Scanning thermal lithography: Maskless, submicron thermochemical patterning of photoresist by ultracompliant probes

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This article introduces a scanning probe lithography technique in which ultracompliant thermal probes are used in the selective thermochemical patterning of commercially available photoresist. The micromachined single-probe and multiprobe arrays include a thin-film metal resistive heater and sensor sandwiched between two layers of polyimide. The low spring constant (<0.1 N/m) and high thermal isolation provided by the polyimide shank is suitable for contact mode scanning across soft resists without force feedback control. The probes provide what is effectively a spatially localized postexposure bake that crosslinks the photoresist in the desired pattern, rendering it insoluble in developer. For 450-nm–1400-nm-thick AZ5214E (Clariant Corp.), line and dot features with sizes of 450 –1800 nm can be printed using probe powers of 13.5–18 mW, and durations of 1–60 s per pixel. Variation of feature sizes with process parameters is described. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1808732]

I. INTRODUCTION

With the increasing costs of photomasks—often in excess of one million dollars for state-of-the-art complementary metal-oxide-semiconductor processes—alternatives to optical lithography have been sought, particularly for low-volume manufacturing and prototyping in conventional processes. As a maskless lithography approach, scanning probe lithography (SPL) offers the promise of high spatial resolution (which is not limited by the diffraction of light) and, for low-volume applications, substantial savings in mask and equipment costs.

It is interesting to note that as methods in scanning probe microscopy developed over the last few decades, most have been applied to lithography.[1] Years after the invention of the scanning tunneling microscope (STM) in the 1960s, scanning probe lithography was born when an STM was later used to selectively oxidize hydrogen-terminated Si surfaces with nanometer resolution.[2] Likewise, the atomic force microscope (AFM), originally used for mapping topography, was later modified to "scratch" thin metals[3] and soft polymers,[4] again with resolution in the tens of nanometers. The near-field scanning optical microscope, which employs scanning probe tips to focus light, was used directly to optically pattern photoresist with resolutions beyond the far-field diffraction limit.[5] Several other lithographic techniques have grown out of AFM and STM technology, two of which are electrostatic[6] and dip-pen lithography.[7]

Scanning thermal microscopy, introduced in 1986, has also found complementary efforts in lithography, but nearly all are based on thermomechanical indentation, that is, the use of heat and pressure in submicron tips to etch pits into polymers with glass transition points. Initally, heat was provided by an external laser pointed at a conventional AFM tip,[8] and later by thin-film heaters embedded in the cantilever.[9] Thermomechanical indentation has been pursued with interest in ultra-high-density data storage, the most notable device being the IBM "millipede."[10] In this work, we demonstrate that scanning thermal probes can be applied towards lithography by thermally catalyzing a chemical reaction in a submicron region (Fig. 1) rather than by thermomechanical indentation. We have demonstrated this principle on the positive tone photoresist AZ5214E (Clariant Corp.) in a process similar to image reversal. The use of localized heat to pattern this resist has been previously explored by focusing semiconductor lasers.[11] Some potential advantages of the proposed method are that it is less prone to tip wear and produces less debris when compared to purely mechanical SPL techniques; however, it does require scanning over soft photoresist. An enabling device for this technique has been the ultracompliant probe technology, reported previously by our group,[12,13] which minimizes damage to both the sample and the probe tip. Both single probes and eight-probe arrays are shown to provide thermochemical patterning of photoresist.

II. PROCESS AND DEVICE CONCEPTS

Several structural features of the ultracompliant probes (Fig. 2) make them well suited for the lithography process, the most important aspect of which is use of a thin-film polyimide as the structural material for the cantilevers. The excellent thermal resistance of the polymer allows the probe tips to be heated to temperatures of nearly 300 °C by embedded thin-film heaters operating at <20 mW, while the low spring constant (~ 0.08 N/m for the single probe) allows for scanning over photoresists and other soft polymers in the absence of mechanical feedback without scratching the resist and with minimal wear to the tip. The elimination of force feedback is especially important when scaling to arrays of probes. If rigid cantilevers are used, tip height nonuniformity

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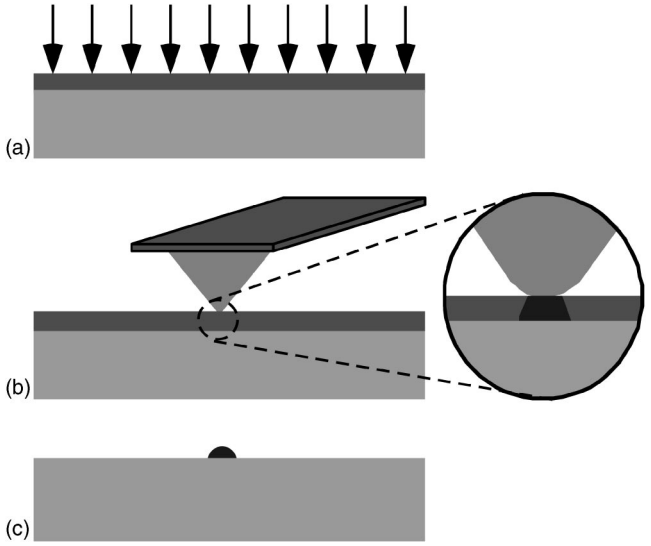

FIG. 1. Process flow for scanning thermal lithography of AZ5214E resist. (a) Flood exposure generates photoacids. (b) Spatially localized thermal crosslinking occurs under the heated probe tip (inset) as a result of the photoacids and elevated temperatures. (c) The insoluble crosslinked region remains after development in TMAH developer.

across the array can result in significant variation in contact force when it is lowered to the substrate,[10] necessitating feedback control at the probe level to prevent excessive force in any one tip. The low spring constant in the ultracompliant array passively accomplishes the same function, thus eliminating the need for force feedback. An additional feature of the array is that each probe has individual heater control which can allow for independent patterning if desired.

Both single probes and multiprobe arrays are fabricated in the same low-cost micromachining process in which a thin-film metal bolometer is sandwiched between two insulating layers of polyimide.[13] The thin metal film, consisting of 300–1200 Å Au between two adhesion layers of 100 Å Cr, is molded into an anisotropically wet-etched notch in the Si substrate to form the scanning tip. Two lines extending outwards from the tip region form the heating element. Electrical connection to the bolometer is provided by thicker metal lines extending the length of the cantilever. The total resistance ranges from 20 to 200 Ω depending on design and process parameters. The probe is then released from the substrate, flipped out over the die edge, and held in place by a thermocompression bond between two thin films of Au.

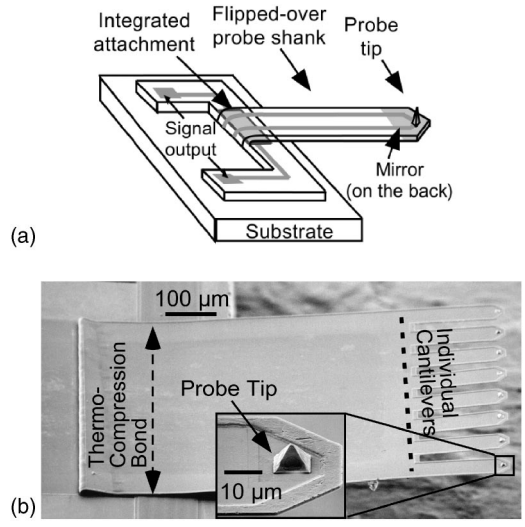

FIG. 2. (a) Schematic of the micromachined single probe, and (b) scanning electron micrograph of the eight-probe array surface micromachined from polyimide on a Si substrate. Thin-film resistors integrated on the tip of the cantilevers allow the individual probes in the array to be heated independently of one another.

With regard to the patterning of the sample by the probes, the photoresist AZ5214E is one of the very few positive tone photoresists that can function as a negative tone resist by a process called image reversal. Conventional image reversal begins with a patterned UV exposure which generates photoacids in unmasked regions. A subsequent postexposure bake (PEB) thermally activates a crosslinking reaction catalyzed by the photoacids in the previously exposed regions.[14] The crosslinked regions become insoluble in alkali developer, and are insensitive to any further UV processing. The substrate is then flood exposed to solubilize all non-crosslinked regions. Development in tetramethyl ammonium hydroxide (TMAH) leaves a negative photoresist image.

III. EXPERIMENTAL RESULTS

Temperature calibration of the single probe is relatively straightforward because the fractional change in the probe resistance ($\Delta R/R$) is directly proportional to the increase in tip temperature (ΔT) by a constant K.[12] The thin-film heater accounts for the majority of the probe's resistance and results in a linear relationship between the measured resistance and tip temperature. To determine the constant K, the single-probe cantilever was immersed in water and the current was ramped until bubble formation and rapid evaporation was observed. Water was found to boil at a 2.16% increase in probe resistance, and by correlating this to a 75 °C increase in tip temperature, K was found to be 288 ppm/°C. Repeating the same experiment with isopropyl alcohol (boiling point 85 °C) resulted in a virtually identical figure. Using the above calibration, the tip temperature can be correlated to the measured resistance during probe operation. The probes can be heated to approximately 300 °C before high temperatures begin to damage the cantilever structures. It should be noted that the temperature versus power relationship differs depending on the degree of thermal isolation from the surrounding environment. A probe operating in proximity or in contact with the substrate requires about 30% more power than when suspended in air due to the heat loss to the substrate. Nevertheless, the typical input powers needed to reach temperatures in excess of 250 °C while in contact was $<$20 mW.

The scanning thermal lithography (Fig. 1) proposed for this effort is similar to the conventional process, except that it involves patterning the PEB instead of the initial exposure. AZ5214E photoresist at full concentration was spun on Si wafers to obtain a thickness of 1.4 μm, and diluted 50% with

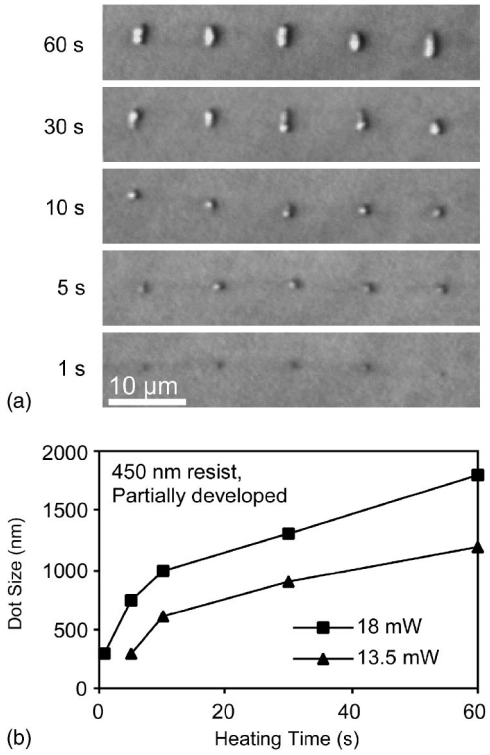

FIG. 3. Dot sizes can be controlled by the heating times as well as heating power. (a) Reduction in size with shorter heating times using a probe biased at 18 mW on 450 nm resist. (b) Dot sizes vs heating time for 18 and 13.5 mW power.

