Applied Surface Science 458 (2018) 503–511

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Enhanced anti-scratch performance of nanopatterned anti-reflective polymer films

Na Eun Yeo[a], Won Kyoung Cho[a], Doo-In Kim[b,*], Myung Yung Jeong[a,c,*]

[a] Department of Cogno-mechatronics Engineering, Pusan National University, Geumjeong-gu, Busan 46241, South Korea
[b] BK21 + Nano-integrated Cogno-mechatronics Engineering, Pusan National University, Geumjeong-gu, Busan 46241, South Korea
[c] Department of Opto-mechatronics Engineering, Pusan National University, Geumjeong-gu, Busan 46241, South Korea

ARTICLE INFO

Keywords:
Anti-reflection film
Nanostructure
Anti-scratch performance
Heat treatment
Residual stresses
Free volume

ABSTRACT

A heat treatment process was proposed to enhance the anti-scratch performance of nanostructured anti-reflection (AR) PMMA films fabricated by thermal nanoimprint lithography (t-NIL). Nanostructured AR films were fabricated using the high-temperature/high-pressure flat pressing (FP) to control free volume and rapid cooling (RC) to induce a compressive residual stress, which are compatible with t-NIL. The effects of the heat treatment process on the optical and the mechanical properties of the nanostructured films were examined by evaluating the optical properties, such as reflectance and transmittance, and measuring the mechanical properties with a pencil hardness test and a nanoindentation. It was found that the anti-scratch performance of the film was significantly improved while the optical properties are degraded slightly by a combination of FP and RC processes. It was further confirmed that the enhanced anti-scratch performance is due to the improved elastic modulus of the film by the optimized sequence of the process consisting of FP, RC and t-NIL. The enhanced anti-scratch performance is attributed to the compressive residual stress on the surface and the minimization of the unevenly distributed free volume in the polymer film.

1. Introduction

Anti-reflective coatings (ARCs) are applied to various applications such as optical systems and displays to minimize reflectance and maximize transmittance at the surface, thus ensuring enhanced functionality with maximized efficiency. Conventional ARCs were typically fabricated by deposition of multi-layer coatings for gradually changing refractive indices. Hence, deposition of the selected materials suitable for the specific refractive index hinder a large-area fabrication with cost-effectiveness [1]. To overcome these limitations, nanostructure mimicking a moth-eye was intensely investigated to achieve AR effect using fully packed patterns of which critical dimension is sub-wavelength scale. The moth-eye structure is known to be able to accept light efficiently by minimizing reflection using parabolic nanocores array [2–3]. Because of parabolic shape, the effective reflective indices gradually increase from air to the substrate. Hence, a sudden change in the refractive index is eliminated and the light can be transmitted at the interface with excellent AR effect (Fig. 1) [4]. Such nanopatterns with high accuracy can be fabricated over a large area using thermal nanoimprint lithography (t-NIL) or ultraviolet nanoimprint lithography (UV-NIL) [5–6]. In order to transform a flat surface of a substrate into a specific high-resolution pattern, a polymer film is heated up to a higher temperature than the glass transition temperature, T_g, of a polymer substrate and then imprinted with a stamp under high pressure. The UV-NIL utilizes low-viscosity UV-curable resist, and the confined resist in some specific patterns by an imprint mold is cured by UV irradiation under room temperature and low-pressure condition [7]. Even though the material property of a UV-resin is adjustable, refractive index mismatch at the interface still exists, and influences transmittance and reflectance [8]. On the other hand, even though optical performance is excellent, the AR film fabricated by t-NIL is vulnerable to scratches due to the limited mechanical properties of applicable polymer substrates. To overcome this drawback, various approaches are being studied, such as direct patterning on a hard material such as glass [9], atomic layer deposition (ALD)-based patterning [10], deposition of a thin hard coating using ALD [11–12], or UV-based curing [13]. However, these methods are mostly based on an expensive and independent process, which significantly degrades the cost-effectiveness and provides a limitation for a large-area fabrication. Hence, it is necessary to investigate a cost-effective approach which is compatible with a conventional t-NIL process to enhance anti-scratch performance of the nanostructured AR film. Heat treatments are widely used to reinforce

* Corresponding authors at: Department of Cogno-mechatronics Engineering, Pusan National University, Geumjeong-gu, Busan 46241, South Korea (M.Y. Jeong).
E-mail addresses: dooin.kim@pusan.ac.kr (D.-I. Kim), myjeong@pusan.ac.kr (M.Y. Jeong).

https://doi.org/10.1016/j.apsusc.2018.07.086
Received 19 February 2018; Received in revised form 8 July 2018; Accepted 11 July 2018

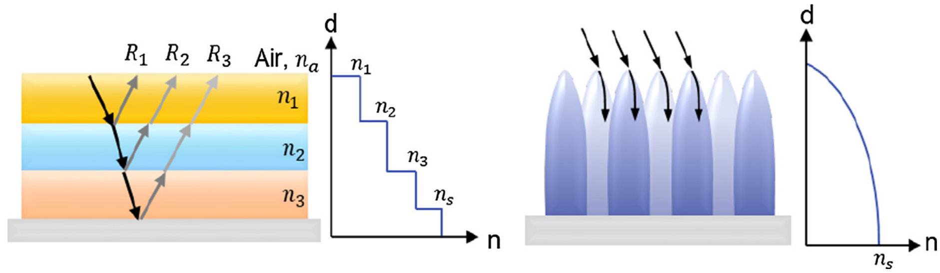

Fig. 1. Schematics of anti-reflection effect of multi-layer coatings and parabolic nanocone structure inspired by moth-eye.

