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Plasmonic 'top-hat' nano-star arrays by electron beam lithography

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ABSTRACT

Lithography techniques play an important role in the fabrication of nanoscale functional devices. In electron beam lithography (EBL) the optimum dose of electron irradiation is a critical parameter. In this paper, we first identify suitable EBL fabrication parameters by writing patterns with different sizes, periods and electron radiation doses. After finding suitable fabrication parameters, we show how five-pointed gold nanostructures with electric field-enhancing 'top hats' can be fabricated using EBL. Reflectance data of these arrays is measured in order to assess their potential applications in biosensing arrays.

1. Introduction

Nanostructures with well-controlled shapes and sizes may be fabricated using focused ion beam (FIB) [1], electron beam lithography (EBL) [2,3] or nanoimprint lithography (NIL) [4]. Gold is a particularly suitable material for such structures [5] especially using EBL which is capable of fabricating patterns down to about 10 nm resolution under ideal conditions [6]. Nanostructures made this way have potential applications in nano-electronic and photonic devices [7]. Poly(methylmethacrylate) (PMMA) is a common positive tone resist for EBL because it has a high resolution, good reproductivity, and stability [8,9]. Typically, PMMA has sensitivity of <100 μC/cm^2 varying with the resist heights, the acceleration voltages, and the development procedures used [10]. Resolution limits [11], surface chemical modification [12] and photoresist [13] effect on the EBL fabrication process have been previously explored for simple shapes such as gold nanorods or deep trenches. Unfortunately EBL in thick resist layers still suffers from the inevitable problem of low resolution due to broadening of the energy deposition profile of the electron beam inside the resist by electron scattering in the resist and the substrate [13]. Therefore it is still challenging to fabricate complex nanostructures using EBL.

In the present work, we investigate the optimum techniques to produce arrays of gold nano-stars for potential use in biosensing. In addition, we demonstrate a reliable technique to place a 'top hat' disk on top of a central hole within the nanostar. Such 'top-hats' have recently been reported to enhance the localised electric field on circular shapes [14] and they should also be effective on star shapes. Two layers of PMMA were used to improve the lift-off process. Patterns with different sizes, periods and doses are designed. The effects of the spin coating parameters on the photoresist thickness and the substrate's effect on the dose requirements are also established. Finally, an array of complex gold nanostars is fabricated using EBL and the optical properties are assessed.

2. Experimental

2.1. Dose test patterns

Patterns with different shapes, periods and doses were designed using ELPHY Quantum design software (Dortmund, Germany). As shown in Fig. 1, stars, star-holes, and star-star holes with different sizes, different periods and different doses (60–360 μC/cm^2) were created. The writing field size was 100 μm × 100 μm. The dose

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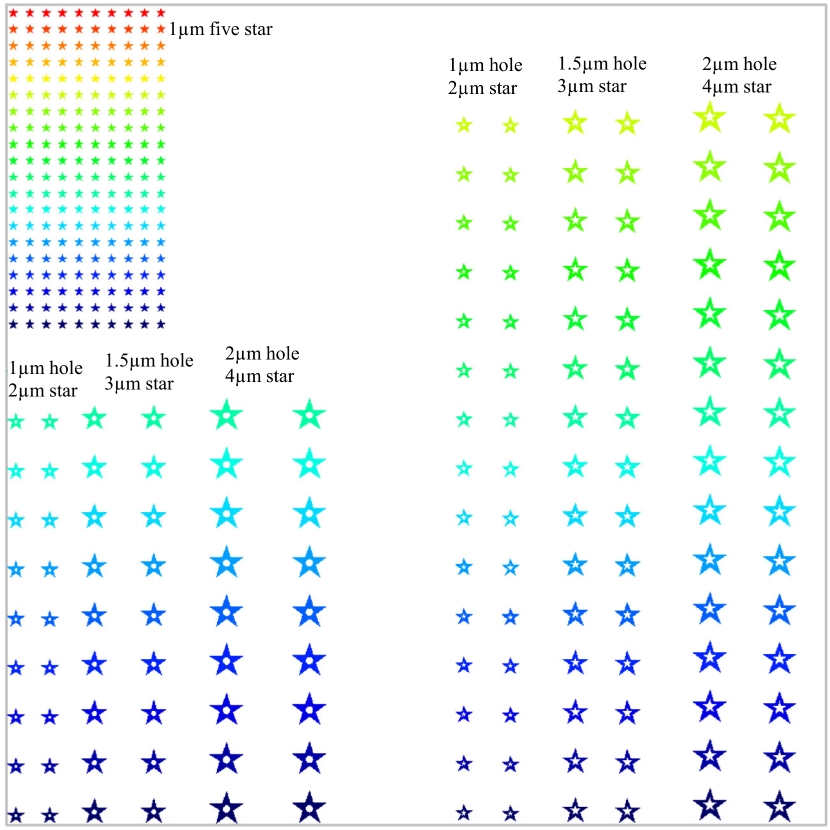

