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Full Length Article

Fabrication of hexagonal star-shaped and ring-shaped patterns arrays by Mie resonance sphere-lens-lithography

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ABSTRACT

Mie resonance sphere-lens-lithography has proved to be a good candidate for fabrication of large-area tunable surface nanopattern arrays. Different patterns on photoresist surface are obtained theoretically by adjusting optical coupling among neighboring spheres with different gap sizes. The effect of light reflection from the substrate on the pattern produced on the photoresist with a thin thickness is also discussed. Sub-micron hexagonal star-shaped and ring-shaped patterns arrays are achieved with close-packed spheres arrays and spheres arrays with big gaps, respectively. Changing of star-shaped vertices is induced by different polarization of illumination. Experimental results agree well with the simulation. By using smaller resonance spheres, sub-400 nm star-shaped and ring-shaped patterns can be realized. These tunable patterns are different from results of previous reports and have enriched pattern morphology fabricated by sphere-lens-lithography, which can find application in biosensor and optic devices.

1. Introduction

Well-ordered surface nanopatterns arrays have been paid much attention due to their widespread use in many areas, such as sensors based on local plasmon resonance [1,2], nanoantennas [3], solar cells [4] and photonic devices [2,5]. Various manufacturing technologies, including conventional lithography [6], X-ray lithography, focused ion beam lithography, electron beam lithography, UV/EUV interference lithography and nanoimprint lithography [7–10], have been proposed and verified experimentally. Although they can be utilized to fabricate highly-ordered nanopatterns arrays with uniform size, low-output or high-cost makes them have fewer advantages in mass production, especially in producing large-area well-ordered nanopatterns. Sphere-lens-lithography (SLL) [11–15], as it is inexpensive and rapid in manufacturing large-area micro/nanopatterns arrays, it has been recognized as a promising technique for industrial production of large-area well-ordered nanopatterns arrays. In general procedure, a monolayer hexagonal-close-arranged latex crystal or silica spheres crystal, self-assembled on a photoresist (PR) layer, serves as a lens array mask to modify incident UV light and form sub-wavelength beam waists in PR [11]. After developing, ordered two-dimensional pore array is formed on the PR layer. The period (lattice constant) of the pore array is equal to the sphere diameter. The sizes of pores are defined by the sphere size, exposure dose and development time. Therefore, by adjusting the sphere size and processing condition, pore array with a tunable pore size can be obtained. One disadvantage for the pore array lies in that the morphology of the pore is circular. This disadvantage hinders its applications, for example, when shape-dependent properties of materials are used to design plasmon resonance devices. To overcome this limitation, researchers carefully select material and size of spheres, wavelength and incident angle of illumination light, and various surface nanopatterns [16,17] and complex three-dimensional nanostructures arrays are obtained [18,19]. They attributed the appearance of various contours of the pores or pillars to the change of optical near-field behavior of a single sphere. However, light coupling between neighboring micro/nano-spheres also exists [20,21], and when the coupling is intense, light field distribution of a periodic model is different from that of a single sphere model [20,22,23]. This is interesting, as some more different surface nanopatterns can be easily fabricated by SLL and they would find applications in sensors and nano-atennas, but no detail theory and experimental evidences are found.

For a selected micro/nano-sphere in vacuum, on thick PR film, or directly on substrate, the light scattering behavior is determined by illuminating light, support layers, substrates, and it can be explained by Mie scattering theory [24,25]. A strong near-field

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enhancement mediated by the Mie resonance scattering was theoretically and experimentally confirmed by Refs. [16,23,25–28]. Based on these studies, super-resolution photolithography/imaging samples and surface-enhanced Raman scattering substrates were achieved [26–28]. However, Mie theory ignores light coupling among adjacent spheres and is not good at finding light field distribution in such cases (i.e., for multiple spheres). Some numerical calculations, such as finite-different time-domain (FDTD) method, have been utilized to simulate the optical scattering behavior of such spheres [17–19,28–30], but they only considered a single microsphere models [17–19,29] for simplicity or simulated the periodic models but failed to find the interactions among adjacent Mie resonance spheres effect on pattern morphology [30]. In addition, non-close-packed spheres lens assisted lithography was not studied experimentally. Furthermore, the influence of thickness of PR layer and substrate on pattern by SLL was only seen in a very few references [24,29,32].

Therefore, this paper studies effect of several main factors on the surface patterns arrays manufactured by SLL. Mie theory is utilized to choose proper transparent latex spheres which are in resonance for a given illumination light. FDTD method is adopted to study the influence of gap size among adjacent spheres, thickness of PR layer, substrate and polarization illumination effect on light field distribution at PR surface. Different field images, consisting of bright hexagonal star-shaped and dark ring-shaped images form on PR film for situations of small gap size and huge gap size, respectively. Experimental results agree well with simulation results. Smaller resonant spheres are finally chosen and size of ~400 nm hexagonal star-shaped images and rings are realized in simulation.

2. Results and discussion

2.1. Results of numerical calculation and simulation

It is well known that micro/nanoparticles can exhibit extremely high enhancement of electromagnetic field, which can be utilized for lithography [11,28] or sensing [1,27]. According to Mie theory, for metallic particles, the enhancement results from surface plasmon which is collective oscillation of free electrons when particles encounter optical scattering. For the dielectric particle, however, it is due to optical scattering and optical resonance. As Mie theory is convenient to analyze resonance scattering modes and Mie near-field efficiency (Q_{nf}, the enhancement times of the local field relative to the incident light) of micro/nanoparticles, here it is utilized to select latex spheres which are in resonance for a chosen wavelength of light. The Q_{nf}, which represented described by Mie scattering theory is shown as [31]

$$Q_{nf} = 2\sum_{n=1}^{\infty}\left\{|a_n|^2\left[(n+1)|h^{(2)}_{n-1}(k_0a)|^2 + n|h^{(2)}_{n+1}(k_0a)|^2\right] + (2n+1)|b_n|^2|h^{(2)}_{n}(k_0a)|^2\right\} \tag{1}$$

where a_n and b_n are the Mie coefficients, and $h_n^{(2)}$ is the Hankel functions of the second kind. The parameter a is the radius of the sphere and k (=$2\pi/\lambda$) is the wavenumber of the exciting light. The Mie scattering coefficients display resonances as a function of the parameter $x = ka$. Thus, by calculation Q_{nf}, a_n and b_n, resonance size and Mie efficiency are obtained.

In order to study light scattering of sphere lenses under different packing conditions of spheres and parameters, electromagnetic simulation was implemented using CST Microwave Studio, a commercial software. The 3D computational domain was composed of a PR layer, a single transparent sphere or periodic model of sphere array from bottom to top. As the reflection from the substrate influenced the field distribution [29,32], a silicon (Si) substrate was added in some of the models. A linearly polarized plane wave, with a wavelength of 400 nm or 365 nm, propagated perpendicularly to PR film. The refractive indexes of latex spheres and PR were 1.59 and 1.67, respectively. We got their indexes from the suppliers' tests. The optical constant of Si was taken from Ref. [33].

2.1.1. Neighboring spheres influence on light field distribution of sphere lens array

Fig. 1(a) shows the Q_{nf} of a latex sphere in air as a function of its diameter. It is obtained by matlab code based on Eq. (1) [31]. The relationship between Q_{nf} and diameter of sphere is complex, like jagged. However, the peak value points in the curve are always repeated. The maximum Q_{nf} is because of electric/magnetic resonance mode emerging [32]. We noticed that when the sphere size is smaller than or close to the illumination wavelength, the maximum efficiency is quite low. However, when the diameter of sphere is big enough, the maximum efficiency becomes high. Especially, some maximum values, close to or bigger than 100, appear at the diameter range from 1.9 to 2.5 μm. The maximum values are attributed to both the big size of sphere and the high-order scattering mode. The fluctuation is attributed to the induction of enhanced near field affected by the reflection at the particle surface. As the focusing property of a resonance sphere is decided by several factors: diameter of the sphere, refractive index (including itself and surrounding index), illumination wavelength and interaction between adjacent spheres [23,26,30], extreme high Q_{nf} may promise stronger light coupling among adjacent spheres, but does not mean a good focus spot. In order to consider focusing of spheres and coupling between neighboring spheres together, we chose resonance spheres with diameters of 2.06 and 2.44 μm, whose Q_{nf} is moderate. Based on Eq. (1), we looked for factors contributing to their high Q_{nf} and found that scattering mode order of electric at $n = 21$ and 25, do it, respectively. In the following study, we will concentrate on latex spheres with diameter 2.06 and 2.44 μm due to their commercial availability.

It was stated that when dielectric spheres are put together, photons in one sphere can tunnel to the next sphere due to the overlap of the neighboring evanescent cavity modes [20,34,35]. We have already proved that latex spheres of 2.06 μm diameter, illuminated by light of 400 nm wavelength are in resonant state in the last paragraph. In order to demonstrate there exists interaction among adjacent latex resonance spheres, simulation as follows was carried out. Periodic models, close-ordered-arranged and non-close-ordered-arranged, where spheres are placed on PR film, were set, respectively. Illumination light is as described before. Fig. 1(b) is cross-section illustration of hexagonally arranged spheres. Gap is the distance between the surfaces of any two adjacent spheres among the ordered sphere arrays. The PR film (2.5 μm) is thick enough to allow light attenuation. Fig. 1(c) shows difference of normalized intensity along z axis (the optical axis of the entered sphere lens) of the periodic model with different gap sizes. Of course, a single sphere model is also presented for comparison. Obviously, electric field enhancement forms at the back of latex spheres for all models. It is due to the focusing of light by wavelength-sized dielectric spheres. However, the intensity curves show non-negligible difference between each models. Near the shadow side of spheres, intensity of periodic model (0 nm gap) reduces more than 10 percent compared to that of the single sphere model. For the model with 30 nm gap, the curve is similar to the 0 nm gap model, but with increasing intensity at z = 1.035 μm (vicinity of sphere-PR interface). When the gap reaches 800 nm, the intensity curve along z axis nearly coincides with that of a single sphere model. These differences between a single sphere model and periodic models indicate that there exists mode overlapping and strong coupling among adjacent resonance spheres. When the gap is 0 nm, the light coupling between the adjacent