# Nanostructure Fabrication by Reactive-ion Etching of Laser-Focused Chromium on Silicon

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## ABSTRACT

We have fabricated chromium nanostructures on silicon by laser-focused atomic deposition, and have further processed these structures by reactive-ion etching in an $SF_6$ plasma.  We show that the result can be an array of parallel wires as narrow as 68 nm, or an array of parallel Si trenches as narrow as 85 nm.  The laser-focused deposition process is inherently parallel, so a large area is patterned simultaneously with an accurate periodicity of 212.78 nm. This method represents a novel way to make large, coherent arrays of sub-100 nm-size structures.

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Because of the increasing demand for smaller and smaller features in microelectronic and data storage devices, many new techniques for microfabrication are currently under intense investigation. While present needs are met for the most part by optical lithography, this approach is fundamentally limited by optical diffraction to about the 0.1-0.2 $\mu$m level. Future technology will demand fabrication deep in the sub-100 nm regime, where entirely new methods will be required. Existing techniques such as electron beam lithography, with its capability of 10-20 nm feature fabrication, have filled the gap temporarily, but wide application in manufacturing is limited because of the serial nature of the process, which results in long exposure times and proximity effects. Other lithographic approaches using collimated parallel broad beams of electrons, ions, or x-rays show promise, but have yet to be proven commercially viable.

A new approach to sub-100 nm fabrication, utilizing laser light to focus neutral atoms as they deposit onto a surface, has been demonstrated recently[1-3]. This process has potential advantages in that it can be used to create, in parallel, a large, coherent array of features with size well below 100 nm. To date, studies of this process have been conducted using sodium[1], chromium[2], and aluminum[3] as the focused atom. With chromium, linear features with full width at half maximum (FWHM) as small as 38 nm[4], and dots with FWHM of 80 nm[5] have been demonstrated, all with a periodicity of 212.78 nm.

In the studies of laser-focused atomic deposition performed so far, a certain amount of unintended background deposition is often observed between the intended nanofabricated features. One source of this background is atoms in the atomic beam that are of a different isotopic species, or are in a non-resonant electronic state, and hence do not interact strongly with the laser. Other sources could be atoms in the high-velocity tail of the thermal velocity distribution in the atomic beam, or possibly surface diffusion during deposition. For some applications, reduction of the background is desirable. A number of approaches can be taken to achieve this, for example removal of the non-interacting atoms from the beam by laser separation, or velocity monochromization of the atom beam.

We discuss here a post-processing approach to the removal of background. Using a reactive-ion etch plasma, we demonstrate that it is possible to sputter-remove chromium uniformly without significantly increasing the roughness. This leads to removal of background material while the features remain essentially intact, being simply reduced in size. The result is a large, coherent (i.e., highly regular) array of clearly separated metallic nanowires on the surface of a silicon wafer.

Once the background is removed, we have also seen that the remaining Cr features act as an etch mask for the reactive ions in the etch plasma, transferring the laser-focused Cr pattern into the silicon wafer. The uniformity of this etching process is greatly enhanced by the smooth, regular nature of the laser-focused Cr features. Thus we have also demonstrated a way to further process a laser-focused atomic deposition pattern to result in nanoscale-patterned silicon.

The basic process in which atoms are focused by laser light into nanostructures as they deposit on a surface has been described elsewhere[1-3]. As shown schematically in Fig. 1, a highly-collimated beam of atoms (usually collimated by laser cooling[6]) passes through a standing-wave laser field tuned near an atomic resonance in the atom. The standing wave is situated on the surface of the substrate, with the light propagating parallel to the surface. As the atoms interact with the near-resonant blue-detuned laser light, the resulting dipole force[7,8] focuses the atoms into the nodes of the standing wave, causing increased deposition there. The final result is an array of nanostructures with a periodicity of half the laser wavelength used. The array is formed simultaneously across the entire area covered by the standing wave, and because the laser frequency is locked to an atomic resonance, its periodicity can be very accurate.

For the present study, two samples ("A" and "B") were made under nominally the same deposition conditions. The chromium beam was produced in an effusive oven at 1615 $^{o}$C with a 1 mm diameter aperture. The beam was pre-collimated by a 1 mm square aperture placed 450 mm from the source, and then further collimated by transverse laser cooling such that 90% of the atoms were contained within an angular range of 0.6 mrad[9].

