



Broadband and wide angle anti-reflective nanoporous surface on poly (ethylene terephthalate) substrate using a single step plasma etching for applications in flexible electronics

Arvind Kumar^a, Shiva V. Yerva^b, Harish C. Barshilia^{a,*}

^a Nanomaterials Research Laboratory, Surface Engineering Division, CSIR – National Aerospace Laboratories, Bangalore 560017, India

^b Birla Institute of Technology and Science Pilani, Hyderabad Campus 500078, India

ARTICLE INFO

Article history:

Received 9 November 2015

Received in revised form

19 April 2016

Accepted 2 June 2016

Available online 14 June 2016

Keywords:

Plasma etching

Poly (ethylene terephthalate)

Nanoporous surface

Broadband

Anti-reflection

ABSTRACT

Poly (ethylene terephthalate) (PET) substrate is a widely used polymer in the optoelectronics industry, its optical properties, such as light transmittance, haze, etc., are of significant importance in organic light emitting diodes and photovoltaics. In this paper, we present a broadband anti-reflective nanostructure on PET substrate prepared by means of plasma etching in a mixture of argon and oxygen gas. Etching time was varied for optimizing the optical transmittance. Field emission scanning electron microscopy images revealed formation of nanostructures of sub-wavelength dimensions resembling pores at the surface. Atomic force microscopy confirmed that the graded porosity was generated from the randomly distributed pores of different sizes and depths. Due to the formation of a gradient refractive index, nanostructured surface exhibited broadband and quasi-omnidirectional anti-reflection properties. A maximum total transmittance of ~99% at 835 nm was achieved for both sides treated PET without significant increase in light scattering or haze. Moreover, both sides treated PET showed polarization insensitivity upto 48°, which was not exhibited by untreated PET. X-ray photoelectron spectroscopy revealed generation of degradation products, which consisted of carbon and oxygen containing functional groups. Durability of the anti-reflection layer was tested and proved to be satisfactory.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Flexible electronics is a diverse industry, comprising of display devices, organic light emitting diodes (OLEDs), flexible solar cells, printed data storage and recording media, other printed circuits etc. [1,2]. It is one of the most rapidly growing sectors, both scientifically and technologically. The feasibility of these applications is dependent on availability of a low-cost flexible substrate that meets the chemical, mechanical and optical requirements for each of the applications. Poly (ethylene terephthalate) (PET), a polyester, is one of the most commonly used polymer substrates in flexible electronics [3–5].

The importance of having a substrate with high optical transmittance and low reflectance is illustrated by the wide spread use of anti-reflection (AR) coatings on displays, OLEDs, flexible solar cells and other optoelectronic devices [6,7]. AR coatings raise the efficiency of energy harvesting devices such as solar cells by decreasing reflection losses at the air/substrate interface [8–10]. They

increase the amount of light extracted from light emitting diodes [8,11,12], in displays, improve aesthetics by eliminating ghost images [9], increase light output, and reduce flickering due to reflections at the substrate [10,13]. Full realization of benefits of AR is possible only when it occurs throughout the relevant spectral range, consequently, PET substrate with broadband AR properties is of interest. PET substrate shows a transmittance of ~89% due to Fresnel reflection of ~11% at the air/PET interface [7,14]. The reflection at each surface for normal incidence can be calculated from the Fresnel reflection model given by [15]:

$$\left(\frac{n_{\text{PET}} - n_{\text{air}}}{n_{\text{PET}} + n_{\text{air}}} \right)^2 \times 100\% \quad (1)$$

A gradient refractive index at the interface ensures AR properties due to elimination of step discontinuity in refractive index [16]. There are three ways to achieve such AR properties. The first involves fabrication of an anti-reflective layer of thickness $d \sim \lambda/4$ at the surface with refractive index given by the Fresnel equation [6,15,17]:

$$n_{\text{layer}} = (n_{\text{sub}})^{1/2} \quad (2)$$

where the refractive index of air is assumed to be 1, and n_{sub}

* Correspondence to: Nanomaterials Research Laboratory, Surface Engineering Division, CSIR – National Aerospace Laboratories, Bangalore 560017, India.

E-mail address: harish@nal.res.in (H.C. Barshilia).

represents the refractive index of the bulk of the substrate. Since this condition is wavelength sensitive, broadband AR remains elusive [9]. The second technique involves fabrication of multiple coatings of increasing refractive index to produce the gradient in refractive index, this technique is not only expensive but is also complex, moreover omni-directionality and adhesion between the layers remains an issue [9].

The third technique involves AR by virtue of nanostructures, such as moth eye structures, nanoporous structures and inverted conical structures [9]. Tapering nanostructures, which are usually nanoporous create a gradient in refractive index and ensure broadband AR [8]. The shape and distribution density of the pores ensure that the amount of air in each layer reduces as we move away from the interface to the bulk. These layers then behave as a surface with a gradient refractive index. The refractive index increases gradually from $n_{air} = 1$ just before the interface to $n_{PET} = 1.57$ in bulk, as the light passes through the nanoporous layers at the interface [13,18]. Thus, reflectance due to step discontinuity is greatly reduced over a broad range of wavelength.