Fig. 1. EBL pattern with different sizes, periods and doses, used to optimize the dose.

factor is indicated by the colour of the stars and was varied on a row-by-row basis. Although stars of 1 μm, 1.5 μm, 2 μm and 3 μm were made, the present study focused on 1 μm size stars.

2.2. Effect of substrate on dose requirements

Different substrates required different dose conditions and when a pattern was exposed on a new substrate, dose tests for that pattern were required. We initially investigated gold, silicon, glass and glass coated with ITO substrates to find which substrate was better for the fabrication of complex nanostructure arrays.

In particular, collisions at the interface between the PMMA and the substrates were investigated. Valuable insights were gained from use of the Casino modeling program V2.42 [15,16] to simulate the impact of 1000 electrons onto different substrates. As shown in Fig. 2, the number of backscattered electrons (BSE) increases significantly as the atomic number of the substrate increased, with the BSE coefficient of a gold substrate being 0.47. BSE contributes to the PMMA chain scission and exposure. Therefore, the gold substrate requires a significantly lower dose than the other substrates. But the gold substrate has background noise, adhesion problems and a large grain size that contributes to increased surface roughness. The high yield of BSE generation can also result in a more severe 'proximity effect' during the patterning in the resist film. Although the ITO glass substrate has more collisions and larger number of BSE paths than the silicon substrate, the number of collisions on the silicon substrate is larger than on the ITO glass substrate. Thus, the ITO dose required was slightly higher than that for silicon. From these results we can see that, of the three substrates considered, silicon is the best substrate for EBL fabrication. Therefore, we selected silicon for the present work.

2.3. EBL fabrication

The EBL fabrication procedures are shown in Fig. 3. First, p-type Si ⟨100⟩ wafers were cleaned by immersing in acetone and isopropanol alcohol for 2 min under sonication, followed by drying with a stream of N_2. The wafers were spin coated with bi-layer polymethylmethacrylate (PMMA) photoresists in which 4 wt% 495 k and 2 wt% 950 k PMMA (Microchem GmbH) were used for bottom and top layer resists. The solvent used in this case was anisole. Each layer of resist was soft-baked at 185 °C for 10 min on a hot plate after spin coating. Measurements with an ellipsometer indicated that the thickness of bi-layer PMMA was about 100 nm (±10 nm).

The wafers were exposed in a customised EBL system equipped with a Raith Elphy Quantum system attached to a JEOL-7800 FE-SEM. The exposures were carried out in the EBL system with accelerating voltage of 20 kV and with dose ranging from 60 to 360 $\mu C/cm^2$. The wafers were then developed in a solution containing a 1:3 ratio of methyl isobutyl ketone (MIBK) and IPA at room temperature for 31 s followed by rinsing in IPA and drying with N_2. The wafers were deposited with 5 nm of titanium (Ti, vacuum: 2×10^{-6} Torr, deposition rate 0.4 A/s) and 40 nm of gold (Au, vacuum: 2×10^{-6} Torr, deposition rate: 1.5 A/s) using Temescal FC-2000 E-beam evaporator, followed by stripping the resist in acetone overnight. (The Ti layer is used to adhere the Au to the surface of the silicon wafer.)

The fabricated devices were then characterised using the JEOL 7800 SEM at 10–15 kV equipped with the upper secondary electron detector (UED). ImageJ software [17] was to measure the radius (r) of the tips of the stars. The reflectances of the various structures were measured with a SCI FilmTek 2000 M (Temescal Headquarters, United States) using a 10× objective.