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A study of polymeric films modified with SiC nanoparticles

Summary — There were studied optical properties of polymeric films of poly(*N*-vinylcarbazole) (PVK), polycarbonate (PC), polystyrene (PS) and films of these polymers modified with SiC nanoparticles of size between 20 and 30 nm. Thin polymeric films were deposited on glass plates with spin coating method, using polymer solution in tetrahydrofuran (THF). In order to determine optical parameters of these new materials, the reflection spectrum was examined in the range between 350 and 860 nm, using a reflection probe and an integrating sphere. In order to determine the thickness of examined films, ellipsometric measurements were performed. The examination demonstrated that a small content of SiC nanoparticles in polymers changes the refractive index of the sample without causing its optical heterogeneity. But an increasing content of nanoparticles causes their aggregation, which strengthens light diffusion.
Key words: thin polymeric films, SiC nanoparticles, nanoparticle-modified polymers, optical properties.

BADANIE CIENKICH WARSTW POLIMEROWYCH MODYFIKOWANYCH NANOCZĄSTKAMI SiC

Streszczenie — Badano właściwości optyczne cienkich warstw polimerowych poli(*N*-winylokarbazolu) (PVK), poliwęglanu (PC) oraz polistyrenu (PS) oraz warstw tych polimerów modyfikowanych nanocząstkami SiC o wymiarach rzędu 20—30 nm. Cienkie warstwy polimerów nanoszono na płytki szklane metodą powlekania wirowego stosując roztwór polimeru w tetrahydrofuranie (THF). Do wyznaczenia parametrów optycznych tych nowych materiałów przeprowadzono badania widm odbicia w zakresie 350—860 nm z użyciem sondy odbiciowej i sfery integrującej. W celu wyznaczenia grubości badanych warstw, wykonano pomiary elipsometryczne. Badania wykazały, że niewielka zawartość nanocząstek SiC w polimerach zmienia współczynnik załamania światła próbki, nie powodując przy tym optycznej niejednorodności (tabela 1, rys. 1 i 2). Jednak zwiększanie zawartości nanocząstek powoduje ich agregację, co skutkuje wzmocnieniem rozpraszania światła (rys. 3 i 4).
Słowa kluczowe: cienkie warstwy polimerowe, nanocząstki SiC, polimery modyfikowane nanocząstkami, właściwości optyczne.

Thin polymeric films are promising materials for production of light-emitting diodes (LEDs) and photovoltaic cells [1, 2], as they combine the photoelectrical properties of semiconductors with the large scale and low cost technology of polymers. Among others, poly(*N*-vinylcarbazole) (PVK) or its modifications [3—5] have been frequently used for fabrication of high quantum efficiency LEDs and photovoltaic cells with the indium tin oxide (ITO) transparent electrode. It also appears that addition of SiC in the form of nanopowder to photoactive PVK causes a further increase of quantum efficiency of photovoltaic conversion [6] and physics of ITO/polymer+SiC photoactive devices is based on photo-induced charge transfer from a donor-type semiconducting conjugated polymer to an acceptor-type nanoparticle [7].

This work concerns optical reflectance studies of thin polymeric films modified with SiC nanoparticles and fabricated with the spin coating technique. The goal of these investigations is to determine the refractive index dispersion, which is very important to future applications of these new materials.

DISPERSION OF REFRACTIVE INDEX

Local magnitudes of reflection coefficients R_1 and R_2 describing reflections from upper and bottom thin film interfaces can be presented in terms of the spectral reflectance envelopes as [8]:

$$R_1^{1/2} = \frac{1+(E_{R+}E_{R-})^{1/2}-[(1-E_{R+})(1-E_{R-})]^{1/2}}{(E_{R+})^{1/2}+(E_{R-})^{1/2}} \quad (1)$$

$$R_2^{1/2} = \frac{1-(E_{R+}E_{R-})^{1/2}-[(1-E_{R+})(1-E_{R-})]^{1/2}}{(E_{R+})^{1/2}-(E_{R-})^{1/2}} \quad (2)$$

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where E_{R+}, E_{R-} — spectral reflectance envelopes for reflectance maximum ($R+$) and minimum ($R-$), respectively.

