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# UHV-STM Nanofabrication and Semiconductor Interface Characterization: Transitions to CMOS Technology

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## 1. Introduction

This paper focuses on the development of ultrahigh vacuum scanning tunneling microscope (UHV-STM) nanofabrication and the spin-off discovery that deuterium can be used to dramatically reduce hot electron degradation in CMOS transistors.

## 2. UHV-STM Nanofabrication

Atomic scale patterning of hydrogen passivated Si(100) surfaces has been achieved using the UHV-STM to selectively desorb hydrogen (fig. 1a,b) [1]. The chemical contrast between clean and H-passivated silicon can be used for selective area chemical processing. Results will be presented

showing the selective oxidation, nitridation, metallization, and molecular functionalization (fig. 1c [2]). of these surfaces.

During the nanofabrication experiments fundamental information was obtained about the underlying mechanisms for electron stimulated desorption of hydrogen [1,3]. Two desorption regimes were observed. At higher energies, above  $\sim$ 5 eV, single electrons directly excite the bonding-to-antibonding transition with a current independent desorption yield of  $\sim$ 1 H atom/10<sup>6</sup> STM electrons. At lower energies, in the tunneling regime, multiple electrons successively excite the Si-H vibrational mode, leading to H desorption that is strongly current dependent [3].



(a)

(b)

(c)

Fig. 1 (a) A 500 Å x 500 Å STM image showing a central 290 Å x 290 Å region where hydrogen has been desorbed at a bias of 5.5 V (tip negative). (b) Individual lines, ~1 nm wide, produced by hydrogen desorption at 4.5 V. (c) Self-assembly of norbornadiene molecules on a previously STM depassivated square region.

### 3. Deuterium vs Hydrogen

To further elucidate the electron stimulated desorption mechanisms, STM experiments were performed on the monodeuteride Si(100) surface where it was found that deuterium is a factor of 50 more difficult to desorb than hydrogen in the single electron desorption regime [4,5]. Simulations show that this is a kinetic isotope effect resulting primarily from the H/D mass ratio during the desorption process [4]. Recent low temperature STM experiments confirm this giant isotope effect (fig. 2a) and show further that there is no temperature dependence to the H or D desorption in the single electron desorption regime. In contrast to this, however, a strong temperature dependence is observed in the tunneling regime with desorption becoming much easier at low temperatures [5]. This results from the interplay between the Si-H(D) vibrational states and the substrate phonon modes.

#### 4. Deuterium Processing for CMOS Transistors

The large isotope effect observed in the STM experiments motivated the use of deuterium instead of hydrogen during post-metal anneals on CMOS wafers [6,7]. In these experiments deuterium improved transistor lifetimes by factors of 10 to 50 for the same level of transconductance variation (fig. 2b). This is consistent with the added difficulty for channel hot electrons to desorb deuterium from silicon at the oxide-silicon interface. Mechanisms involving carrier injection into the oxide are not necessary to explain these results. Furthermore, we believe that at lower device operating voltages the dominant degradation mechanism involves multiple vibrational excitations of Si-H(D) by channel hot electrons. Recent STM experiments [5] show the isotope effect to be orders of magnitude larger (fig. 2c) in the tunneling regime than in the single electron desorption regime. This is consis-

tent with our recent findings showing lifetime improvements by factors of  $10^4$  or more in deuterium annealed transistors [8].

CMOS device lifetime improvements as a function of processing conditions will be presented along with SIMS data used to determine the extent of deuterium incorporation relative to background hydrogen.



Fig. 2 (a) STM desorption yield data showing that hydrogen is a factor of  $\sim$ 50 easier to desorb than deuterium from the Si(100) surface in the single electron desorption regime. (b) Accelerated stress tests for NMOS transistors showing transconductance degradation for hydrogen and deuterium annealed devices. (c) STM desorption experiments in the tunneling regime (3 V) showing that the isotope effect increases by orders of magnitude compared to the factor of 50 observed in the single electron desorption regime (a).

## 5. Conclusions

UHV-STM experiments are providing a means to explore nanofabrication on silicon surfaces down to the atomic level. At the same time they are providing fundamental new insight into long-standing problems such as hot electron degradation in CMOS transistors.

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