Burghoorn et al. reported the fabrication of moth eye like structures on poly (methyl methacrylate) (PMMA) and polycarbonate by step-and-flash nano imprint lithography. It was also reported that replication of the same technique on PET substrate produced an increase in transmittance of 3–4% [9]. But scalability of lithography technique makes it unfeasible. Plasma etching of PMMA substrate for AR as demonstrated by Hsu et al. produced a maximum increase of only 3.6% in transmittance to 95.6% in the visible region even after both sides were etched [19]. But Sakata has demonstrated an increase of 3–4% in transmittance of metallophthalocyanine substrate by plasma etching with a gas mixture of nitrogen and CF_4 when only one side was treated [20]. An alternative technique that is note-worthy is that demonstrated by Bravo et al. which consists of fabrication of a multilayer AR coating of SiO_2 and polymers to create a nanoporous structure [21]. But such a technique would require an unfeasible multi-step procedure [10].

High broadband AR for PET with total transmittance (specular + diffusive) as high as ~99% by plasma etching technique has not been reported so far. Plasma treatment offers the advantage of uniform treatment and scalability while being environmentally friendly [22].

In this paper, we study surface morphology of PET substrate subjected to plasma etching with argon (Ar) and oxygen (O_2), and the resulting AR properties. An increase in light transmittance from ~89% in untreated PET to ~99% by virtue of a single step plasma etching process is observed. This is accompanied by significant increase in transmittance throughout the 350–2100 nm spectral range. Further we briefly discuss the changes at the surface due to plasma treatment, physical changes include generation of nanostructures and chemical changes include generation of new products (primarily consisting of oxygen functionalities) and degradation of the polymer chain [23–25]. Moreover, tests revealed that the AR structure was relatively stable in a basic environment, while it showed a marginal decrease in transmittance in acidic and outdoor environment. Adhesion of the AR coating was demonstrated to be more than satisfactory.

2. Experimental details

Transparent PET film of thickness $125 \pm 1 \mu m$ was taken for the current study. The film was cut into $\sim 50 \times 50 \text{ mm}^2$ samples, and cleaned in isopropyl alcohol through ultrasonic treatment in a water bath for 10 min. The cleaned substrate was mounted onto a stainless steel holder. The rotatable holder was then loaded into the vacuum chamber of the plasma reactor. Further information about

the plasma reactor system can be found in an earlier paper [26]. A base pressure of $8.8 \times 10^{-4} \text{ Pa}$ was created in the vacuum chamber. Ar and O_2 flow rates were maintained at 20 sccm and 10 sccm (cm^3/min at STP), respectively. A pulsed DC bias of -700 V was applied to generate the Ar+ O_2 plasma at room temperature. The plasma current, power and operating pressure during the plasma treatment process were measured to be 167 mA, 116 W and 2.33 Pa, respectively. The treatment was allowed for durations of 15, 30, 60, 90, 120, and 150 min, respectively.

The surface morphology of the untreated and plasma treated PET was studied using field emission scanning electron microscopy (FESEM, Supra 40VP, Carl Zeiss). The average surface roughness of both sides of untreated and treated PET samples was calculated from atomic force microscopy (AFM, Bruker) measurements. Optical properties including transmittance and reflectance of the samples were recorded in the UV–vis–NIR region using Lambda 950 spectrophotometer (PerkinElmer). The polarization and angle dependent AR properties were studied using universal reflectance accessories. Chemical analysis was done by X-ray photoelectron spectroscopy (XPS, SPECS) measurements carried out with monochromatic Al K_{α} radiation (1486.6 eV) operated at 150 W. The Fourier transform infrared (FTIR) spectra of untreated and treated PET were recorded using Bruker spectrometer (Vortex 80v) in transmission mode from 400 to 4000 cm^{-1} .

The optimized samples were subjected to chemical resistance, environmental stability, adhesion and mechanical bending tests and performance evolution was studied. The tests are further discussed in the subsequent sections.

3. Results and discussion

3.1. Effect of etching time on transmittance

In order to optimize the etching time, PET substrate was etched for different durations. Fig. 1 shows the total transmittance (T_{tot}) spectra of single side treated PET with different etching times along with that of untreated PET. Increasing etching time until 120 min increases the T_{tot} over the broadband. With further increase in the etching time, the transmittance increases in the NIR region but decreases in the visible region. To understand the behavior of transmittance spectra, the surface morphologies of the treated PET substrate were examined and the evolution of surface morphology with etching time can be seen in Fig. 2(a)–(d). The surface morphology of untreated PET substrate is shown to be even and dense with some cracks that are believed to have originated during the manufacturing process. After etching, a nanoporous network is formed on the surface, which has a lower refractive index than bulk PET due to presence of air in the nano-voids [14,17,27]. To suppress the reflection as much as possible, the volume of air in the porous structure should increase while restricting the pores to sub-wavelength dimensions. Larger pore size will lead to scattering and increased haze, thus compromising the transparency [28,29]. It must be noted that if the etching time is increased to 150 min, the pores grow and merge to form longer and wider pores of size greater than the visible wavelength and are no longer restricted to sub-wavelength dimensions (Fig. 2(d)). A further increase in etching time gives a reduced transmittance for wavelengths below NIR region. This is attributed to the pores being larger than the effective size for shorter wavelengths. These results are consistent with reported literature of polymer AR coatings [14,28,29]. For a low etching time of 15 min (Fig. 2(b)), the nanoporous network does not exhibit broadband AR as the etching time is too short to produce an effective pore depth as evident from Fig. 3(a), which shows the AFM line profile of treated PET surface with different etching times. It is evident that pore depth is

دانلود مقاله



<http://daneshyari.com/article/77504>



- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات