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Implementation of sub-Rayleigh-resolution lithography using an *N*-photon absorber

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A nonlinear optical, phase-shifted-grating method for improving the resolution of feature sizes is implemented experimentally using an *N*-photon lithographic material. For the recording medium, we used poly(methyl-methacrylate) (PMMA), which is a UV lithographic material that can be excited by multi-photon absorption in the visible region. We achieved a two-fold enhancement of the resolution over the standard Rayleigh limit of half of the wavelength.

1. Introduction

Over the past few decades, significant effort has been invested towards improving the resolution of lithographic systems beyond the conventional diffraction limit [1]. In standard linear interferometric lithography, the interference fringes have the form $I = 1 + \cos(Kx)$, where $K = 4\pi \sin\theta/\lambda$, where θ is the angle of incidence. Thus, the highest resolution that can be written is $\lambda/2$ at grazing incidence $\theta \to \pi/2$, and it is called Rayleigh limit [2, 3].

Several proposals have been suggested to achieve an *N*-fold resolution enhancement over the diffraction limit by using lithographic materials that work via *N*-photon absorption. In particular, a recent proposal of Boto *et al*. [4] has received a great deal of attention. In this proposal, they suggest exposing an *N*-photon absorbing lithographic material to an interference pattern created from a quantum mechanically entangled source. Following this method, a fringe pattern will be recorded with unit visibility and with a period *N*-times smaller than the period $\lambda/2$ given by the Rayleigh limit. D'Angelo *et al*. reported a proof-of-principle experimental demonstration of quantum lithography that mimicked the lithographic recording material by use of an electronic coincidence circuit [5]. However, quantum lithography has yet to be experimentally realized with a true lithographic material.

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Other methods for improving resolution employing only classical light sources are also possible, but always with reduced visibility. Yablonovitch and co-workers [6, 7] using an interference technique with multiple-frequency beams were experimentally able to obtain a doubling of the spatial frequency of interference fringes formed on a two-photon commercial film. However, the film is not a lithographic material and the resulting pattern had a visibility of only 3%. Recently, Bentley and Boyd have demonstrated that an N-fold enhancement in resolution can be achieved by exposing an N-photon absorber N times, and adjusting the phase difference between the two recording beams after each exposure [8, 9]. In their experiment, an N-photon absorbing medium is simulated by Nth harmonic generation followed by a CCD camera.

As mentioned above, these classical methods suffer from reduced fringe visibility with increasing N. Quantum lithography as proposed by Boto does not suffer from this problem. However, their source is required to produce states of the form $|\psi\rangle = 1/2^{1/2}(|N, 0\rangle + |0, N\rangle)$, so-called high-NOON states [10, 11]. An efficient source capable of producing such states has not yet been developed. Nagasako and co-workers proposed using a high-gain optical parametric amplifier (OPA) as a compromise between the high intensity achievable with classical light sources and the strong correlations achievable with quantum light sources [12–14]. A high-gain OPA is able to produce an intense source of photons while partially preserving the quantum statistics of the high-NOON states. Even with large N, the fringe pattern has a non-vanishing visibility. Nevertheless, an efficient N-photon lithographic media that works via N-photon absorption must be developed.

In the present paper, we demonstrate that poly(methyl-methacrylate) (PMMA), a UV lithographic material, is a viable candidate for the realization of quantum lithography. The technique proposed by Bentley and Boyd is used for verifying the possibility of PMMA as a multi-photon absorbing lithographic material. We are able to write a fringe pattern with a period of 213 nm using recording beams at 800 nm, roughly a two-fold enhancement over the Rayleigh limit. We also show the possibility of recording non-sinusoidal patterns with this technique.

