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REFLECTANCE STUDIES OF POLYAZOMETHINE THIN FILMS

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Abstract. The results of study of the total, diffuse and specular reflectance of polyazomethine thin films deposited on various substrates are reported. The main optical parameters, i.e the energy loss function, absorption, and scatter refraction coefficient were determined, and the values of rms roughness were found using AFM, Talysurf profilometer and integrating sphere. It appears that the films studied are characterized by a small rms roughness (4–7 nm), and the main reason of light scattering in this material is the volume scattering by crystalline centers inside the films, being essentially amorphous. It has been also found that, apart from a strong absorption in the range 350–500 nm, a strong Rayleigh scattering occurs above 600 nm.

1. INTRODUCTION

Polyazomethine thin films are promising materials to obtain organic (light-emitting diodes) (LEDs) [1,2]. In this work, we present one of polyazomethines, namely poly(1,4-phenylenemethilidenenitrolo-1,4-phenylenenitrilomethilidene) (PPM) which has been obtained by polycondensation of two components, terephtaldehyde (TPA) and para-phenylene diamine (PPDA) using the chemical vapor deposition (CVD) method with pure Ar as a transport agent [3]. Thin films of PPM were deposited on fused silica, BK7 glass and crystalline Si.

For a proper characterization of PPM films, the thickness of films, surface roughness and optical parameters (i.e refraction and absorption coefficients) should be known. Those parameters strongly depend on the technology of film deposition. Also the quantum efficiency strongly depends on thickness of the films (usually in the 50-500 nm range). In the first step, we have tried to find the optical and geometrical parameters using a multiangle-one-wavelength ellipsometer of Sentech 400E, but measured values were strongly unreliable. Usually, ellipsometry gives good results for parallelly sided, smooth layers with root mean square (rms) roughness much less than the wavelength of illuminating beam.

It appears that in PPM layers obtained by polycondensation method, the main role in optical losses play the scattering and absorption processes. The optical losses L of a single layer follows from absorption a and light scaterring s in the film:

$$L = a + s. \quad (1)$$

The losses of single layers can be calculated from reflectance R and transmittance T using the following equation:

$$R + T + L = 1. \quad (2)$$

The scattering of light originates from roughness of the surface layers, as well as from the volume scattering caused by small particles concentrated

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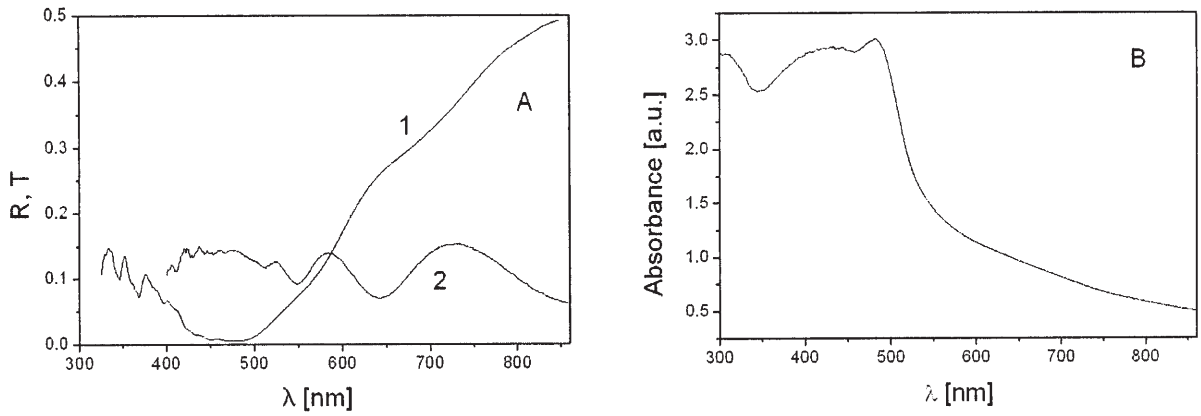

Fig. 1. The spectra of reflectance and transmittance (A) and loss function (B) for the 220 nm thin PPM film on fused sillica substrate.

in the medium layer. The factor *s* in Eq. (1) is therefore a sum:

$$s = s_s + s_v, \quad (3)$$

with s_s and s_v describing the surface and volume scattering, respectively.

