Direct write electron beam patterning of DNA complex thin films

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The authors report on the first use of direct write electron beam lithography (DW-EBL) patterning of DNA-based materials. Water insoluble and organic solvent soluble DNA:CTMA complexes were formed by reaction of DNA polymers with cationic surfactants and other molecular species. Thin films with thicknesses ranging from 85 to 300 nm were prepared by spin coating. DW-EBL was conducted using a Raith 150 system. The resulting exposed areas demonstrated either positive or negative resist properties depending on development solution. The characteristics of the DNA:CTMA material as a patternable electron sensitive resist medium are presented for different exposure conditions (10–30 kV), development conditions, structure sizes (100 nm to 20 μm), and structure complexities. Contrast values of ~2 have been obtained in both positive and negative resist modes. Both simple (20 μm diameter circle and square) and complex (Fresnel lens) patterns with nanometer scale features (<100 nm) in DNA films are possible using this method. © *2008 American Vacuum Society.* [DOI: 10.1116/1.2993258]

I. INTRODUCTION

Interest in using the unique properties of DNA has grown rapidly in the areas of bioelectronics and photonic device applications.[1–4] Several properties and processing characteristics are required in order for DNA materials to be usefully incorporated into devices. These include the formation of functional complexes and thin/thick films, ability to pattern the films, and incorporation of the patterns into device structures. The ability to form well characterized DNA complexes in solution and to form thin films with predictable properties by spin coating has been established.[5] We have previously demonstrated the use of DNA complex thin films in high performance organic light emitting diodes[6] and in optically pumped laser applications.[7] To date, several indirect techniques such as surface functionalization,[8] molecular lift-off,[9] or charge trapping[10] have been reported for obtaining DNA nano- and micro-scale features. In these patterning techniques, the DNA thin film is patterned by either the topography or the surface modification of the underlying material. Given the interest in DNA-based devices and material applications at the micro- and nano-scale (such as quantum wires, biosensors, and others) it is important to develop techniques for fine feature patterning of the DNA material. We present the first results, to our knowledge, of direct patterning of DNA thin films by electron beam lithography.

The exposure mechanism is well established for typical electron beam sensitive polymers such as poly(methyl methacrylate) for positive resist[11] and SU-8 for negative resist.[12] In positive resists, energetic secondary electrons break chemical bonds and release acid groups that in turn cut the long chain polymer into many smaller chains with lower molecular weights (MWs). This process results in development selectivity between unexposed longer chains and exposed shorter chains, with the lower MW chain polymers being removed during development. In the case of negative resist, the absorbed secondary electron energy promotes cross-linking of the polymer chains, leading to higher MW material. The lower MW material is again selectively removed during development. Natural DNA is water soluble, which greatly limits its ability to form uniform thin films and is incompatible with standard chemical processes. Reacting DNA with cationic materials forms DNA complexes which are insoluble in water but readily soluble in organic solvents. We have utilized the reaction of DNA with $CH_3(CH_2)_{15}N(CH_3)_3{\bullet}Cl$ [hexadecyltrimethylammonium chloride (CTMA)] to form a DNA:CTMA (Ref. 2) complex which is soluble in butanol (and other organic solvents) and leads to the formation of uniform thin films by the spin-coating technique. Exposure to energetic electrons, shown schematically in Fig. 1, locally modifies the DNA:CTMA complex such that the exposed areas are selectively developed in aqueous solutions and the unexposed areas are selectively developed in specific organic solvents.

II. EXPERIMENT

The formation of DNA:CTMA solutions and the related material properties are discussed in previous work.[5] The film thickness is determined by the concentration of DNA:CTMA in butanol and the spin speed. In this experiment the 3 and 5 wt % DNA:CTMA in butanol solutions were used to spin coat uniform thin films ranging from 85 to 300 nm. The reproducibility of these results was verified by profilometry and ellipsometry. The thin films were then soft baked at 100 °C for 60 s. Previous work[13] suggests that the DNA:CTMA material is stable at temperatures ≤240 °C.

