

Effect of nanoimprinted surface relief on Si and Ge nucleation and ordering

T.I. Kamins^{a,*}, A.A. Yasseri^{a,1}, S. Sharma^{a,2}, R.F.W. Pease^b, Q. Xia^c, S.Y. Chou^c

^aQuantum Science Research, Hewlett-Packard Laboratories, Palo Alto, CA 94304-1100, USA

^bDepartment of Electrical Engineering, Stanford University, Stanford, CA 94305, USA

^cNanoStructure Laboratory, Department of Electrical Engineering, Princeton University, Princeton, NJ, 08544 USA

Available online 5 July 2006

Abstract

Surface relief formed by nanoimprinting and etching into a thermally grown SiO₂ layer on Si was used to position the initial nuclei formed by chemically vapor deposited Si and Ge. By controlling the deposition conditions, the surface diffusion length was adjusted to be comparable to or larger than the spacing between features, thus favoring nucleation adjacent to steps, rather than random nucleation. Random nucleation was further suppressed by a two-stage deposition process. Ge nucleation on oxide by chemical vapor deposition was enhanced by coating the oxide surface with an organic self-assembled monolayer (SAM) and by the nanoimprinted surface relief. The nanoimprinted surface relief also provides long-range order in the SAM.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Epitaxy; Graphoepitaxy; Self-assembled monolayers; Nucleation

1. Introduction

Forming single-crystal semiconductors on amorphous insulating layers has been an elusive goal of integrated-circuit technology for at least three decades. Early radiation-hardened integrated circuits used deposition of thick polycrystalline silicon (polysilicon) layers on an oxidized silicon wafer, followed by grinding and polishing of the single-crystal substrate, to achieve a thin single-crystal Si layer on an insulator. The process was expensive, and control of the polycrystalline-silicon deposition was difficult. Wafer warpage during polysilicon deposition made alignment difficult and decreased yield.

Bonding of a handle wafer to an oxidized Si wafer avoids the need to deposit a thick layer of polysilicon. Implantation of high doses of oxygen into a single-crystal silicon wafer, followed by extremely high-temperature annealing, also allows forming the desired silicon/oxide/silicon struc-

ture, but is expensive. Both techniques allow formation of a single-crystal Si layer on an insulated substrate. The latter is limited to one layer, while the former can be extended to multiple layers of Si.

The possibility of directly depositing a single-crystal semiconductor layer on an insulated Si substrate remains attractive, however, to avoid the mechanical complexity of wafer thinning techniques and the extreme temperatures associated with annealing after oxygen implantation. The ability to form multiple layers of devices on a silicon wafer is especially attractive.

Early investigation of Si deposition on insulating layers with surface topography produced intriguing results, but the technique, labeled as “graphoepitaxy,” [1–3] was not pursued aggressively. One difficulty was the large lateral size of patterned surface relief that could be formed at the time that the technique was being investigated. If the diffusion length of the depositing species is small compared to the spacing between features, the surface relief cannot significantly influence the deposited material, and random nucleation between features produces a disordered layer.

For a given materials system, the diffusion length is controlled by the temperature and arrival rate of the

*Corresponding author. Tel.: +1 650 857 1501; fax: +1 650 236 9885.

E-mail address: kamins@hp.com (T.I. Kamins).

¹Now at Lam Research, Fremont, CA, USA.

²Now at Spansion, Inc., Sunnyvale, CA, USA.

depositing atoms. At higher temperatures, the adsorbed atoms can diffuse farther in a given time to find favorable sites at the patterned features for nucleation. At lower adatom arrival rates, the adatoms can diffuse for a longer period of time before encountering other adsorbed atoms and forming random nuclei on the surface. Therefore, the diffusion length L_D relevant to this discussion depends on temperature and arrival rate. A useful functional expression to help visualize the behavior follows:

$$L_D = (D\tau)^{1/2} = D_0^{1/2} \exp(-E_{as}/2kT)/R^{1/2},$$

where D is the surface diffusion coefficient, which depends on a slowly varying pre-exponential factor D_0 and a rapidly varying exponential factor containing the surface diffusion energy E_{as} and the temperature T , and τ is a characteristic time associated with the arrival rate R of adatoms. For CVD, the effective arrival rate can be limited by either transport of the gaseous precursors to the surface or by the reaction rate at the surface.

