



ISSN: 0067-2904

The Potential Barrier and Thermal Stability Dependence on PI Thickness of Al/PI/c-Si Schottky Diode

Hussein Kh. Rasheed*, Aseel A. Kareem

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Received: 23/8/2020

Accepted: 9/10/2020

Abstract

This research investigated the effectiveness of using different thickness values of polyimide (PI) interfacial layer in order to improve electrical and thermal properties of Al/PI/c-Si capacitor. The PI spectra produced by poly(amic acid) (PAA) were characterized by using FT-IR analysis. After imidization of PAA, some absorption peaks vanished, whereas PI peaks appeared, due to the complete conversion of PAA to PI.

The dependence of current-voltage and Capacitance-Voltage characteristics of Al/PI/c-Si on PI thickness (10, 20, 30, 40 nm) was exhibited through the increase of potential barrier and built-in potential and the decrease of the saturation current. These results may be interpreted in terms of the decrease in the interfacial defects, such as surface states and interface defects, which leads to reduce the potential barrier between Aluminum and crystalline Silicon and increase saturation current.

The results show that thermal decomposition resistance of polyimide films increases with the increase of polyimide thickness, because of the increase of the imide bond and the decrease of the average distance between amide groups.

Keywords: Metal semiconductor, Electrical properties, Polyimide, Schottky diode

اعتماد حاجز الجهد والاستقرارية الحرارية على سمك البوليميد لثنائي شوتكي Al / PI / c-Si

حسين خزل رشيد*، اسيل عبدالامير كريم

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، لعراق

الخلاصة:

درس هذا البحث فعالية استخدام اسماك مختلفة للطبقة البينية البوليميد (PI) من أجل تحسين الخواص الكهربائية والحرارية لمتسعة Al / PI / c-Si.

تم تشخيص طيف البوليميد (PI) الناتج من البوليميد اميك اسيد (PAA) باستخدام تحليل FT-IR. لوحظ بعد عملية امدزة البوليميد اميك اسيد اختفاء بعض قمم الامتصاص، وظهور قمم البوليميد اميك وهذا بسبب التحول الكامل للبوليميد اميك اسيد الى بوليميد اميك.

يُظهر اعتماد خصائص تيار-فولتية وسعة-فولتية لـ Al / PI / c-Si على سمك PI (10، 20، 30، 40) نانومتر زيادة في حاجز الجهد و جهد البناء الداخلي ويقلل من تيار الاشباع، ويمكن تفسيره من خلال تقليل العيوب البينية كحالات السطح و عيوب التداخل، مما يؤدي إلى تقليل حاجز الجهد بين الألوومنيوم (Al) و السليكون البوليميد c-Si وزيادة تيار الاشباع.

أوضحت النتائج أن مقاومة التحلل الحراري لأغشية البولي إيميد تزداد مع زيادة سماكة البولي إيميد بسبب زيادة رابطة الإيميد وانخفاض متوسط المسافة بين مجموعات الأيميد.

1. Introduction

Technology is continuously trending toward high-efficiency, high-speed, and large-scale integrated circuits (LSIs) as well as lower power dissipation in electronic and optoelectronic devices [1].

In the recent time, semiconductors are present in most of the modern electronic devices, because of the foundation of the electronic systems that play a crucial role in technology [2]. Metal-organic insulator-semiconductor structures obtained remarkable interest, due to the fact that these devices serve as a cost-effective alternative to traditional common junctions on low grade polycrystalline silicon thin films [3-5]. The device performance and stability are affected by the interface properties. In addition, the metal-organic insulator semiconductor (MOIS) structure has a much higher barrier than the traditional metal-semiconductor Schottky junction, causing MOIS to be more reliable than the other types of junctions [4]. Several factors are affected by the fineness and execution of the electronic metal-semiconductor (M/S) structures, such as the interfacial layer (IL), barrier height (BH), and homogeneity between the metal and semiconductor [5].

Polyimide has become an attractive compound in microelectronics applications, because of its high operating temperature, high adhesion to substrate, and high thermal stability, compared with those of common polymers [3,6].

The aim of this study involves the fabrication of PI by mixing the solutions of PMDA and PDA and studying the dependence of electrical and thermal properties of Al/PI/c-Si Schottky diode on PI thickness.

