Near-field scanning optical nanolithography using amorphous silicon photoresists

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(Received 31 August 1998; accepted for publication 29 October 1998)

Near-field scanning optical microscopy (NSOM) patterning of hydrogenated amorphous silicon (*a*-Si:H) has been explored. Our sample preparation technique produces films that are stable over several days. The etching process used is highly selective, allowing the unexposed *a*-Si:H to be completely removed while patterns with line heights equal to the original film thickness remain in exposed regions. We are able to generate patterns with and without the use of light. We have found that the probe dither amplitude greatly affects the linewidth and height of patterns generated without light. We also find that the exposure required for the NSOM to optically generate patterns agrees with threshold dosages determined by far-field exposure studies. Feature sizes of approximately 100 nm, comparable to the probe diameter, were obtained. © *1999 American Institute of Physics.* [S0003-6951(99)04001-2]

In this letter, we report the results of using a near-field scanning optical microscope (NSOM) in conjunction with a hydrogenated amorphous silicon (*a*-Si:H) photoresist for nanolithography. NSOM is a scanning probe technique that allows optical excitation of materials at spatial resolutions well below the diffraction limit. While near-field techniques are not new,[1] the recent interest in NSOM has been stimulated by the development of near-field apertures which are suitable for visible to UV wavelengths.[2] The apertures are formed by tapering an optical fiber and are typically 100 nm or less in diameter. The fiber tip is scanned across the sample surface while maintaining a fixed tip-sample separation using shear force feedback.[3] The separation is much less than the wavelength of light and, hence, in the near field. Light emitted or collected from the fiber is used to record optical images such as transmittance, reflectance, photovoltage, or photoluminescence with lateral resolutions much better than 100 nm. Images of surface topography are obtained simultaneously.

NSOM can also be used as a tool for photolithography on the submicron length scale. In this application the fiber optic probe is used as a light source to expose a photoresist, and patterns are generated by scanning the probe over the resist surface. Because this technique is not diffraction limited, it has the potential to generate features with widths less than those achievable by conventional far-field optical lithography. NSOM patterning of conventional photoresists, photosensitive polymers, and ferroelectric surfaces has been demonstrated.[4–6]

Amorphous silicon has been shown to be a potentially useful resist for nanoscale lithography based on scanning microscope techniques.[7–9] In general, patterning *a*-Si:H involves selectively oxidizing the *a*-Si:H surface by local removal of hydrogen passivation. The oxide layer formed in this way then becomes a mask for subsequent etching of the surface. Madsen *et al.* have shown that NSOM can be used to pattern *a*-Si:H optically with dimensions less than 100 nm.[10] They have also observed that proximity of the fiber tip to the *a*-Si:H surface can lead to patterning even in the absence of optical illumination. Their work was done on sputtered *a*-Si:H using wet chemical etching for development.

In the present work we have examined both proximity effect and optical patterning of *a*-Si:H photoresist using NSOM. Resists were deposited by plasma enhanced chemical vapor deposition (PECVD) and etching was done in a hydrogen plasma using the same PECVD system. The required optical doses needed for film exposure at various wavelengths were determined and the effects of the probe dither amplitude and optical exposure on pattern generation were studied using secondary electron microscopy (SEM), atomic force microscopy (AFM), and NSOM.

For this study, *a*-Si:H films were grown on crystalline silicon wafers to a thickness of ~100 nm using standard PECVD.[11] Silane was used as the source for deposition, which was typically done at 500 mTorr and 50 °C. The films were removed from the vacuum system at room temperature to avoid native oxide growth.[12] Samples were patterned in open air using the NSOM at room temperature. NSOM tips were prepared both by chemical etching[13,14] and by pulling using a Sutter Instruments Co. P2000 micropipette puller.[15] The probes were coated with approximately 100 nm of aluminum. For proximity effect studies uncoated tips were also used. Both ultraviolet (UV) and visible light tips were prepared. The results discussed here were obtained using visible

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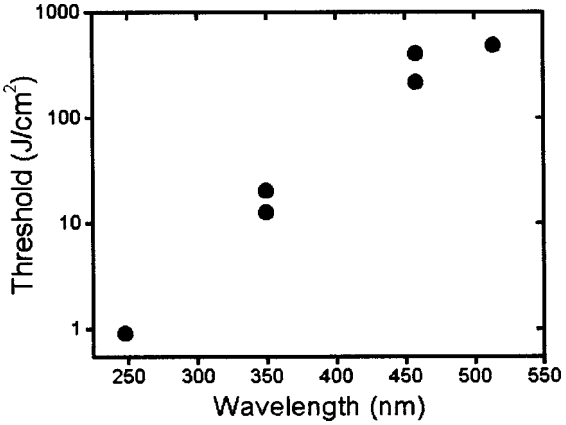

FIG. 1. Optical doses required to fully expose the *a*-Si:H resist are shown as a function of illumination wavelength. Exposure was done through a shadow mask using the cw lines of an Ar-ion laser except for the 248 nm point which was obtained using a pulsed excimer laser.

light tips and the lines of an Ar-ion laser as the light source. The NSOM probe was attached to a piezoelectric tube, which was oscillated (dithered) parallel to the sample surface. This dithering provided the necessary signal for maintaining a constant probe-sample separation of approximately 5–20 nm.[3] The sample was scanned in a serpentine pattern beneath the tip.

After patterning with the NSOM, the samples were developed in a hydrogen plasma etch in the PECVD system. The etch selectivity between oxidized and hydrogen terminated *a*-Si is greater than 500 to 1 allowing the unexposed *a*-Si:H to be removed even if the thickness of the oxide produced by the NSOM is only a few Angstroms.[12] This etch selectivity is an order of magnitude larger than typically observed with wet chemical etches or other plasma chemistries. Since the hydrogen passivated surface is not entirely stable, exposure to atmosphere eventually leads to the formation of oxides on the surface and patterning is no longer possible. A study of the air stability of the *a*-Si:H was performed to determine the limit this places on the handling time of samples. A sample was stored in the dark in a normal laboratory environment. A section of the sample was etched periodically to determine the time required to remove the *a*-Si:H layer. No change in the etch rate was detected until after eight days, when it began to drop. In agreement with this, we patterned samples several days after *a*-Si:H deposition with no noticeable difference relative to a fresh layer.

The optical dose required to induce oxidation of the *a*-Si:H was measured as a function of illumination wavelength as shown in Fig. 1. For this study, a 100-nm-thick *a*-Si:H film was exposed to a light source through an aluminum shadow mask. The power densities used at each wavelength were generally kept low (<3 W/cm^2) to avoid thermal heating of the sample. The threshold dose was defined as the dose which left the exposed region untouched when the unexposed region was completely removed by the etch. This threshold definition leads to an exposure that would give rise to well defined features in lithographic applications. We note, however, that partially developed patterns could be observed for doses an order of magnitude less than threshold. A continuous wave (cw) Ar-ion laser was used as the light source for 350, 458, and 514 nm illumination. Measurements were also made using the 632.8 nm HeNe laser line. Although all exposures at 632.8 nm were below threshold, partial patterns were visible. The generation of patterns at low power and photon energy suggests that electron hole recombination is involved in the hydrogen desorption.[16] A pulsed excimer laser was used for the 248 nm point. While we cannot rule out the possibility that high peak intensities due to pulsed operation may contribute to a reduced threshold at 248 nm, Fig. 1 makes it quite clear that shorter wavelengths decrease the required dose and allows us to estimate maximum write speeds for NSOM lithography. Assuming a tip aperture of 0.1 μm, 1–2 mW of light at 350 nm coupled into the fiber, and transmission efficiencies ranging from 10^{-6} to 10^{-2},[17] the write speeds range from 0.1 to 1000 μm/s.

In agreement with Madsen *et al.* we observed that proximity of the NSOM tip to the *a*-Si:H resulted in oxidation of the surface and pattern generation even in the absence of light.[10] Figure 2(a), for example, shows an AFM image of a serpentine pattern written in an *a*-Si:H layer using an NSOM tip with no light. To explore this effect further, patterns were generated while varying NSOM scan conditions. For the range of scan speeds (1–100 μm/s) and tip-sample separations (~4–20 nm during feedback) used in this study, linewidth and height were not significantly affected by varying these parameters. Dither amplitude, however, strongly influenced linewidth and height. A series of patterns was generated while varying dither amplitude and holding all other parameters fixed. The dither amplitude was monitored using conventional optical detection of laser light scattered off the tip.[3] Since the relationship between the absolute dither amplitude and this signal depends on factors such as the tip taper and the location of the light on the tip, absolute dither amplitudes were not determined. For a given tip, however, this method allows relative changes in dither amplitude to be

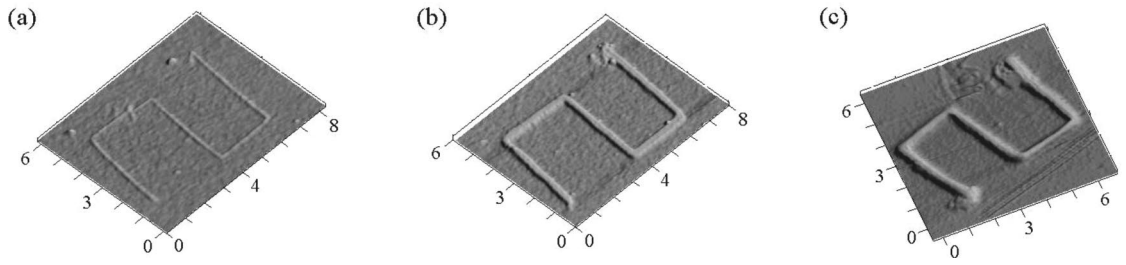

FIG. 2. Contact AFM images of three patterns generated by NSOM are shown. Dimensions are in microns. Images (a) and (b) were obtained by proximity effect in the absence of optical illumination. Increased dither amplitude was used for (b) relative to (a) with all other parameters held constant. Average line width increased significantly, from ~140 to 320 nm. A change in line height from ~15 to ~45 nm was also seen. In (c), light was used with an intermediate dither amplitude resulting in a line height of ~58 nm. Without the use of light, these parameters produced lines only ~27 nm tall.

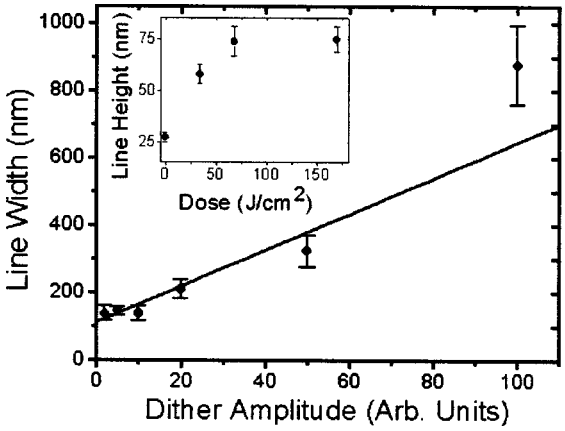

FIG. 3. The dependence of the linewidth on dither amplitude in the absence of optical exposure is shown. Linewidth decreases to approximately 100 nm as dither amplitude is decreased. The inset shows the dependence of line height on optical exposure for fixed dither amplitude. Patterns are more fully developed as the optical exposure is increased. Error bars represent fluctuations in linewidth or height along the trace.

easily determined. We report relative values in this letter. The trace in Fig. 2(a) was written with no light at a scan speed of 1 μm/s using a small dither amplitude. The lines are $\sim$140 nm wide and 15 nm tall. The trace in Fig. 2(b) was drawn after increasing the dither amplitude. Its lines are $\sim$320 nm wide and 45 nm tall. The resulting linewidths for this series of patterns are presented in Fig. 3 as a function of dither amplitude.

It seems likely that the linewidths are to first order determined by the probe movement and the diameter of the probe. The minimum linewidth extrapolated to zero dither amplitude would then be expected to be comparable to the probe diameter. The value of roughly 100 nm extracted from Fig. 3 is consistent with this. The decrease in line height with decreased dither amplitude indicates that lower dither amplitudes result in incomplete exposure of the *a*-Si:H.

Given the dependence of linewidth and height on dither amplitude during proximity effect patterning, it is natural to speculate that the shear force interaction removes the hydrogen surface termination in the absence of light. The origin of the shear force interaction is, at present, poorly understood. Proposed explanations include long range van der Waals forces, contamination layers, image-charge current dissipation, and physical contact between the probe and sample.[18] Shear force has been shown to depend on ambient conditions and on humidity in particular.[3,19] If the probe were, for example, interacting with a surface water layer, this layer could be responsible for removing hydrogen. Future experiments will explore the effects of background humidity and ambient gas on nonoptical patterning.

Using a medium dither amplitude and 458 nm cw illumination, true optical exposure of the resist was explored by writing a series of patterns while all parameters were held constant except for light intensity. The optical dose was varied from 0 to $\sim$170 J/cm^2, roughly the threshold dose at 458 nm which is shown in Fig. 1. We note that dose estimates were based on the far-field intensity emitted by the probe, and the actual dose may have been higher. As dose increased from zero to the maximum value, linewidth increased by only a few percent. Line height, however, changed dramatically as shown in the inset to Fig. 3. The line height of 75 nm for the maximum dose is comparable to the original film thickness. Figure 2(c) shows an AFM image of the pattern obtained with a dose of $\sim$30 J/cm^2.

In conclusion, we present results of using NSOM for photolithography of *a*-Si:H. Our sample preparation technique produces films with relatively long-term stability. Our etching process is highly selective, allowing the unexposed photoresist to be completely removed while patterns with line heights equal to the original film thickness remain. We are able to generate patterns with and without the use of light. We have found that the probe dither amplitude greatly affects the linewidth and height of patterns generated without light. We also find that the exposure required from the NSOM tip to optically generate patterns agrees with threshold doses calculated by illuminating samples through a shadow mask.

The authors profited from valuable conversations with A. T. Hunter and T. F. Kuech as well as the technical support of O. Wolf, J. P. Kitner, S. C. Lindstrom, and J. Flory throughout the course of this work. They would like to thank Connie Volz for depositing and etching the *a*-Si:H films. They also gratefully acknowledge the support of the Defense Army Research Projects Agency through STTR Contract No. DAAH01-97-C-R225 and support from the National Science Foundation through Grant No. DMR-9704780.

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