Optical properties of polyimide layers prepared by vacuum deposition in the presence of gas

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Abstract. Thin polyimide (PI) layers were prepared by simultaneous vacuum evaporation of the polyimide precursors pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). After deposition the layers were thermally treated 1 hour at 170°C followed by 1 hour at 250°C. Precursors were deposited in a residual atmosphere of different gases - argon, nitrogen, helium and air at a pressure \( 10^{-2} \) Pa. Conditions for fabrication of PI layers with reproducible composition, uniform and smooth surface, without mechanical and chemical defects have been established. It was found that the preparation conditions do not significantly affect the optical properties of the layers. The PI layers before and after thermal treatments are transparent over 85% in the studied spectral range (from 350 to 900 nm). The thermal treatment leads to a bathochromic shift, in a consequence of the transmission edge shift to the longer wavelengths, for all the samples, independently of the deposition conditions in the vacuum chamber. The average refractive indices at 633 nm varied from 1.67 towards 1.72 depending on the deposition conditions and thermal treatment.

1. Introduction

In the last few years, the interest in the field of thin organic layers has grown dramatically due to their successful application in optical and electronic devices, such as light emitting diodes or field effect transistors [1]. Organic and polymer thin layers will play a pivotal role in the development of next-generation electronic devices, passivation coatings, and chemical and biological sensors. The superior dielectric and thermal performances of polyimides (PI) have led to their widespread use for electronic applications (as an insulator, barrier layer or capsulation layer) [2-6]. PI layers are used in photovoltaic (PV) cells due to its dielectric properties, but also have requirements for their optical properties [7]. Polymide-based materials are expected to have potential applications in the field of organic optical waveguides [8]. PI layers are conventionally prepared from polyamic acid solution (the precursor of PI) [9, 10] by coating on a substrate and transformation to PI through thermal or chemical dehydration. One of the used methods for PI layer preparation is physical vapour deposition (PVD) of precursors, like diamines and dianhydriedes [11] followed by a thermal treatment.

It is known that there is a relationship between the conditions of preparation and structure of the layers on the one hand, and their structure and physical and chemical properties on the other. Our previous studies have shown that the introduction of gas into a vacuum chamber leads to a change in micro-mechanical and electrical properties of polyimide layers [12]. FTIR spectroscopy summarized that presence of an inert gas (regardless of its type) results in an increase of the degree of imidization [12]. The layer produced in nitrogen atmosphere is with the
highest degree of imidization. The degree of imidization decreases around 10% for layers produced in the presence of air compared with the layers produced in the presence of nitrogen [12].

The aim of this study is to investigate the optical properties of thin PI layers, obtained by PVD depending on the residual gas in the vacuum chamber – helium, argon, nitrogen and air. The results obtained could lead to a better understanding of the relationship between preparation conditions, structure, and optical properties of thin PI layers.

2. Experimental

2.1. Sample preparation

The vacuum deposited polyimide (VDP) layers with thicknesses of 300 nm and 1000 nm were prepared on soda-lime-glass plates. The vacuum chamber was evacuated by oil diffusion pump to a pressure of < 7x10^{-4} Pa. The precursors used pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA), were evaporated from two independent thermally-heated Knudsen type evaporation sources and deposition rates from 0.2 to 2 A/sec, the latter being carefully controlled by quartz oscillators. Thus, the optimal ratio in the flux of 1:1 for the ODA:PMDA vapours was ensured [13]. The process of maintenance of a definite permanent residual pressure of the inert gas in the vacuum chamber was performed by the introduction of the corresponding gas by a mass flow controller which is computer-controlled via information obtained from the vacuum meter. The precursors condensed on the substrates in the presence of gas atmosphere at vacuum 10^{-3} and 10^{-2} Pa. Thus the mixed (precursors-gas) layers were built-up. The co-deposited precursor layers were transformed into PI layers by a two-step thermal treatment at strictly controlled temperatures (1 hour at 170°C followed by 1 hour at 250°C). The goal of the thermal treatment is to accelerate the polycondensation solid state reaction between the monomers, leading to the PI formation [6].

