Nanolithography with metastable neon atoms: Enhanced rate of contamination resist formation for nanostructure fabrication

S. J. Rehse, A. D. Glueck, and S. A. Lee[a)]
Department of Physics, Colorado State University, Fort Collins, Colorado 80523

A. B. Goulakov and C. S. Menoni
Department of Electrical Engineering, Colorado State University, Fort Collins, Colorado 80523

D. C. Ralph
Department of Physics, Cornell University, Ithaca, New York 14853

K. S. Johnson and M. Prentiss
Department of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 15 April 1997; accepted for publication 26 June 1997)

We report a sevenfold improvement in the rate of contamination resist formation over previous experiments by using metastable neon atoms for nanolithography. Chemically assisted ion beam etching was used to transfer the resist pattern into the substrate. We demonstrate the fabrication of 50-nm-wide features in GaAs with well-defined edges and an aspect ratio >2:1. These are the best resolution and highest aspect ratio features that have been achieved with metastable atom lithography. The resist formation rate by the metastable neon atoms and the etch selectivity of the contamination resist with GaAs were measured. © *1997 American Institute of Physics.* [S0003-6951(97)00936-4]

There has been increased interest recently in using neutral atomic beams as the lithographic source for the fabrication of nanostructures. Atoms have small de Broglie wavelengths, typically of the order 10 pm for thermal atomic beams, thus diffraction effects are negligible and resolution of a few nanometers is potentially possible. Atom beams have large cross sections, thereby allowing large areas to be patterned simultaneously. The key difference and potential advantage of atom lithography over e-beam or x-ray lithography are that atoms have internal energy levels which provide a mechanism for manipulation with laser light.[1] The wavelength of the manipulating laser maintains excellent long range spatial-phase coherence that is difficult to achieve with e-beam lithography. One important area in atom lithography is to investigate the use of atoms to expose or to deposit resist materials that have high resolution and that can withstand etching.[2–5] In this regard metastable rare gas atoms are particularly attractive as the source for lithography.[4,5] The atoms are inert and do not bind to the substrates. The internal energy of the atoms is delivered directly to the resist, and the atoms may be easily manipulated by lasers for future applications. For these techniques to become practical, it is important to have a short resist exposure time and to quantify the resist formation rate and etching performance. Thus far quantitative results are lacking.

In this work we report the use of metastable neon (Ne*) atoms to deposit contamination resist on a GaAs substrate and subsequent anisotropic etching of the resist and GaAs by chemically assisted ion beam etching (CAIBE). The resist formation rate is almost an order of magnitude increase over previous results.[4] Our technique offers excellent control over both the resist formation and the etching process, provides a high degree of selectivity, and allows the characteristics of the lithographic process to be quantified. We demonstrate the fabrication of sharply defined 50-nm-diam pillars with an aspect ratio greater than 2:1 in GaAs. These are the best resolution and highest aspect ratio that have been achieved with metastable atom nanolithography. We also present measurements on the etch rates of GaAs and the resist, and the etch selectivity as a function of the ion beam voltage.

In a diffusion pumped vacuum system, background pump oil vapor molecules tend to adsorb on the inner surfaces of the system. A layer of carbon atoms is formed when a surface is impinged by a beam of Ne* atoms. Previously, electron beams[6] and metastable argon (Ar*) atoms[4] have been shown also to deposit this contamination resist. In the case of Ne*, the physical mechanism responsible for resist formation is well defined. The large metastable energy of Ne*, 16.6 eV per atom, ensures that the dominant de-excitation process of Ne* in collisions with the surface is through Penning ionization of the adsorbed hydrocarbon molecules.[7] Recombination of the molecular ions with electrons follows rapidly on the surface, resulting in the dissociation of the molecules.[8] The volatile fragments are pumped away, leaving carbon atoms on the surface. The Penning ionization by Ne* is only weakly dependent on the adsorbate and the underlying substrate. In contrast, Ar* has low metastable energy ($\sim$12 eV) and its de-excitation mechanism efficiency is strongly dependent on the exact nature of the adsorbate since typical ionization energy for hydrocarbons is 10–15 eV. Large uncertainties also exist for the determination of the metastable Ar* beam flux;[7] thus reliable quantitative results for Ar* nanolithography are difficult to attain. Our experiment allows us to reliably control the resist formation by the use of Ne*.

