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Simulation and Fabrication of Large-Area 3D Nanostructures

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ABSTRACT

Three-dimensional (3D) nano-structures are vital for emerging technologies such as photonics, sensors, fuel cells, catalyst supports, and data storage. The Proximity-field nanoPatterning[1] method generates complex 3D nanostructures using a single exposure through an elastomeric "phase mask" patterned in x, y, and z, and a single development cycle. We developed a model that predicts the phase mask required to generate a specific desired nanostructure. We have compared this inverse model with experimental 3D structures to test the validity of the simulation. We have transferred the PnP fabrication process to a class-10 commercial cleanroom and scaled-up the processed area to >2000mm^2, tested photopolymer additives designed to reduce resist shrinkage, incorporated atomic layer deposition (ALD) to coat the 3D patterned resist with metals/metal-oxides to improve structure robustness, and generated quasi-crystal patterned 3D nanostructures.

Keywords: nanostructure, lithography, quasicrystal, photonic, model

1 INTRODUCTION

Three-dimensional (3D) nano-structures are vital for emerging technologies such as photonics, sensors, fuel cells, catalyst supports, and data storage. Conventional fabrication (repeated cycles of standard photolithography with selective material removal) is costly, time-consuming, and produces limited geometries. Unconventional methods (colloidal self assembly, template-controlled growth, and direct-write or holographic lithography) have uncertain yields, poor defect control, small areas, and/or complicated optical equipment. The Proximity-field nanoPatterning (PnP)[1] method overcomes these limitations by generating complex 3D nanostructures using a simple optic and one lithographic exposure and development cycle. The optic is an elastomeric "rubber phase mask" patterned in x, y, and z with dimensions roughly equal to the exposure wavelength. Exposure through this mask generates a complex 3D light intensity distribution due to diffraction (Abbe theory) and the Talbot effect (self-imaging).[2] The underlying photoresist is thus exposed in certain regions, baked, and developed, producing a 3D network of nanostructures with one lithography cycle. Our goals are to create full models of this process and scale this method to 150mm.

2 METHODS AND RESULTS

2.1 FDTD Model and Simulation

We have developed a model using Finite Difference Time Domain (FDTD) methods that predicts the 3D nanostructure resulting from light passing through a phase mask with a given geometry.[3] We have also developed a model to identify the phase mask parameters required to generate a specific desired nanostructure. This "inverse" approach is much more complex than the simplistic modeling of the diffraction pattern produced by passing light through a phase mask. The integrated tool starts with a desired pattern and an initial guess on the PnP mask parameters. Next, the interference pattern is simulated using the mask information and filtered to reveal the expected photoresist burn image, which is then evaluated against the desired pattern. An integrated optimizer makes improvements to the mask parameters and cycles again with a simulation using the new mask parameters. The simulation engine is a high performance, Open MP parallelized FDTD simulator optimized to run on shared memory symmetric multiprocessor (SMP) systems. The product from the simulation is the actual resist burn pattern.

We have compared this model with experimental 3D structures for a hexagonal array (Figure 1) to test the validity of the forward simulation. The phase mask was patterned in a hexagonal array of posts with diameter (d) = 450 nm, period (p) = 600nm, height (h) 420 nm. SU-8-2 (MicroChem) photoresist was spun twice forming a 4.5 μm

