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Nanometer table-top proximity x-ray lithography with liquid-target laser-plasma source

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A compact laser-plasma proximity x-ray lithography system suitable for laboratory-scale low-volume nanometer patterning is presented. The laser-plasma source, which is based on a fluorocarbon liquid-jet target, generates high-brightness $\lambda = 1.2\text{--}1.7$ nm x-ray emission with only negligible debris production. The Au/SiN_x x-ray mask is fabricated by employing ion milling and a high-contrast e-beam resist. With SAL-601 chemically enhanced resist we demonstrate fabrication of high-aspect-ratio, sub-100 nm structures. The exposure time is currently 20 min using a compact 10 Hz, $\lambda = 532$ nm, 70 mJ/pulse mode-locked Nd:YAG laser. However, the regenerative liquid-jet target is designed for operation with future, e.g., 1000 Hz, lasers resulting in projected exposure times of ~ 10 s. © 1997 American Vacuum Society. [S0734-211X(97)01004-4]

I. INTRODUCTION

Proximity x-ray lithography shows promise of becoming a suitable technique for the fabrication of nanometer structures.¹⁻⁵ Pattern transfer with feature sizes of a few tens of nanometers is feasible.² Most current systems are, unfortunately, based either on expensive synchrotron sources^{1,2} having limited accessibility, or conventional low-intensity electron impact sources^{3,4} that result in long exposure times. This has limited the spread of the technology into the nanofabrication community. The laser plasma is an alternative high-brightness x-ray source.⁵ However, previous laser-plasma-based lithography has utilized larger-scale lasers and conventional target systems, such as bulk metal⁶⁻⁸ or thin metal films.⁹ Such target systems have a limited operating time between the necessary changes of the target. They do not allow a high laser repetition rate, which results in a limited average x-ray flux. They also suffer from severe debris emission making mask damage a problem. By using microscopic liquid fluorocarbon droplets as the target, the debris problem is reduced by several orders of magnitude.¹⁰ Furthermore, the droplet x-ray source¹¹ is compact, may be operated at high repetition rate, provides nearly 4π steradian access and is practically unlimited in operating time. In the present article we combine a modified version of the droplet x-ray source with a simple method for x-ray mask fabrication, demonstrating laboratory-scale lithography of high-aspect ratio sub-100 nm structures. This compact system has potential for short-exposure times and is particularly appropriate for low-volume laboratory-scale applications of nanolithography.

II. EXPERIMENTAL ARRANGEMENT

The operation of the original table-top fluorocarbon-droplet source¹⁰ was modified by employing a microscopic liquid jet for enhanced long-term stability and simpler tem-

poral synchronization.¹² The experimental arrangement of the lithography system is shown in Fig. 1. A fluorocarbon liquid is forced through an ~ 10 μm capillary glass nozzle by a pressure of ~ 40 bar into a $\sim 10^{-4}$ mbar vacuum chamber. This produces a microscopic fluorocarbon liquid jet that is a few mm long. The diameter is ~ 15 μm and the velocity is ~ 50 m/s. The jet is irradiated from the side by the focused beam from a 10 Hz mode-locked Nd:YAG laser (Continuum PY61C-10). The laser generates 120 ps, $\lambda = 1064$ nm, 140 mJ pulses. By the frequency conversion and mixing in three nonlinear crystals this is converted into a 3 mJ, $\lambda = 355$ nm prepulse which hits the liquid-jet target 7 ns before the 70 mJ, $\lambda = 532$ nm main pulse.¹³ The laser pulses are converted into x rays in the $\lambda \approx 1.2\text{--}1.7$ nm spectral range with a conversion efficiency of approximately 4%, resulting in $\sim 1.8 \times 10^{12}$ ph/sr/pulse. The conversion efficiency is slightly smaller than that in Ref. 10, which may be attributed to the longer laser pulses used in the present experiment. The $\lambda < 1.7$ nm x rays are mainly due to F IX and F X emission. The full width at half-maximum (FWHM) diameter of the x-ray emitting plasma was measured to be 30 μm with a pinhole camera. The small size of the plasma as well as negligible debris make it possible to use a small distance (40 mm) between the plasma and the mask/substrate unit, while still maintaining an acceptable penumbral blur. This increases the x-ray intensity at the substrate. The target liquid not used for x-ray generation is collected in a liquid nitrogen trap.

The lithography exposure chamber is equipped with a loadlock system for rapid exchange of mask/substrate units while the liquid-jet x-ray source is operating in vacuum. Three spring-loaded screws on a stainless steel chuck press the mask against the resist-coated Si substrate via a 13 μm polyimide spacer. The mask/substrate unit is then inserted into the exposure chamber so that the substrate surface is positioned ~ 40 mm from the plasma.

The x-ray mask was manufactured on a 250 nm thick SiN_x membrane¹⁴ covered by an absorbing layer of 185 nm Au and 3 nm NiCr. Patterning of the mask's absorbing metal

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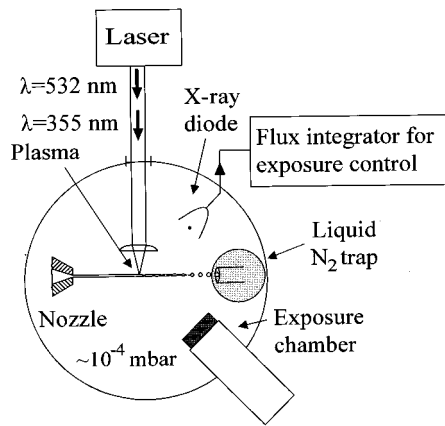


FIG. 1. Experimental arrangement for table-top nanometer x-ray lithography using liquid-jet laser-plasma source.

layers was performed by Ar^+ ion milling. The resist mask for the ion milling was prepared by e-beam exposure of the high-contrast positive resist Zeonrex ZEP-520.¹⁵ To minimize proximity effects, 50 keV electrons were used for the e-beam writing (JEOL JBX-5DII). Electrons with this energy were found to pass through the Au/NiCr/SiN_x substrate without any significant backward scattering. This resulted in a considerable reduction of the long-range proximity effect, whereas the short-range effect was noticeable at distances shorter than the thickness of the Au film. The resist development conditions were chosen to obtain the highest possible contrast ($\gamma=8$ for a 0.25 μm thick film), which made it possible to obtain resist profiles with better than 2:1 height-to-width ratio. After the e-beam lithography, the gold was patterned by Ar^+ ion etch through the resist mask. During the etching the mask was rotated and the axis of rotation was tilted approximately 5° to the direction of the ion beam. This method allowed us to control the height of the edge fences resulting from redeposition of etched material onto the resist walls. The smallest resolved Au features of the mask were below 100 nm in size. Structures larger than 200 nm exhibit nearly uniform 185 nm thickness and very sharp edges. Figure 2 shows a part of the mask. The pattern on the mask was chosen to allow critical evaluation of the x-ray lithography method. It included similar features to those based on 100, 250, and 500 nm design rules. Due to the proximity effect

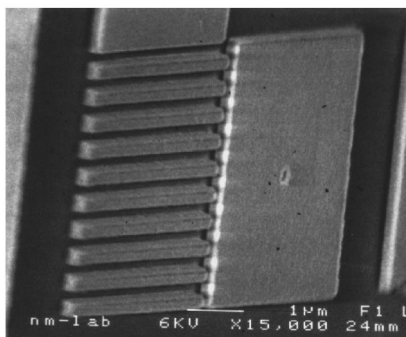


FIG. 2. Scanning electron micrograph of a section of the Au/Si_x x-ray mask.

mentioned above, the features with sizes below 200 nm were difficult to reproduce in the resist without active proximity correction.

The 185 nm Au/250 nm SiN_x mask provides an x-ray transmission contrast of about 11:1 for the $\lambda \approx 1.5$ nm laser-plasma emission. To suppress the longer-wavelength emission in the spectrum, which is mainly due to C V and C VI ions, a free-standing metal filter consisting of 130 nm Cu and 1 μm Al is inserted between the mask and the plasma. The total transmission of the $\lambda < 1.7$ nm radiation through the SiN_x mask and filter combination is approximately 40%. The SiN_x membranes employed for the mask were 0.5 mm \times 0.5 mm on a Si substrate.¹⁴ Much larger-area membranes (1–2 μm thick) with extreme strength are routinely manufactured.³ Naturally such membranes can be combined with the system described in this article. If such a membrane would be used for the mask instead of the ones we had available, the metal filters could be omitted. Compared to conventional x-ray lithography around $\lambda = 1\text{--}1.2$ nm, the slightly longer wavelength in our experiments makes mask fabrication simpler due to increased gold absorption, thereby avoiding the need for fabrication of very high aspect ratios in the absorber material.

An x-ray diode covered by 2 μm Al and 260 nm Cu free-standing metal filters is used for on-line determination of the x-ray flux in the $\lambda < 1.7$ nm region. The higher filter thickness was chosen to avoid saturation of the diode. From diode sensitivity data and filter transmission calculations, the x-ray intensity was calculated to be 4 $\mu\text{J}/\text{cm}^2/\text{pulse}$ at the substrate surface. The absolute accuracy of this data is 50%; the uncertainty is due to the filter thickness, the x-ray diode sensitivity data and the relative strength of the spectral lines.¹¹ In order to obtain a controlled x-ray dose in each exposure, the diode signal, which corresponds to the emitted x-ray flux in each shot, was electronically integrated over time. Since the x-ray flux was determined to be approximately uniform in all directions, the total deposited energy in the resist could be accurately estimated.

III. RESULTS AND DISCUSSION

X-ray lithography was performed with the acid-catalyzed, novolak-based negative resist Microposit SAL-601 ER7,¹⁶ which is approximately 20 times more sensitive than PMMA. An approximately 0.6 μm thick film was spin coated onto Si substrates. The resist processing included a 110 $^\circ\text{C}$ postexposure baking step in a convection oven followed by 2 min of development in Microposit MF-322.¹⁶ The sensitivity curve obtained with these exposure/development parameters and with a 22 min postexposure baking time is shown in Fig. 3. After optimization of the process, we used an exposure dose of 45 mJ/cm^2 and a postexposure baking time of 18 min for the best lithography results.

Figure 4(a) shows a scanning electron microscope (SEM) micrograph of a typical lithographic pattern. The exposure time was 20 min. In Fig. 4(b) the pillars in the frame of Fig. 4(a) are displayed at a higher magnification. These high-

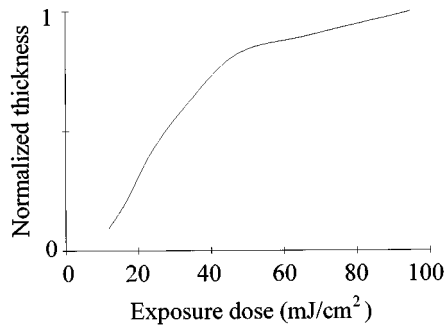


FIG. 3. Sensitivity curve of SAL-601 negative resist with 22 min postexposure baking time.

aspect-ratio pillars have a typical diameter of 70 nm, which is determined mainly by the mask. The wall profiles are vertical or even leaning slightly backward, indicating that this lithography procedure may be suitable for lift-off processing of metal patterns on the nanometer scale. The slight undercut may result from the comparatively high absorption ($\sim 25\%$) of the incident $\lambda \approx 1.2\text{--}1.7$ nm x rays in the resist layer. Thus, a slightly larger fraction of the absorbed energy is deposited in the top layers of the negative resist resulting in a higher density insoluble resist there, while the less exposed lower layers are less crosslinked.

Resolution in proximity x-ray lithography is primarily limited by diffraction and by the photoelectron range.^{2,3} The photoelectron range sets the ultimate limit since diffraction, in principle, can be reduced by reducing the mask-substrate

gap. For wavelengths of the present liquid-jet x-ray source, i.e., $\lambda \approx 1.5$ nm, the maximum range of the photoelectrons is 20–30 nm while most of the energy deposition is due to the short-range (~ 5 nm) Auger electrons.³ Thus, with $\lambda \approx 1.5$ nm, < 20 nm features would be feasible when considering only the photoelectrons.² Shorter wavelength lithography systems will increase the photoelectron range.

The minimum linewidth w due to diffraction may be estimated from

$$w = k_1 \sqrt{\lambda \cdot g}, \quad (1)$$

where g is the gap distance between the mask and the substrate, λ is the wavelength, and k_1 is a factor that depends on the mask and the illumination system. Using $k_1 \approx 0.6$ (cf. Ref. 2) and the parameters used in the present article ($\lambda \approx 1.5$ nm, $g \approx 13$ μm) results in a minimum achievable linewidth of ~ 90 nm. With a 2 μm gap, routinely used in Ref. 3 even for large-diameter masks, this reduces to ~ 35 nm. Finally, it may be noted that previous investigations show that some spatial incoherence in the source is favorable to avoid edge ringing.³ In our experiments we had a penumbral blur δ of ~ 10 nm, resulting in the blur-to-width ratio $\beta = \delta/w$ being approximately 0.1. Studies show that a somewhat larger β (approximately 0.3) provides better contrast.¹⁷ Thus, a larger plasma diameter or smaller plasma-mask distance may improve the current arrangement.

The exposure time is approximately 20 min in the current arrangement, which is based on the 10 Hz laser-plasma source. Although this is reasonable for many low-volume laboratory-scale projects, several applications require shorter exposure times. This is especially true for larger-volume fabrication. Fortunately, the average x-ray flux from our negligible debris laser-plasma source may be increased significantly since the liquid-jet target allows much higher repetition-rate lasers to be used. This is in contrast to many other laser-plasma sources and is due to the fact that fresh target material is supplied in a continuous flow at a rapid rate (jet velocity ~ 50 m/s). Lasers aiming at a 1000 Hz repetition rate, and with suitable pulse energy and pulse width, are currently being developed.¹⁸ With a 1000 Hz laser the exposure time would be on the order of 10 s. Furthermore, the effective throughput may be increased since the nearly 4π steradian geometric access allows several exposure chambers at the source to be operated simultaneously. Finally, it might be of importance that the cost of the target is very low (approximately $\$10^{-7}$ /pulse for a 1000 Hz system¹⁰) due to the small liquid flow and the intrinsic accurate forming and positioning of the target material.

IV. SUMMARY

We have demonstrated a compact laser-plasma proximity x-ray lithography system appropriate for low-volume nanometer patterning. It combines a Au/SiN_x mask and a sensitive negative x-ray resist with a fluorocarbon liquid-jet target laser-plasma x-ray source with negligible debris emission. The lithography system with its 10 Hz current source is already suitable for low-volume small-scale appli-

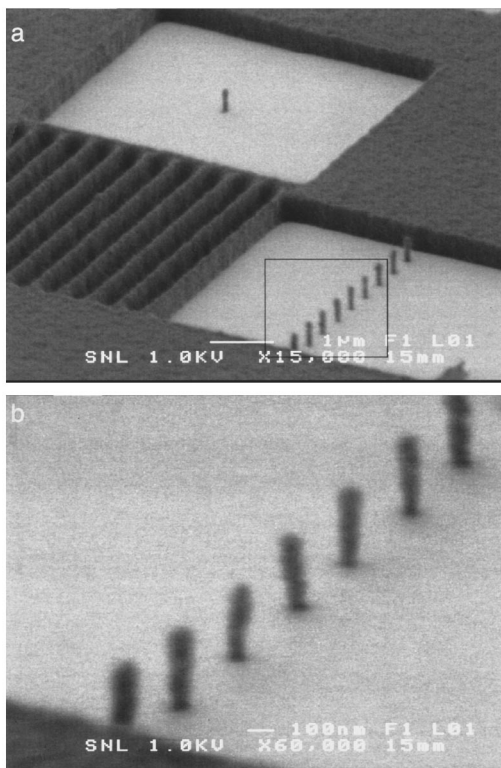


FIG. 4. Electron micrographs at low (a) and high (b) magnification of high-aspect-ratio 70 nm diameter pillars fabricated in SAL-601 negative resist.

cations in, for example, research environments, and has the potential for larger-scale applications using higher-repetition-rate lasers.

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