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Current-dependent growth of silicon nitride lines using a conducting tip AFM

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Abstract

The measurement of a picoamp current accompanying silicon nitride line growth in an ammonia atmosphere, using a conducting tip atomic force microscope, is reported for the first time. The observed total charge per nanolithographed volume is found to be consistent with a process where the reduction of H^+ ions belonging to the ammonia gives rise to the nitridation of the silicon substrate.

Keywords: Atomic force microscopy; Compound formation; Growth; Silicon nitride; Surface chemical reaction

1. Introduction

Silicon nitride is currently being used extensively in the semiconductor industry as an alternative to, or in combination, with silicon oxide because it is an insulator with a higher dielectric constant that can also be used to mask Ga, Zn, O_2 and In, for example. It is of interest, therefore, to explore its utility as a material for nanolithography using a conducting-tip atomic force microscope (CT-AFM). To optimize conditions for the growth of the nanolithographed nitride lines, one must first understand the chemical processes taking place under the intense tip–sample electric field. Evidence of growth of silicon nitride lines by a CT-AFM has already been demonstrated by replacing the ambient humid air in the controlled-environment chamber by ammonia [1]. The study also showed that, as with nanolithographed oxide lines, the nitride lines exhibit a high dielectric strength evidenced by Fowler–Nordheim emission maps. Similar studies have already been conducted for the nanolithography of silicon oxide [2–7], where it was shown that the oxide growth is accompanied by a Faraday current attributed to the transport of OH^- ions through the oxide [8–10]. In this letter, we present evidence that such an accompanying Faraday current also exists during the growth of nanolithographed nitride lines, from which one can (1) deduce a possible growth mechanism and (2) control the growth rate by using a constant current.

2. Experimental

The silicon-nitride lines were written with commercially available chrome/platinum-coated,

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n-type (0.025 Ω-cm) Si tips on H-terminated Si(100) substrates (n-type, 100 Ω-cm). The AFM (Digital Instruments, Santa Barbara, CA) was placed in a chamber, which was pumped to 10 mTorr and purged with ultra-high purity (UHP) (99.999%) dry nitrogen three times. The chamber was then pumped to 10 mTorr, and anhydrous ammonia was bled into the chamber to a pressure of 254 Torr and then up to atmospheric pressure with dry UHP nitrogen.

The lines were written with a positive sample bias with respect to the tip. As previously mentioned, the bias is known to cause the nitridation of the silicon substrate in the presence of a small amount of ammonia [1]. This was confirmed using a phosphoric acid etch, although the exact stoichiometery is unknown. The current was recorded while writing five adjacent lines (from left to right, each line written top to bottom), the topography of which is shown at the bottom of Fig. 1a and b. The bias was increased by 1 V with each successive line from 4 V on the left-hand side to 8 V on the right-hand side. The averaged cross-section of the topography along the length of the 7 and 8 V lines, and the their averaged recorded current, are shown at the top and center of Fig. 1a and b, respectively.

To correlate the current and volume, it is proposed that the reaction of the ammonia with the silicon, under the intense tip–sample electric field, proceeds by

$$3Si+4NH_3 \rightarrow Si_3N_4+6H_2+12e^- . \quad (1)$$

Note that this model assumes, for simplicity, that the grown material is stoichiometric Si_3N_4. Therefore, the formation of one molecule of silicon nitride requires the release of 12 H^+ ions, which are reduced at the tip, giving rise to the measured Faraday current. The integrated current for the 7 V line yielded 2.3×10^8 C, and the total volume, determined by measuring the volume above the silicon surface using the bearing analysis of the AFM and assuming that an additional 13% of the total volume was below the surface [1], was 7.3 $\times 10^5$ nm^3. The average number of charges per