Both laser cooling and laser focusing were carried out using the $^7S \rightarrow {}^7P$ atomic transition in Cr at 425.55 nm (vacuum wavelength). Laser light was supplied by a single-frequency, stabilized ring-dye laser operating with stilbene-3 laser dye and pumped with a UV argon-ion laser. The laser cooling utilized a polarization-gradient (*lin* $\perp$ *lin*) scheme[8] with 33 mW of single-beam laser power detuned by 5 MHz (one atomic linewidth) below the atomic resonance. The cooling laser beam was nominally Gaussian and elliptical in shape, with $1/e^2$ widths 23 mm along the atom beam and 4.2 mm transverse to the atom beam.

The standing-wave laser beam, with single-beam power of 30 mW, was frequency-shifted to 500 MHz above the atomic resonance with an acousto-optic modulator. Its profile was Gaussian, with $1/e^2$ diameter 130 $\mu$m, and the position was adjusted so that the substrate surface cut this profile in half. The beam waist was located on a mirror mounted rigidly to the sample at a distance of 3 mm (sample A) or 5 mm (sample B) from the deposition location.

The substrate consisted of a polished Si (100) wafer with native oxide, cleaned before installation into the vacuum with ultrasonic baths of acetone followed by methanol. Chromium was deposited for a total of 30 minutes for each sample, and the result in each case was a 1 mm square pad of Cr. The nominal thickness of Cr was 12 nm for sample A and 10 nm for sample B, as determined by atomic force microscope (AFM) measurements of the step height of the shadow cast by a 25 $\mu$m wire placed across the corner of each pad during deposition.

AFM studies of the samples in the regions covered by the laser standing wave revealed modulation of the deposited Cr into an array of lines oriented perpendicular to the laser direction. The depth of modulation essentially followed the laser intensity profile, dropping off at about 65 $\mu$m on either side of the laser beam axis, but remaining uniform along the direction of the laser across the full 1 mm of the Cr pad. In the central 0.1 mm x 1 mm area, the modulation depth was nominally 12 nm for sample A and ranged from 8 to 10 nm for sample B[10]. The full-width at half-maximum of the lines was nominally 60 nm for sample A, and ranged from 60-100 nm for sample B. The thickness in the minima between the lines (background level) was nominally 6 nm for sample A and 8 nm for sample B. This quantity was estimated by normalizing and offsetting the AFM line scan such that its mean height equalled the measured average thickness of the pad.

To investigate the uniformity of the deposited lines, a series of AFM images were taken across sample B. On a local level, up to 10 $\mu$m, the lines were found to be highly uniform. Over a longer range slight variations were observed, as indicated by the range of measured values given above. The reasons for these variations, and also the differences between the two samples, are not fully understood at present. Possibilities include variations of laser mode, alignment or power, variations in local growth conditions (e.g., contamination), or variations in local deposition rate arising from nonuniformities in the atom beam.

After formation of the Cr nanostructures and characterization by AFM, the samples were exposed to reactive ion etching in a commercial parallel-plate reactor with $SF_6$ as the etchant gas. Both samples were exposed to a 50 W RF plasma with -150 volts DC self-bias. The operating pressure was 2.3 Pa (17 mtorr) and the flow of $SF_6$ was $7.5\times10^{-6}$ mol/sec (10 sccm). Utilizing test samples, the Cr sputter rate in this plasma was found to be 0.5 nm per minute, but appeared to vary by 30-50%, possibly due to oxides or contamination on the surface of the Cr or at the Cr/Si interface, or residues from the plasma chamber surfaces. The Si etch rate was found to be 100 nm/min on an open area of the substrate, though this could be dramatically slower in the narrow trenches between the Cr lines. For each sample, the etching was periodically checked visually and was stopped when a clear change occurred. After 17 minutes for sample A, and 23 minutes for sample B, the regions covered by the Cr lines had turned a brownish-black color.

The results of reactive ion etching of the Cr nanostructures were observed by surveying both samples with scanning electron microscopy (SEM) and in addition by coating sample A with $SiO_2$ and polishing it for cross-sectional SEM. Overall, the appearance was that of a large array of uniform, parallel trenches etched into silicon with Cr lines along the surface.  On close examination, three distinct types of structure were observed.

The first type of structure, shown in plan view in Fig. 2a and in cross section in Fig. 3a, consisted of an array of 68 nm wide Cr wires on top of Si ridges 200 nm high[10]. Because of undercutting in the etch process, the Si was thinned to about 10 nm underneath the Cr wires, and in several locations the Cr wires appeared to have become detached (Fig 2a).  These narrow Cr wires were found only on sample A, and only in some random portions of the areas whose visual appearance was darkest.  The occurrence of this type of structure is thought to be associated with a locally stronger etch rate and/or a locally smaller average Cr thickness.