2. Experimental Work

First, the c-Si wafer was cleaned with deionized water, then dipped in ammonia water (30% by weight of NH_3) and hydrogen peroxide (30% by weight of H_2O_2) for 30 sec. This was followed by rinsing in distilled water to remove the thin oxide layer and the ionic contamination. After that, the wafer was dried.

To prepare the polyimide, 2 g (10 mmol) of p-phenylene diamine (PDA) and 40 mL NMP were placed in a container and stirred for 30 min. Then 2g (10 mmol) of pyromellitic dianhydride (PMDA) was added to the solution and stirred for 3h at room temperature to prepare poly(amic acid) (PAA) solution. Next, the resulting solution was coated with silicon wafer substrate with different thicknesses (10, 20, 30 and 40 nm) by utilizing the spin method. Aluminum with high purity (99%) was vacuum evaporated onto the back side of the silicon wafer and onto the front side of the polymer films, using a mask to form circular dots of a thickness of 220 nm.

Current-Voltage measurements were performed in the dark by using Keithley 616 and D.C. power supply. A voltage variation of -4 to 4 Volt was applied in the cases of forward and reverse bias.

From current-voltage (C-V) measurements, we can determine the height of potential barrier (Φ_b) by the relation (1) :

$$J_s = A^* T^2 e^{\frac{-q\Phi_b}{k_B T}} \dots \dots (1)$$

where A^* is Richardson constant, T is temperature, q is the magnitude of the electron charge, and k_B is Boltzmann's constant.

The built-in voltage (V_{bi}) of the junction can be determined from the plots between inverse-square capacitance ($1/C^2$) - applied bias voltage (V) in eq.(2). The C-V characteristic was measured as a function of the reverse bias voltage, applied in the range of 0-3 V with an electrode area of $1.5 \times 10^{-4} \text{ m}^2$ at a fixed frequency of 100 KHz, by using HP- 4275A LRC meter.

$$C^{-2} = \frac{2}{q\epsilon N_A} \left(V_{bi} + V - \frac{2k_B T}{q} \right) \dots \dots (2)$$

The thermal stability of the junction was evaluated by using a thermo gravimetric analyzer (STA PT100). The samples were heated from 0 to 800 °C at a heating rate of 10°C/min under Nitrogen .

3. Results and Discussion

The FT-IR spectra of PAA PI are shown in Fig.1. The characteristic ammonium multiple peaks appeared around 3098 cm^{-1} . The PAA characteristic peaks were observed, including the aromatic carboxyl peak (C=O) at 1714 cm^{-1} , C=O amide peak at 1662 cm^{-1} , N-H and C-N peaks in secondary amide at 1601 cm^{-1} and 1408 cm^{-1} , respectively, aromatic amine peak at C-N 1362 cm^{-1} , and diphenyl ether at 1117 cm^{-1} . When gradually heated, the PAA would be thermally imidized to prepare polyimide. The FT-IR characterization of PI showed the absorption bands of the C=O aromatic imide group which appeared around 1774 cm^{-1} , the asymmetrical C=O stretching at 1710 cm^{-1} , and the C=O bending vibration at 739 cm^{-1} . When comparing the spectrum of PI with the spectrum of PAA, the peak at 1362 cm^{-1} was significantly increased, indicating the increase of C-N bond number after thermal imidization [7,8]. It could be seen that, after imidization of PAA, some characteristic absorption peaks vanished, whereas the characteristic peaks of PI appeared. This indicates that PAA was completely converted to PI.