The goal of our measurements was finding reliable optical parameters using spectrophotometric devices described below. PPM films on glass or Si substrates exhibit various proportions of amorphicity and crystallinity, depending on the deposition condition. The crystallinity of PPM films may be high enough, reaching even 40% [4]. As a result of crystallization, big spherical structures (spherolites) are created in PPM films, being responsible for the volume scattering of light.

2. EXPERIMENTAL

The specular reflectance and transmittance measurements were performed by means of a reflection probe R200-7. This probe consists of a bundle of 7 optical fibres, 6 illumination fibres around one 'read fiber' (which reads the reflected light), each with a diameter of 200 μm. The probe is coupled by a read fiber to a miniature optic spectrometer PC 2000 and by an illumination fiber to a tungsten lamp as a light source. The light reflected from sample illuminated by 6 fibers, reaches the spectrophotometer input, then it is dispersed via fixed grating across a CCD linear detector which is responsive in the range 400-860 nm. The thicknesses of films are measured by means of the Talystep Hobson profilometer.

Fig 1. shows reflectance, transmittance and loss function for a PPM film with thickness of 220 nm versus wavelength of light in range 300-860 nm. In the reflectance spectra, the interference maxima and minima are observed, while in the transmittance spectrum, the extrema do not appear. Using the SCOUT2 program, we have determined an average refraction coefficient as being equal to n = 1.78. By means of the Topometrix atomic force microscope (AFM) we studied the surface relief of PPM samples. The surface roughness (rms) has been determined for an area of 2.5 μm x 2.5 μm. The values of rms roughness for three samples are very similar, i.e 5.6, 5.2 and 4.9 nm. In the first approximation, the relation between surface scattering coefficient s_s and rms roughness is [5]

$$s_s = \frac{I_{spec}}{I_0}\left[-\frac{(4\pi\sigma)^2}{\lambda^2}\right], \quad (4)$$

where I_{spec} and I_0 are specular and incident intensity of the light, respectively, σ is the rms surface roughness and λ is the wavelength of illuminating light.

The contribution of surface scattering to the loss function appears to be very small because λ >> σ. Therefore for further studies of optical properties of PPM, we used a goniometer yielding the angular dependence of the scattered light. Fig. 2. shows such a dependence for a PPM film and, for comparison, for a polyvinylocarbazole (PVK) film. Despite of very similar relief of roughness for both films, curves from Fig. 2 are very different. Therefore, one may conclude that the main part of light scattering in the PPM film comes from the volume scattering.

We have also measured total and diffuse reflectances using a complementary reflection method, applying a single-beam sphere technique

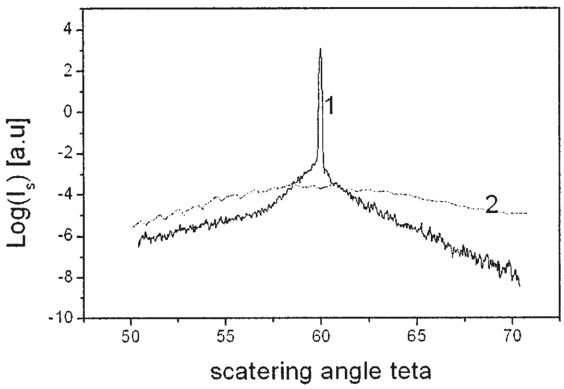

Fig. 2. Dependence of intensity of scattered light on the scattering angle for two surfaces with very similar rms roughness 1 – PVK film with σ = 6.7 nm, 2 – PPM film with σ = 5.6 nm.

