Atomic force microscopy studies of self-assembled $Si_{1-x}Ge_x$ islands produced by controlled relaxation of strained films

R. Bashir[a)]
School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47906

K.-J. Chao
Charles Evans and Associates, Sunnyvale, California

A. E. Kabir
Linear Technology Corporation, Vancouver, Washington

(Received 13 April 2000; accepted 15 January 2001)

Self-assembled $Si_{1-x}Ge_x$ islands were studied in detail using atomic force microscopy. The self-assembled $Si_{1-x}Ge_x$ islands were formed by a novel two-step process. First, highly strained $Si_{1-x}Ge_x$ thin films (with $x \sim 0.4$) were selectively grown on a silicon wafer by chemical vapor deposition at 650 °C. The growth was followed by an annealing step performed in hydrogen at 750 °C at reduced pressure conditions for specific times. The size and distribution of the islands was found to be a function of the annealing conditions and an ordered pattern could be achieved with specific annealing conditions. This growth process shows a new way of creating device islands, which are confined within oxide regions and could be ordered, for applications in optical and electronic devices on silicon. © *2001 American Vacuum Society*. [DOI: 10.1116/1.1354976]

I. INTRODUCTION

Self-assembly of semiconductor islands on a crystalline substrate for the formation of quantum optical and electronic devices has become increasingly important in recent years. One of the motivations behind these efforts is to find cost effective means to form nanoscale device regions without the use of expensive lithography techniques. Another motivation is to form devices and functions that take advantage of quantum confinement effects for electronic and optical applications such as light emitting diodes (LEDs), tunneling diodes, detectors, etc. The well-known Stranski–Krastanov (SK) growth concept for self-assembly of semiconductor crystals was initially demonstrated on III–V and II–VI families of semiconductor materials. The main goal of the efforts in this area is to form ensembles of identical quantum size systems. For example, three-dimensional InAs,[1,2] InSb, GaSb, and AlSb[3,4] nanometer-scale dots have also been grown on GaAs. Similarly, in recent years, the SK growth technique has been applied to silicon-based heterostructures and pure Ge islands have been grown on silicon substrates.[5–10] The islands were grown using a modified SK growth process with chemical vapor deposition of germane from 10 T to atmospheric pressure in a commercially available reactor.[5] The same authors also show that preferential formation of Ge islands takes place at the edges of a selective silicon region facet.[6] In a later study, the authors also showed that once the islands are formed, subsequent annealing changes the shape and size of the islands as a function of annealing time.[7] Atoms can detach from one island and diffuse to other larger islands as function of thermal conditions, a phenomenon known as Ostwald ripening.[5,8,11] The positioning of single-crystal Ge islands at specific locations by Silicon mesas formed by nanoimprinting and etching has also been demonstrated in an effort to achieve an ordered array of device islands.[9] We have also reported on the formation of ordered SiGe islands by annealing of thin SiGe films, thus providing a method to localize the formation of SiGe islands.[10]

The silicon–germanium ($Si_{1-x}Ge_x$) materials system is quite attractive since the possibility of integrating self-assembled nanostructures with silicon technology for electronic and optical applications provides great promise to extend the silicon technology roadmaps. LEDs in SiGe nanostructure diodes have been reported as possible examples of such technology.[12] Lithographic positioning of germanium quantum dots, which was demonstrated earlier,[6] has also been used to propose a prototype dot register for quantum computing.[13] For optical applications, random positioning of the germanium dots is sufficient, but for electronic applications, such as the dot register described above, ordered placement of dots within a device region is necessary. This article provides further details on the process flow, the formation, and atomic force microscopy (AFM) characterization of self-assembled SiGe islands that can be formed in ordered arrays within device regions bounded by oxide. A novel two-step process has been devised consisting of growth and subsequent thermal annealing of a metastable $Si_{0.6}Ge_{0.4}$ film. This process can potentially be used to form devices, which can have applications as electronic devices (active device regions, dot registers, etc.) and optical devices (LEDs, etc.).