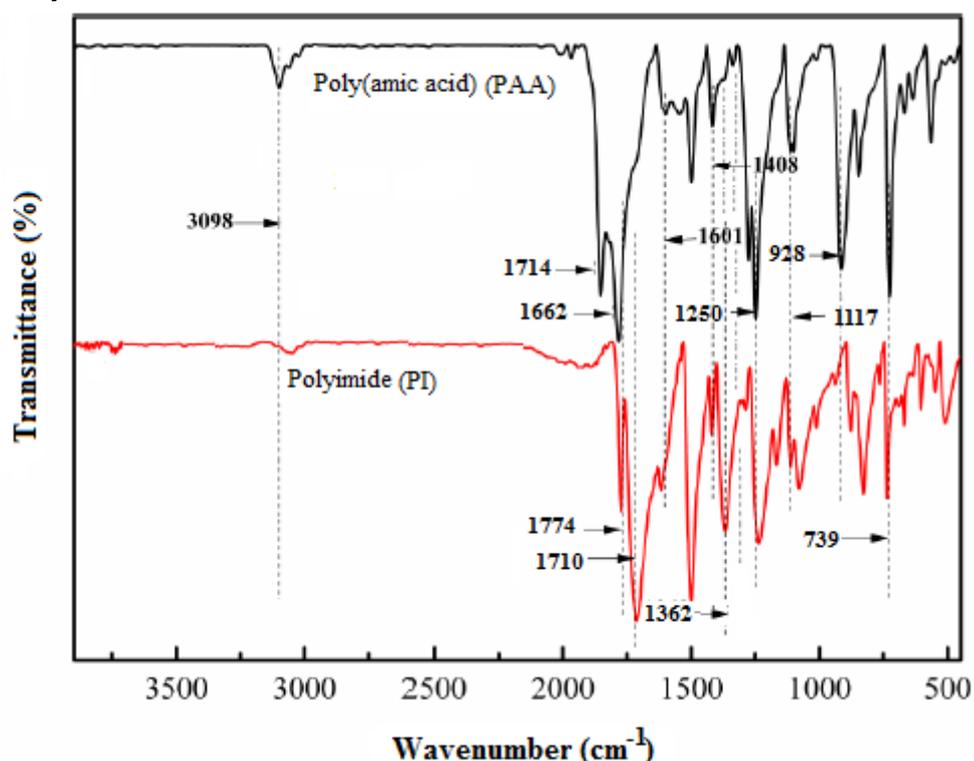


Figure 1-FT-IR spectra of Poly(amic acid) (PAA) and polyimide(PI)

The I-V characteristics of Al/ PI /c-Si in the dark, with the applied bias voltage (forward and reverse) at different thicknesses of PI, are shown in Figure-2.

From this figure, it can be observed that the non-linearity of the I-V characteristic curve indicates that the non-ohmic conduction mechanism in nature is caused by thermionic and diffusion mechanisms [9]. The good rectifying nature of the device refers to the presence of barriers on its two sides. It was observed from I-V characteristics that the forward direction characteristics do not differ markedly from those in the reverse direction. This indicates that the interfaces between metal (Al)-polymer (PI) at the bottom and top electrodes (layers) were identical in nature.

Fig. 3 shows that the value of the current decreases with increasing thickness of PI films, which refers to the reduction of the interfacial defects and the scattering of carriers at the interface region [10]. Also, these defects allow the energy levels to be within the energy gap and act as an active recombination center within the depletion region, which causes the decrease in current flow across the junction [11].

The saturation current density increases with increasing PI thickness, as shown in Table-1, where the potential barrier height increases by increasing PI thickness [10,12].