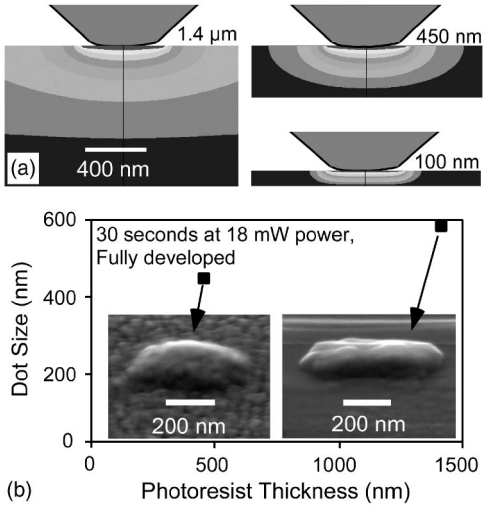

FIG. 4. (a) Finite element simulations with photoresist thicknesses of 1.4 μm, 450 nm, and 100 nm show that the geometry of heat flow becomes vertical as the photoresist is thinned below the diameter of the tip, resulting in smaller features. (b) Dots obtained after fully developing 1400 and 450 nm resists follow the same trend. The roughened surfaces in the micrographs are due to an Au/Pd layers sputtered for scanning electron microscopy.

polyethylene glycol methyl ether (PGMEA) solvent (Nano EBR, Clariant Corp.) to obtain 450 nm thickness. Further dilution resulted in poor uniformity; however, in general it is expected that thinner resists will permit smaller feature sizes to be patterned (discussed later in this article). After softbaking, the resist was flood exposed to generate photoacids globally. The heated thermal probes were then scanned across the surface point by point, each point being heated anywhere between 1 and 60 s. Regions under the probe tip crosslink and become alkali insoluble. The resist was developed in diluted TMAH (0.21 N) in order to maintain the highest contrast between crosslinked and noncrosslinked regions.[15]

To fully crosslink, AZ5214E requires temperatures of about 90 °C, but it was found that simply biasing the probe tip at this temperature was inadequate due to the thermal contact resistance between the tip and the photoresist. Except where indicated, the single probe was biased at 18 mW, corresponding to a tip temperature of 275 °C. In addition, the substrate was biased at 45 °C using a hot plate in order to further reduce the amount of heat that the probe needed to provide. Tests showed that when the contact force was made excessively high by flexing the cantilever towards the substrate, the increased pressure in combination with the high tip temperature resulted in thermomechanical indentations penetrating all the way through the resist, and no thermal patterns were observed after development. Conversely, weak contact forces resulted in poor thermal contact, also resulting in no pattern formation. An intermediate contact force of about 480 nN was found to be successful. The advantage of using flexible probes is again noted here in that once the probe is biased at some contact force, that force does not change significantly over the sample topography, thereby increasing the uniformity of the patterned structures.

Using the process described above, submicron dots and lines were obtained, in some cases when the photoresist was partially developed, and in other cases when it was fully developed. It was found that dot sizes could be well controlled by the changing the probe temperature as well as the heating times (Fig. 3). Using an 18 mW bias on 450 nm resist resulted in features that ranged from 400 to 1800 nm as heating times were increased from 1 to 60 s. Reducing the power to 13.5 mW power resulted in the same feature sizes, but required longer heating times. The above results were found after partially developing the 450 nm photoresist. Features patterned at 18 mW for longer than 30 s remained after full development of both 1.4 μm and 450 nm resists (Fig. 4). Biasing at high powers and heating for longer times results in a higher degree of crosslinking because the crosslinking reaction is, in effect, both temperature and time dependent.

Feature sizes shrink with photoresist thickness due to the decreased lateral flow of heat. Two-dimensional ANSYS heat flow models [Fig. 4(a)] qualitatively show that as the thickness of the resist is reduced below the diameter of the scanning tip, the cylindrical flow of heat results in features of approximately the same size as the tip. A thick resist permits the heat to spread laterally, increasing feature sizes. For example, using identical heating powers and times (18 mW, 30 s) on both 1.4 μm and 450 nm resists produced dot sizes of 590 and 450 nm respectively, after full development of the