The experimental arrangement for the deposition of contamination resist is shown in Fig. 1. A beam of neon atoms was produced by a supersonic nozzle source.[9] The atoms

[a)]Electronic mail: salee@lamar.colostate.edu

Downloaded 22 Oct 2006 to 128.84.158.108. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

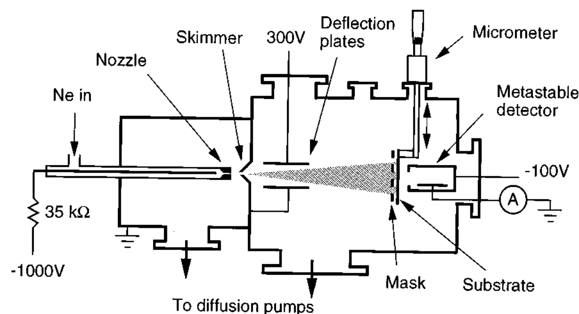

FIG. 1. Schematic setup of the neon metastable beam apparatus for the deposition of contamination resist.

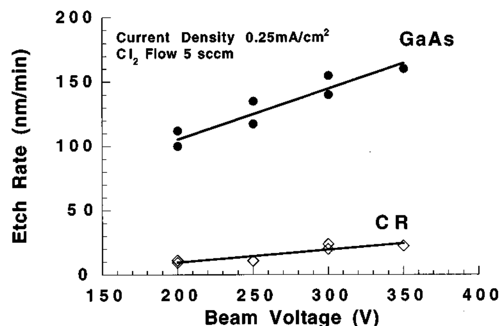

FIG. 2. The etch rates of GaAs and of the contamination resist (CR) as a function of Ar ion beam voltage.

were excited to the metastable $3s[3/2]^{\circ}_{J=2}$ and $3s'[1/2]^{\circ}_{J=0}$ levels by a dc discharge operating between a sharp needle and a cone-shaped skimmer electrode. The atoms passed through the 1-mm-diam skimmer hole and entered a deposition chamber. The average velocity of the atoms was $1000\ \mathrm{m/s} \pm 10\%$. The electrons and ions contained in the beam were steered away by a set of deflection plates. The flux of Ne* atoms was measured with a metastable detector, which was located 50 cm downstream from the skimmer. The Ne* flux was $\sim 4.6 \times 10^{11}$ atoms $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$. The vacuum system was pumped with diffusion pumps[10] that were cold trapped with liquid nitrogen. The background pressure in the deposition chamber was 1×10^{-7} Torr with the neon beam off, and 2×10^{-6} Torr when the beam was on.

The substrates were mounted on a micrometer stage 40 cm downstream from the skimmer, and could be translated to intercept the metastable beam. The $\langle 100 \rangle$ p-doped GaAs wafers were exposed to the Ne* beam patterned by physical masks mounted on the substrate surface. Two different types of masks were used. E-beam fabricated masks,[11] which consisted of a 50-nm-thick, 100 μm$\times$100 μm Si_3N_4 membrane with nanoscale perforations supported on Si, were used to pattern nanometer scale features on the substrates. These will be referred to as nanomasks in this letter. Transmission electron microscopy (TEM) grids with μm-scale openings were used in studies pertaining to deposition and etching rates. The metastable beam diameter was approximately 3 cm in this region, allowing simultaneous exposure of several samples. Exposure times ranged from 2 to 36 h. The thickness of the contamination resist was measured with an atomic force microscope (AFM). The resist height for a 24 h exposure through the TEM grids was found to be 40 ± 3 nm. For comparison, the previous experiment[4] with Ar* had a resist height of 6 ± 2 nm. Thus the use of Ne* increased the resist depth by a factor of 7.

The patterns of the contamination resist were transferred to the GaAs substrates using CAIBE.[12] CAIBE was performed using chlorine as the reactive gas together with an Ar ion beam produced from an Ion Tech model 3-1500-150 ion source. Typical etching conditions were as follows: 200–350 V Ar ion beam voltages, 0.25 mA/cm^2 ion beam current density, 5 sccm Cl_2 flow, and 2 mTorr pressure in the etching chamber.

We investigated the dependence of the etch rates of GaAs and the contamination resist on the ion beam voltage (Fig. 2). For these studies, clean GaAs substrates were exposed to the Ne* beam through TEM grids for 24 h. Auger electron analysis showed that greater than 98% of the resist was composed of carbon. The contamination layer performed well as a resist, as shown by the results of Fig. 2. The selectivity, defined as the ratio of the etch rates for GaAs and the contamination resist, varied from 7.3 at 300 V to 11 at 200 V. We also measured the etching rate of GaAs and the contamination resist when no chlorine gas was present. The sputtering rate at 200 V and 0.25 mA/cm^2 argon ions was found to be 12 nm/min for GaAs and 2.5 nm/min for the resist. Thus CAIBE improves the selectivity while increasing the etching rate for GaAs and the contamination resist.