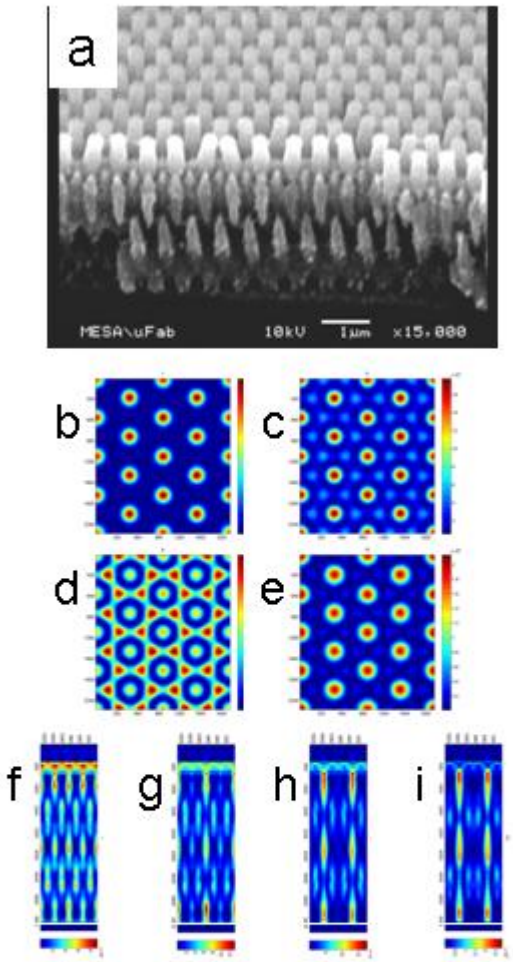


Figure 1. Scanning electron micrograph of an angled cross section of a 3D resist nanostructure made with a hexagonal geometry (1a), corresponding horizontal (x,y) and vertical (x,z) model slices, (1b-e, 1f-i, respectively). The horizontal slices are 160 nm apart and the vertical slices are 80 nm apart.

thick film. Passage of 365 nm light through the phase mask (placed in direct, conformal contact with the resist surface) generated a complex 3D light intensity pattern, which is transferred directly into the photoresist. Normal post-exposure baking, developing, and drying followed [1,2] generating a 3D nanostructure. A scanning electron micrograph of an angled view of the cross section of the 3D resist structure is shown in Figure 1a.

For reference, the surface is defined as the x-y plane and the direction from surface to substrate is z. The 3D structure has an alternating array of resist columns with air gaps, corresponding to the ABAB design of the hexagonal array. The corresponding modeled structure is shown in Figs. 1b-e (horizontal or x,y slices, 160 nm apart) and Figs. 1f-i. (vertical or x,z slices, 80 nm apart). The model used the same phase mask dimensions and exposure wavelength as inputs, and a given threshold value to generate the resist burn. The horizontal model slices show the hexagonal arrangement of resist columns in the 3D resist structure. The vertical model slices show the alternating patterns of resist columns with air holes. The ABAB nature of the resist columns in the resist cross sectional cleave matches the vertical model slice (compare Fig. 1a with Fig. 1f).

2.2 Fabrication and Scale-up

We have successfully transferred the PnP fabrication process to a class-10 commercial clean room and scaled-up the processed area from 490mm^2 to >2000mm^2 using commercial lithography exposure tools. We use a Karl Suss MA-6 contact proximity printer for the exposure. The broad band output of the Hg lamp is narrowed to 364.75±1.25 nm by a multiple thin film narrow bandpass filter and a 350 nm longpass filter. Conventional pre-bake (65°C, 10 min /95°C, 15 min), post-exposure bake (65°C, 20 min) and development in SU-8 developer (MicroChem) processes are used to complete the fabrication. We have produced 3D resist structures for cubic arrays of posts and holes (Fig 2a), hexagonal arrays of posts (Fig 1a) and aperiodic Penrose quasicrystal structures (Fig. 2b). We have also obtained similar comparisons between the aperiodic 3D resist structures and the simulated structures for these geometries.[4]

Our scale-up has recently progressed to exposure of a full 150 mm wafer using the MA6 exposure tool (17600 mm^2). An optical photograph of the wafer is shown in Figure 3a, along with SEM images of 3D nanostructures taken from the center (Fig. 3b) and edge (Fig. 3c) of the 150 mm wafer. No significant difference is observed in the structures across the wafer.

2.3 Chemical Modifications

One of the properties of epoxy-based resists is their shrinkage upon exposure/development. This shrinkage is a function of primarily solvent loss from the resist, compounded by the strong epoxy linkages formed during the cross-linking process. In order to address the issue of resist shrinkage, we have tested photopolymer additives designed to reduce resist shrinkage by replacing a percentage of the resist solvent with reactive solids. We have identified diglycidyl ether, diepoxyoctane, and diglycidylglycidioxyaniline as reactive diluents. We have