If a film is transparent, R_1 and R_2 can be expressed as functions of the refractive indices n_i of upper and bottom interfaces ($i = 1, 2$):

$$R_i = \left| \frac{n_{i-1} - n_i}{n_{i-1} + n_i} \right| \quad (3)$$

From formulas (1), (2) and (3), the refractive index dispersion can be obtained.

EXPERIMENTAL

Materials

The optical studies have been performed for layered structures involving three types of polymers, *i.e.* poly(*N*-vinylcarbazole) (PVK), polycarbonate (PC) and polystyrene (PS) with averaged molecular weights $\overline{M}_w$ of 6400, 20 200 and 50 000 respectively (all purchased at Sigma-Aldrich). As a polymer solvent, tetrahydrofuran (THF) with purity ≥ 99.9 % (also from Sigma-Aldrich) has been used.

The SiC nanopowder was synthesized by laser pyrolysis of silane (SiH_4) and acetylene (C_2H_2) using the experimental set-up described elsewhere [9]. During the synthesis, the ratio between the gaseous precursors [SiH_4]/[CH_2] monitors the nanoparticle stoichiometry (C/Si ratio) which is manifested mainly at the nanocrystallites (nc) boundaries [10]. The present experiments deal with large-sized SiC nanoparticles (20—30 nm) synthesized with a silicon excess. Their annealing at 1400 °C under the inert gas atmosphere improves the crystalline order [11].

As substrates for the polymer and polymer+SiC thin film deposition, we have used glass BK7 and finely polished Si wafers.

Sample preparation

For the thin film preparation, the SiC nanopowder was inserted into the polymer solution in THF and then deposited on substrates with spin coating method at 1000 rpm. The layers were poured out from solutions with 10 mg/cm^3 polymer concentration. Two SiC-polymer solid solutions with the weight ratios 1:30 or 1:10 were used for preparation of PVK, PS and PC layers modified with SiC nanoparticles. It corresponds to 3.3 and 10 wt. % of SiC content, respectively. Before spilling, the solutions were mixed with an ultrasonic probe. The final lateral dimensions of samples were 15 × 15 mm.

Methods of testing

As for the optical studies, first the thickness of the polymer+SiC films has been determined with a one-wavelength (633 nm) null ellipsometer EL-86. The ellipsometry [12] determines two angles Ψ and Δ. Ψ angle is defined by the equation:

$$\tan \Psi = |r_p|^2 / |r_s|^2 \quad (4)$$

where: r_p, r_s — *complex Fresnel reflection indices for 'p' and 's' polarizations, respectively.*

Δ is a phase shift between both polarized waves. Both angles satisfy the equation:

$$r_p / r_s = \exp(i\Delta) \cdot \tan \Psi \quad (5)$$

allowing to determine the refractive index (n), extinction index (k) and the layer thickness (w). The determined thicknesses of layers are in the range 200—300 nm and the refractive index found for 633 nm has been subsequently used as a starting parameter for determining the spectral dispersion.

The specular reflectance measurements were performed by means of a reflection probe R200-7 [13]. This probe consists of a bundle of 7 optical fibers, 6 illumination fibers around a single "read fiber" (which read reflected light), each 200 μm in diameter. The probe is coupled with a read fiber to a miniature fiber optic spectrometer PC 2000 and with illumination fibers to a tungsten lamp as a light source. The light reflected from the 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.

We have also measured the diffuse reflectance using an ISP—REF Avantes Co. integrating sphere [14]. The sphere 60 mm in diameter has a build-in tungsten-halogen lamp as a light source (type 0°/d). Applying the single-beam technique, one can measure the total and diffuse reflectances in the range 400—1100 nm. As a reference we have used the white standard Spectralon®.

RESULTS AND DISCUSSION

The refractive indices obtained from ellipsometric measurements for polymer layers of PVK, PC and PS without and with 10 wt. % of SiC nanoparticles are shown in Table 1. It can be seen that polymer films containing SiC nanoparticles have higher refractive indices than pure polymers.