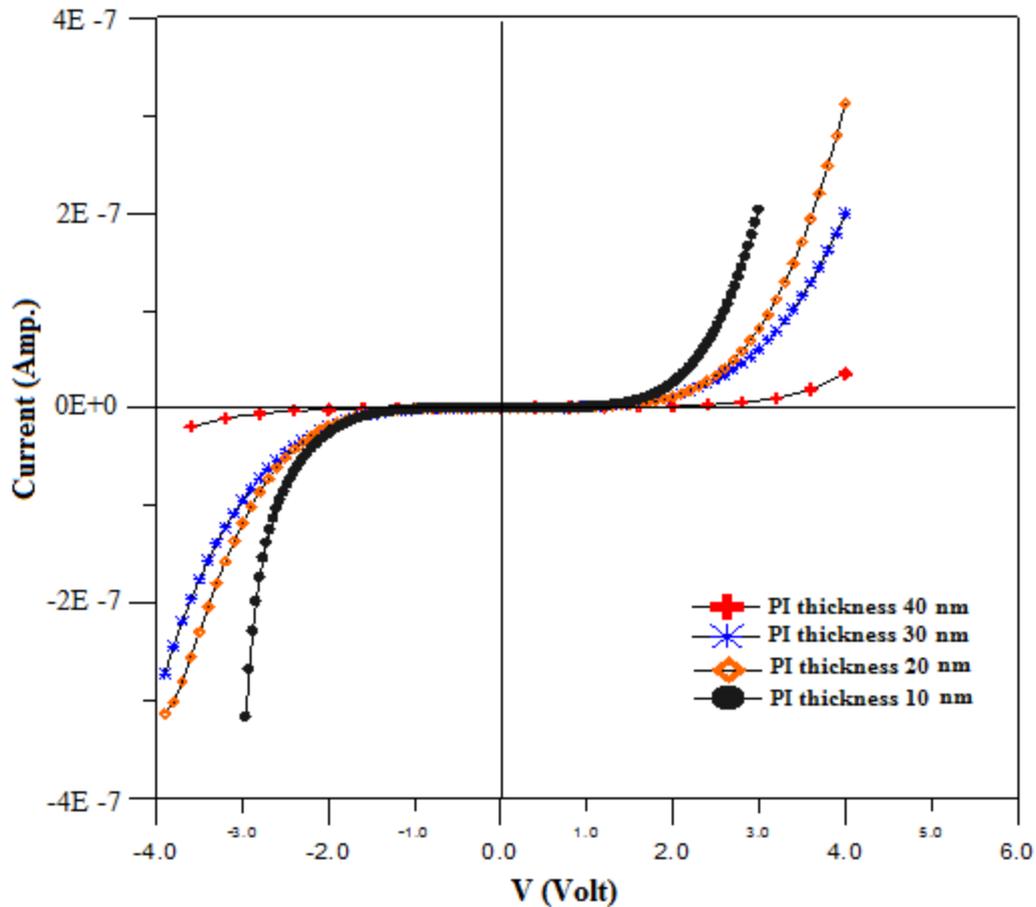


Figure 2-I-V characteristics in the dark for Al/ PI /c-Si at different thicknesses of PI layer (10, 20, 30 and 40 nm).

The resulting C-V characteristics are shown in Figure- 3. When a large positive bias is applied to the metal gate, electrons are pushed back to the silicon surface [12]. The silicon then behaves much like a metal and the capacitance measured is that of the PI layer alone. This is denoted as an accumulation case, which is consistent with the observations of Hatta *iet al.*[13]. When a small positive bias is applied to the metal gate, electrons are repelled and a region depleted of majority carriers is formed at the silicon surface. The depletion region adds to the width of the dielectric polymer and the measured capacitance begins to drop [10, 11].

Table 1-Values of saturation current density, barrier height and built in potential for Al/ PI /c-Si with different thicknesses of PI layer.

p	Js (Amp./cm ²)	Φ _b (Volt)	V _{bi} (Volt)
10	1.5*10 ⁻⁷	1.2	1.13
20	9.3*10 ⁻⁸	1.45	1.27
30	6.45*10 ⁻⁸	1.62	1.478
40	2.5*10 ⁻⁹	1.85	1.65

Also C-V characteristic curve increases with the increase of the thickness of polyimide film , which is due to the increase in the width of the depletion layer which leads to an increase in the value of built-in potential and a decrement in the capacitance [12].