The electron beam patterning of the DNA:CTMA thin films was carried out using a Raith 150 direct write electron beam lithography (DW-EBL) system. All initial experiments involving development and beam conditions were conducted using two dose matrix designs consisting of arrays of 20 μm circles or squares. The exposure dose ranged from 0 to

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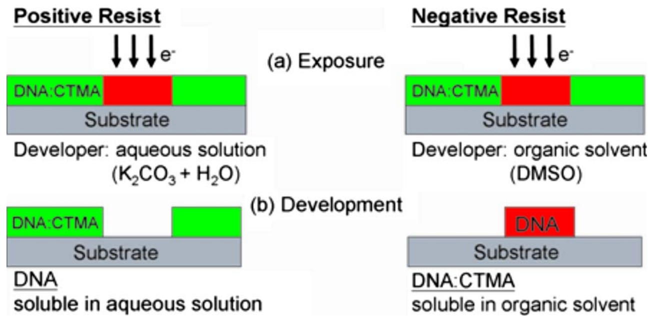

FIG. 1. Electron beam lithography patterning process of DNA complex thin films: (a) exposure and (b) development.

742.5 $\mu C/cm^2$ in 7.5 $\mu C/cm^2$ increments (circles) and 15 to 600 $\mu C/cm^2$ in 15 $\mu C/cm^2$ increments (squares). Development conditions were determined using aqueous solutions and organic solvent solutions, with and without ultrasonic assistance. The effects of electron beam conditions were determined by varying the accelerating potential from 5 to 30 kV. In addition, the effect of beam current density was investigated by using two apertures (30 and 60 μm) at each accelerating potential. The beam spot size as a function of accelerating potential is constant in the selected current range but decreases with increased accelerating potential. For example, the spot size for a 20 kV accelerating potential is ~2 nm for beam currents from a few picoamperes to 100 nA. DNA:CTMA films with thicknesses from 85 to 300 nm were exposed. The results in this study used 85 and 100 nm films. Finally, the Raith "demo pattern" was exposed to determine resolution and the effect of complex geometries for the exposure/development process.

III. RESULTS

Development chemistry for the exposed dose matrix patterns was tested for a variety of aqueous solutions and organic solvents. The results summarized in Table I demonstrate that both positive and negative mode developments are possible. Using water or water with a weak salt solution removed the exposed areas. Water by itself removed the exposed areas but required a fairly long development time (~20 min) while immersed in an ultrasonic bath. The addition of small amounts of the salt potassium carbonate (K_2CO_3; 0.1–0.25 wt %) drastically reduced the development time to ~60 s and increased the resolution. K_2CO_3 is soluble in water (insoluble in alcohols), forming strongly alkaline solutions. Thus, aqueous development of DNA:CTMA acted like a positive resist developer. Several organic solvents such as butanol, propanol, and dimethylsulfoxide [$(CH_3)_2SO$; (DMSO)] were found to remove the unexposed DNA:CTMA regions. DMSO is a highly polar solvent and is usable with both water and other organic liquids. Short (<5 s) development with DMSO in an ultrasonic bath yielded the best results. Thus, development of DNA:CTMA using specific organic solvents yielded a negative resist behavior.

Resist parameters of contrast (γ) and clearing dose (D_{80}) for DNA:CTMA were measured using the square pattern dose matrix developed for 30, 60, and 90 s with H_2O +0.1 wt % K_2CO_3 solution for the positive resist process and 5 and 30 s for the DMSO negative resist process. The results for the positive process are shown in Fig. 2 for a 60 μm aperture, accelerating potentials of 10, 20, and 30 kV, and 60 s development time. The γ for these curves increased from ~1.3 to ~1.9 with increased accelerating potential, while D_{80} increased from 160 to 410 $\mu C/cm^2$. D_{80} is

TABLE I. Development conditions and results for electron beam exposed DNA:CTMA films for various positive- and negative-tone solvents.