2. Theory

A schematic representation of this technique is illustrated in figure 1. In one arm of the interferometer we inserted a phase-shifter which is used to adjust the phase difference between two recording beams of light. The two recording beams are then brought together on an N-photon absorber and interference fringes are formed. We then expose the PMMA M-times where we increase the optical path-length difference by λ/M between the two arms after each exposure. Thus, we record an interference pattern with a fringe period of $\lambda/(2M \sin\theta)$, where θ is the incidence

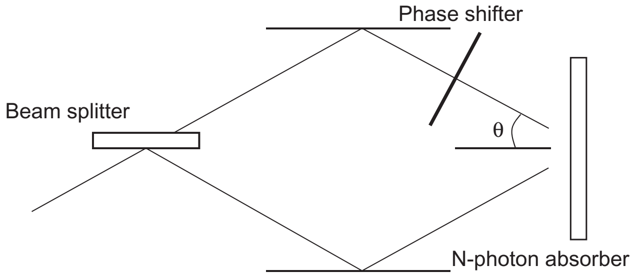

Figure 1. Schematic representation of the method.

angle of the recording beams. To see this, note that the recorded interference pattern is given by

$$\sum_{m=1}^{M} I_m^N = \sum_{m=1}^{M} \{1 + \cos[Kx + 2(m-1)\pi/M]\}^N, \tag{1}$$

where I is the intensity of the interference pattern for each exposure, M is the total number of exposures and $K = 4\pi \sin\theta/\lambda$. For example, if one uses a 3-photon absorber ($N = 3$) and two exposures ($M = 2$), where the second exposure is shifted as described above, the resulting pattern on the 3-photon absorber is given by

$$\begin{aligned} I_1^3 + I_2^3 &= (1 + \cos Kx)^3 + [1 + \cos(Kx + \pi)]^3 \\ &= 4 + 3\cos(2Kx) \\ &= 4[1 + V\cos(2Kx)], \end{aligned} \tag{2}$$

where $V = (I_{\max} - I_{\min})/(I_{\max} + I_{\min}) = 3/4$ is the visibility of the fringes. $I_{\max}$ and $I_{\min}$ are the maximum and minimum values of the interference patterns. In figure 2(*a*), we plot the theoretical surface profile calculated from equation (2) under the assumption that the surface profile varies linearly with the exposure pattern. Note that this method reduces the fringe period by a factor of two, although the visibility is also reduced. Moreover, if one does not use uniform phase shifts between exposures, then non-sinusoidal patterns can also be formed. Let us assume that the lithographic material is a 3-photon absorber and is exposed twice with a $\pi + \Delta$ phase shift on the second exposure, where Δ is a small phase deviation. Using equation (1) we calculate the fringe pattern as compared to the uniformly phase-shifted result. The results are presented in figure 2(*b*). This figure shows that the various combinations of the phase shifts between the two arms can cause various non-sinusoidal patterns.

3. Experimental details

The sample film was prepared as follows. PMMA (molecular weight ~120 000, Aldrich) was dissolved in toluene (Fisher Scientific) at 20 wt% and was spin-coated

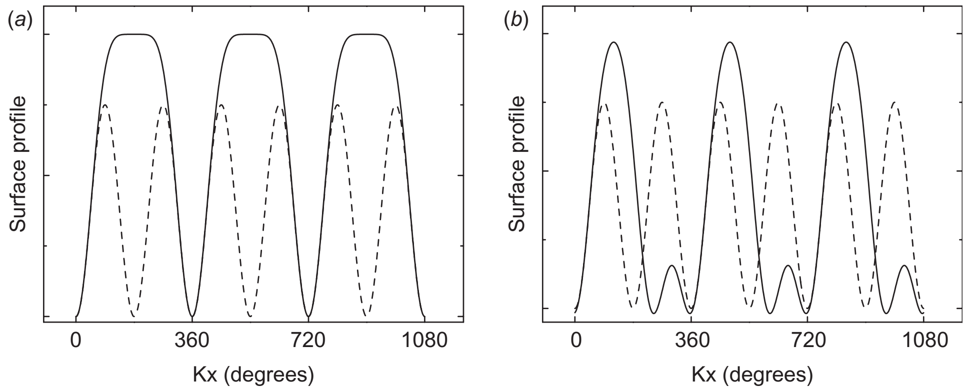

Figure 2. Theoretical surface profile for various experimental parameters. (*a*) Solid curve is for $N=3$, $M=1$; dotted curve is for $N=3$, $M=2$. (*b*) Solid curve is for $N=3$, $M=2$ and the phase shift of the second shot is $\pi+\Delta(\Delta=\pi/3)$; dotted curve is for N=3, M=2, and the phase shift of the second shot is π.