In this study, we attempted to extend the concept of graphoepitaxy to the finer patterns that can be formed by advanced patterning techniques such as nanoimprint lithography (NIL). By depositing Si and Ge under conditions where the diffusion length is comparable to or larger than the feature spacing formed by NIL, we attempted to obtain nucleation adjacent to the features while minimizing random nucleation between features. Si nucleates well on SiO_2 , but nucleation of Ge by CVD is difficult; we attempted to enhance the nucleation of Ge by using an organic, self-assembled monolayer (SAM) on the patterned SiO_2 . This paper contains a preliminary report of the work.

2. Experimental techniques

Surface relief was formed in thermally grown SiO_2 by NIL [4]. After oxidation to form an SiO_2 layer approximately 200 nm thick, a 180 nm thick thermoplastic imprint resist was applied and baked at 70 °C for 15 min. The pattern was then imprinted into the resist using 4-in Si molds with gratings over the entire mold area using an NX-2000 imprint machine. The Air Cushion Press (ACP™) in the NX-2000 ensures uniformity over the entire 4-in wafer. After removing the residual resist layer in the regions to be etched, the pattern was transferred into the oxide by reactive ion etching using a CHF_3/O_2 gas mixture. Details of the NIL procedure have been previously described elsewhere [4]. After patterning, the substrates were cleaned in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (1:1:5, heated to 80 °C for 15 min), rinsed and dried.

Fig. 1 shows atomic-force micrographs of the array of raised regions and recessed trenches after etching. The recessed regions were typically 115 or 155 nm wide with a pitch of 190 nm (“narrow” and “wide” trenches, respectively), allowing investigation of the effect of the ratio of

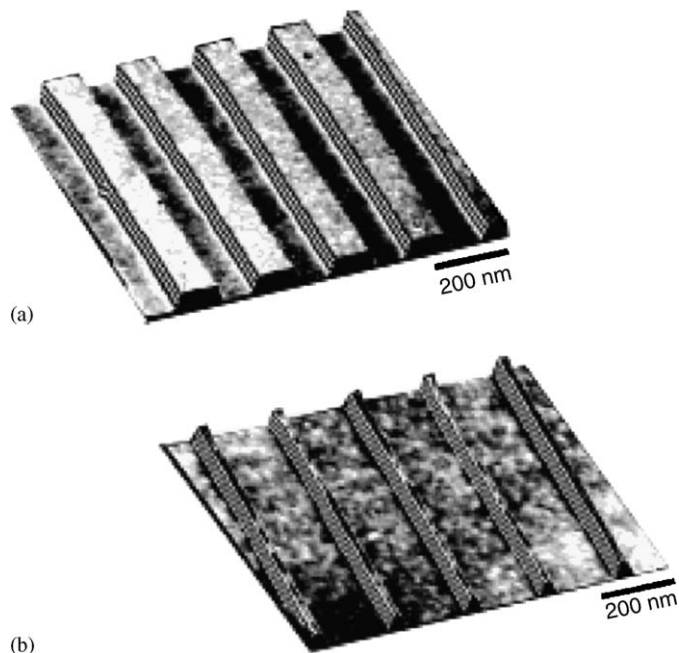


Fig. 1. Atomic-force micrographs of nanoimprinted patterns with 190 nm pitch and (a) 115 nm or (b) 155 nm recessed regions etched ~12–15 nm into the 200 nm thick thermally grown oxide layers.

width to diffusion length. The trenches were etched 12–15 nm into the 200-nm-thick SiO_2 layer.

