Optical properties of thin films of polyazomethine with triphenylamine unit in the main chain prepared by spin-coating method

M. Palewicz[a,b], A. Iwan[b], J. Doskocz[c], W. Stręk[c], D. Sęk[d]

[a] Institute of Electrical Engineering Fundamentals, Wroclaw University of Technology, 27 Wybrzeze Wyspianskiego Street, 50-370 Wroclaw, Poland
[b] Electrotechnical Institute Division of Electrotechnology and Materials Science, M. Sklodowskiej-Curie 55/61, 50-369 Wroclaw, Poland
[c] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okolna 2, 50-422 Wroclaw, Poland, P.O. Box 1410, 50-950 Wroclaw 2, Poland
[d] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Sklodowska – Curie Street, 41-819 Zabrze, Poland

*Abstract-*Thin films of a polyazomethine (PAZ) were prepared from a chloroform solution by spin-coating technique. The solution of the polymer was spread on microscopic cover glass and quartz under nitrogen atmosphere at room temperature and atmospheric pressure. The optical properties of the PAZ were investigated at room temperature under atmospheric pressure. An absorbance, transmission and reflectance were determined from spectrophotometric measurements. The absorption coefficients and bang gap of films material were developed. Surface structure of the PAZ thin layer was checked by AFM measurements. Thickness of the PAZ thin layer on the glass and quartz were determined with ellipsometer at the range from 150 to 220 nm.

I. INTRODUCTION

Investigation of a new kinds of organic materials for photovoltaic devices were begun because of increasing demand of logging energy. Solar panels produced hitherto on industrial scale are based on inorganic crystals like silicon. However, manufacturing of such devices are still expensive and has negative effect on natural environment. For these reasons an organic materials for photovoltaic devices are investigated. Use of the organic materials are supposed to be very promising in photovoltaic devices because of economic reasons and high demand of a products [1]. One of the first solar cells which could be considered as organic origin was characterized by Tang [2]. A thin-film, two-layer organic photovoltaic cell was fabricated from copper phthalocyanine and a perylene tetracarboxylic derivative [2]. However, no product of conducted research has been used in commercial application.

Among them, much attention is paid to triphenylamine (TPA) derivatives because they are promising candidates for photo- and electro- luminescence materials. TPA is a unique molecule possessing useful function such as redox-activity, fluorescence, and transport of positive charge centers via the radical cation species. Being efficient hole conductors TPA are commonly used us photoconductors. Introduction of azomethine moieties (HC=N) in TPA may lead to new functional materials based on the synergistic effect of both of them. Additionally, polyazomethines are known to display interesting thermal, mechanical, electrical, optical and fiber-forming properties and they are promising materials in optoelectronic and photonic application [3].

PAZ with TPA in the main chain can be used as one of the layers in organic solar cells. The aim of this article is to describe optical properties and texture of thin layer composed from PAZ by spin–coating method.

II. EXPERIMENTAL

PAZ was prepared from dialdehyde and diamine via high temperature solution polycondensation. Properties of the PAZ were confirmed by elemental analysis, FTIR and ^{1}H, ^{13}C NMR spectroscopy and are described in [4]. Structure of the PAZ is shown in Fig. 1. The absorption spectrum of the PAZ in chloroform solution was characterized by one well defined band at 413 nm being responsible for π-π^* transmission in the imine group. PAZ emitted blue light in chloroform solution with maximum of emission band at 480 nm under 400 nm excitation wavelength [4].

Solution to spread on substratum was prepared from PAZ and chloroform. Quantity of the used polyazomethine in solid state and chloroform was 36 mg and 2 ml, respectively. Dissolution of the PAZ was executed at room temperature.
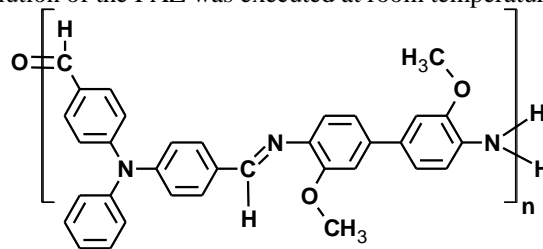

Fig. 1. Chemical structure of the PAZ.

Basis from microscopic cover glass and quartz were situated in ultrasonic washer with deionised water for ten minutes period and then were cleaned in solution of deionised water and 2-propanol (1:1 relation), toluene, lavaged in deionised water and acetone [5].

The thin layers of the PAZ were spread by spin-coating method via drift process on the glass and quartz. To avoid a contamination and defects in thin stratum this process was carried out at room temperature in atmosphere of nitrogen under atmospheric pressure. The values such as rotational speed and time of turn were set on 880 turns per minute by 10 seconds. Two – beam spectrophotometer Cary 5000 was used to measure optical properties of the thin PAZ layer. The absorption (A), transmission (T) and reflectance (R) measurements were performed at room temperature.

Topography of the surface was tested by an atomic force microscope (AFM) in the contact mode. Thickness (d) of the layer was measured using ellipsometer at constant angle.

III. RESULTS AND DISCUSSION

The absorption spectra of the PAZ film on the glass (PAZ/Glass) and on the quartz (PAZ/Quartz) substratum are shown in Fig. 2. Maximum of the absorbance was observed for both samples at 405 nm. Also, on a spectrum related with layer deposited on the glass was noticeable oscillation behavior below 260 nm (See Fig. 2). That phenomenon is related with crystalline structure of basis. Electromagnetic wave in ultraviolet (UV) range was absorbed and converted into phonon oscillation in background of the sample based on the glass, while for light at that length quartz was transparent. To describe dependence of the obtained thin layers form substratum two kinds of them have been used. Besides of the chemical purification quartz was polished. Therefore appropriate prepared basis capacitate to obtained good quality of the thin layer. From the analysis of the absorbance spectrum it was possible to notice the variation of the thickness layer for the glass and quartz, which was confirmed by elipsometric measurements

From transmission (T) and reflectivity (R) measurements an absorption coefficient α is calculated according to the equation (1) given in reference [6,7], where d is film thickness. The typical absorption coefficient plot of the PAZ thin layer on glass and quartz at entire energy scale from 1.2 to 6.0 eV is illustrated in Fig. 3. An increase of the absorption coefficient α was observed on plot from energy value equal to 2.5 eV.

$$\alpha = \frac{1}{d} ln\left(\frac{(1-R)^2}{T} \right) \qquad (1)$$

The absorption edge of the PAZ on the glass and on the quartz was observed between 2.5 and 3.0 eV. For semiconductor materials it is possible to calculate an energy gap (E_G) from relation given by formula (2) [8].

$$\alpha \cdot E = A(E - E_G)^r \qquad (2)$$

Where α is absorption coefficient, A is parameter independent of photon energy, E, E_G represent photon and band gap energy, respectively. Index r accepts two values 1/2 or 2 connected with direct and indirect band to band transition. Type of the transition in the investigated material is determined by subscript $r = 2$. Such approach leads to equation (3).

$$(\alpha E)^{1/2} = f(E) \qquad (3)$$

Delimitation value of the energy gap (E_G) is determined from linear approximation of equation (3), as is mentioned in [8] for
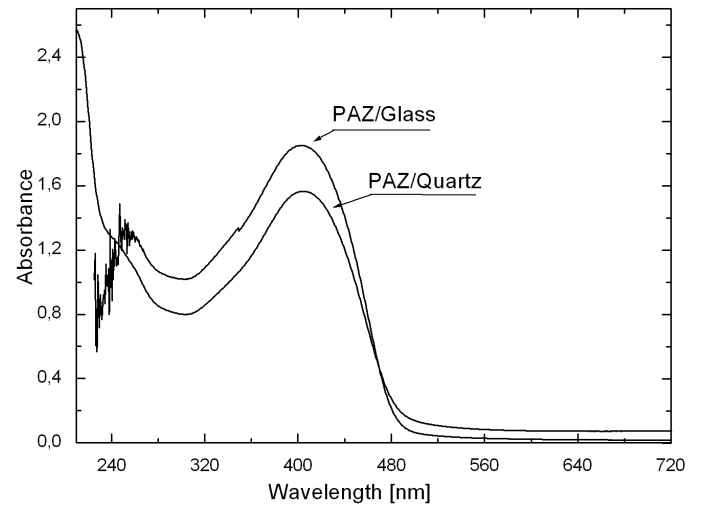
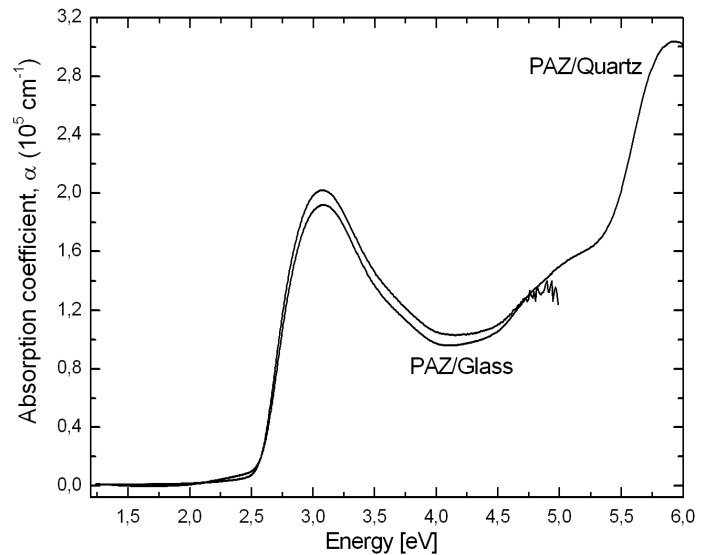Fig. 2. Absorption spectra of the PAZ film coated on the glass and quartz.

Fig. 3. Absorption coefficient of the PAZ thin layer on the glass and quartz.

amorphous semiconductors. The absorption edge of the PAZ thin layer on the glass and quartz is shown in Fig. 4. Value of the energy gap for samples deposition on the glass and quartz is elevated (2.45 ± 0.02 eV).

Energy gap ($E_G = 2.45$ eV) of the polyazomethine film on the glass and quartz are similar. Insignificant changes into value of E_G related with amount of the solvent in solution were observed. Increasing or decreasing of the band gap about 0.01 eV was caused by different concentration of the chloroform.

Characteristic broad and strongest section at the absorption coefficient allocated at about 3.0 eV (Fig. 3) is due to inter-band transition between delocalized states which are related with interaction of π-orbitals in the polyazomethine [9].

Measurements of the PAZ thickness layer on the glass or quartz substratum were performed with ellipsometer equipment working at constant angle. Real refraction coefficients (n) of the glass, quartz and polyazomethine layer were required to conduct a measurements. Real refraction coefficient $n = 1.42$ of the PAZ was estimated from equation (4) [10], where k, R are imaginary refractive and reflection coefficient, respectively.

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}, (k = 0) \qquad (4)$$

Thickness of the thin PAZ layer on the glass and quartz was changing from 150 to 220 nm (Table I). About 50 nm variation of width between the PAZ spread on the glass and quartz were noticed. Difference in thickness of the PAZ films are related with used basis and technological parameters of the spin-coating method.

Atomic force microscope (AFM) was used to describe surface structure of the PAZ. Images of the PAZ on the glass and quartz are represented in Fig. 5. Relatively homogenous and smooth surface for the PAZ coated on the glass and quartz
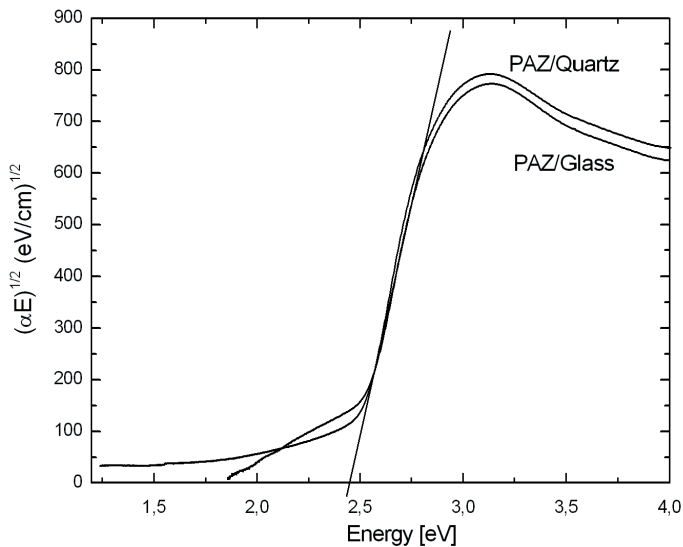

Fig. 4. Absorption edge of the PAZ thin layer on the glass and quartz.

Code	Thickness of layer, d [nm]				
PAZ/Glass	200	218	203	208	211
PAZ/Quartz	155	162	155	157	154

films was observed by AFM. Characteristic granulation is typical for the polymers thin layers and also agglomerates are visible in Fig. 5. Scale of the granulated polymers concentration are related with a porosity of the substratum and technological parameters implemented to spin-coater equipment.
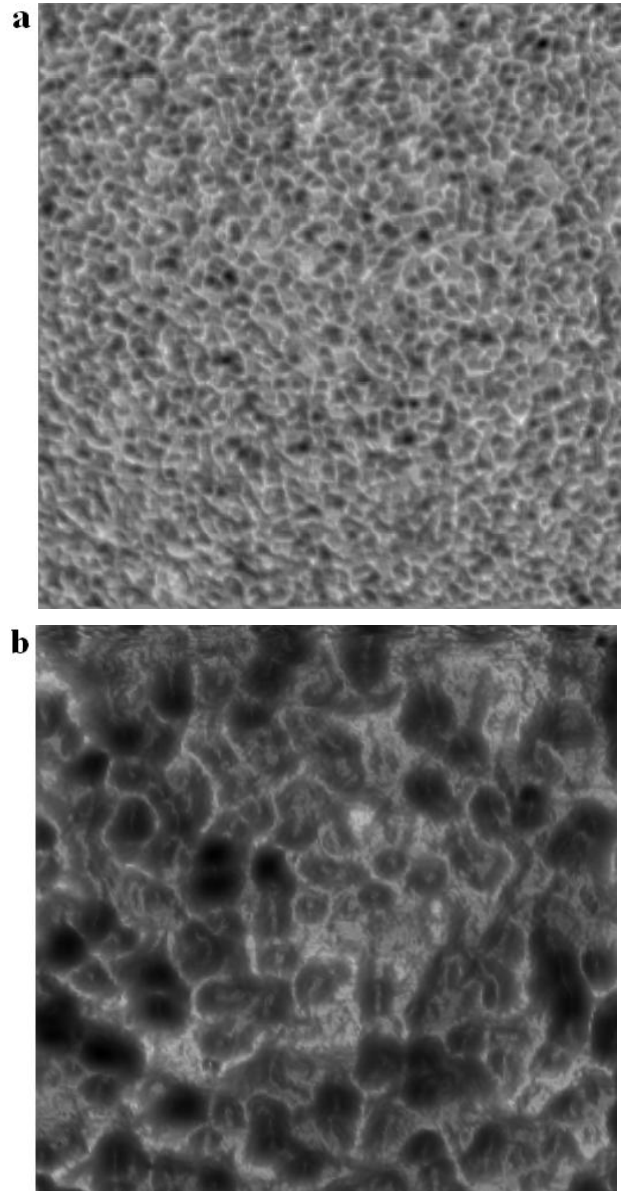

Fig. 5. AFM images (5 x 5 μm^2) of the a) PAZ/Glass and b) PAZ/Quartz.

IV. CONCLUSION

Spin-coating method appeared to be an effective tool to prepare good quality of the polyazomethine (PAZ) thin layer. Optical properties such like the energy gap was obtained in typical way for the amorphous semiconductors. The technological parameters have influence on the energy gap, thickness and surface structure of the investigated polyazomethine. Presented results seem to be helpful to better understanding of the physical properties of that polyazomethine. It can be concluded that the investigated polyazomethine is an amorphous semiconductor with the wide energy gap. Therefore such polyazomethine with the TPA in the main chain could be used to produce photovoltaic devices.

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