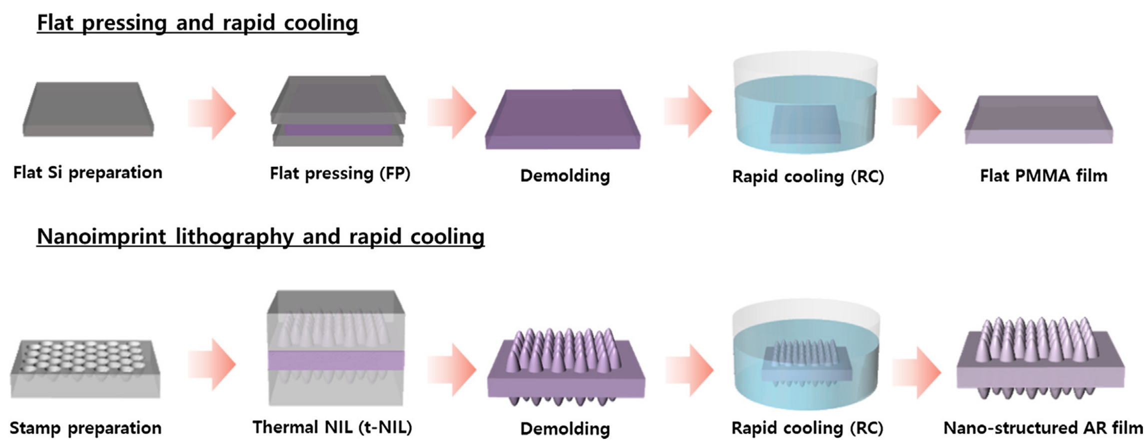

Fig. 2. Schematic illustrations of a flat pressing and rapid cooling process (top), and thermal nanoimprint lithography and rapid cooling process for fabrication of nanopatterned anti-reflection film (bottom).

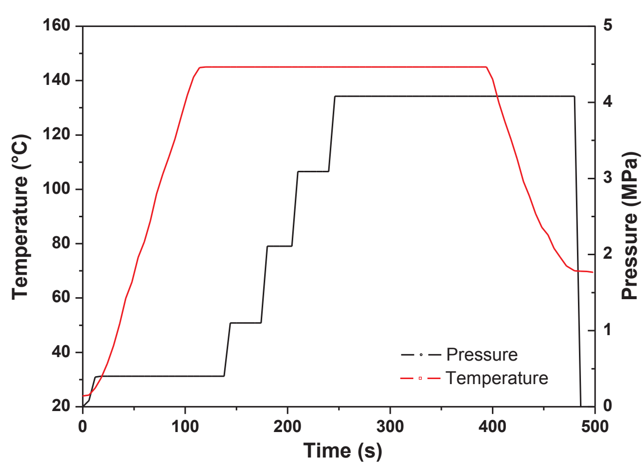

Fig. 3. The temperature and pressure conditions for nanostructure fabrication on PMMA film using thermal nanoimprint lithography.

mechanical property by altering microstructure of materials, typically metals. It was reported that this approach is applicable by controlling relatively low temperature to improve the mechanical properties of a polymer film [14–15]. Therefore, it is necessary to investigate effects of a heat treatment on optical and mechanical properties of nanostructured AR polymer film.

In this work, the heat treatment process which can be conducted using a conventional t-NIL was proposed to improve anti-scratch performance of a nanopatterned AR film. The effects of the heat treatments on the optical properties and mechanical properties of the nanopatterned film were investigated by measuring reflectance and pencil hardness test [16]. Nanoindentation was further conducted for quantitative assessment of improved mechanical properties of the treated PMMA, which is one of excellent base materials for t-NIL [17]. It was found that the optical properties are degraded slightly whereas the elastic modulus of the film was significantly improved by the optimized process. The observed contrary effects were ascribed to the effects of the unevenness of a free volume in PMMA film and compressive residual stress.

2. Experiments

2.1. Surface design and master stamp fabrication

The suppression of the reflected light at a range of 400–900 nm by fully packed nanostructures in hexagonal array was evaluated using a commercially-available software (VirtiaulLab, LightTrans, Germany), which employs the rigorous coupled-wave analysis (RCWA) method [18]. The master stamp covered with the designed nano-cone array was fabricated by the sequential process of the E-beam lithography, dry etching and electroplating [19]. The 8-inch Si wafer coated with double layers of photoresists was exposed under 248 nm KrF excimer laser source (KrF Scanner System, ASML Co., Netherlands) through a stepper using a reticle. Subsequently, the nano-cones were fabricated by dry etching process using Cl_2 and HBr gases. Cr and Cu seed layers coated on the fabricated Si and followed by the electroplating with current density of 0.5 A/mm^2 for 25 min. The analysis using a field emission scanning electron microscope (FE-SEM, S-4700, HITACHI, Japan) confirmed that the diameter, height and pitch of the fabricated nanocones in hexagonal lattice of on Ni mold surface were approximately 236 nm, 312 nm and 311 nm, respectively.

2.2. Nanostructure fabrication and characterization

Fig. 2 (top) illustrates a flat pressing (FP) and a rapid cooling (RC) processes proposed in this work. During the FP process, a 200 μm-thick PMMA film was pressurized between Si wafers with elevated temperature using imprint equipment (NIL-60-ss-UV, Obducat, Sweden).