T a b l e 1. Refractive indices (n) at 633 nm of the pure polymers and polymers modified with 10 wt. % of SiC

Material	n
PVK	1.82
PVK+SiC	2.16
PC	1.76
PC+SiC	2.12
PS	1.62
PS+SiC	1.95

The SiC nanoparticles embedded in the polymer matrices substantially modify their optical properties. The changes depend on the nanoparticle material, size and

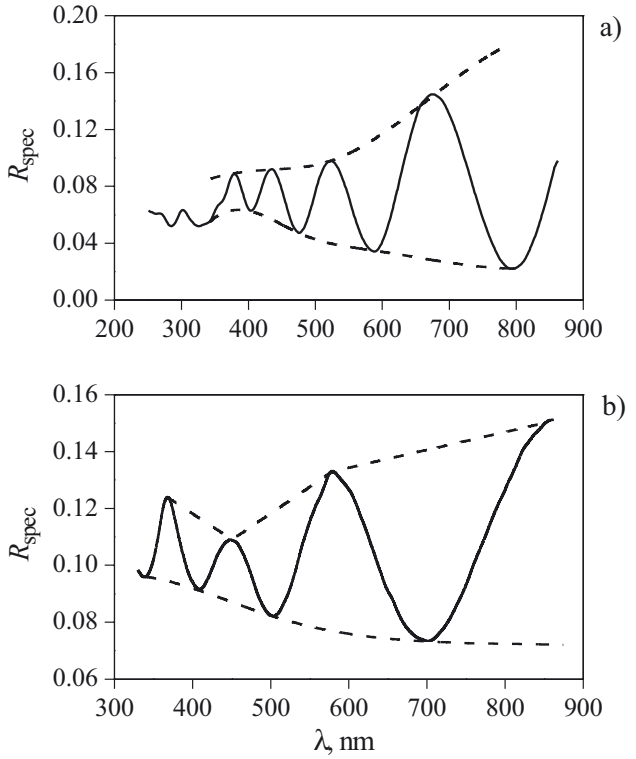

Fig. 1. Specular reflectance (R_{spec}) of polymers modified with 10 wt. % of SiC deposited on glass BK7: a) PVK+SiC, b) PC+SiC; dashed lines show spectral reflectance envelopes

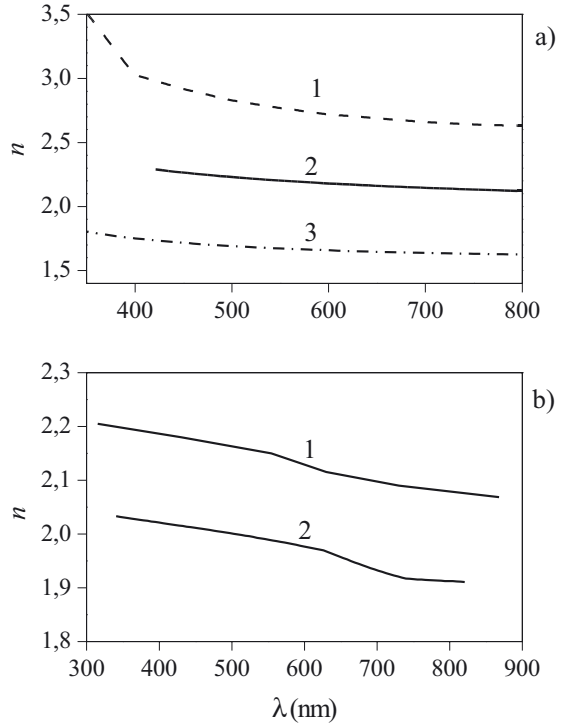

Fig. 2. Dispersion of refractive indices for: a) 1 — SiC, 2 — PVK modified with 10 wt. % of SiC, 3 — PVK; b) 1 — PC modified with 10 wt. % of SiC, 2 — PS modified with 10 wt. % of SiC

aggregation rate. To a good approximation, the refractive index of a modified polymer depends linearly on the inorganic particle concentration (c) [11]:

$$n = n_p(1 - c) + n_i c \tag{6}$$

where: n_p, n_i — *refractive indices of a polymer and particles, respectively*.

Inserting SiC nanoparticles with $n_i > n_p$ into the polymer matrix results in enhancing of the refractive index of the system.

Reflectance spectra measured with R200-7 reflection probe for layers of PVK+SiC (with the thickness d = 330 nm) and PC+SiC (d = 360 nm), deposited on glass BK7, are shown in Figs. 1a and 1b, respectively. These spectra show interference patterns typical of thin film structures enabling to draw the envelopes E_{R+} and E_R for both samples.

Fig. 2 displays the refractive index dispersion calculated for polymer+SiC films from the refractive indices of pure PVK, PC and PS, obtained from spectroscopic ellipsometry [9], and SiC from [12]. For comparison, Fig. 2a shows also the refractive indices of SiC and PVK and it can be seen that the refractive index of PVK+SiC film lies between those of SiC and PVK.

For pure polymers presented in this work the refractive index (n) decreases slowly with wavelength (λ) and this dependence can be described with the Cauchy relation. To the first approximation below the absorption edge this relation is

$$n(\lambda) = n_o + \frac{A}{\lambda^2} \tag{7}$$

where: n_o — *refractive index for long wavelength*, A — *a constant*.

In the visible and near infrared (NIR) ranges the refractive index of SiC and PVK practically obeys this formula and one may suppose that the extinction coefficient is close to zero. However, in PS+SiC and PC+SiC films the refractive index slightly increases with wavelength in the measured range.

Fig. 3 shows the reflection spectra of two PVK+SiC films with different SiC concentrations deposited on crystalline silicon, along with the spectrum of the latter

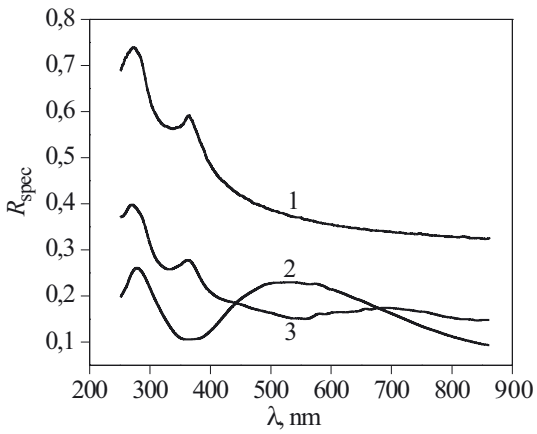

Fig. 3. Specular reflectance (R_{spec}) of PVK+SiC films on Si substrate: 1 — PVK modified with 3.3 wt. % of SiC, 2 — PVK modified with 10 wt. % of SiC, 3 — pure Si

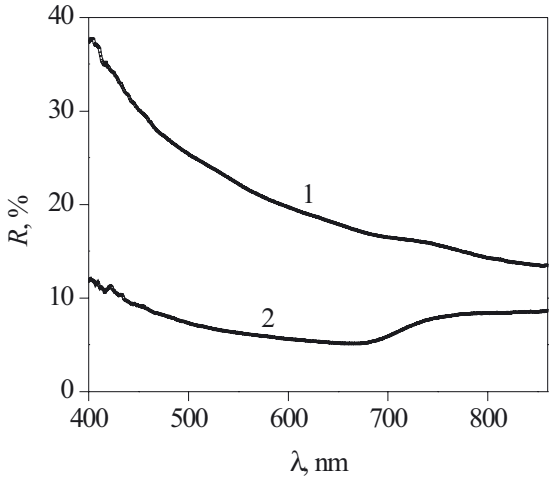

Fig. 4. Diffuse reflectance of PVK+SiC films on Si substrate; description of curves as in Fig. 3

for comparison. As it can be seen in Fig. 3, the reflectivity level and interference extremes weaken with the SiC content. For higher SiC concentrations interference patterns disappear because of increasing light scattering by surface- and volume irregularities.

To learn additional information on quality of PVK+SiC samples with different SiC concentrations, the diffuse reflectance measurements have been performed with a reflection sphere and the appropriate data are shown in Fig. 4. It can be concluded that an increasing SiC nanoparticle content in the PVK matrix results in a gradual loss of the optical uniformity of the materials studied.

CONCLUSIONS

This work demonstrates that SiC inorganic nanoparticles embedded in the polymer matrices, like PVK, PS and PC, form transparent hybrid nanocomposites with high refractive indices (1.9—2.4) in the visible range. It appears that small amounts of nanoparticles modify the effective refractive index of the system without any noticeable optical heterogeneity. On the other hand, an increasing concentration of nanoparticles results in their aggregation, which in turn strengthens the light scattering. These results can allow to project appropriate films in order to enhance efficiency of photovoltaic devices due to the internal reflection phenomena occurring in the films.

ACKNOWLEDGMENT

This work was financially supported by grant F166N-SINGAPORE/2007/0.

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Received 27 III 2008.
Received in revised from 16 XI 2009.