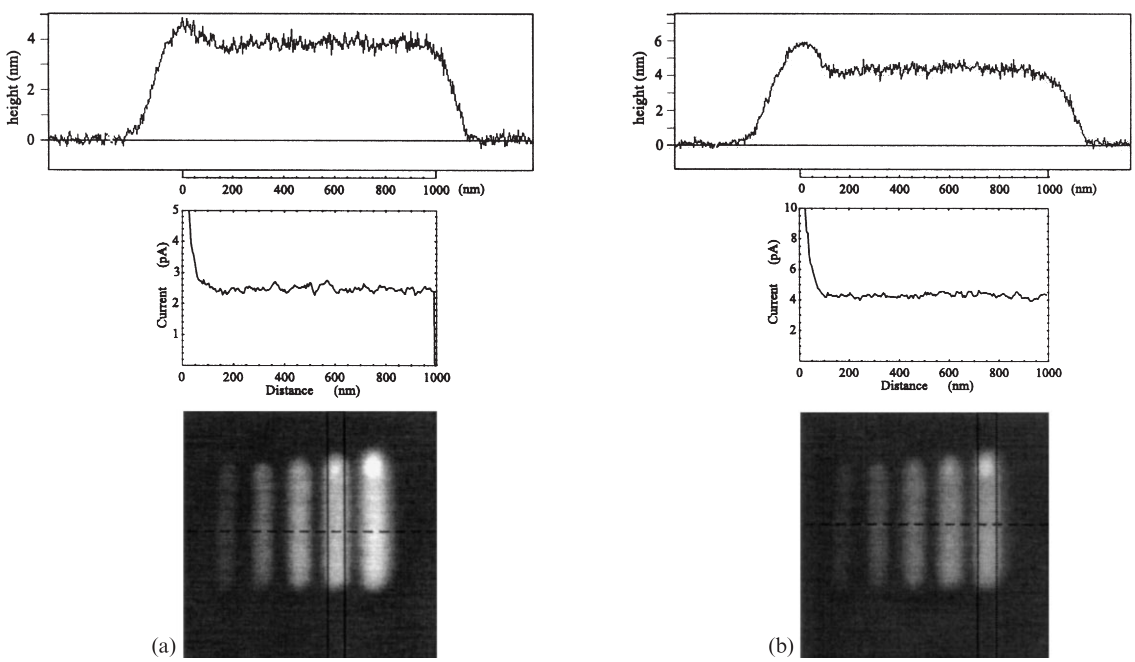

Fig. 1. Nanolithography with (a) +7 V and (b) +8 V sample bias. Topography sections along the length of the silicon nitride lines (top), averaged current recorded while writing these line (middle), and top view of the lines showing the regions over which the topography sections were averaged (bottom). Note the correlation between the bulges at the begining of the lines and their associated currents. Image size: 2.3 × 2.3 μm^2; black-to-white contrast: 5 nm.

molecule was 18.5, a charge efficiency of 65%. For the 8 V line, the average number of charges per molecule was 22, a charge efficiency of 55%, while the charge efficiency over all of the 7 and 8 V lines varied from 26 to 90%.The low efficiency is attributed to the presence of a tunneling current. Since this current is exponential in distance, d, as shown by the Fowler–Nordheim tunneling equation[11]

$$J \propto \left(\frac{V}{d}\right)^2 \exp\left(\frac{-8\pi\sqrt{2m_{\mathrm{eff}}}}{3he}\,\frac{\phi^{3/2}d}{V}\right), \quad (2)$$

whereas the ionic conduction current has approximately a linear dependence on distance[11],

$$J \propto \frac{V}{d}\exp(-\Delta E_{\mathrm{a}}/kT), \quad (3)$$

one can increase the efficiency by having an additional insulating layer on the tip apex. The presence of such an insulating layer will suppress tunneling currents without overly affecting the nitride growth, making it possible to control the growth rate using a current feedback system.

3. Summary

It was found that the growth of silicon nitride lines by a CT-AFM under an ammonia environment is mediated by a predominantly Faraday current. A model explaining the growth mechanism has been presented, and a possible application of this current to control the growth rate has been identified. These results can pave the way for more advanced device fabrication than previously possible using silicon oxide.

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