Developer	Time (s)	Ultrasonic (min)	Development selectivity	Resist type (+/−)
Water		20	Yes (fair)	(+)
K_2CO_3+water (0.1 wt %)	60	1	Yes (good)	(+)
K_2CO_3+water (6.25 wt %)		1	No (all material removed)	
Butanol		11	Yes (poor)	(−)
Toluene	60	5	No (all material removed)	
Dichloromethane	70	5	No (no development)	
Chlorobenzene	60	10	No (no development)	
Tetrahydrofuron	60		No (all material removed)	
DMSO		30	No (all material removed)	
DMSO		<5	Yes (good)	(−)
Amino-ethanol	60		No (all material removed)	
2-propanol	80	5	Yes (poor)	(−)

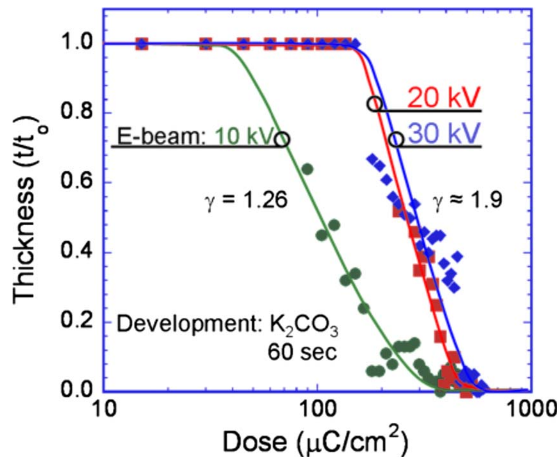

FIG. 2. Contrast curves for K_2CO_3 "positive" resist development: normalized remaining DNA:CTMA film thickness as a function of electron dose for 10, 20, and 30 kV. Contrast (γ) ranges from ~1.3 to ~2 and clearing dose (D_{80}) ranges from ~160 to 440 $\mu C/cm^2$.

defined as the dose where 80% of the material is developed. The results for the negative process are shown in Fig. 3 for a 60 μm aperture, 10 kV accelerating potential, and 5 s development time. For the negative resist development case, the γ is 2.1 and D_{80} is 400 $\mu C/cm^2$. The results for the exposures with the 30 μm aperture and different development times are similar.

Examples of DW-EBL patterning of DNA:CTMA films are shown in Fig. 4 for positive (K_2CO_3) development and in Fig. 5 for negative (DMSO) development. Atomic force microscopy (AFM) was used to scan the exposed and developed surface and create the surface and line scans. The scanned feature for both the positive and negative resist processes is part of the circular dose matrix, namely, a 20 μm diameter circle exposed at 10 kV with a dose of 240 $\mu C/cm^2$. The positive resist feature (Fig. 4) was developed with 0.1 wt % K_2CO_3 solution for 60 s in an ultrasonic bath, while the negative resist process (Fig. 5) was developed with DMSO for 5 s. The original DNA:CTMA film thickness was 85 nm. The exposure dose of 240 $\mu C/cm^2$ at 10 kV is below the clearing dose for both development processes in Figs. 4 and 5. Therefore, the feature depths of ~60 and 30 nm for the positive and negative developments are less than the original 85 nm original DNA:CTMA film thickness. Both development methods produce fairly uniform features with sharp sidewall profiles. The lateral feature measurement deviates from the nominal 20 μm pattern size by <10%.

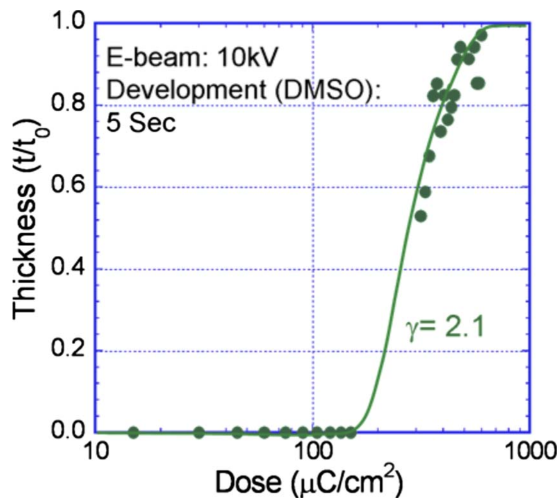

FIG. 3. Contrast curves for DMSO "negative" resist development: normalized remaining DNA:CTMA film thickness as a function of 10 kV electron dose for 5 s development. The contrast (γ) is 2.1 and the clearing dose (D_{80}) is ~400 $\mu C/cm^2$.

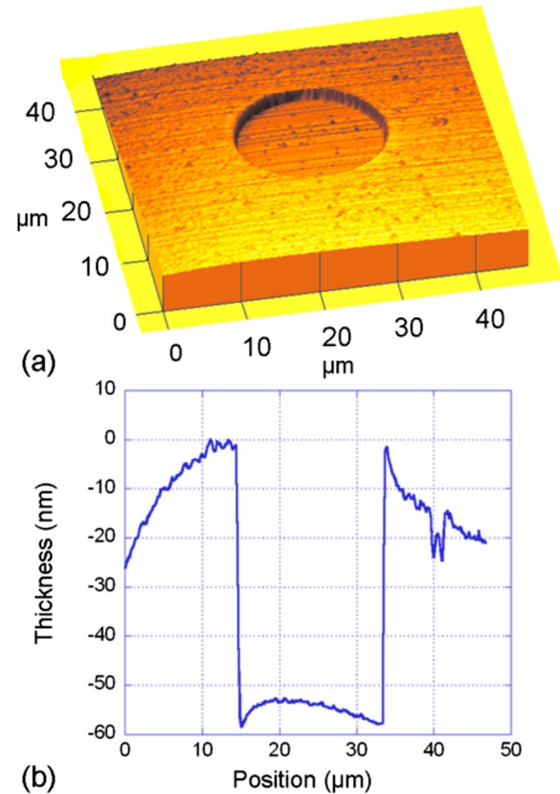

FIG. 4. AFM surface and line scan of DNA:CTMA pattern electron beam exposed at 10 kV and developed in K_2CO_3 for 60 s.

With the exposure parameters determined, several patterns involving nanoscale features and complex patterns were exposed. Feature sizes as small as 70 nm were confirmed for both the positive and negative resist processes. The AFM area and line scan in Fig. 6 of the Raith demo pattern Fresnel lens structure demonstrate both the ability to directly write complex patterns with DW-EBL in the 85 nm thin film DNA:CTMA material and resolve <100 nm features. The positive-tone pattern was obtained by electron beam exposure at 10 kV with a dose of 500 $\mu C/cm^2$ and development in 0.1 wt % K_2CO_3 solution for 60 s. The line scan shows clear features with depths of ~40–60 nm. The narrow outer ring of the lens structure has a width of ~100 nm. Features ranging from 75 nm to 1 mm have been written using the Raith 150 DW-EBL system.

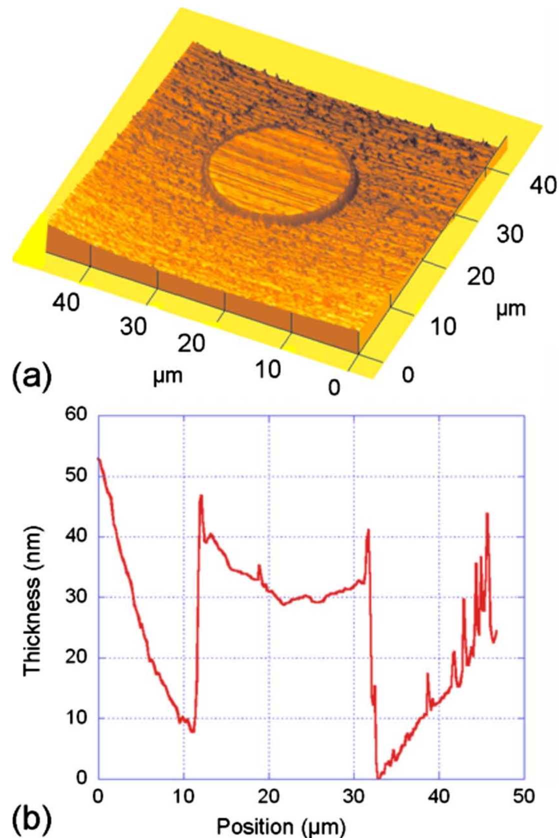

FIG. 5. AFM surface and line scan of DNA:CTMA pattern electron beam exposed at 10 kV and developed in DMSO for 5 s.

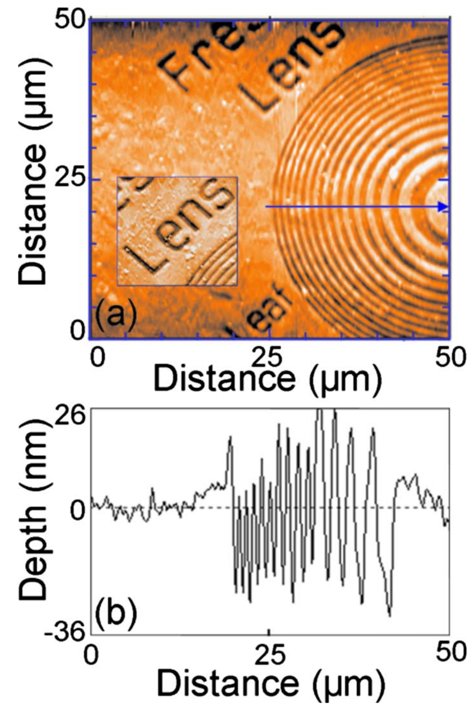

FIG. 6. AFM surface and line scan of micro/nanoscale features using the Raith demo pattern: (a) surface image of the Fresnel lens structure; (b) line scan of the Fresnel lens structure with smallest features measuring 100 nm. Positive-type pattern developed with K_2CO_3 for 60 s. Insert shows a section of the surface scan modified to improve resolution.

IV. DISCUSSION AND CONCLUSIONS

In this work we have shown that DNA:CTMA thin film material is sensitive to electron beam energies and that DW-EBL is a viable and relatively simple method for nanoscale patterning of such materials. In addition, development chemistry provides an avenue for either positive- or negative-type resist development by simply changing the development solution. Thin films of DNA:CTMA can be formed by spin coating ranging from ~50 nm to greater than 2 μm by increasing the wt % of DNA:CTMA in butanol and varying the spin speed. Contrast coefficients of 1.9–2.1 for positive and negative resist developments are comparable to commonly used positive and negative resists.[11,14] Clearing doses ranging from 160 to 450 $\mu C/cm^2$ are also comparable to these for existing resists.

We have also demonstrated features that can be exposed/developed by both positive and negative resist development processes. The larger features are shown to have a precise shape and sharp sidewalls. This process has the potential for increasing the basic knowledge of the DNA molecule and is well suited for incorporating DNA:CTMA and DNA complex materials in device applications.

The working hypothesis for the exposure/development mechanisms is still under investigation and will be published elsewhere. Possible mechanisms that need to be considered include the following: (1) electron energy breaks the ionic bond of the DNA:CTMA, resulting in the disassociation of the DNA and CTMA; (2) electrons directly charge the DNA:CTMA molecule, changing the hydrophobic character of the material; (3) electrons dissociate the alkyl tail of the CTMA molecule, reducing its hydrophobicity; (4) electrons break the double helix structure of the DNA, resulting in small double helix or single strand DNA segments, with higher solubility. All the above mechanisms can lead to the formation of water soluble DNA and CTMA or the DNA:CTMA itself becoming soluble in aqueous solution.

DNA thin films have remarkable potential for photonic applications. The discovery of direct e-beam patterning of DNA complex films creates new opportunities for incorporating DNA in novel biodevices. To fulfill these opportunities, we plan to investigate in detail the exposure/development mechanisms and their effects on the DNA material properties. We will be exploring electronic and electro-optic device applications for the DW-EBL patterning process of DNA.

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