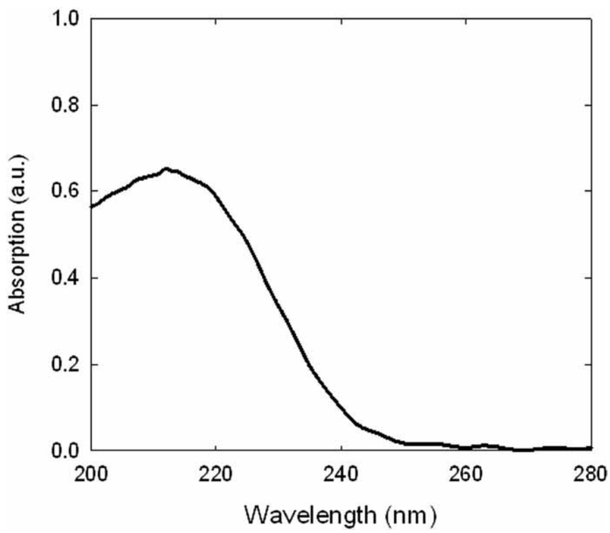

Figure 3. The UV absorption spectrum of the PMMA film.

on a glass substrate at 1000 rpm. The film was dried on a hotplate for 3 min. To fabricate a thicker film, we spin-coated the sample again on top of the first coat of film and dried it. We measured the absorption spectrum of the PMMA film to confirm its linear absorption properties. The spectrum is shown in figure 3.

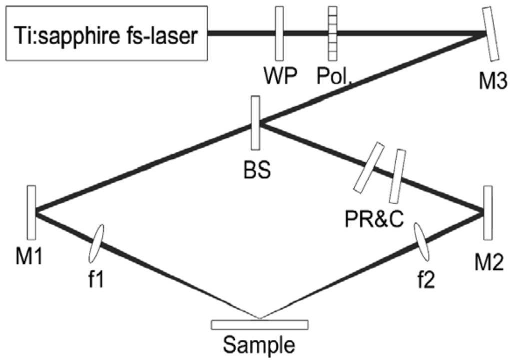

Figure 4. Experimental set-up. WP, half-wave plate; Pol, polarizer; M1,M2,M3, mirrors; BS, beam splitter; f1,f2, lenses; PR&C, phase retarder and compensator.

The PMMA film is transparent throughout the visible region down to a wavelength of 250 nm. Thus, we selected an 800 nm Ti:sapphire laser with regenerative amplification (120 fs, Spectra-Physics) for the light source. We expect that the PMMA film is a 4-photon absorber at 800 nm.

We interfered beams at an angle of incidence of $\theta = 70^{\circ}$, which is close to the grazing angle limit, $\theta \rightarrow \pi/2$. Hence, the fundamental period of the fringes is 425 nm. The experimental set-up is shown in figure 4. To introduce a phase-shift between the two arms, we use a glass plate that can be rotated. A second glass plate is used to compensate for the lateral beam displacement caused by the first plate. The focal length of two lenses is 50 cm. After each exposure, we observed the diffraction pattern of a green diode laser incident on the exposed area (Beam of Light Technologies, $\lambda = 532$ nm, $\sim$5 mW).

After irradiating the sample, we put it in the developer, 1:1 MIBK (MicroChem Corp.) for 10 s and rinsed it in deionized water for 30 s. After development, we used an atomic force microscope (AFM) to confirm the fringe pattern recorded onto the surface of the film.