Far more prevalent on both sample A and B was the structure type shown in Figs. 2b and 3b.  This was found over the entire central region of sample B, and most of the central region of A.  It consisted of Cr "ribbons," nominally 100 nm wide and 16 nm thick, lying on top of Si pedestals that had been thinned to a width of 60 nm by undercutting.  The uniformity was quite high over a 5-10 $\mu$m range, with slight variations in ribbon width observable over a 20-50 $\mu$m range.

The third type of structure consisted of narrow trenches separated by regions of essentially flat Cr-covered Si (Figs 2c and 3c).  The width of the trenches was nominally 85 nm, and the depth was about the same.  This type of structure occurred at the edges of the laser-focused region, where the Cr thickness modulation depth was beginning to drop off. Within a plane perpendicular to their length, the trenches had nearly identical cross section. However, variation in cross section was observed along the trenches, i.e., in going from outside of the laser-focused region toward the central area: the trenches changed over a distance of about 20 $\mu$m from regions of incompletely-removed Cr, to structures of the type shown in Figs 2b and 3b.

To shed further light on the relationship between the precise profile of the patterned Cr film and the resulting etched structure, a series of AFM images taken across sample B before etching was compared with a series of SEM images taken in the same region after etching. Surprisingly, little correlation was seen between either the FWHM or the modulation depth of the Cr lines and the dimensions of the etched features. However, a smaller minimum thickness (background level) of the Cr did appear to be associated with wider trenches in the Si. This is consistent with a model in which (a) the minimum thickness of the Cr film regulates how long before etching in the Si begins and hence how much time is allowed for etching of the trench, and (b) the Cr feature-shape is significantly altered during sputtering by redeposition of material, so the process is not sensitive to the exact original shape. We note that some evidence of redeposition is seen in Fig 3c.

We have demonstrated that an array of sub-100 nm structures can be made in parallel by using laser-focused atomic deposition to form a patterned Cr film on Si and then exposing this pattern to a reactive ion etch. In this feasibility study we have learned that an array of distinct, well-formed Cr wires can be made with dimensions as small as 68 nm on the surface of a Si wafer, and also that an array of trenches in Si with width as small as 85 nm can be made. The precise dimensions of the etched features appears to depend on the minimum thickness of Cr between the features on the laser-patterned film, and also the total amount of etching performed.

Based on the demonstrations described here, it is clear that several processes could be developed with further work. On one hand, emphasis could be placed on covering a large area with a uniform array of Cr wires of width 68 nm or below. A single exposure area of several square milimeters is conceivable, with the limitation set by the diffraction-determined geometry of the standing-wave laser beam. To achieve uniform wires over this area, it will be necessary to (1) precisely control the etch, possibly reducing the undercutting by varying the plasma parameters, (2) make Cr structures with as little background material as possible. and (3) explore the role of contamination and oxides. Alternatively, emphasis could be placed on the patterned Si below the Cr wires. The Cr can be easily removed by a wet etch (commercial chrome etchant), leaving a variety of possible Si shapes. For example, using the etch parameters described in the present work, with the significant amount of undercutting, an array of very sharp features could be made with sharpness on the 10 nm level. Alternatively, the plasma could be optimized for straighter sidewall etching, resulting in much deeper, more nearly rectangular trenches.

In addition to basic extensions of the process, a broader range of possibilities also exists. Other substrates besides silicon could be used, for example sapphire if an array of wires on an insulator were required, or GaAs if very-high-aspect-ratio features were desired[11]. Also, more complex patterns could be generated. Laser-focused atom deposition has already been demonstrated to be useful for making a two-dimensional array[5], a pattern which now could be etched to provide an array of isolated dots, or transferred into the substrate. With new developments, such as scanning the substrate during deposition, this two dimensional deposition could be extended to generate complex patterns in a highly parallel fashion with very accurate registry.

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**References**

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10. All dimensions quoted are those found in representative AFM or SEM images taken at various locations on the sample. A full statistical analysis was not carried out over the entire sample, so the values should be considered as nominal representations of the actual widths and feature heights. Horizontal scales were calibrated against the pitch of the lines, the average of which is considered accurate to at least 0.02% (see, e.g., R. Gupta, Z. J. Jabbour, J. J. McClelland, and R. J. Celotta, in proceedings of the Industrial Applications of Scanned Probe Microscopy, NIST, Gaithersburg, MD, March 24-25, 1994). The accuracy of nominal horizontal dimensions was limited by the variation of measurements within a given image: ±2% (one standard deviation) for FWHM of Cr lines, ±3% (one standard deviation) for SEM images. The accuracy of the AFM vertical measurements was ±10%. In addition, the minimum value of the Cr thickness was obtained by subtracting an average thickness, so variation of Cr thickness across the sample contributes to the uncertainty in this quantity. In the region of the wire shadow, this variation was ±2 nm (one standard deviation).

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## Figure captions

1. Focused deposition of atoms in a standing-wave laser field.

2. Scanning electron microscope images of the three types of structures found on specimens prepared by laser-focused atomic deposition of chromium on silicon, followed by reactive-ion etching with $SF_6$. (a) Cr wires 68 nm wide on top of silicon ridges, as found in some regions of sample A (see text); (b) Cr ribbons separated by Si trenches, as found over most of the area of both samples A and B; (c) 85 nm wide trenches cut into the Si substrate, as found around the edges of the region covered by the laser in both samples A and B.

3. Cross-sectional scanning electron microscope images of the three types of structures found on specimens prepared by laser-focused atomic deposition of chromium on silicon, followed by reactive-ion etching with $SF_6$. Samples were prepared by coating with quartz, sectioning, and polishing. (a) Corresponding to Fig 2a, Cr wires 68 nm wide on top of silicon ridges, as found in some regions of sample A (see text); (b) corresponding to Fig 2b, Cr ribbons separated by Si trenches, as found over most of the area of both samples A and B; (c) corresponding to Fig 2c, 85 nm wide trenches cut into the Si substrate, as found around the edges of the region covered by the laser in both samples A and B. Note that material seen in trenches is most likely debris resulting from polishing.

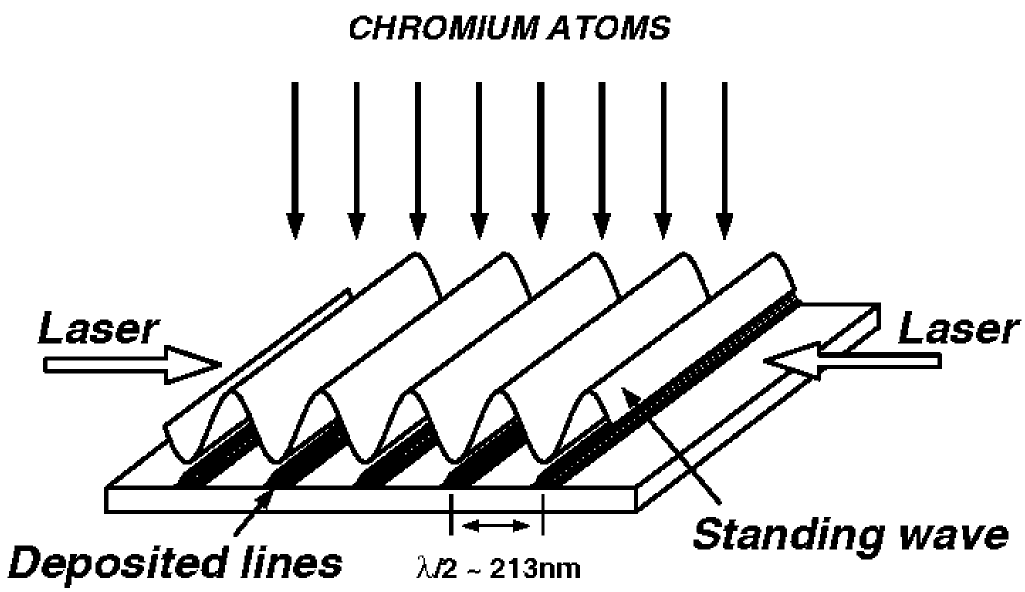


