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Two-surface-plasmon-polariton-absorption based nanolithography

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We propose and demonstrate the two-surface-plasmon-polariton-absorption (TSPPA), which is a nonlinear effect by absorbing two surface-plasmon-polaritons (SPPs), as well as a nanolithography technique based on TSPPA. The TSPPA effect is verified with the plasmonic interference structure to exclude the possibility of two photon absorption. Benefiting from the short wavelength and the field enhancement of SPP as well as the selective transfer of plasmonic patterns into photoresist induced by TSPPA, resist strips with the linewidth of $\sim\lambda_0/11$ are achieved by a single illumination on the plasmonic mask with the femtosecond laser for only 15 s, which shows great potential for future large-area nanolithography. © *2013 American Institute of Physics*.
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Photolithography is one of the most important techniques which allow the large-scale fabrication for micro/nano structures nowadays. However, limited by the optical diffraction, the conventional photolithography technique becomes much more complicated and expensive in order to further reduce the pattern linewidth.[1,2] In the past decades, a number of techniques were proposed and studied to realize overcoming-diffraction-limit nanolithography, such as two photon absorption (TPA) lithography, plasmonic lithography, and nano-imprint lithography.[3–7]

TPA induced polymerization referring to a nonlinear effect in the photoresist (PR) is a powerful method to break the optical diffraction limit in micro/nano fabrication.[3,4,8–10] Most of the TPA lithography applications today focus light into a small spot to achieve the required energy level for substantial TPA and to realize extremely small linewidth. However, this kind of lithography configuration is a point-by-point direct-writing scheme which is time-consuming and impractical for the large-scale fabrication. In recent decades, surface plasmon polariton (SPP)[11] has been used for realizing subwavelength lithography due to its ability of compressing the light field and carrying the subwavelength information.[5,6,12–22] However, the current lithography techniques based on SPP have difficulty in meeting the requirement of both extremely small linewidth and large-area fabrication. For example, the focusing of SPP can squeeze light into the nanoscale region as small as a few nanometers resulting in the resist pattern with the linewidth beyond the diffraction limit.[12,13] However, this method is a point-by-point-scanning scheme, which is usually time-consuming and low-throughput. Even though it was reported that this problem could be overcome to some extent, where both the plasmonic lens array with 22 nm-linewidth and flying head are employed,[12] the lithography configuration used there is still sophisticated. A simple, cost-efficient, and high-throughput lithography method would be more attractive and desirable for the practical nanofabrication.

In this letter, we propose and observe the two-surface-plasmon-polariton-absorption (TSPPA) ruling out the possibility of TPA. And a TSPPA based nanolithography is preliminarily demonstrated aiming to realize large-area fabrication of extremely fine patterns. The periodic resist strips with the linewidth of ~1/11 of the exposure wavelength are obtained by a single illumination on the plasmonic mask with the femtosecond laser for 15 s. The feature size of resist could be further reduced by controlling the illumination power. And we prove that the SPP field enhancement could reduce the input power density of exposure source and in turn enlarges the TSPPA exposure area.

According to the quantum optics, SPPs can be quantized and treated as quantum in term of energy.[24–26] Therefore, similar to TPA, TSPPA referring to a nonlinear effect could occur in the nonlinear medium near the metal surface, where two SPPs are absorbed to excite an electron state. However, the participation of SPP would make the TSPPA process different from the conventional TPA and result in interesting phenomena. As shown in Fig. 1(a), although the energy of the photon and SPP are identical for the same frequency, the wave vector (wavelength) of SPP could be much larger (shorter) than that of the photon. Hence, the TSPPA based lithography is able to realize nanopatterns beyond the diffraction limit, which is similar to TPA: (1) The absorption rate quadratically depends on the light intensity which can further squeeze the exposure spot; (2) the pronounced power threshold provides a possibility for precisely controlling the linewidth by manipulating the illumination power. Meanwhile, this TSPPA based lithography possesses unique advantages due to the special properties of SPP. First, unlike the TPA lithography which focuses light into a single spot and scans point by point, the TSPPA method could obtain the subwavelength field pattern by simply illuminating the plasmonic mask. And this subwavelength field pattern due to the short wavelength of SPP would further result in the overcoming-diffraction-limit resist pattern through the proposed TSPPA process. Besides, the highly concentrated SPP field leads to the strong electromagnetic field enhancement at the metal-dielectric interface, which could reduce the input power density of exposure source and enlarge the exposure area. Therefore, the proposed TSPPA based lithography

