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Injection moulding antireflective nanostructures

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ABSTRACT

We present a method for injection moulding antireflective nanostructures on large areas, for high volume production. Nanostructured black silicon masters were fabricated by mask-less reactive ion etching, and electroplated with nickel. The nickel shim was antistiction coated and used in an injection moulding process, to fabricate the antireflective surfaces. The cycle-time was 35 s. The injection moulded structures had a height of 125 nm, and the visible spectrum reflectance of injection moulded black polypropylene surfaces was reduced from $4.5 \pm 0.5\%$ to $2.5 \pm 0.5\%$. The gradient of the refractive index of the nanostructured surfaces was estimated from atomic force micrographs and the theoretical reflectance was calculated using the transfer matrix method and effective medium theory. The measured reflectance shows good agreement with the theory of graded index antireflective nanostructures.

1. Introduction

The optical properties of injection moulded plastic products can be altered by nano-scale surface textures [1,2]. Antireflective (AR) structures which reduce reflectance by 2% can significantly improve the optical properties of a dielectric, in terms of reducing glare, with possible use for displays or polymer lenses [3]. AR structures in opaque materials have also been shown to enhance the colour appearance (chroma) of coloured plastics [4]. Other functionalities can be achieved using nanostructures, such as super hydrophobicity, and anti-fogging [5]. While these functionalities have been shown on lab-scale, there are still great challenges in developing industrial fabrication methods that can reduce the cost of such nanostructured materials.

Saarikoski et al. previously reported injection moulding of antireflective nanostructures in polycarbonate, from nanoporous anodized aluminium oxide, decreasing the reflectance from 5% to below 1% in the visible spectrum [1]. Black silicon [6] can likewise be used as a template for fabricating antireflective structures [7], despite the random nature of the structures. We have previously shown that black silicon can be optimized in order to minimize the scattering of light on the structured surface [3]. The antireflective properties of the nanostructures depend on the height of the structures, as well as the gradient profile of the refractive index, generated by the structures [8–10].

Although early works show that injection moulding of high aspect ratio nanostructures with low cycle times is possible [11], recent results still indicate that it is a challenging matter. Recent reports rely on dynamic heating and cooling [12–14], in order to obtain high aspect ratio structures.

Here we present a low cost method for fabricating antireflective polymer surfaces, based on mask-less reactive ion etched black silicon masters, and 35 s cycle-time conventional injection moulding from antistiction coated, electroplated nickel (Ni) shims. The reflectance of the black, injection moulded polypropylene (PP) was measured using an integrating sphere, and was reduced from $4.5 \pm 0.5\%$ to $2.5 \pm 0.5\%$, in the visible spectrum. We compare the measured reflectance to the theoretical gradient index antireflectance, by estimating the gradient from atomic force micrographs of the nanostructured surfaces, and calculating the reflectance using the effective medium theory and the transfer matrix method.

We thus show the direct relation between the incomplete filling of the nanostructures, and the impact it has on the desired optical property. This is useful for future optimization of the injection moulding process. Despite the shortcomings of the injection moulding process, we still obtain the desired optical effect of the nanostructures.

2. Theory

Light incident on an interface between two materials with different refractive indices, is subject to reflection, given by the Fresnel equation (at normal incidence) [15]

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$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 \quad (1)$$

where n_1 and n_2 are the refractive indices of the first and second medium respectively. For light in air ($n_1 = 1$), incident on a polymer surface ($n_2 = 1.5$), the reflectance amounts to 4%. Since the expression for R is quadratic in the difference between the value of the two refractive indices, the reflectance can be lowered by introducing one or more intermediate layers on the interface, with a refractive index, n, which obey $n_1 < n < n_2$. This can be realized by nanostructuring the surface using so-called moth-eye nanostructures [16]. Tapered moth-eye nanostructures provide a gradient in the effective refractive index over the interface which can be described as multiple thin layers, each with a gradually increasing refractive index. Due to the very small difference in refractive index, the reflectance at each interface becomes very small, and the total reflectance of the surface can in principle go to zero.

Clapham and Hutley [17] showed that very good antireflective properties can be obtained by gradient structures that obey the relation $d/\lambda > 0.4$, where d is the height of the nanostructures, and λ is the wavelength of the incident light. If we consider the visible spectrum of light, with wavelengths of 380–700 nm, the nanostructures should then have a height of around 280 nm or more. Structures with a smaller height will still be antireflective, but less effective.