**Figure 1** Focused deposition of atoms in a standing-wave laser field.

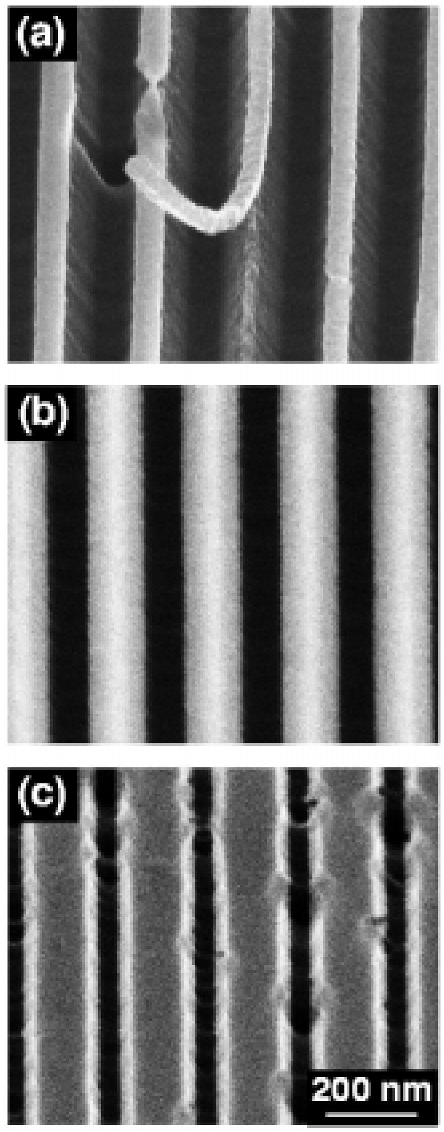


**Figure 2** Scanning electron microscope images of the three types of structures found on specimens prepared by laser-focused atomic deposition of chromium on silicon, followed by reactive-ion etching with $SF_6$. (a) Cr wires 68 nm wide on top of silicon ridges, as found in some regions of sample A (see text); (b) Cr ribbons separated by Si trenches, as found over most of the area of both samples A and B; (c) 85 nm wide trenches cut into the Si substrate, as found around the edges of the region covered by the laser in both samples A and B.

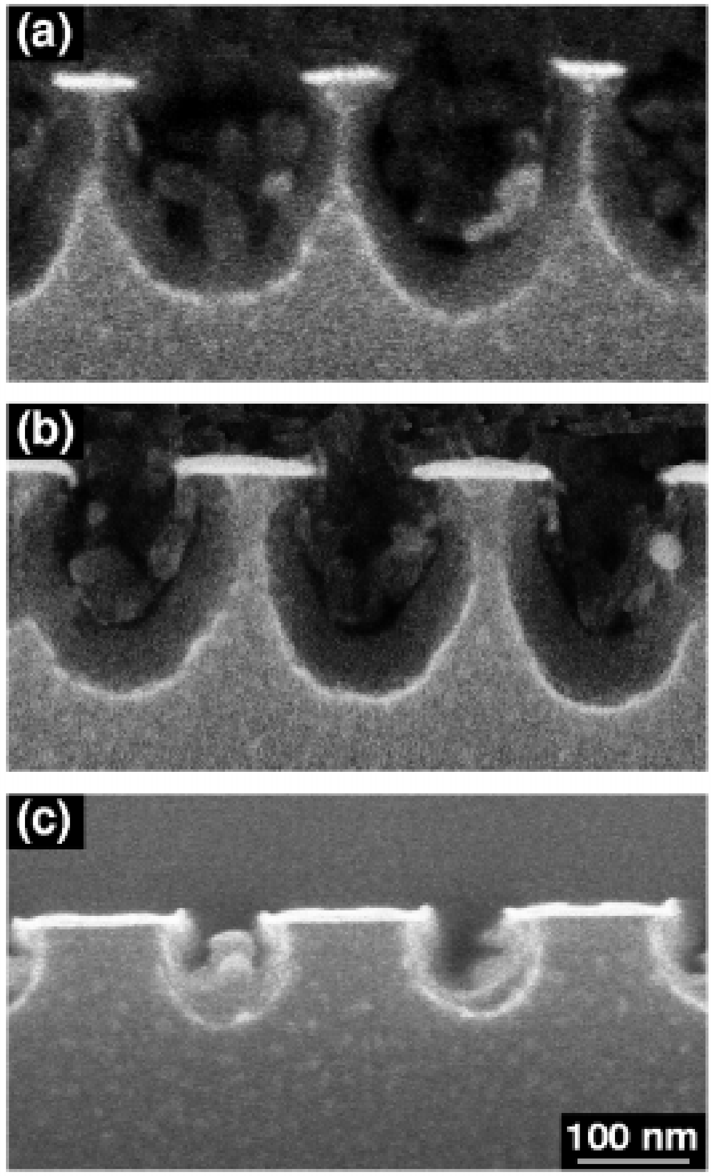


**Figure 3** Cross-sectional scanning electron microscope images of the three types of structures found on specimens prepared by laser-focused atomic deposition of chromium on silicon, followed by reactive-ion etching with $SF_6$. Samples were prepared by coating with quartz, sectioning, and polishing. (a) Corresponding to Fig 2a, Cr wires 68 nm wide on top of silicon ridges, as found in some regions of sample A (see text); (b) corresponding to Fig 2b, Cr ribbons separated by Si trenches, as found over most of the area of both samples A and B; (c) corresponding to Fig 2c, 85 nm wide trenches cut into the Si substrate, as found around the edges of the region covered by the laser in both samples A and B. Note that material seen in trenches is most likely debris resulting from polishing.