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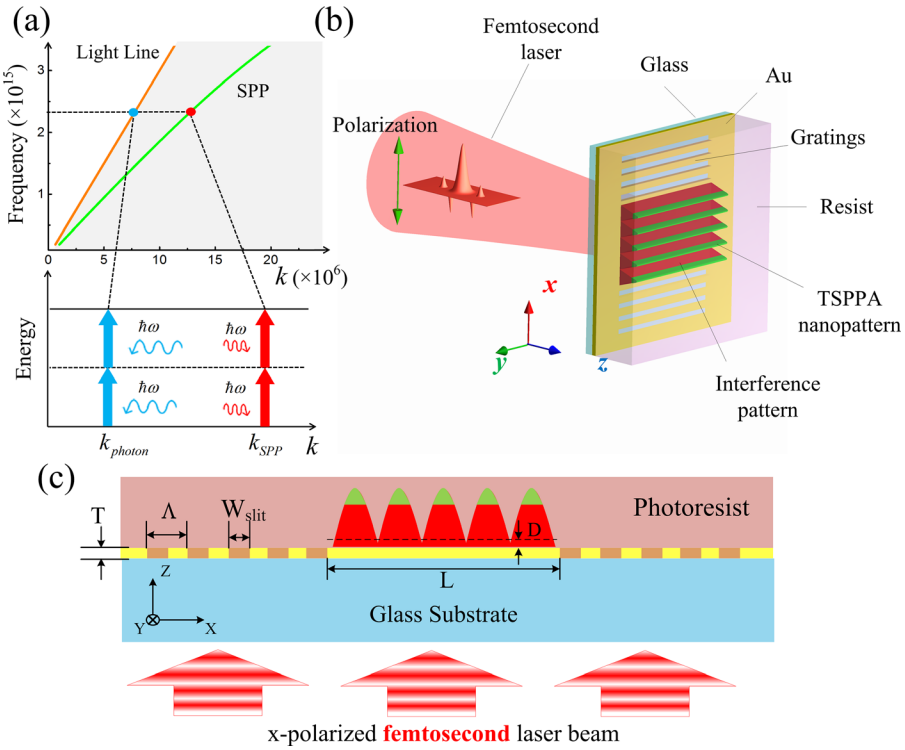

FIG. 1. The schematic of the proposed TSPPA based lithography. (a) The schematic mechanisms of TPA (blue arrows) and TSPPA (red arrows). The SPP dispersion is calculated with the experimental data taken from Ref. 23. (b) The plasmonic interference structure with photoresist is illuminated by a femtosecond laser. (c) The cross section of the simulated structure. The plasmonic interference pattern (red) is generated by the two sets of gratings. By controlling the illumination power, the nanopattern (green) recorded by the resist through TSPPA process can be much narrower than that of the interference pattern.

shows great potential for extremely small patterning fully exploiting the overcoming-diffraction-limit abilities of both SPP and the nonlinear absorption in resist, and overcomes the aforementioned problems encountered in both plasmonic and TPA lithography, which is promising for future large-area nano-fabrication.