The exact reflectance of a nanostructured surface can be calculated analytically, from the geometry of the nanostructures. If the volume fraction profile of the structures is known, this can be related to the effective refractive index profile, using effective medium theory. The effective refractive index n of two materials can be calculated using the Maxwell Garnett model [9,18]

$$\left[\frac{n^2 - n_1^2}{n^2 + 2n_1^2}\right]^2 = (1 - f_1)\left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right]^2, \quad (2)$$

where n_1 and n_2 are the refractive indices first and second medium, respectively, and f_1 is the volume fraction of the first medium.

In this paper, the volume fraction of the surface was measured with atomic force microscopy. The topographic data was divided in layers with a thickness of 1 nm. The effective refractive index of each of the layers was calculated using Eq. (2). The total reflectance of the resulting multilayer structure was calculated using the transfer matrix method [15]. In this way the theoretical reflectance was calculated, using actual topographical data.

3. Fabrication

The black silicon (BSi) substrates were structured by reactive ion etching (Pegasus DRIE, STS), see Fig. 1. The structures were formed in a single etching cycle with an O_2/SF_6-based etch [6]. The masters were patterned using conventional photolithography and isotropic dry etching to remove the nanostructures from the unmasked areas. A 90 nm seed layer of NiV was deposited on the Si masters using sputtering, and the masters were electroplated with Ni, to a thickness of 300 µm. The Si was subsequently dissolved in a 8.9 M KOH solution at 80 °C. The etch time was approximately 9 h. The nickel shims were coated with perfluorodecyltrichlorosilane (FDTS) using molecular vapor deposition. The Ni shims were inserted in the injection moulding tool, and the samples were fabricated using cycle times of up to 35 s.

An Ormocomp (a hybrid organic-/inorganic UV curable resin from Microresist Technologies GmbH) sample was casted from the Ni shim as well, using UV moulding (see Christiansen et al. [3] for details on the fabrication process). The Ormocomp replica has a very high resolution, and served as a reference for the characterization of the nanostructures and optical properties.

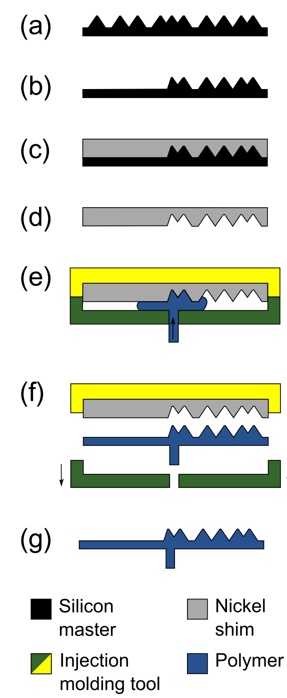

Fig. 1. Fabrication process. (a) Reactive ion etching of Si master. (b) Patterning using UV lithography. (c, d) Electroplating Ni shim. (e, f) Injection moulding. (g) Final part.

4. Results

4.1. SEM and AFM characterization

The Si master, Ni shim, injection moulded samples, and the Ormocomp replica were characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM). A PPP-NCH tip from Nanosensors (www.nanosensors.com) was used for the AFM characterization. Fig. 2 shows scanning electron micrographs of the fabricated samples. The images show good resemblance between the nanostructures of the Ni shim, and those of the injection moulded samples. The characteristic distance between the nanostructures is around 210 nm (measured by Fourier analysis. See Christiansen et al. [3]). No significant changes to the Ni shim were observed after the injection moulding process.

The heights of the nanostructures were measured from atomic force microscopy micrographs, and are shown in Table 1. The standard deviation on the heights was estimated by measuring two to three AFM scans on different positions on each sample. The height

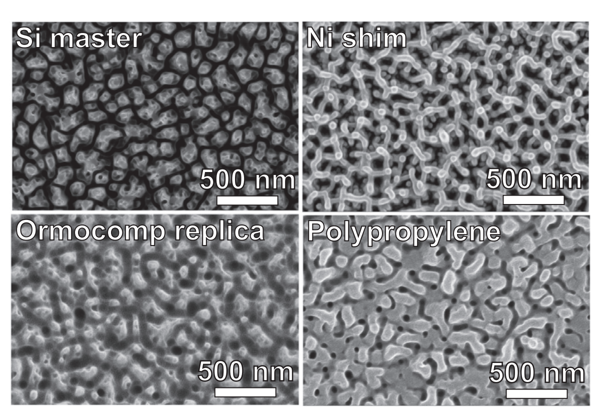

Fig. 2. Scanning electron micrographs of nanostructured surfaces.