Optics Communications 382 (2017) 462–469

Contents lists available at ScienceDirect

Optics Communications

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

The fabrication of flip-covered plasmonic nanostructure surfaces with enhanced wear resistance

Joo-Yun Jung, Sang-Keun Sung, Kwang-Seop Kim, So-Hui Cheon, Jihye Lee, Jun-Hyuk Choi*, Eungsug Lee*

Nanomechanical Systems Research Division, Korea Institute of Machinery and Materials, Yuseong-gu, Daejeon 305-343, South Korea

ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form
23 July 2016
Accepted 9 August 2016
Available online 23 August 2016

Keywords:
Plasmonic resonance
Nanoimprint
Transfer
Tunable photonics

ABSTRACT

Exposed nanostructure surfaces often suffer from external dynamic wear, particularly when used in human interaction, resulting in surface defects and the degradation of plasmonic resonance properties particularly in terms of transmittance extinction rate and peak-to-valley slope. In this work, a method for the fabrication of flip-covered silver nanostructure-arrayed surfaces is shown to enhance wear resistance. Selectively transferred silver dot and silver webbed-trench exposed reference samples were fabricated by metal nanoimprint, and flip-covered samples were created by flipping and bonding reference samples onto a PET film coated with an adhesive layer. The samples' spectral transmittance was measured before and after a dynamic wear test. Some spectral shift was observed due to the change in refractive index of the surrounding media, but this was not as significant as the effects of the other chosen geometry factors. It was found that dynamic wear had a greater effect on the plasmonic resonance behavior of the exposed samples than in those that had been flip-covered. This suggests that flip-covering may be an effective strategy for the protection of plasmonic resonators against dynamic wear. It is expected that the slight variations in spectral transmittance could be compensated through proper tuning of the sample geometry.

1. Introduction

Periodic nanostructure arrays have been shown to be effective for various modes of electromagnetic manipulation such as refractive index gradients, waveguide gratings, diffractive-coupling, and plasmonic resonance. Through the design of periodic nanostructure arrays, various unique nanophotonic properties have been assigned to films, windows, lenses, and various nanophotonic devices [1–3]. In particular, plasmonic metal nanostructures can be used to control light–matter interactions at nanoscale through resonant matching of the radiating photons, resulting in resonant extinction, localized field confinements and out-coupling to near-field optical modes, and enhanced radiative decay rates [4–6]. These effects have been reported to be useful for improving the efficiency of sensing, light-emitting and optoelectronics [7–11].

Nanoimprinting is a simple, inexpensive, and high-quality nanolithographic technique, commonly used in the fabrication of periodic metal nanostructure arrays. Additional process steps require deposition [12–15], lift-off [16,17], direct nanoimprinting [18,19], metal etching [20,21], or transfer [22–25] processes to be performed on the predefined nanoimprint template patterns. These nanostructures are often contained by additional layer deposition in multilayer devices [26–28] or exposed by a window or flexible film. In the latter case, wear resistance should be guaranteed, particularly when exposed to environmentally harsh conditions, or human interaction [29–31]. Therefore, attempts have been made to identify harder and more robust nanostructure materials, particularly for use in antireflective windows [32–34]. Robust plasmonic substrates are more demaded to applications such as tip-enhanced Raman spectroscopy, surface-enhanced spectroscopy, and enhanced optical and optoelectronic nanosensors. Hence, protective films such as diamond-like carbon [35,36], ultrathin (3 nm) SiO_x [37], and ultrathin (3 nm) AlO_x [38], have been investigated to enhance surface hardness and wear resistance in working environments.

Unprotected nanostructures have a limited resistance to repetitive external abrasion, the evaluation of which requires dynamic wear testing, rather than static hardness tests. According to the dynamic wear test scheme described in [36,39], the contact force is moved across the sample surface with a fixed normal force and speed. More effective protection strategy of the

* Corresponding authors at: Nanomechanical Systems Research Division, Korea Institute of Machinery and Materials, Yuseong-gu, Daejeon 305-343, South Korea.
E-mail addresses: junhyuk@kimm.re.kr (J.-H. Choi), eungsug@kimm.re.kr (E. Lee).