TSPPA should play an important role in early reported near-filed lithography with the help of localized surface plasmon (LSP).[27,28] Nevertheless, their experiments cannot rule out the influence of TPA induced by the incident and scattered light. In our experiment, the subwavelength field distribution is provided by the interference of SPPs without the influence of the incident and scattered light. The schematic of the proposed TSPPA based lithography is shown in Fig. 1(b). It is worth noting that the application of the TSPPA based lithography is not limited to the proposed SPP interference structure and can be extended to various plasmonic structures. The simulated structure is shown in Fig. 1(c). The light source is assumed as a femtosecond laser ($|E_{\text{input}}| = 1$) with a central wavelength of $\lambda_0 = 800\,\text{nm}$ and a pulse length of 150 fs. The structure consists of a transparent glass substrate, an Au mask layer with nano-gratings, and a PR layer. The thickness of the Au mask is assumed to be $T = 100\,\text{nm}$ and the photoresist above the mask is thick enough compared with the field penetration depth of SPP. The permittivity ($\varepsilon_{\text{metal}} = -25 + 1.8 \times i$) of the Au film is taken from the experiment data in Ref. 23. The refractive indices of the glass and the SU-8 photoresist are $\varepsilon_{\text{glass}} = 1.520$ and $\varepsilon_{\text{PR}} = 1.574$,[29] respectively. The period ($\Lambda = \lambda_{\text{spp}} = 2\pi/k_{\text{spp}} = 480\,\text{nm}$) of the gratings is determined by the wave vector of the SPP at the Au/PR interface.[19]

According to the finite difference time domain (FDTD) simulation shown in Fig. 2(a), the counter-propagating SPPs are excited by the two sets of metal gratings in the Au film and form the interference patterns with the period of ~240 nm in the interference region ($-1\,\mu\text{m} < x < 1\,\mu\text{m}$.). It is clear in the simulated result that the interference region between the two sets of gratings cannot be disturbed by the incident and scattered light, which enables us to rule out TPA and to directly observe the TSPPA effect. The length of the cavity is carefully optimized to meet the resonant condition for better intensity contrast.[19] The maximum electric field ($|E_{\text{max}}|$) in the interference region is ~15 times higher than the input electric field ($|E_{\text{input}}| = 1$), which results from the near-field enhancement of SPPs. Compared with TPA, this field

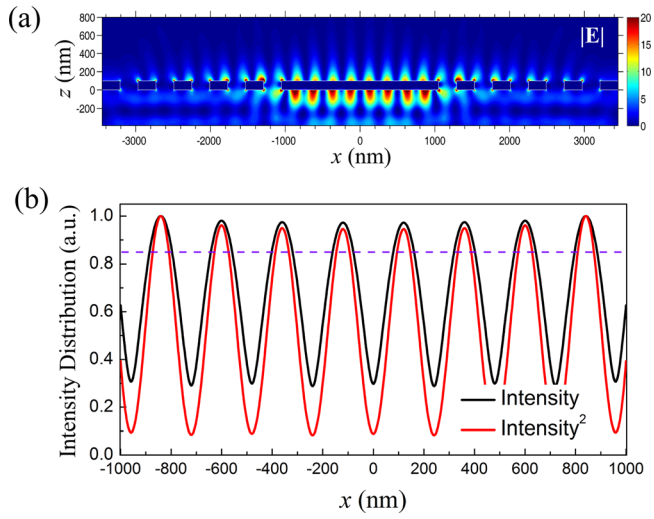

FIG. 2. FDTD simulation of the interference pattern under the illumination of a femtosecond laser beam (a) $|E|$ distribution of the interference pattern generated by the proposed structure. (b) Normalized intensity I (black line) and I^2 (red line) along the black dashed line in Fig. 1(c) at the distance $D = 20\,\text{nm}$ from the Au/PR interface. The purple dashed line indicates the threshold for TSPPA exposure.