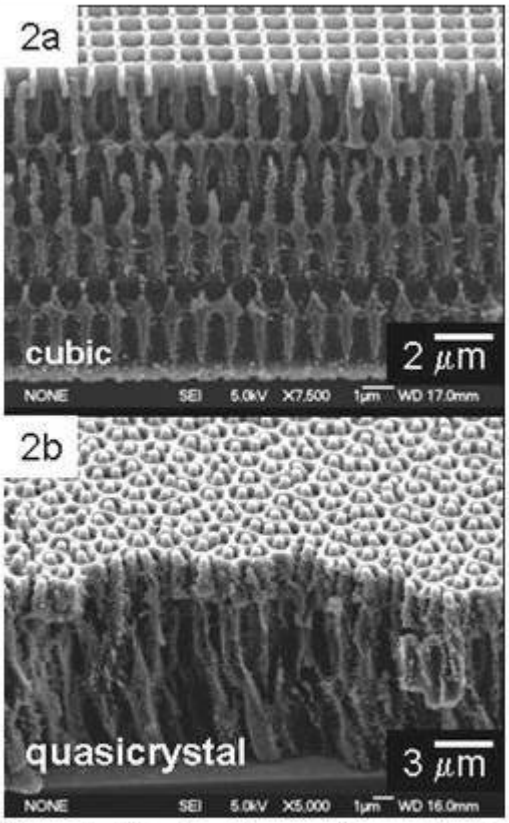


Figure 2. Scanning electron micrographs of 3D resist nanostructures made from a cubic array of holes (2a) and a Penrose quasicrystal array of posts (2b).

successfully fabricated 3D structures with these components at replacement volumes of between 10 and 30 wt%. Measurements of shrinkage reduction are commencing.

PnP 3D nanostructures can also be formed by a 2-photon (2ph) exposure process. In this case, light with a wavelength (λ) double the normal exposure λ (350-400nm) is used, but with much greater energy, ~1TW/cm^2, enabling a 2ph energy absorption that is sufficient to initiate the photoacid generation reactions in the photoresist.[5] Lasers at this power level are often in the near infrared, thus photoresists require a red-shift in sensitization for exposure. We have chemically modified SU8-10 photoresist with Rose Bengal and Uvacure 1600 (photoacid generator) (Fig. 4a) and successfully fabricated 3D nanostructures with a 1-photon exposure at 532 nm (equivalent to doubling of 1064 nm YAG for 2ph mode). Examples of those structures are shown in Figures 4b and 4c.

Epoxy-based photoresists such as SU8, are inherently robust due to the epoxide cross-linking. However, a 3D nanostructure made in SU8 is still an organic resist-based material. We have used atomic layer deposition (ALD) to coat the 3D resist nanostructure to improve the robust nature of 3d structure and also alter the chemical and physical properties of the material.

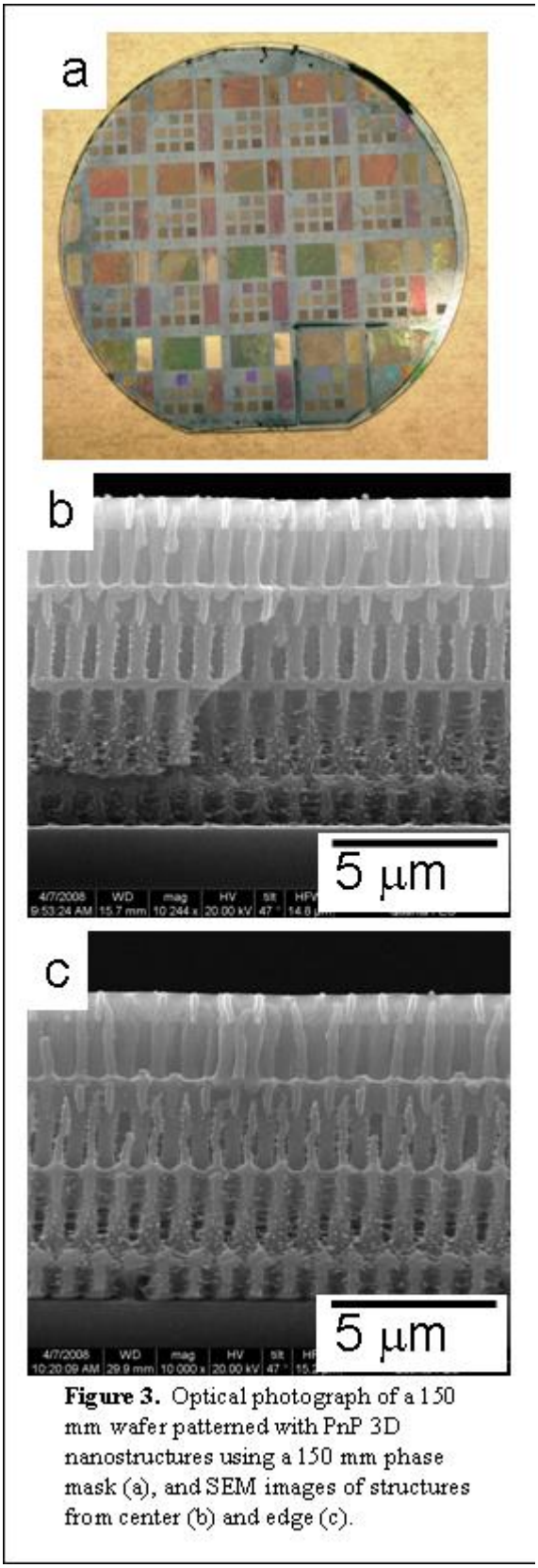
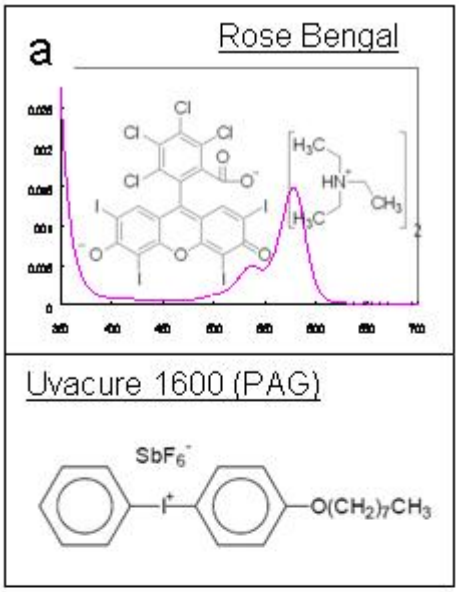
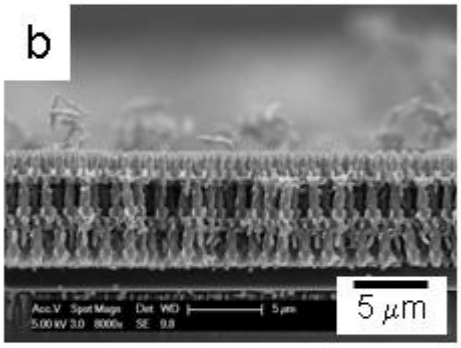


Figure 3. Optical photograph of a 150 mm wafer patterned with PnP 3D nanostructures using a 150 mm phase mask (a), and SEM images of structures from center (b) and edge (c).





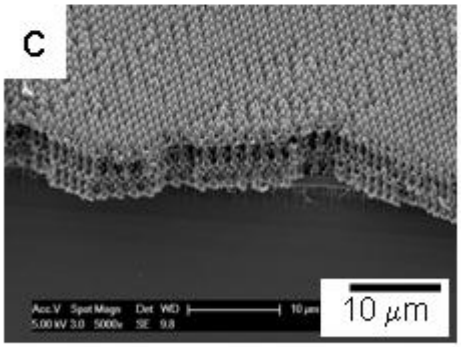


Figure 4. Chemical structure and absorption spectrum for Rose Bengal additive and Uvacure 1600 (3a), SEM images of 3D nanostructures from chemically modified SU8-10 resist exposed at 532 nm in 1-photon mode (3b, 3c).

We have developed a proprietary, graded-temperature deposition approach which does not cause deformation or degradation of the resist structure. Both Al_2O_3 and TiO_2 have been used with this approach, rendering the structure

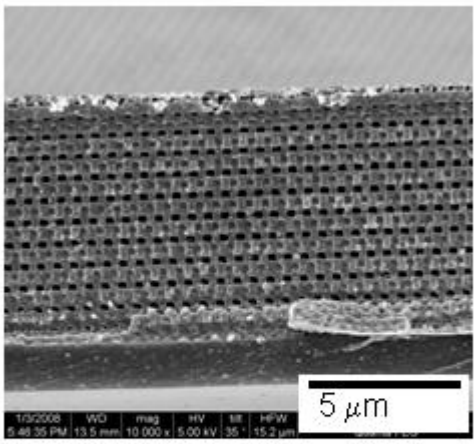


Figure 5. SEM image of PnP 3D resist nanostructure coated with Pt by ALD, showing no degradation of structural features.

capable of withstanding high ALD deposition temperatures above 250°C. High-temperature ALD materials we have deposited onto these structures include Pt, ZnO, and ZrO_2. Examples of 3D nanostructures made using a 2ph exposure (800 nm) and a square array of posts pattern and coated with Pt using ALD are shown in Figure 5. Deposition of the high-temperature Pt does not degrade the 3D nanostructure. Optical measurements of this structure, with an eye towards photonic crystal properties, are commencing.

3 SUMMARY

The PnP lithography technology, coupled with accurate FDTD modeling, enables predictive simulation and fabrication of 3D nanometer-scale structured materials with specific, desired optical and structural properties.

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