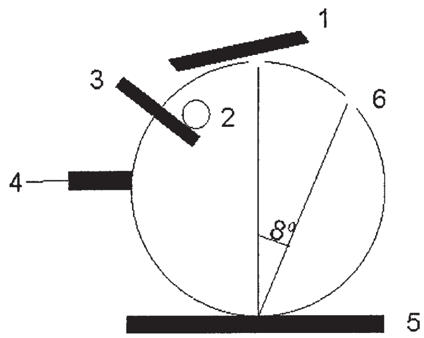

Fig. 3. Scheme of integrating sphere of *d*/0° type. 1 – light trap, total (switch on) and diffuse (swich off) reflectance, 2 – light source, 3 – trap for diffuse illumination, 4 – reference fiber, 5 – sample or reference.

with an OOI ISP-REF integrating sphere [6] of a diameter of 60 mm with a built-in tungsten-halogen lamp as a light source. In this arrangement, sample is illuminated with diffuse light. The reflected light signal is then collected under an angle of 8° from the normal (the so-called d/0° geometry). A light trap switch has made it possible to include the specular reflectance (switch on) or only the diffuse reflection (switch off). For the initial reference measurement, a white reference tile WS-2, made from spectralon, is placed on the same port. From the output port, the collected light is transmitted through an optical fiber to a PC-2000 spectrofotometer.

The method used allows one to separate the light intensity reflected from sample in the specular mode from the diffuse part of radiation. This measurement enabling one to derive data to calculate the scattering factor according to Eq. (3). The quantity s_s, being mainly related to the rms roughness, can be neglected to simplify the model. Fig. 3 shows the experimental setup for the reflection measurements in the range 340–860 nm and for the transmittance measurements in the range 200–2500 nm, while Fig. 4 presents the obtained results. It can be seen that the diffuse part, as well as reflection and transmission show long tails in their spectra above 600 nm, disappearing with increasing wavelength of light. This fact suggests a strong Rayleigh scattering (I_{diff} ~ $1/\lambda^4$ in PPM thin films which is also supported by the angular distribution of the scattered light from a PPM sample (see Fig. 2).

3. CONCLUSIONS

The results obtained for PPM films deposited on silicon and fused silica substrates yield new information about scattering of light by this material. It seems that the films studied exhibit a very small rms roughness (4–7 nm), comparable even with that observed for superpolished films of other materials. The main problem, which concerns the PPM layers, is the volume scattering by crystalline centers inside the films. Analysis of angular behavior of scattered light (Fig. 3) and long, disapearing asymptotic tailes in diffuse reflectance and transmittance spectra (Fig. 4) suggest a high Rayleigh scattering for wavelength higher than 600 nm [7]. For shorter wavelengths

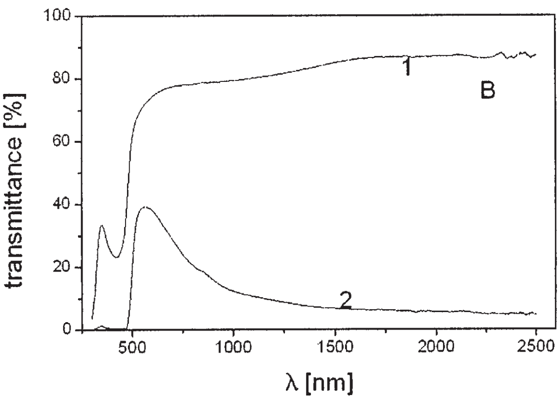

Fig. 4. Total and diffuse refectance (A) and transmitance (B) spectra for the a PPM film on fused silica substrate obtained by means of the integrating sphere.

(350–500 nm), one observes a strong absorption (Figs. 1B and 4B). The main component of the loss function, particularly over 600 nm, is the volume scattering with small absorption and surface scattering. In authors' opinion, the integrating sphere measurements of PPM films give much more reliable results than ellipsometry.

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