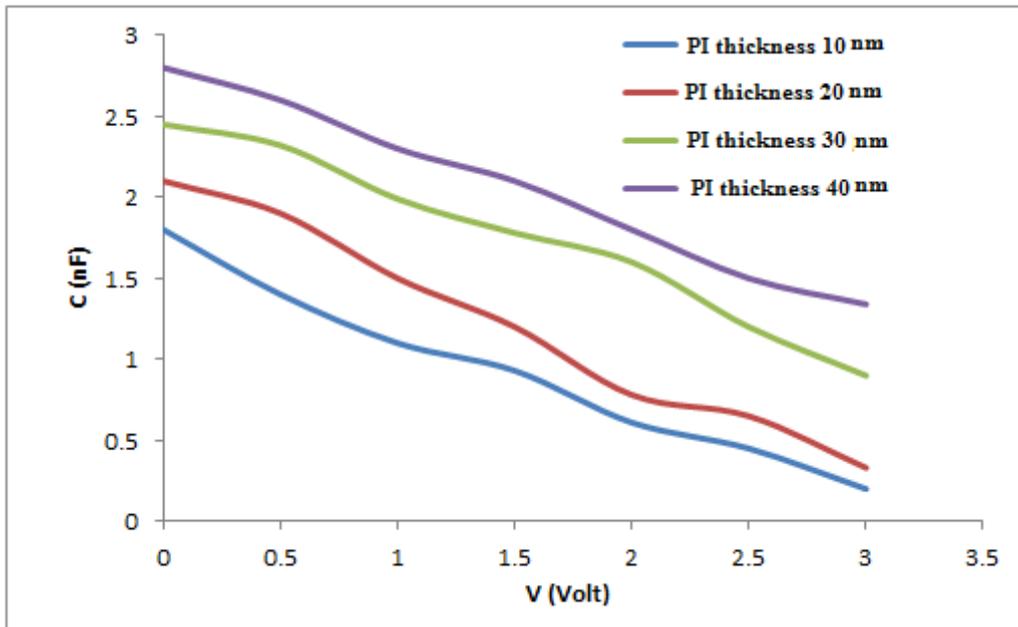


Figure 3-The C-V characteristic curve for Al/ PI /c-Si at different thicknesses of PI layer (10, 20, 30 and 40 nm).

The intersection of the straight line with the voltage axis at $1/C^2=0$ represents V_{bi} , as given in Fig.4 and Table-1. V_{bi} value increases with increasing the thickness of PI film, because of an increase in the defect concentration as a result of a mismatch between the two materials. These defects act as recombination centers that extinguish charge carriers, which lead to decreasing the width of the depletion region [12, 13].

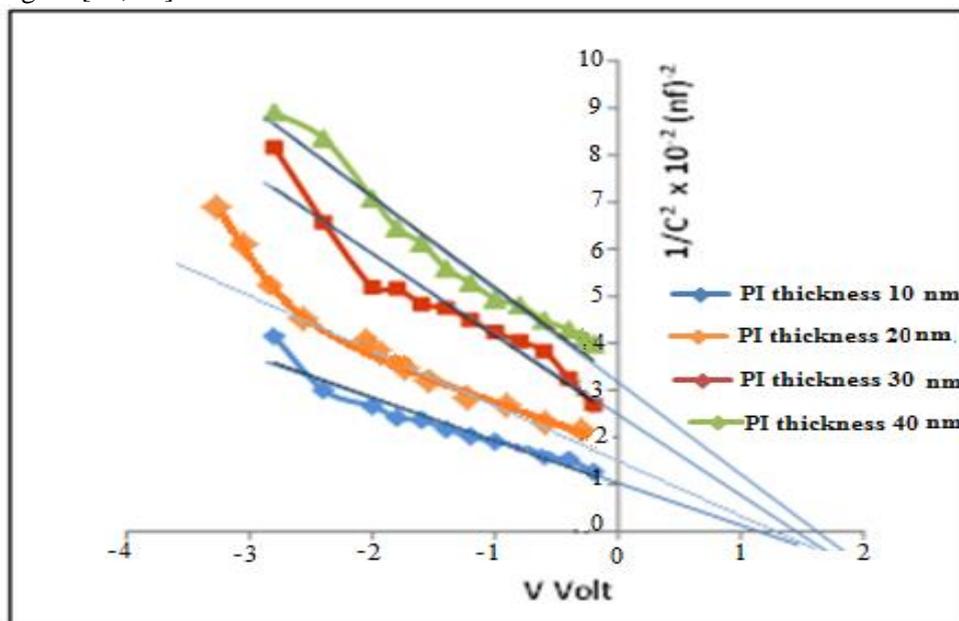


Figure 4-The inverse-square capacitance ($1/C^2$) - applied bias voltage (V) curve for Al/ PI /c-Si at different thickness of PI layer (10, 20, 30 and 40 nm)

Figure-5 shows the thermal stability of Al/ PI /c-Si at different thicknesses of PI layer.

A small amount of weight loss can be observed in the initial stage, which may be due to the residual water and evaporation of solution during heating [8].

As shown in Figure-5 and Table-2, the values of decomposition temperature for 5% weight loss (T_5), the decomposition temperature at 10 % weight loss (T_{10}), and the glass transition temperature (T_g) were measured from the PI film with different thicknesses.

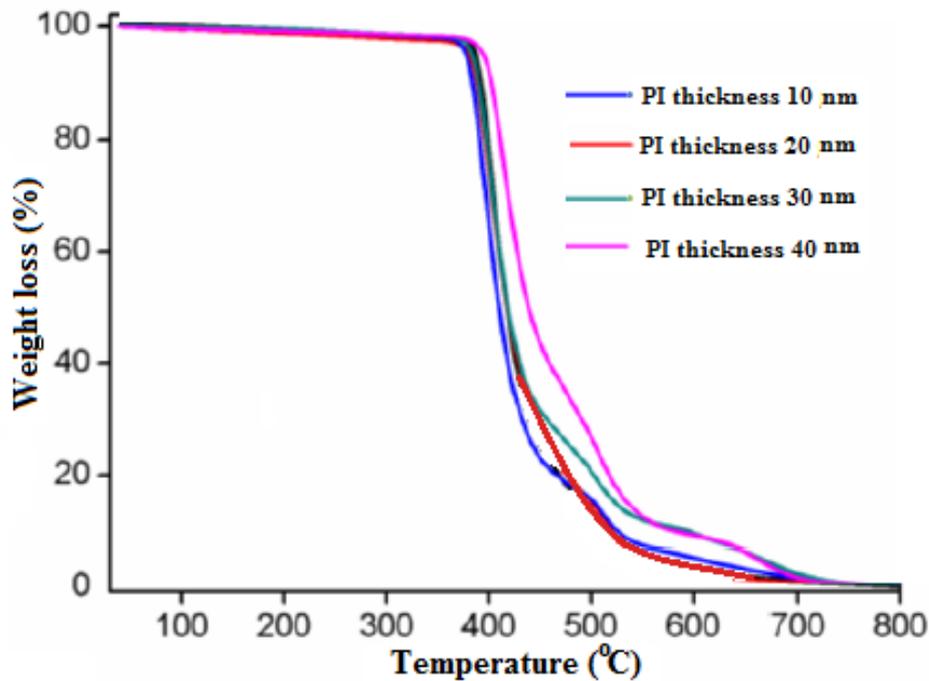


Figure-5 TGA curves for Al/ PI /c-Si with different thicknesses of PI layer (10, 20, 30 and 40) nm.

It was observed that the decomposition temperature (T_5 , T_{10} and T_g) of the PI was increased by about 38, 35 and 40 °C, respectively, when the thickness of PI film was increased. This behavior is due to the increase of the number of imide bonds and the decrease of average distance between imide groups which enhances the intermolecular interaction [14, 15].

Meantime, the incorporation of rigid bipyridine units into the polymer backbone can be also attributed to the high T_g and excellent thermal stability.

Table 2-Thermal analysis data of Al/ PI /c-Si at different thicknesses of PI

Thickness of PI (nm)	T_g [°C]	T_5 [°C]	T_{10} [°C]
10	256	365	373
20	276	381	389
30	283	390	398
40	297	403	412

Conclusions

This research investigated the effectiveness of using different thicknesses of PI interfacial layer in order to improve electrical and thermal properties of Al/ PI /c-Si capacitor. The results of the electrical parameters of the capacitor (J_s , Φ_b , V_{bi}) were obtained by using I-V for the forward and reverse cases and on the C-V measurements at room temperature.

The I-V characteristic curve indicated that the non-ohmic conduction mechanism in nature is caused by thermionic and diffusion mechanisms.

The results also indicated that the PI interfacial layers are more effective on the conduction mechanisms. The electrical characteristics which must be taken into account in the relevant applications were also clarified.

The decomposition temperature (T_5 , T_{10} and T_g) of the PI was increased by about 38, 35 and 40 °C, respectively, when the thickness of PI film was increased. The use of PI interface layer can be lead to an improved thermal stability of this structure.

References

1. Tu, L. W., P. H. Tsao, K. H. Lee, Ikai Lo, S. J. Bai, C. C. Wu, K. Y. Hsieh and J. K. Sheu. **2001**. Polymer PBT /n- GaN metal–insulator–semiconductor structure. *Appl. Phys. Lett.* **79**: 4589-4591. doi:10.1063/1.1429297
2. Manda P. K., L. Karunakaran, S. Thirumala, A. Chakravorty and S. Dutta. **2019**. Modeling of Organic Metal-Insulator-Semiconductor Capacitor. *IEEE Trans. Electron Devices.* **66**: 3967-3972. doi:10.1109/TED.2019.2927535.
3. Abdul-Rassol H. K. and Abdul-Hussein A. M. **2017**. Manufacture of Graphene-based Supercapacitors. *Iraqi J. Sci.* **58**: 1829-1838.
4. Ahmed H. M. and Aziz S. B. **2009**. Structure, AC conductivity and power loss in PVC and PMMA polymers. *Iraqi J. Sci.* **50**: 3349-3354.
5. Al-Rehamey H. J., Al-Hilli M. F. and Rasheed H. Kh. **2015**. Effect of thickness on some physical properties of α -Fe₂O₃ thin films prepared by PLD. *Iraqi J. Sci.* **56**: 417-423.
6. Peng X., W. Xu, L. Chen, Y. Ding, Sh. Chen, X. Wang and H. Hou. **2016**. Polyimide Complexes with High Dielectric Performance: Toward Polymer Film Capacitor Applications. *J. Mater. Chem. C.* **4**: 6452-6456. doi:10.1039/C6TC01304J
7. Hlali S., N. Hizem and A. Caboose. **2017**. Electrical characteristics of metal–insulator–semiconductor and metal–insulator–semiconductor–insulator–metal capacitors under different high-k gate dielectrics investigated in the semi-classical and quantum mechanical models. *Bull. Mater. Sci.* **40**: 67–78. doi:10.1007/s12034-016-1341-5
8. Cheek G. and R. Mertens. **1983**. Metal-Insulator-Semiconductor Silicon Solar. *Solar Cells.* **8**:17-32. doi:10.1016/0379-6787(83)90037-6
9. Uryanarayana D. and K. L. Mittal. **1985**. Effect of Polyimide Thickness on Its Adhesion to Silicon Nitride Substrate with and without Adhesion Promoter, *J. Appl. Polym. Sci.* **30**: 3107-3111. doi:10.1002/app.1985.070300730
10. Peng X., W. Xu, L. Chen, Y. Ding, T. Xiong, Sh. Chen and H. Hou. **2016**. Development of high dielectric polyimides containing bipyridine units for polymer film capacitor. *React. Funct. Polym.* **106**: 93-98. doi:10.1016/j.reactfunctpolym.2016.07.017
11. Diahm S., S. Zemat, M. L. Locatelli, S. Dinculescu, M. D. Cup and T. Lebey. **2010**. Dielectric Breakdown of Polyimide Films: Area, Thickness and Temperature Dependence. *IEEE Trans. Dielect. Elect. Insulat.* **17**: 18-27. doi: 10.1109/TDEI.2010.5411997
12. Bala S. **2012**. The Role of Interface State Density in I-V Characteristics of Metal-Semiconductor Contact With Interfacial Layer. *Inter. J. Emerg. Techno. Adv. Eng.* **2**: 364-368. Doi:10.1. 1.414. 4096
13. Tanrikulu E. E., S. Demirezen, Ş. Altındal and İ. Uslu **2017**. Analysis of electrical characteristics and conduction mechanisms in the Al/(%7 Zn-doped PVA)/p-Si (MPS) structure at room temperature. *Mater Sci: Mater Electron.* doi: 10.1007/s10854-017-6613-3
14. Hatta H., Y. Miyagawa, T. Nagase, T. Kobayashi, T. Hamada, S. Murakami, K. Matsukawa and H. Naito. **2018**. Determination of Interface-State Distributions in Polymer-Based Metal-Insulator-Semiconductor Capacitors by Impedance Spectroscopy. *Appl. Sci.* **8**: 1-11. doi: 10.3390/ app 8091 493
15. Yao J., C. Wang, C. Tian, X. Zhao, H. Zhou, D. Wang and C. Chen. **2017**. Highly optical transparency and thermally stable polyimides containing pyridine and phenyl pendant. *Des. Monomers Polym.* **20**: 449-457. doi:10.1080/15685551.2017.1351766