4. Results

To verify the multi-photon nature of absorption in PMMA, in our first experiment we irradiated the sample with a single pulse. To determine the appropriate pulse energy, we repeated this measurement several times with different pulse intensities. We found that whenever the pulse energy of either light beam exceeded 135 μJ damage of the surface of the PMMA occurred. We also found that pulses weaker than 80 μJ could not produce a change in surface morphology even after development. We therefore used pulse energies in the range of 80 to 135 μJ. The film's surface profile after exposure to the single pulse is shown in figure 5(*a*). In this case, the pulse

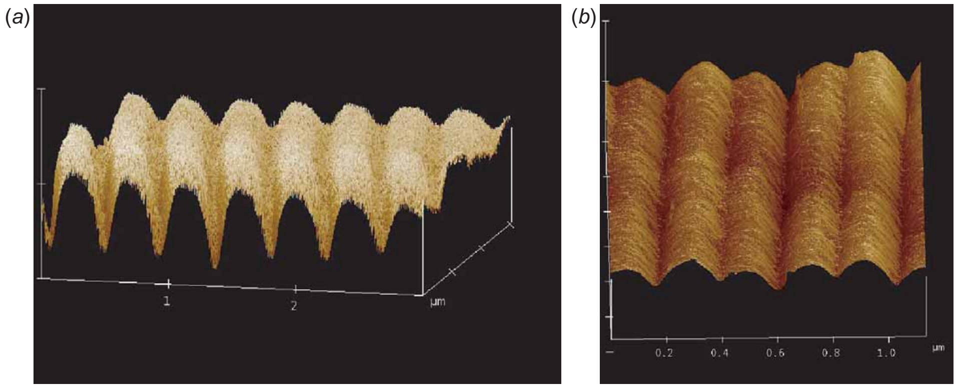

Figure 5. AFM images of the fringes recorded on a PMMA film. (*a*) Result for a single exposure, leading to fringes with a period of 425 nm. (*b*) Results for a sequence of two exposures, leading to a period of 213 nm.

energy was 130 μJ. As shown in the figure, the surface profile is sharp and not sinusoidal indicating that the fringes are due to multi-photon absorption. From the ratio of the depth to the sharpness of the grooves, we can conclude that PMMA is an N-photon absorber with $N \geq 3$.

Next to enhance the resolution of the fringes, we irradiated the sample twice in sequence. For the second exposure, the field in one arm is phase-shifted by π with respect to another arm. After the exposures, we performed the same development procedures as mentioned above. The surface profile is shown in figure 5(*b*). One can see that the fringe period is nearly 213 nm. This shows that we achieved a resolution that exceeds the Rayleigh limit by a factor of two.

In figure 6, we show a cross-section of a non-sinusoidal pattern, which is created by use of a $\pi + \Delta$ phase shift for $\Delta = \pi/3$. This result might be useful in making arbitrary patterns from sinusoidal patterns [2, 11, 15]. The smallest distance between any two fringes is 140 nm. Thus, PMMA should be able to support feature sizes of 140 nm or less, and a 3-fold enhancement beyond the diffraction limit should be possible in PMMA.

5. Conclusions

We have demonstrated the use of PMMA as a multi-photon lithographic recording medium and have experimentally demonstrated resolution enhancement beyond the classical Rayleigh limit by means of the phase-shifted-grating method using a classical light source. We also demonstrated a two-fold enhancement in resolution by writing fringes with a period of $\lambda/4$. These results suggest that PMMA can be useful as a nonlinear lithographic material for the realization of quantum lithography.

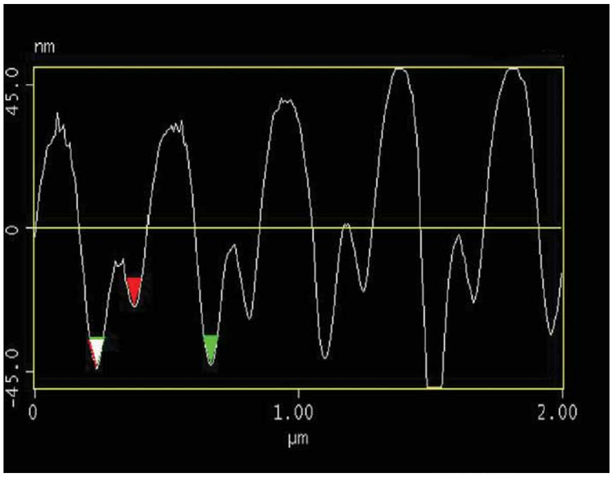

Figure 6. Surface profile of the non-sinusoidal fringes. In this case, we shifted the phase of the second shot by $\Delta = \pi/3$.

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