Figure 3 shows the structures etched into $\langle 100 \rangle$ p-doped GaAs. The exposure time to the Ne* beam was 15 h for Figs. 3(a)–3(c) and 36 h for Figs. 3(d) and 3(e). The samples were etched for 2 and 6 min, respectively, at an ion beam voltage of 200 V. The nanomask consisted of arrays of 500-nm-sq holes and 50-nm-round holes. This pattern was transferred to GaAs [Fig. 3(a)]. Figure 3(b) shows the 50-nm-round features formed in GaAs. They have well-defined edges, indicating that even smaller features may be fabricated with this technique. Figure 3(c) is a 60° scanning electron microscopy (SEM) image of the features. The pillars are ~ 130 nm tall, giving an aspect ratio of better than 2:1. This is the highest aspect ratio nanostructures created using neutral atom lithography. Figures 3(d) and 3(e) show the 500 nm squares. The feature height is ~ 500 nm. The 50-nm-diam pillars, however, did not survive the 6 min etch due to undercutting in the sidewalls. The undercutting is most likely due to the divergence of our ion beam. This may be improved by optimizing the ion beam focusing conditions and by increasing the source to substrate distance.[13] With modifications in our present CAIBE setup, it is not unreasonable to expect that an aspect ratio of greater than 5:1 is possible for the 50 nm pillars.

In summary, using metastable neon atoms to deposit contamination resist and the standard CAIBE technique, we achieved significant improvements in the resist formation rate, etch anisotropy, etch rates, and selectivity for fabricating nanoscale structures in GaAs. The resolution obtained in this Ne* experiment is already quite comparable to that of e-beam lithography. The ability to manipulate atoms with laser light provides additional possibilities.[1,14] In addition, enhancement in the metastable beam flux by more than a

Downloaded 22 Oct 2006 to 128.84.158.108. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

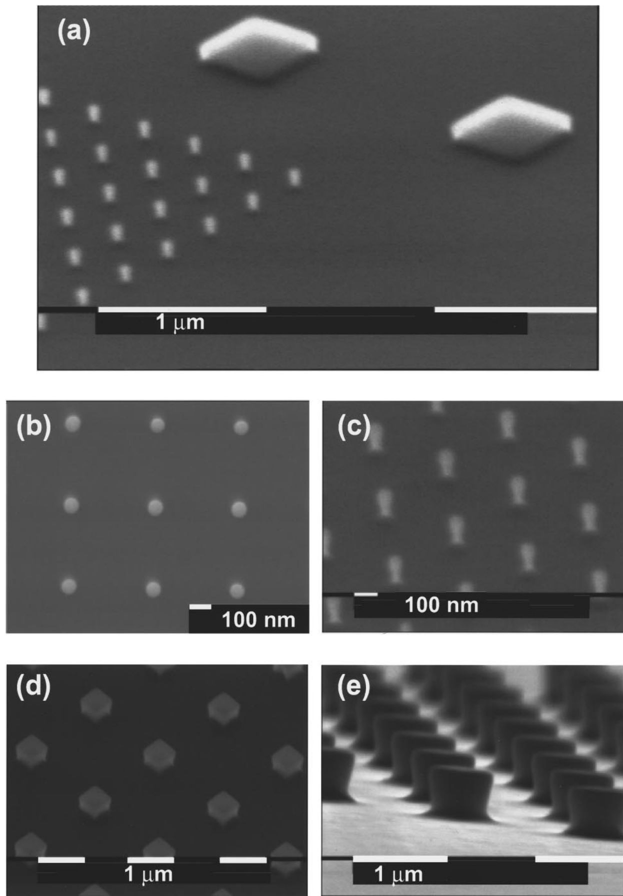

FIG. 3. SEM images of the nanostructures fabricated in GaAs. (a) The structures contain 500-nm-sq posts and 50-nm-round posts. (b) A magnified view of the 50 nm pillars. The SEM view angle is 0°. (c) Same as (b) but viewed at 60°. (d), (e) The 500 nm squares viewed at 60° and at 90°, respectively. For (a)–(c), the neon exposure time was 15 h, and the CAIBE etch time was 2 min. For (d) and (e), the exposure time was 36 h, and the etch time was 6 min.

factor of 10 may be obtained with laser cooling.[15] With these improvements, the atom lithographic technique demonstrated in this work may become attractive for practical applications.