For the study of Ge nucleation, organic SAMs were formed on unpatterned or patterned, oxidized Si substrates. Alkylsiloxane monolayers were spontaneously formed on SiO_2 by immersing the oxidized Si into a solution containing the octadecyltrichlorosilane (OTS) precursor for varying durations. As will be discussed below, on the unpatterned layers isolated domains formed initially, and extended times (~20 h) were needed to obtain a completely saturated monolayer. The completely saturated SAM formed in a much shorter time on nanoimprinted substrates. To minimize effects of water on SAM formation, the solutions of OTS were prepared in bicyclohexyl, toluene, or chloroform, in a glove box. Bicyclohexyl produced the most reproducible and highest quality films. The samples were rinsed repeatedly before using.

Si and Ge were deposited by chemical vapor deposition (CVD) in a lamp-heated, reduced-pressure reactor, in which the walls of the process chamber remain at a much lower temperature than the substrates. The substrates were placed on a SiC-coated graphite support plate of moderate thermal mass in a load lock before being introduced into the process chamber, so that the process chamber was not exposed to air during normal operation. Silane (SiH_4) and germane (GeH_4) were used as gaseous precursors in a hydrogen ambient. The total pressure was in the range of 10–90 Torr during deposition. Deposition temperatures were 400–600 °C for Ge and 700–900 °C for Si.

After the samples were removed from the reactor, they were analyzed by scanning electron microscopy (SEM),

atomic-force microscopy (AFM), and X-ray diffraction. To determine the stability of the SAMs, they were annealed in hydrogen in the same reactor and analyzed by X-ray photoelectron spectroscopy (XPS) and water contact angle.

3. Experimental results

To study the initial stages of deposition, patterned substrates were exposed to SiH_4/H_2 for short durations (from 30 s to 2 min), with the results shown in Fig. 2. For the shorter deposition time of 30 s (Fig. 2(a)), only a very few nuclei formed. These nuclei were adjacent to the step edges, as desired, indicating that the surface diffusion length was sufficient for the adsorbed atoms to reach a step edge before random nucleation occurred. A typical island was 35 nm in lateral dimension and 3 nm in height. After 2 min of deposition, islands were again positioned adjacent to the step edges. Most islands were located in the recessed areas, but some were on the raised regions. The typical island dimensions in the recessed region were 75 nm in

lateral dimension and 13 nm in height. As seen in Figs. 2(b) and (d), the island top is relatively flat. For comparison, islands on unpatterned substrates (Figs. 2(e) and (f)) have a rounded profile without a distinct flat top.

As the deposition continues, the islands adjacent to the edges become larger, but the probability of random nucleation increases with increasing deposition time. To minimize random nucleation during additional deposition and enlarge the silicon nuclei formed at the pattern edges, in a second deposition step the temperature was lowered and the silane partial pressure was reduced (by decreasing the total pressure). Fig. 3(a) shows an SEM of a deposit formed by two-step growth on a patterned substrate. Silicon nuclei initially formed adjacent to the pattern edges at 900 °C were further grown for 5 min at 800 °C at a lower total pressure. Some islands appear to extend completely across the 115 nm-wide recessed region or the 75 nm-wide raised region, indicating that the two-step deposition can suppress random nucleation. Discontinuities along the length of each region show that the nucleation is random