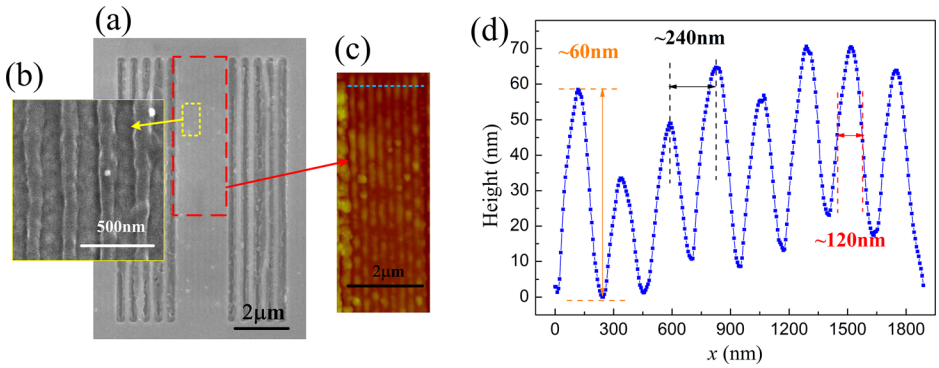

FIG. 3. The plasmonic interference structure with SU8 is exposed at average power of 630 mw for 10 s. (a) The SEM photo of the interference structure after the exposure and development. (b) A SEM photo of the resist pattern details in the yellow dashed area in (a). (c) The AFM photo of the resist pattern in the red dashed area in (a). (d) The surface profile along the blue dashed line in (c).

enhancement could effectively reduce the input power density of the femtosecond laser required for generating the nonlinear reaction. Equivalently, the illumination area for TSPPA can be much larger than that of TPA with the same input power density. Similar to TPA lithography,[9] the effective exposure region only depends on the illumination part above the TSPPA threshold rather than the overall illumination area, which results in the lithography resolution beyond the diffraction limit. As shown in Fig. 2(b), it is the square intensity distribution above the TSPPA threshold (purple dashed line) that determines the linewidth of resist pattern instead of the overall interference pattern. Hence, the linewidth of the resist nanopatterns can be predicted to be as small as ten-nanometer scale by controlling the exposure dose. Given the fact that SPP is a surface wave which is quite sensitive to the medium near the metal surface, the period of interference pattern which is equal to half of the SPP wavelength would depends on both the thickness of the resist layer and the refractive index of the medium surrounding the resist. Here, we first investigate the case in which the PR layer is thick enough compared with the field penetration depth of SPP.

Furthermore, the experiment has been carried out to realize the subwavelength pattern based on TSPPA. To obtain the Au mask for the TSPPA lithography, a 105 nm-thick Au film is sputtered on a glass substrate. Using the focused ion beam (FIB), the gratings with period of 480 nm and duty cycle of 0.5 are written in the Au film. The distance between the two sets of gratings (interference region) is $L = 2100$ nm. Then, a 2 μm-thick film of resist (SU8-2002) is spin-coated on the Au mask and then prebaked for 2 min at 95 °C. The wafer is illuminated by a femtosecond laser (Tsunami + Spitfire) with a central wavelength of $\lambda_0 = 800$ nm, a pulse length of $<= 150$ fs, and a repetition rate of 1 kHz. The linewidth of the laser is narrower than 20 nm. The laser beam is focused by an objective lens whose focal length is $f = 501$ mm. The Au mask coated with SU8 is placed behind the lens at the distance $R = 38$ cm, where the diameter of the light spot is about 1.6 mm. The light spot in our experiment is much larger than that used in the conventional TPA fabrication, which implies the feasibility for large-area fabrication with our proposed TSPPA based lithography. After being exposed by the laser beam, the wafer with SU8 resist is developed and baked. The developed SU8 resist is then inspected by both the scanning electron microscope (SEM) and the atomic force microscope (AFM).

The SEM photo shown in Fig. 3(a) illustrates a resist pattern between two sets of gratings after an exposure at average power of 630 mw for 10 s and the development. Fig. 3(b) illustrates the details of the resist pattern. The AFM picture also reveals obvious periodic strips between the gratings, as shown in Fig. 3(c). The surface profile along the blue dashed line in Fig. 3(c) illustrates an array of nanostrips with a period of ~240 nm, a linewidth of ~120 nm, and an average height of ~60 nm, as shown in Fig. 3(d). The experiment result validated the occurrence of the nonlinear TSPPA effect according to the following reasons: (1) SU8 can only be polymerized with light shorter than 400 nm (Ref. 29) and would not absorb the input light at 800 nm through the usual single-photon-absorption, which means that the nonlinear process participates in the polymerization of SU8. (2) The Au film in the interference region is thick enough to block the direct incident light, which excludes the possibility of the TPA process. (3) The period of the resist pattern is nearly consistent with our simulation result. This result preliminarily demonstrates the overcoming-diffraction-limit nanopattern through TSPPA, achieving the linewidth of ~1/8 of the exposure wavelength.

