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Nanometer-scale metal lines are fabricated onto Si(100) substrates by scanning tunneling microscope (STM) based lithography and subsequent chemical vapor deposition. An STM tip is first used to define areas for metal layer growth by electron stimulated desorption of adsorbed hydrogen. Exposure to Fe(CO)₅ at 275 °C results in preferential deposition of Fe onto Si dangling bond sites (i.e., depassivated areas defined by the STM tip), while the monohydride resist remains intact in surrounding areas. Fe metal lines with widths ~10 nm are constructed using this selective-area, autocatalytic growth technique. [S0003-6951(96)00816-8]

The scanning tunneling microscope (STM) has become useful not only for the study of surface structure and thinfilm growth but as a lithographic tool for building small devices. In the past, several scanning probe based techniques have shown potential in patterning sub-0.1 μ m feature size components. This includes processes that involve field evaporation,¹ electric-field manipulation of atoms,² local chemical reaction under a scanning probe tip,³⁻⁵ and exposure of conventional polymeric^{6,7} and self-assembled monolayer resists.^{8,9} In general, these scanning probe based techniques provide improved resolution compared with conventional lithography, because tip-sample working distances are small for operation in both field-emission and tunneling modes. Small spacings provide a large current density $(\sim MA/cm^2)$ and a high field strength at low voltages. It is also apparent from previous work that these techniques are capable of patterning what may accurately be referred to as nanostructures. Recently, scanning tunneling microscopes have been used to build structures of single atom width¹⁰ as well as nanometer-scale test structures, e.g., magnetic arrays of 10 nm sized Fe particles.11

Despite the progress made using these techniques, practical fabrication of sub-10 nm sized devices requires significant improvements in dimensional control, reproducibility, and the ability to transfer patterns from a resist to a functional material. In many cases, lack of control and reproducibility are due to changes in tip geometry that occur during lithography. Tips are susceptible to growth or deformation when local chemical reaction⁴ or scratching of the surface is involved. Pattern transfer requires robust resists that can withstand subsequent processing.

In this letter, we discuss a technique for producing nanometer-scale metal structures that provides better control over feature size without drastically altering tip geometry. This technique combines STM-based lithography of atomic-scale resists^{12,13} with thermal chemical vapor deposition (CVD).^{14,15} Atomic-scale resists are useful for defining small features because the monolayer thickness prevents significant beam scattering. We choose to use hydrogen as a resist because the conditions (i.e., current density and voltage) required to remove H from a Si surface have already been determined. Becker *et al.*¹⁶ and Boland¹⁷ showed that hydrogen can be desorbed from a Si surface using very low energy electron beams (~10 eV). In more recent work, Shen *et al.*¹⁸ measured the cross section for H removal for various inci-

dent electron energies. Above ~6 eV, hydrogen removal occurs by electron stimulated desorption, whereas at lower energies, hydrogen is desorbed by a multiple-vibrational excitation process.¹⁹ Also, we have characterized the lithographic performance of monohydride resists by determining the electron doses required for 5–50 nm sized feature definition.²⁰

The goal of the present study is to test the usefulness of hydrogen as a resist for pattern transfer selective area CVD by growth. Selective chemical vapor deposition of metals has been used in the past, primarily for fabrication of large-scale structures.²¹ In this work, we take advantage of our ability to pattern nanometer-sized features in H-terminated Si(100) surfaces by local desorption using the STM. Metal CVD involves pyrolysis (thermal decomposition) of Fe(CO)₅ precursor molecules with the tip withdrawn from the surface. We choose pyrolysis of Fe(CO)₅, because previous studies indicate that the nucleation kinetics are dominated by site-specific reactivity of the precursor with the substrate.²² In addition, Fe layer growth on Si(100) via pyrolysis occurs at temperatures below the monohydride desorption temperature (520 °C) with little C or O contamination.²³

All experiments are conducted within an ion-pumped, ultrahigh vacuum system (base pressures= 6×10^{-11} Torr). Si(100) samples [Virginia Semiconductor, *n*-type (P)] are first heated to 1250 °C *in vacuo* to remove impurities and reveal a clean, well-ordered starting surface. Si(100):H 2×1 surfaces are prepared by exposure to an atomic H beam with the samples maintained at ~350 °C. The H doser consists of a hot (1600 °C) W filament fixed 1 in. from the sample and a UHV leak valve attached to a glass bottle of high purity (99.9995%) H₂. Formation of a hydrogenated surface is accomplished using exposures of 1200 L.

After hydrogen dosing, the sample is placed into the Ta clip holder of a variable-temperature STM and equilibrated at 275 °C for 6 h. In this holder, samples are scanned to ensure that higher-order hydride species did not form during dosing. Selected areas of the monohydride terminated surface are then stripped of H using sample-tip biases greater than 6 V. For CVD, the tip is withdrawn from the surface and the sample is dosed with 60 L of freshly distilled $Fe(CO)_5$. $Fe(CO)_5$ is contained in a covered Pyrex bottle that is kept cold (77 K) when not in use to avoid decomposition to $Fe_2(CO)_9$.

Scanning tunneling microscopy is used to monitor the



FIG. 1. STM micrograph of a Si(100):H 2×1 surface. The micrograph is taken using a sample bias of -2.30 V and a tip-sample current of 0.15 nA.

sample surface after depassivation and selective area growth. The images presented in this work are acquired using a sample bias of -2.30 V and a tunneling current of 0.15 nA. These particular operating conditions do not result in additional hydrogen desorption.

Figure 1 shows a typical H-passivated Si(100) surface used in this study. This surface is monohydride terminated and contains a small defect density. As demonstrated in previous work, H-passivated dimers are aligned in rows, with each dimer having an oblong shape.²⁴ After depassivation, bright features appear due to the H-free Si dangling bonds. This is shown in Fig. 2 for a line drawn onto a single terrace using a sample bias of +8 V and a line dose of 100 μ C/cm. For this particular line, the depassivated area is continuous over a width of ~8 nm; a limited amount of electron stimulated desorption occurs outside the central region.



FIG. 2. STM micrograph showing a single line stripped of H in the $\langle 110 \rangle$. Electron beam stimulated desorption involved a sample bias of +8 V and a line dose of 100 μ C/cm. Depassivated Si dimer rows are seen within the central portion of line. Scattered bright sites in the vicinity of the patterned line, in part, represent areas "exposed" by the electron beam. The micrograph is taken using a sample bias of -2.30 V and a tip-sample current of 0.15 nA.



FIG. 3. STM micrographs taken after Fe(CO)₅ dosing of the patterned Si monohydride surface. T_{growth} =275 °C. Two separate lines are shown. In each, the metal has been selectively deposited onto more reactive Si dangling bond sites. In the bottom micrograph, the metal line is drawn ~25° with respect to the dimer row direction. Monohydride-terminated Si dimer rows are seen in neighboring areas on the surface. The micrograph is taken using a sample bias of -2.30 V and a tip-sample current of 0.15 nA. The contrast is line adjusted.

Metal is *selectively* deposited onto the patterned areas by pyrolysis of Fe(CO)₅ at 275 °C, as demonstrated in Fig. 3. Metal lines formed on clean Si have a rough surface morphology and are most likely polycrystalline. STM and heavy ion backscattering spectrometry (HIBS) confirm that \sim 2 monolayers of Fe are locally deposited during a 60 L dose. Figure 4 shows representative HIBS spectra for Fe(CO)₅-dosed Si(100) and Si(100):H 2×1 surfaces. In separate experiments, x-ray photoelectron spectroscopy indicates very small C and O impurity levels, characteristic of pyrolysis onto Si substrates at elevated temperatures.^{25,26}

These results show that metal nanostructures can be grown on patterned H-terminated Si substrates. STM confirms that the adsorbed hydrogen is still intact as a monohydride in the unexposed areas of the surface and is not disrupted by the $Fe(CO)_5$. There are a few bright objects present on H-terminated areas after $Fe(CO)_5$ dosing that have an areal density approximately equal to the density of defects on the as-prepared H-terminated surface. These may be metal clusters that have nucleated at specific defect sites, such as higher order hydrides or metal impurities, but additional work is required to confirm this.



FIG. 4. HIBS spectra showing Fe metal content after 60 L Fe(CO)₅ dose at 275 °C for (a) a clean Si(100) surface and (b) a Si(100):H 2×1 surface.

Nucleation during Fe CVD growth is dominated by sitespecific chemical reactivity of the precursor with the substrate. Previous work has shown that decomposition of the Fe(CO)₅ molecule occurs predominantly at Si dangling bond sites.²² Passivation of the dangling bond sites with hydrogen removes the active site for pyrolysis and effectively raises the activation barrier for nucleation. Previous studies have also shown that Fe CVD is autocatalytic on Si-i.e., the barrier to dissociation of the precursor on an existing Fe cluster is smaller than on the clean Si surface (about 0.14 eV on Fe and 0.40 eV on Si).^{22,23} Therefore, once a nucleus is created, it grows rapidly compared to the formation of additional clusters. This highly nonlinear growth rate is advantageous in maintaining the area selectivity of metal deposition.

This technique appears to be well-suited for fabrication of sub-10 nm sized metal structures. Control over feature size at this level is evident. The two Fe metal lines shown in Fig. 3 have approximately the same width as the depassivated areas defined by the STM, ~10.0 nm. Further reduction in linewidth may be achieved by defining even smaller areas during H removal. In this work, we have produced continuous depassivated lines of Si with a width as small as 2.5 nm. Other studies have demonstrated continuous lines with widths as small as 1.0 nm, i.e., of single dimer width.¹⁹ In general, depassivated Si linewidths can be tailored by changing line dose, tip voltage, or tip-sample separation.²⁰ Future work will focus on how the width of metal lines is influenced by continued metal precursor exposure and growth. It is expected that lateral, i.e., in-plane, growth will occur as the line is thickened. We note that the lines shown in Fig. 3 are only partially continuous. Since growth is autocatalytic, however, metal deposits may easily be thickened without nucleating an appreciable number of additional clusters on H-covered areas.

To conclude, we have shown that a two-step technique, that combines STM patterning of atomic-scale resists (H) with thermal CVD can be used to deposit metal nanostructures. Fe is grown selectively onto depassivated regions of Si(100):H 2×1 surfaces by Fe(CO)₅ pyrolysis at 275 °C. The monohydride resist remains intact during gas exposure, with only limited nucleation occurring on H-terminated Si. The effect of hydrogen is to increase the barrier to nucleation compared with growth on clean Si(100). This is demonstrated with the construction of 10 nm wide lines. In general, we feel that this technique could be useful for locally depositing other metals via CVD or for fabricating novel quantumeffect electronic devices. The success of this technique relies upon choosing a CVD gas system in which nucleation is dominated by site-specific chemical reactions.

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