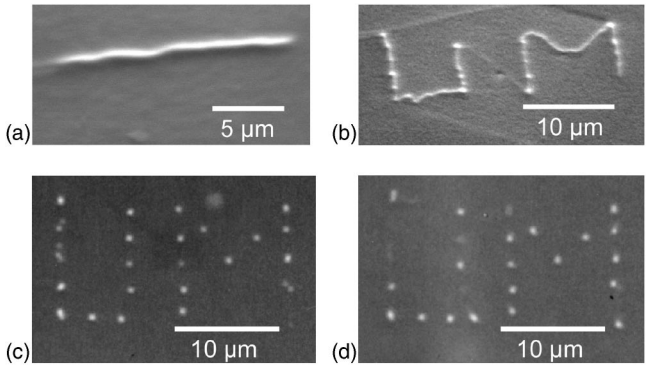

FIG. 5. (a) and (b) Lines of 500 nm width written by patterning successive dots with 200 nm spacing (1 s heating per dot) can be seen after partial development of the photoresist. (c) and (d) Parallel lithography is demonstrated in which two adjacent probes in the eight-probe array simultaneously generate the same pattern.

photoresist [Fig. 4(b)]. The use of a thick resist also runs the risk of creating reentrant cross-sectional profiles that can be undercut during development.

Fully developed dots of 450 nm minimum diameter were obtained with photoresist layers of approximately 450 nm thickness. Further scaling down of features sizes for the purposes of lithography can be accomplished by using sharper tips and thinner resists, particularly those that are chemically amplified (chemical amplification can also help to reduce heating times and increase throughput). The diameter of the scanning tips in the present design can be made as small as 50 nm using oxide sharpening,[16] and others have reported custom fabrication of thermal probes with tip sizes as small as 20 nm.[17]

Line patterns formed by heating successive pixels are shown in Fig. 5(a). Linewidths of 500 nm were observed in partially developed resist at effective speeds of 200 nm/s, while slower speeds of 10–20 nm/s were needed to retain the lines after full development. This is likely because a stronger degree of crosslinking was required to prevent undercutting of the resist. The torsional flexing of the compliant cantilever resulted in some line distortion [Fig. 5(b)], but this can be minimized by lifting the probe between each pixel. The structure of the probe itself could also be modified to provide a stiff torsional spring constant while maintaining a low vertical spring constant.

The final experiment demonstrated the use of the multiprobe array to perform parallel lithography. The eight-probe array was used to write pixels at 5 μm pitch, and the patterns produced by two adjacent probes are shown in Figs. 5(c) and 5(d), respectively. Probe tips were lifted up between pixels, thereby reducing the line distortion; however, during the course of this experiment, external vibrations shifted some of the probes, resulting in double patterning in some areas. With this exception, the feature sizes are fairly uniform between probe tips. Although not shown in this experiment, the probes can also be operated at different powers, allowing the formation of independent patterns.

During the course of the experiments, reliability of the probes was found to be excellent in that all of the probes appeared to run many samples with no noticeable tip damage or deterioration in thermal performance. Longevity of scanning probe tips is an important aspect to consider if they are to be used in a manufacturing process.

In conclusion, this effort has demonstrated that scanning thermal probes can be used, both singly and in parallel, in the thermochemical patterning of AZ5214E. The resolution of this technique can be scaled down in a relatively straightforward manner. The lessons of this effort are as follows: first, the throughput can be addressed to some degree by the use of multiprobe arrays; second, pixel sizes can be controlled by heating times and powers, and finally, the procedure is less costly in the sense that it does not require photomasks or optics, nor does it require a vacuum or UV filtered environment. Ultimately, the resolution and throughput of this technique are determined by the size of the tips, the number of probes that can be scanned in parallel, and the thickness and thermal sensitivity of the resist. In a broader sense, this work has shown that scanning thermal lithography can be used for patterning any thin film for semiconductor and biological applications or for triggering a chemical reaction at the surface of a material.

ACKNOWLEDGMENTS

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