBT:PCBM doping ratio exhibits more ideal behaviour in terms of their ideal factor, maximum current values, and leakage currents when compared to the diode produced using a 2:1 PCPDTBT:PCBM doping ratio. As previously calculated, the ideal factor of the diode with a 1:1 doping ratio is 2.97, while the ideal factor of the diode produced with a 2:1 doping ratio is 3.09. This is thought to be due to a reduction in defects and cracks within the structure as the PCBM doping increases.

RR (Rectification ratio) values of both diodes were calculated using the ratio of the forward current value at +3V and -3V voltage values to the current value at reverse bias. The RR of the diode with a 1:1 PCPDTBT:PCBM blend ratio was calculated as 7.77×10^2. RR of the diode with a 2:1 blend ratio was obtained as 1.65×10^2. The high RR is an important parameter for electronic applications [18]. It is crucial for diodes that will be used in rectifier circuit designs to have a high RR as it will provide better current control and higher efficiency during rectification. Additionally, the obtained RRs show that there is a higher injection of charge into the polymer layer in the forward bias state and much less in the reverse bias state as the PCBM blend ratio increases [19].

In conclusion, a significant increase in RR was observed in the Au/PCPDTBT:PCBM/n-Si heterojunction SBD with an increase in PCBM blend ratio. Therefore, the heterojunction SBD with a 1:1 PCPDTBT:PCBM blend ratio exhibits better diode properties.

In this part of the study, the performance of the proposed machine learning algorithms for I-V data estimation was investigated. The evaluation of PCBM concentration prediction was carried out using the dataset of Au/PCPDTBT:PCBM/n-Si MPS SBD. The dataset was used contains I-V values as input data and mixing ratio as output data. Traditional validation and k-fold cross-validation approaches were utilized to evaluate the proposed algorithms. The I-V data were tested with various machine learning techniques such as Logistic Regression, NB, Linear SVM, Cubic SVM, Quadratic SVM, Fine Gauss SVM, Medium Gaussian SVM, Coarse Gaussian SVM, Fine KNN, Medium KNN, Coarse KNN, Cosine KNN, Cubic KNN, Weighted KNN, Subspace KNN, Boosted Trees, Bagged Trees, Fine Tree, Medium Tree, Coarse Tree, RUSBoosted Trees, Subspace

Discriminant, and Multi-layer Neural Network (with 1–2–3 hidden layers) methods. The classification performance results obtained with different classifiers using all features (with PCA or not) are presented in Table 2.

Table 2. Comparison of ANN methods.

Model No	Model name	Model Type	Success Rate (%)	Cost	Estimation speed	Estimation time (s)
1	Tree	Fine Tree	30.00	42	19629	7.909
2	SVM	Cubic SVM	100.00	0	50.466	24.974
3	KNN	Fine KNN	100.00	0	9176.4	0.58721
4	Ensemble	Boosted Trees	100.00	0	1876.3	0.84399
5	Ensemble	Bagged Trees	100.00	0	1660.2	27.864
6	Ensemble	Subspace KNN	100.00	0	650.78	27.338
7	Ensemble	RUSBoosted Trees	35.00	39	1206.8	20.562
8	Neural Network	Wide Neural Network	100.00	0	21242	32.664
9	Neural Network	Trilayered Neural Network	100.00	0	15951	15.843
10	Kernel	Logistic Regression Kernel	100.00	0	55.45	45.832

In this study, the proposed machine learning algorithms showed more successful accuracy performance for the same dataset compared to other machine learning methods in the literature. Despite the imbalance in the dataset, Cubic SVM, Fine KNN, Boosted Trees, Bagged Trees, Subspace KNN, Wide Neural Network, Trilayered Neural Network and Logistic Regression Kernel algorithms that showed the best performance in I-V data achieved a successful prediction score (100%).

When examining the performance analysis of different feature engineering methods on the dataset, it was found that the structure of the used dataset is decisive. As shown in Table 2, data segmentation reduces performance in all methods similarly. In addition, different parameter variations were tried in the PCA method, and the best results are given in the table. When these results were examined, it was seen that they did not affect the performance much.

3. Conclusion

Measurements of Au/PCPDTBT:PCBM/n-Si heterojunction SBDs with 1:1 and 2:1 PCPDTBT:PCBM doping ratios were performed in a closed environment creostat at a pressure of approximately $1x10^{-4}$ mbar with a voltage range of -3V to +3V in the dark at 300K room temperature. When both diodes were compared, it was found that the diode with a 1:1 PCPDTBT:PCBM contribution ratio, i.e. the diode with more PCBM, both reached higher current values and had a lower ideality factor. In other words, the heterojunction diode with a high amount of PCBM showed more ideal behaviour. The reason for these values obtained as a function of the PCBM content was that the passivation of the surface defects in the structure increased as the PCBM content increased, and thus it had a better transmission mechanism.

In this study, all the features in the I-V data set for Au/PCPDTBT:PCBM/n-Si MPS SBD were classified by machine learning methods and predicted with 100% accuracy. In this respect, our study has shown that machine learning can be used effectively in the dual classification of I-V data of SBDs. For comparison, different types of machine learning methods with different variants were tried and classification accuracies between 30 and 100% were achieved.

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