Further decreasing the exposure power to 230 mw for 15 s, the linewidth of the resist strips is reduced. As shown in Fig. 4, the surface profile along the blue dashed line of the inset illustrates that the minimum linewidth is only about 70 nm which is ~1/11 of the exposure wavelength. Although the resist strips are nonuniform and broken, the measurement result proves that the resist patterns with much smaller

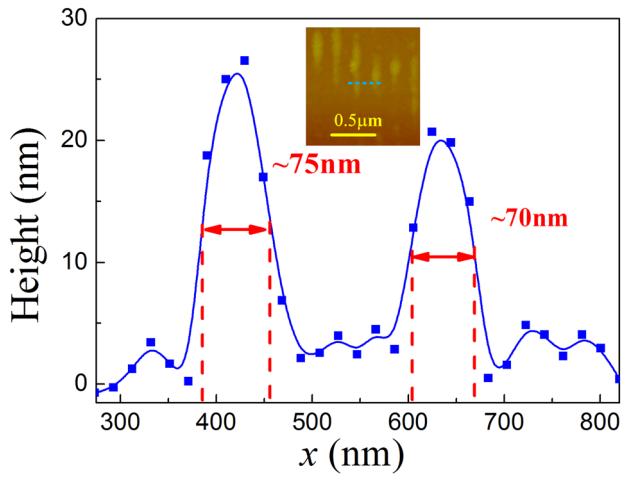

FIG. 4. The plasmonic interference structure with SU8 is exposed at average power of 230 mw for 15 s. The surface profile along the blue dashed line in the inset. The inset is the AFM photo of the resist pattern.

linewidth can be obtained through controlling the illumination power, which benefits from the TSPPA effect. It is worth noting that the polymerization of resist by TPA cannot be found when the same light source directly illuminates the SU8 resist, which is the evidence of the SPP field enhancement mentioned in the previous analysis. In another word, TSPPA can occur at a relatively low input power compared with TPA, which equivalently enlarges the exposure area with respect to the enhancement factor. Moreover, by choosing photoresists with low nonlinear threshold and utilizing the TE-polarized-excited SPP in designer plasmonic metamaterials,[30] the exposure area of the proposed TSPPA lithography can be possibly expanded to several square centimeters, which makes it feasible for the nano-fabrication.

The imperfection of the resist pattern shown in Figs. 3(c) and 4 is possibly attributed to the following reasons: (1) the interference patterns are distorted by the imperfect gratings as shown in Fig. 3(a). Besides, the roughness of the Au surface would cause unexpected scattering of SPP; (2) the finite length of the gratings would cause reflection along the direction parallel to the grating in the interference zone, which would disturb the interference pattern; (3) the lithography conditions, such as the pre/post bake time, the development time, and so on, are very important for the final result. The quality of the resist pattern can be further improved by optimizing the fabrication process and the lithography conditions.

Although the absolute linewidth in our preliminary demonstration is not so small, the TSPPA based lithography shows great potential for reducing the lithography linewidth with respect to the exposure wavelength ($\sim$1/11 of 800 nm in the preliminary result). This ratio can be further reduced by optimizing the exposure power, which fully utilizes the threshold effect of TSPPA. Besides, the absolute linewidth can be further reduced by decreasing the exposure wavelength. In principle, the proposed lithography with the help of TSPPA can be operated at the shorter wavelength, for example, 365 nm or even the ultraviolet wavelength, to greatly improve the lithography resolution as long as the following requirements are met: (1) the photoresist is transparent to the light at the operating wavelength λ_0, while the resist should be absorptive at $\lambda_0/2$ for the single-photon photochemical process and (2) the metallic material should be carefully chosen to support the SPP wave at the operating wavelength. Moreover, this TSPPA scheme could be realized with help of other plasmonic structures which opens up a new route for large-area plasmonic lithography beyond the diffraction limit.

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