http://dx.doi.org/10.1016/j.optcom.2016.08.017
0030-4018/

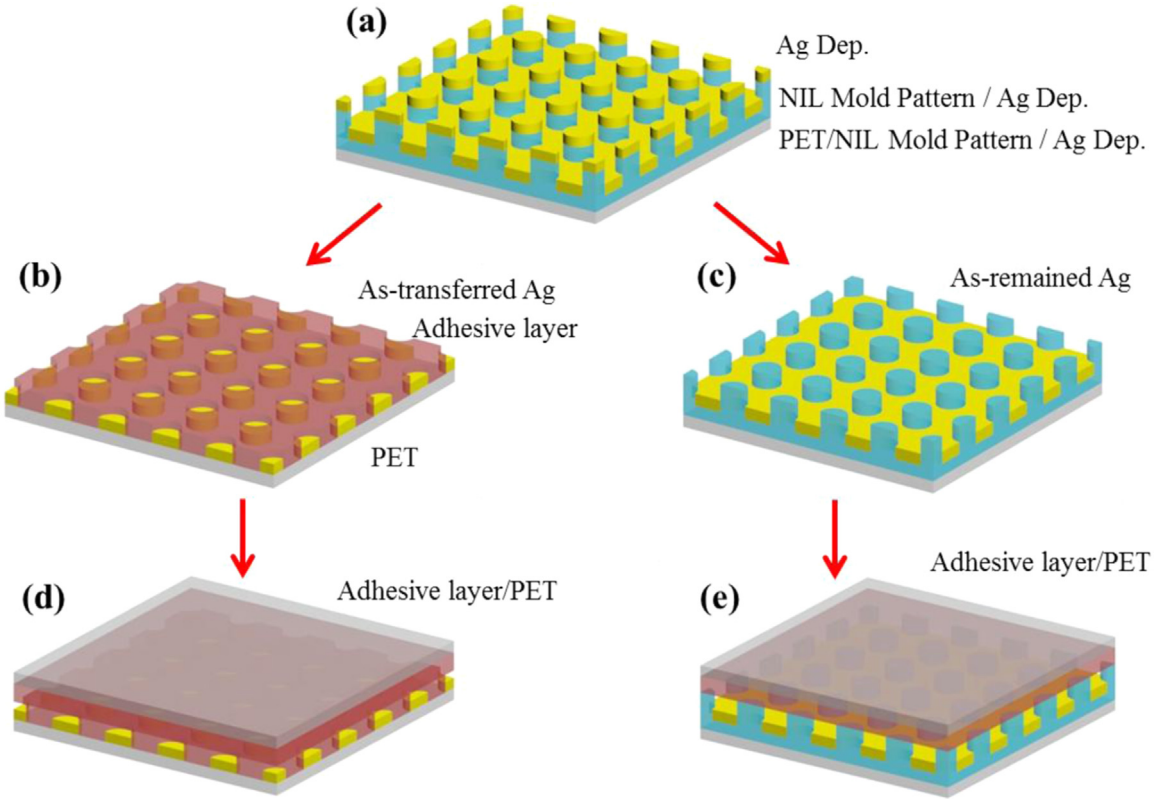

Fig. 1. Fabrication process for the exposed silver nanostructure surface and its flip-covered sample counterpart. (a) Silver deposition on a nanoimprinted mold nanopattern, (b) the receiver with the transferred silver dot array, (c) the donor after transfer, (d) flip-covered receiver film, and (e) flip-covered donor film.

nanostructured surfaces is required against repetitive dynamic forces. Planarization with coating materials and physical bonding are methods that could be used to provide protection. Planarized nanostructures have been shown, using various filling techniques [40–44], to reduce corrugation-drive current leakage in multilayer optoelectronic devices. Alternatively, physical bonds form air-gaps between the nanostructure surfaces and bonding substrates, reportedly optimizing light extraction efficiency [45–47]. This is achieved through anodic bonding of the patterned surface to the device substrate [45,46] using thermal degradation-induced calcination [47] to decrease the dielectric constant in a nanochannel-formed poly-methyl-silsesquioxane (PMSSQ) layer. The basic idea of these techniques can contribute to optimizing the dynamic wear stability of the metal nanostructure surfaces, given that the protection methods used do not significantly alter the plasmonic resonance properties of the exposed nanostructure surface.

In this work, a method for the fabrication of flip-covered flexible plasmonic films is developed, based on previously reported metal nanoimprint transfer techniques [48], enhancing dynamic wear resistance with respect to exposed reference samples. Spectral transmittance profiles were measured, to investigate the wavelength shift and profile variations between the exposed and flip-covered samples, before and after the dynamic wear tests. The damage caused by the wear testing was evaluated qualitatively and quantitatively by scanning electron microscopy (SEM) analysis and measurement of the spectral transmittance and its variations. The results suggest that flip-covering may be an effective technique by which plasmonic resonators can be protected against dynamic wear, increasing the number of potential applications.

2. Experiments

The metal imprint transfer process starts with the preparation of nanoimprint molds replicated in polyethylene terephthalate (PET), as shown in Fig. 1. Two designs of the hexagonal hole array patterns were used in this work, 150 nm diameter holes with a 300 nm period, and 200 nm diameter holes with a 400 nm period. These master patterns were fabricated by KrF optical lithography, followed by a well-established anisotropic etching procedure, at the National Nanofab Center in Daejeon, Korea. The patterns were replicated in mold resin (OrmoStamp®, MRT GmbH, Berlin, Germany) dispensed on a PET film with the reversed pillar pattern profiles for the transfer-imprint mold. The surface of the replicated mold nanopattern was made hydrophilic by surface treatment with trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (Sigma-Aldrich), so that the metal layer could be removed more easily in the afterward.

A 10–30 nm layer of silver was deposited on the replicated nanoimprint mold, using an E-beam evaporator under the optimized condition to minimize the side wall deposition, as shown in Fig. 1(a). An epoxy-based hybrid (thermal & UV curable) resist (mrI-6000E; MRT GmbH, Berlin, Germany) was deposited on PET film with the thickness of 50–100 nm for the adhesion to the silver, prior to the imprint transfer. The silver-coated mold pattern was placed on the adhesive layer-coated PET film, and roll-pressed with a mild pressure (~0.1 MPa) at 65 °C to ensure that only the silver on the top surface of the mold pattern came into contact. The mold was released after UV exposure, transferring the silver to the adhesive layer. As a result, the receiving film in Fig. 1(b) and the donating mold in Fig. 1(c) were produced simultaneously. As-transferred silver dots were trapped in the imprinted trenches of the adhesive layer in the receiver, whereas the silver in the trenches of the mold patterns remained to create the silver webbed-trench and pillar array in the donor. Both the receiver and the donor had exposed nanostructure surfaces at this stage. Flip-covered samples were obtained by flip-bonding them onto additional adhesive layer-coated PET films, as shown in Fig. 1(d) and (e).

The dynamic wear tests for exposed and flip-covered samples