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Fabrications of Nanocomposite Gold-Polymer Metamaterials Consisting of Periodic Microcavities with Tunable Optical Properties

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ABSTRACT

Nanocomposite gold-polymer metamaterials (MMs) were developed in a series of steps. The colloidal gold nanoparticles (Au NPs) were prepared using seeding growth technique. The NPs were then electro-deposited into the micro-pattern structure of polymer thin film formed on the surface of indium tin oxide substrates (ITO). This micro-pattern structure made of positive photoresist (PR) polymer were present in the well-ordered square microcavities in the size range of 52–65 μm (length), 1.3–1.6 μm (depth) and 17–29 μm (interspace length). Field emission scanning electron microscopy (FESEM), scanning transmission electron microscopy (STEM) and atomic-force microscopy (AFM) images confirmed the presence of Au NPs within the microcavities. This nanocomposite was named as patterned Au-PR/ITO and was compared with random-patterned Au-PR/ITO and the bare PR/ITO. The change of refractive index and complex permittivity in the UV–vis range revealed that the periodic arrangements of microcavities containing the Au NPs could result in new exploration in the optical and electromagnetic properties.

1. Introduction

Metamaterials (MMs) or artificial electromagnetic materials are meta-atoms made where the nanoscale inclusions are substantially smaller than the electromagnetic wavelength and the average distance between them is also in subwavelength scale. These features enable MMs exhibiting unusual electromagnetic responses such as negative refraction index, subwavelength imaging and optical cloaking [1,2]. Presently, even in the infancy stage, MMs have demonstrated potentials benefits in some applications including optical sensing, subdiffraction-limited imaging, antennas, nanoscale photolithography, and various electronic devices [3,4]. The unparalleled electromagnetic properties are largely determined by a delicate arrangement of the meta-atoms within a host material (dielectric), and thus, resulting in the need of a simple and low-cost development

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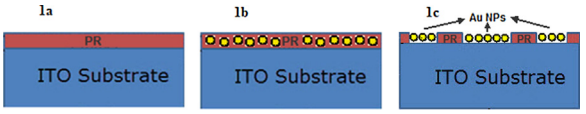

Fig. 1. Three sample configurations are prepared. a: The bare PR/ITO sample without the presence of Au NPs; b: The random-patterned Au-PR/ITO sample without microcavities; c: The Au NPs were electro-deposited within the microcavities on ITO substrate, which was previously formed by UV-lithography process.

of metal-dielectric MMs as an alternative, as compared to the currently used top-down technologies. The Au NPs display excellent optical properties due to the nature of noble metal [5,6]. The positive photoresist (PR) polymer offers a convenient way to modify its morphology and thickness to create desired pattern during a UV-lithography process [7]. Therefore, the arrangement of the Au NPs in the correct spatial arrays within the PR material is possible to realize the real MMs. We believe that by arranging Au NPs (certain range of small size) in a periodic pattern via the lithography method utilizing a suitable fixed thickness of PR (to provide flexibility of a desired pattern on ITO substrate), the optical path of light beams will be within control because the light manipulation is achieved via propagation through media of a designed refractive index n. This gives advantage of engineering the n in a desired range when developing a new optical component. In this work, the PR was spin-coated onto ITO substrate. The Au NPs were electro-deposited into micro-pattern structures made of positive PR, known as microcavities which were successfully created under UV-lithography process. Meanwhile, the random mixture of Au NPs and PR spin-coated onto ITO substrate without undergoing UV-lithography were also prepared, as well as the only PR spin-coated onto ITO substrate without the presence of Au NPs. These three configuration samples were then studied for their optical and permittivity properties.

2. Experimental

The stable colloidal Au NPs (18.4 ± 3.0 nm) in 2.5×10^{-4} M were prepared by using the seeding growth technique which utilizing chemicals such as hydrogen tetrachloroaurate ($HAuCl_4$) (CAS Number: 16961-25-4), trisodium citrate dihydrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) (CAS Number: 6132-04-3), sodium borohydride ($NaBH_4$) (CAS Number: 16940-66-2), cetyl trimethylammonium bromide (CTAB, $C_{19}H_{42}BrN$) (CAS Number: 57-09-0), and ascorbic acid (AA) (CAS Number: 50-81-7). The preparation steps in detail as well as particles stability were explained elsewhere [8]. In UV-lithography process, positive PR and developer named as Microposit-S1813 and MF-319 developer (Dow Electronic Materials) were used, respectively. Two drops of PR were spin-coated onto ITO thin sheet substrate (2.3 cm (H) × 2.3 cm (W) × 0.7 mm (H)) under configuration of 5k rpm for 60 s to produce bare PR/ITO (Fig. 1a). The ITO thin sheet has sheet resistance $\leqq 7\ \Omega$/sq and transmittance $\geqq 80\%$. In addition, the random mixture of the as-synthesized Au NPs colloidal and PR (two drops) were also spin-coated onto ITO substrate using the same previous spinning working parameters to prepare so-called random-patterned Au-PR/ITO (Fig. 1b). During UV-lithography process, the TEM copper grid (3000 mesh) was used as photomask. The dry PR/ITO thin film was exposed under UV (G-line) for 12 s by using mask aligner instrument (MDA–400 M by MIDAS, Korea), followed by immersing it into the developer to remove some region of PR/ITO thin film, which was previously under UV exposure. The successfully formed micro-pattern structures of the PR/ITO thin film as well as bare ITO substrate were used as electrodes, together with the as-synthesized Au NPs colloidal (2.5×10^{-4} M) as electrolyte to conduct the electrophoretic deposition (EPD) to form the patterned Au-PR/ITO sample (Fig. 1c). The EPD was done at 30 DV for 120 s with electrode separation distance of 12 mm.

Characterizations using FESEM, STEM and AFM were conducted to reveal the pattern formed for PR on top of ITO substrate and the arrangement of Au NPs within the PR layer. The electromagnetic characterization using spectroscopic ellipsometry (SE) involved the measurements of real refractive index (n), extinction coefficient (k) and complex permittivity (ε_r). The SE spectra (two independent ellipsometry parameters: Ψ and Δ) were measured in a range from 370 to 1000 nm (1.24–3.35 eV) in multi-angular mode at room temperature using a rotating-compensator instrument (M-2000 by J.A. Woollam, USA).

3. Results and discussion

3.1. Optical surface texture analyser and AFM analysis

The preparation of a stable colloidal Au NPs was detailed in a previous work [8]. The stability of Au NPs was studied by using Turbiscan Classic MA 2000 screening stability tester with the support of optical absorption and zeta potential measurements, which the Au NPs could suffice to remain stable within two months. During UV-lithography process, under UV exposure for 12 s, the top surface of as-prepared PR/ITO thin film revealed micro-pattern structures. As evidenced by 3D optical surface texture analyser (Alicona, Austria), both micrographs in Fig. 2a and b are belonged to the PR/ITO sample after undergoing both UV-lithography and development processes. It is confirmed that the patterns of TEM copper grid (photomask) were transferred and thus the well-ordered squares were successfully formed. The structures displayed dimensions of 52–65 μm (length and width) and 17–29 μm (interspace length). Fig. 3 shows the AFM image where the micro-patterns display a certain range of depth profile (1.3–1.6 μm). In fact, the transparent square patterns in pale colour shown in Fig. 1b also indicate the