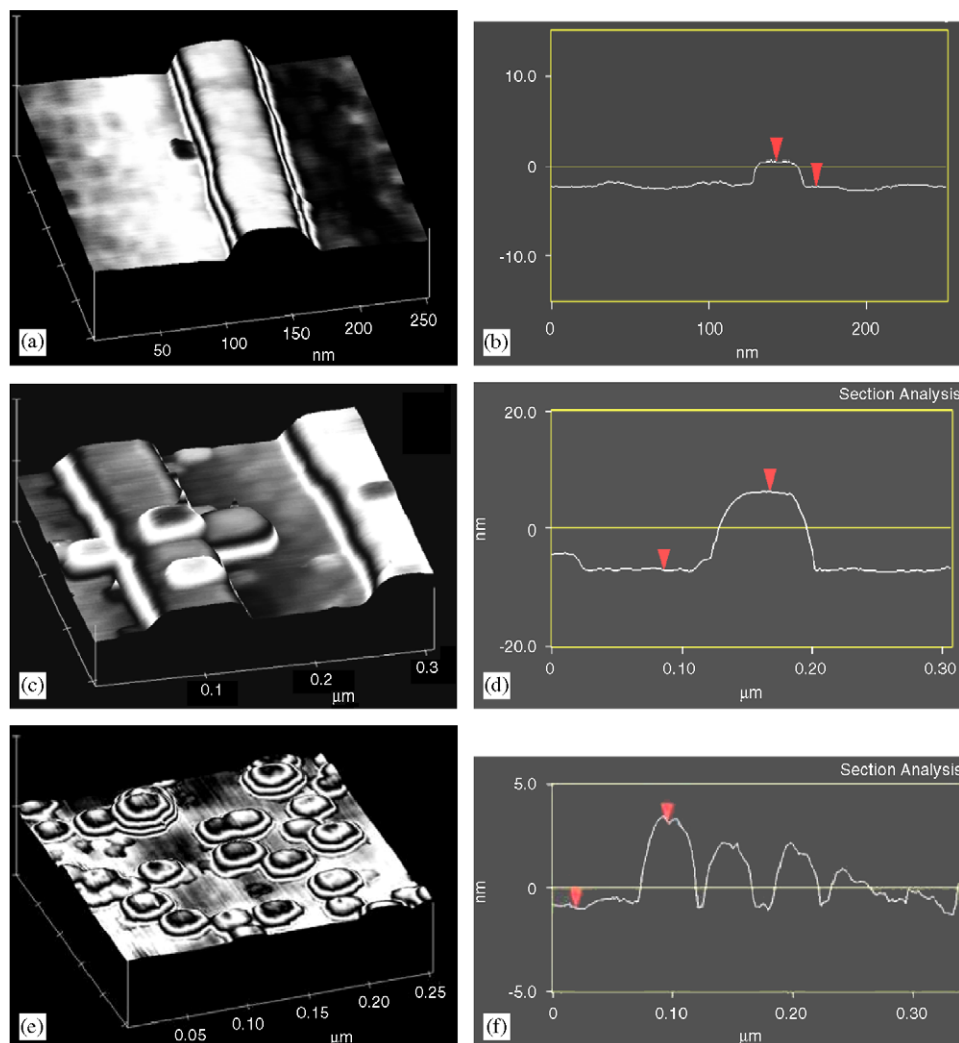


Fig. 2. Atomic-force micrographs of Si nucleation at 900 °C for (a) 30 s and (c) 2 min on nanoimprinted substrates. Corresponding sections are shown in (b) and (d), respectively. (e) 2 min deposition on an unpatterned substrate. (f) Typical section of islands shown in (e).