The authors wish to thank R. S. Robinson, G. W. Whitesides, F. B. Dunning, and C. Howard for helpful discussions, and B. Parkinson for use of the AFM. They acknowledge the technical assistance of J. Chandler, D. Bell, and L. Shaw for SEM imaging and Auger analysis. One of the authors (K.S.J.) was supported by an AT&T graduate fellowship. This work was supported by the National Science Foundation under Grant Nos. PHY-9312572 and EEC-9015128, and by the Colorado Advanced Technology Institute under Grant No. 0594.75.0738.

[1] G. Timp, R. E. Behringer, D. M. Tennant, J. E. Cunningham, M. Prentiss, and K. K. Berggren, Phys. Rev. Lett. **69**, 1636 (1992); J. J. McClelland, R. E. Scholten, E. C. Palm, and R. J. Celotta, Science **262**, 877 (1993); R. W. McGowan, D. M. Giltner, and S. A. Lee, Opt. Lett. **20**, 2535 (1995); U. Drodofsky, J. Stuhler, B. Brezger, T. Schulze, M. Drewsen, T. Pfau, and J. Mlynek, Microelectron. Eng. **35**, 285 (1997).

[2] K. K. Berggren, A. Bard, J. L. Wilbur, J. D. Gillaspy, A. G. Helg, J. J. McClelland, S. L. Rolston, W. D. Phillips, M. Prentiss, and G. M. Whitesides, Science **269**, 1255 (1995).

[3] See, for example, M. Kreis, F. Lison, D. Haubrich, D. Meschede, S. Nowak, T. Pfau, and J. Mlynek, Appl. Phys. B **63**, 649 (1996); see also K. K. Berggren, R. Younkin, E. Cheung, M. Prentiss, A. J. Black, G. M. Whitesides, D. C. Ralph, C. T. Black, and M. Tinkham, Adv. Mater. **9**, 52 (1997).

[4] K. S. Johnson, K. K. Berggren, A. Black, C. T. Black, A. P. Chu, N. H. Dekker, D. C. Ralph, J. H. Thywissen, R. Younkin, M. Tinkham, M. Prentiss, and G. M. Whitesides, Appl. Phys. Lett. **69**, 2773 (1996).

[5] S. Nowak, T. Pfau, and J. Mlynek, Appl. Phys. B **63**, 203 (1996).

[6] W. W. Molzen, A. N. Broers, J. J. Cuomo, J. M. E. Harper, and R. B. Laibowitz, J. Vac. Sci. Technol. **16**, 269 (1979); see also A. N. Broers, Philos. Trans. R. Soc. London, Ser. A **353**, 291 (1995).

[7] H. Hotop, in *Experimental Methods in the Physical Sciences*, edited by F. B. Dunning and R. G. Hulet (Academic, San Diego, 1996), Vol. 29B, pp. 191–215.

[8] See, for example, D. R. Bates, in *Dissociative Recombination: Theory, Experiment, and Applications*, edited by B. R. Rowe, J. B. A. Mitchell, and A. Canosa (Plenum, New York, 1993), and references therein.

[9] Our metastable beam source is similar to the one described by D. W. Fahey, W. F. Parks, and L. D. Schearer, J. Phys. E **13**, 381 (1980).

[10] The diffusion pump oil used was Neovac SY (alkyldiphenylether) from Varian Vacuum Products.

[11] K. S. Ralls, R. A. Buhrman, and R. C. Tiberio, Appl. Phys. Lett. **55**, 2459 (1989).

[12] M. W. Geis, G. A. Lincoln, N. Efremow, and W. J. Piacentini, J. Vac. Sci. Technol. **19**, 1390 (1981).

[13] G. A. Lincoln, M. W. Geis, S. Pang, and N. N. Efremow, J. Vac. Sci. Technol. B **1**, 1043 (1983).

[14] A. P. Chu, K. K. Berggren, K. S. Johnson, and M. Prentiss, Quantum Opt. **8**, 521 (1996).

[15] F. Shimizu, K. Shimizu, and K. Takuma, Chem. Phys. **145**, 327 (1990); M. D. Hoogerland, J. P. J. Driessen, E. J. D. Vredenbregt, H. J. L. Megens, M. P. Schuwer, H. C. W. Beijerinck, and K. A. H. van Leeuwen, Appl. Phys. B **62**, 323 (1996).

Downloaded 22 Oct 2006 to 128.84.158.108. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp