Growth of silicon nitride by scanned probe lithography

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Scanning probe lithography has been used for the first time to grow silicon nitride nanostructures on silicon substrates. The lithography was performed by an atomic force microscope (AFM) placed in an evacuated chamber with a partial pressure of annhydrous ammonia. The silicon nitride nanostructures were grown by negatively biasing the silicon tip with respect to the sample. By changing the environment of the AFM, both silicon oxide and silicon nitride can be grown and subsequently processed. © *1997 American Vacuum Society.* [S0734-211X(97)01801-5]

I. INTRODUCTION

Since the demonstration of silicon oxide growth induced by scanning tunneling microscopy and atomic force microscopy (AFM),[1,2] the field of scanning probe lithography has expanded to include the local oxidation of many materials, including chrome[3] and titanium,[4] as well as the local electron bombardment of PMMA,[5] and other resists.[6] The generated patterns have been used to create devices[7] and serve as growth and etch masks for both silicon[8] and gallium arsenide.[9,10] The mechanism for field-induced oxide growth has been investigated,[1] and recent measurements of current flow during the lithography process support this theory.[11] However, to date no studies have succeeded in expanding this technique to the growth of material other than oxides.

In this article, we present evidence of silicon nitride growth by scanning probe lithography under a controlled environment. Here, lithography was attempted under air, nitrogen, vacuum, and annhydrous ammonia environments using different bias conditions. Growth characteristics were obtained and material specific etchants were used to verify the composition of the grown nanostructures. The ability to change the grown material by changing the AFM environment has many ramifications for the nanofabrication of Si-SiO_2-Si_3N_4 structures in particular, and the growth of other materials in general.

II. EXPERIMENT

H-terminated type Si(100) wafers with a resistivity of 100 Ω cm were used as substrates for the reported experiments. The lithographed lines shown here were written using a conducting AFM system[12] with commercially available Si tips[13] biased at -10 V with respect to the sample. In this study, a single pass with a write speed of 60 nm/s was used, while write speeds of 600 nm/s have also been successful. An initial set of silicon oxide lines was written under ambient conditions. The AFM chamber was then evacuated to 300 mTorr and purged with ultrahigh purity (UHP) N_2 (99.999%) three times. The chamber was then evacuated to <1 mTorr. At this point, NH_3 was bled into the chamber until the pressure reached 50 Torr, and a set of lines was written in this environment. Finally, the system was purged several times with UHP N_2 and brought back to an ambient environment for imaging. The four lines in the upper left of Fig. 1 were written under ambient conditions, and the four lines in the lower right were written in the NH_3 environment.

III. RESULTS AND DISCUSSION

It has been well established that lithography performed under ambient conditions results in silicon oxide growth. We have observed that this growth is etched by a buffered HF solution in only a few seconds, in agreement with previous observations.[2] To distinguish the lines written under ambient conditions from the lines written under an NH_3 atmosphere, a concentrated (85%), 80 °C phosphoric acid etch was chosen because of its highly selective etching of Si_3N_4 over both Si and SiO_2. Figure 2 shows the same area as Fig. 1 after a 2 min phosphoric acid etch. The lines written under the NH_3 atmosphere have been completely etched away, producing a shallow trough where silicon nitride grew beneath the surface, while the silicon oxide lines written under ambient conditions have not been etched at all.

In our system, there are essentially two pathways through which Si_3N_4 growth can occur:

$$3\ Si + 2\ N_2 \rightarrow Si_3N_4, \tag{1}$$

$$3\ Si + 4\ NH_3 \rightarrow Si_3N_4 + 6\ H_2. \tag{2}$$

To determine which of these mechanisms dominated silicon nitride growth in our system, we also attempted lithography while the system was at a pressure below 1 mTorr, and in an UHP N_2 environment at STP, and saw no evidence of material growth under these conditions. The lack of lithography under the above conditions demonstrates the necessity of NH_3 to write the lines in the lower right of Fig. 1, indicating that only the reaction of Eq. (2) is significantly enhanced by the localized electric field of the AFM tip. The higher reactivity of NH_3 is expected because of its polar nature, and the dissociation energy of the H—NH_2 bond, 460 kJ/mol, is much smaller than the 945 kJ/mol for the N_2 triple bond. The presence of a pure NH_3 atmosphere during growth, coupled with the fact that the lines are readily etched by phosphoric acid, strongly supports the presence of silicon nitride growth under these conditions.

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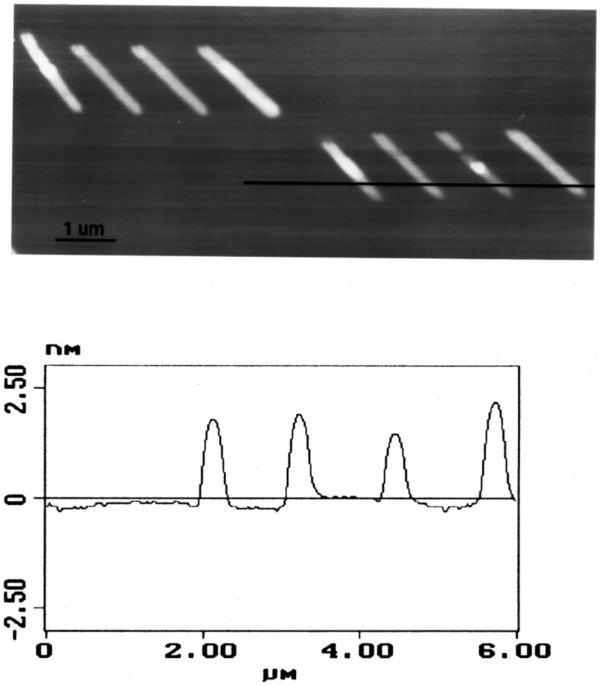

FIG. 1. AFM image of silicon oxide (upper left) and silicon nitride (lower right) lines written on a Si substrate with a Si tip. The tip was biased at −10 V with respect to the sample and a write speed of 60 nm/s was used. The line scan along the black line of the topography image shows the height of the silicon nitride lines.

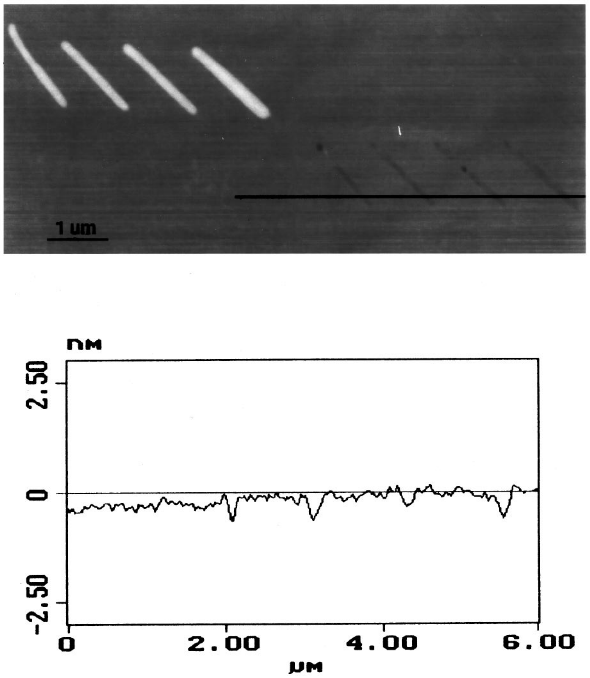

FIG. 2. After etching in phosphoric acid, the silicon nitride lines are completely etched away. The line scan shows that most of the silicon nitride growth occurs above the substrate.

We believe the growth of silicon nitride to be regulated by a mechanism similar to that proposed for silicon oxide.[1,14] Attempts to induce silicon nitride growth with a negatively biased sample produced sporadic, irregular results, similar to observations made during oxide growth, indicating that both the magnitude and direction of the local electric field are important growth parameters. Silicon nitride growth using Cr-coated silicon nitride tips, which are effective for writing silicon oxide,[11] has also been observed. The cross sections in Figs. 1 and 2 show that the average height of a silicon nitride line is about 2.35 nm above the surface, but that silicon nitride growth extends only 0.35 nm below the surface, indicating most of the silicon nitride growth occurred above the surface. This is in sharp contrast with silicon oxide-growth, which produces roughly equal amounts of silicon oxide above and below the surface.[2]

IV. CONCLUSION

Scanning probe lithography has been used for the first time to grow silicon nitride nanostructures on silicon substrates. The lithography was performed by placing the AFM in an evacuated chamber with a partial pressure of NH_3. By changing the environment from ambient to NH_3 conditions, both silicon oxide and silicon nitride structures can be written during the same session for subsequent processing. Expanding the nanolithography process to include silicon nitride growth greatly increases its utility. The ability of silicon nitride to mask dopants like Ga, Zn, O_2, and In, as well as its higher dielectric constant, paves the way for more advanced device fabrication than previously possible using only silicon oxide nanolithographic techniques.

ACKNOWLEDGMENTS

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