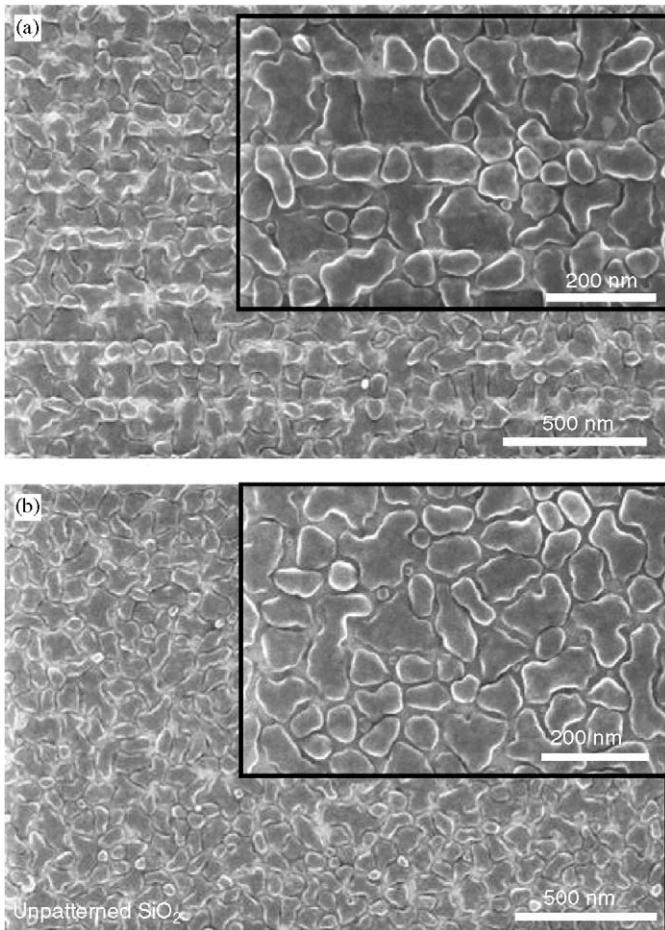


Fig. 3. SEM of deposits formed by nucleation at 900 °C and 10 Torr for 45 s followed by continued deposition at 800 °C and 3 Torr for 5 min on (a) patterned substrate and (b) unpatterned substrate.

along the length of the pattern, as expected. An unpatterned control sample on which Si was deposited at the same time is shown in Fig. 3(b) for comparison.

To observe the effect of a SAM on the nucleation, unpatterned samples with and without a SAM were exposed to SiH_4 at 700 °C. Atomic-force and scanning-electron micrographs show much finer grains on the SAM than on bare oxide, suggesting that the SAM aids nucleation even though the majority of the C was removed by the 700 °C heat treatment. After extended Si deposition (90 min), the differences between samples with and without a SAM were less readily observed.

When Ge is deposited on SiO_2 by CVD, nucleation does not occur readily. Therefore, a SAM was formed on the oxide surface in an attempt to improve nucleation. Ge was deposited at either 400 or 600 °C. The lower deposition temperature does not degrade the SAM significantly; the higher temperature is expected to degrade, but not completely remove, the SAM [5]. On an unpatterned surface the SAM enhances nucleation at both temperatures, but the grains do not grow together readily at either temperature.

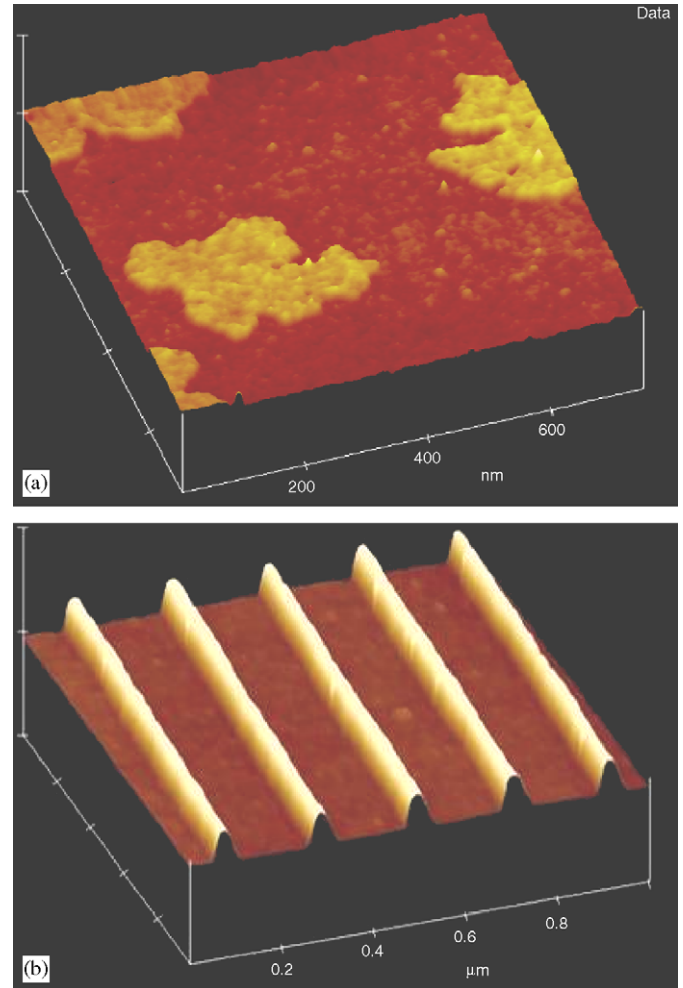


Fig. 4. (a) Atomic-force micrograph of OTS SAM showing isolated domains after 5 min deposition onto unpatterned thermal SiO_2 surfaces; $x = y = 800$ nm full scale. (b) Continuous SAM on nanoimprint-patterned SiO_2 reacted with OTS for 5 min; $x = y = 1$ μm full scale.

One difficulty with using SAMs is the limited domain size over which lateral order is obtained. The disordered domain boundaries might be locations of preferential semiconductor nucleation, and the different in-plane ordering in different domains prevents growth of large areas of single-crystal semiconductor. In an attempt to impose longer-range order, a SAM was formed on nanoimprinted substrates. To obtain information about the domain size, SAMs were formed on unpatterned substrates for limited lengths of time so that the domains remained isolated and could be readily observed by AFM. Fig. 4(a) shows isolated domains of a SAM formed for the limited time of 5 min. The islands are 1.9 nm high, as expected for this type of SAM [6], and extend laterally about 300–400 nm. When the islands coalesce to form a saturated SAM, the boundaries are less readily imaged, but are still expected to influence the nucleation of a subsequently deposited semiconductor.

When the SAM is formed on a nanoimprinted substrate even for a short time, it appears to cover the entire surface

(Fig. 4(b)). The presence of C corresponding to the SAM was confirmed by XPS. No isolated islands are visible by AFM. We speculate that the edges of the nanoimprint pattern serve as efficient nucleation sites for the SAM, so that ordered islands quickly coalesce to form a continuous film.

To compare the effect of SAM and nanoimprinting on Ge nucleation, substrates with nanoimprint-patterned surfaces and unpatterned and patterned surfaces covered with SAMs were compared with bare, unpatterned surfaces. Both the SAM and the nanoimprinted surface aided Ge nucleation, and the combination (SAM on a nanoimprinted surface) was even more effective. We speculate that the discontinuity in packing of the SAM at the feature edges provides effective sites for Ge nucleation.

4. Summary

Surface relief formed by nanoimprinting and etching into a thermally grown oxide layer was used to position the initial nuclei formed by chemically vapor deposited Si and Ge. By controlling the deposition conditions, the surface diffusion length was adjusted to be comparable to or larger than the spacing between features, thus favoring nucleation adjacent to steps, rather than random nucleation. Random

nucleation was further suppressed by a two-stage deposition process. Ge nucleation on oxide by CVD was enhanced by coating the oxide surface with an organic SAM and by the nanoimprinted surface relief. The nanoimprinted surface relief also provides long-range order in the SAM.

Acknowledgement

The authors thank Dr. R. Stanley Williams of Hewlett-Packard for useful discussions and Filip Crnogorac and Daniel Witte of Stanford University for their assistance in the fabrication of NIL samples. This work was supported in part by the Defense Advanced Research Projects Agency (DARPA) and the Office of Naval Research (ONR).

References

- [1] M.W. Geis, D.C. Flanders, H.I. Smith, *Appl. Phys. Lett.* 35 (1979) 71.
- [2] E.I. Givargizov, *Heterogen. Chem. Rev.* 2 (1995) 69.
- [3] H. Mori, *Jpn. J. Appl. Phys.* 20 (1981) L905.
- [4] S.Y. Chou, P.R. Krauss, P.J. Renstrom, *Science* 272 (1996) 85.
- [5] A.A. Yasseri, et al., Unpublished.
- [6] Y. Wang, M. Lieberman, *Langmuir* 19 (2003) 1159.