2.2. Methods of investigation

Thickness of the PI layers was measured using profilometer Talystep.

Surface structure and morphology of vacuum deposited PI layers was examined with a scanning electron microscope (SEM) Philips 515 mode secondary electron image (SEI). To increase the contrast of the image, the sample surface was tilted relative to the primary electron beam. The angle between the normal of the sample surface and the direction of the scanning beam was altered from 0 to 40 °.

UV-Vis spectra of PI layers deposited in presence of different gas before and after thermal treatment were investigated by UV-Vis-NIR spectrophotometer Cary. The refractive index values of the different layers were determined by Swanepoel method [14] through a program developed in our institute by Konstantinov and associates [15].

3. Results

By means of SEM the surface morphology of the layers deposited in presence of different gas has been investigated. Figure 1 presents the surface morphology of PI layer deposited in an atmosphere without gas and vacuum with pressure (p) of 10^{4} Pa. In figure 2 the surface morphology on PI layer obtained in a residual of gas He with p ~ 10^{2} Pa is presented. The PI layers deposited by varying residual gas atmosphere (air, argon, nitrogen) have similar surface morphology.

Figures 1 and 2 show, that thin PI layers remain homogeneous, devoid of micro-cracks and defects independently of the residual gas. The surface of the PI layers is smooth, without noticeable peculiar defects or granular structure. Therefore it can be concluded that there was no influence of the different gas atmosphere on the surface morphology of the different samples.

Figures 3 and 4 present the cross section of the above PI layers - deposited in an atmosphere without presence of gas in the vacuum chamber and in a residual of gas helium, respectively.

As seen in the both pictures, without gas (vacuum 10^{4} Pa) and in the presence of helium, the observed growth of the columns from the substrate to the surface, determines the presence of free volume in the layers.
The layers obtained in an atmosphere of helium introduced in the vacuum chamber have narrower columns. The layers are built up of fine grain structure compared to the layer deposited in an atmosphere without gas.

Figures 5 and 6 show UV-Vis spectra of PI layers deposited in presence of different gases before and after thermal treatment, respectively. As seen after the thermal treatment all spectra are displaced to a long wavelength region. The effect of bathochromic shift, as well as the colorization of PI layers are due to the charge transfer complexes that occur between the donor and acceptor units in the polyimide chain [16]. The color of the samples changes from colorless before thermal treatment, to light brown – after treatment for 1 h at 170 °C and 1 h at 250 °C.

The layers possess a high transmission (>80%) in the range of 440–900 nm. Our experiments show that the shape of the curves and the optical parameter values do not depend on the gas in the vacuum chamber, when the PI layer is formed.
Figure 5. Optical spectra of PI layers deposited in presence of different gas in the vacuum chamber before thermal treatment.

Figure 6. Optical spectra of PI layers deposited in presence of different gas in the vacuum chamber after thermal treatment.

Figure 7 shows the refractive index distribution of PI layers deposited in the presence of different gases after thermal treatment and figure 8 shows the diagram of refractive index values depending on the residual gas.

Figure 7. Refractive index distribution of PI layers deposited in presence of different gas in the vacuum chamber.

Figure 8. Diagram of the refractive index values of PI layers depending on the residual gas in the vacuum chamber.

The results obtained have shown that there is a small difference in the refractive index value of the different layers with the exception of these obtained in the residual atmosphere of helium. The other layers have refractive index values comparable to that of the layer deposited in an atmosphere without gas and vacuum with pressure of $10^{-4}$ Pa.

4. Conclusion
The study was associated with the possibility of modifying the properties of a thin vacuum deposited PI layers by varying the conditions of their preparation. The surface of the PI layers is smooth, without
noticeable peculiar defects or granular structure. There was no influence of the different gas atmosphere on the surface morphology of the different samples. The PI layers display a high transmission (>80%) in the studied range independently of the residual gas. The most significant changes in the refractive index values were found for polyimide layers obtained in the presence of helium atmosphere. The optical properties of these VDP PI layers make them suitable for various applications in the photovoltaic industry or in the field of organic optical waveguides.

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