II. PROCESS FLOW

The process for the formation of structures described here is shown in Fig. 1. A 3500 Å thick oxide was formed using local oxidation of silicon on 8 in. silicon wafers. Various

a)Author to whom correspondence should be addressed; electronic mail: bashir@ecn.purdue.edu

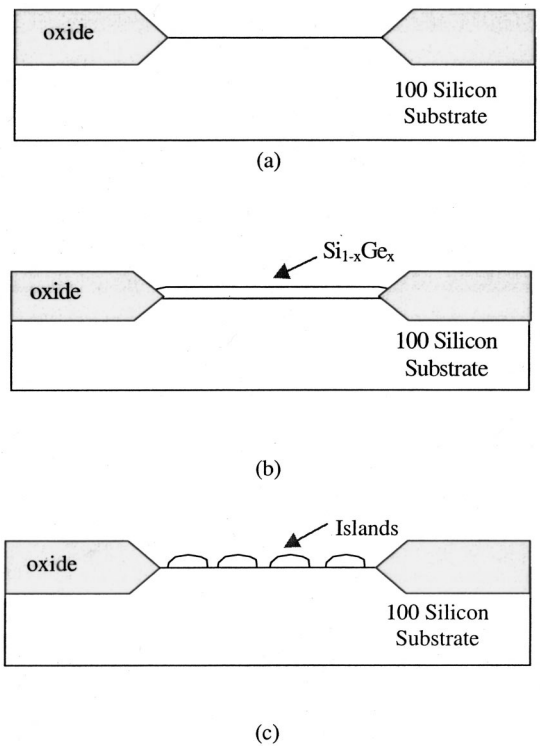

FIG. 1. Process flow for the island formation. (a) Local oxidation of silicon to form active device regions, (b) selective growth of silicon–germanium alloy, and (c) controlled relaxation and nucleation of islands.

regions were defined on the wafers with an overall exposed area of about 15%. Thin $Si_{0.6}Ge_{0.4}$ films are selectively grown on silicon wafers using a commercially available epitaxial system (ASM Epsilon-1) in reduced pressure chemical vapor deposition conditions. A high temperature (950 °C) H_2 bake for 10 min at 30 T was used to remove any native oxide prior to the growth. The films were then selectively deposited directly on the silicon exposed area at 40 T and 650 °C. GeH_4 and $Si_2H_2Cl_2$ were used as the source gases and HCl was used to enhance selectivity over the oxide. The HCl to $Si_2H_2Cl_2$ ratio was 100 sccm/75 scccm. Hydrogen was used as the carrier gas at flow rates of 20 slm.

After growth, the wafers were visually inspected and no sign of defects or dislocations were observed. The growth was perfectly selective and nucleation did not occur on the oxide regions. Different regions were analyzed on the wafer. Region A consisted of a large square of silicon germanium opening in the oxide, which was 50 μm on a side. Region B had the same overall size as region A but had 1 μm silicon germanium spaces between the 2 μm$\times$2 μm oxide islands distributed evenly in a 50 μm square region. Region C consisted of small 3 μm$\times$4 μm silicon germanium windows with oxide spaces in between them. After structure growth, all of the wafers were brought to atmosphere and analyzed using AFM, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

III. CHARACTERIZATION AND DISCUSSIONS

Scanning electron microscopy was first used to inspect the as-grown films, which did not go through any subsequent anneals. Results showed a smooth film surface within the selective growth regions, as shown in Fig. 2. A high-resolution cross-sectional TEM image, performed through region A, shows a film thickness of 55 Å, as shown in Fig. 3. Even though the film does not show any defects or dislocation, it is most likely in a metastable regime, as given by the well-known Mathews–Blakeslee curves and stability criteria[14] and hence should relax when annealed. A similar TEM was also performed in region C along the narrow 2 μm width and the results showed a film growth of about 160 Å and thus there were microloading effects present due to non-optimized growth conditions.

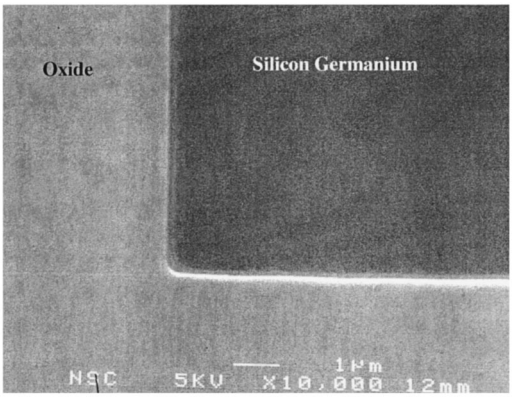

FIG. 2. SEM of the as-grown selective SiGe film in region A in wafer No. 1 showing a smooth film.

After the selective film growth as described above on another wafer (No. 2), it was *in situ* annealed at 750 °C in H_2 at 40 Torr for 6 min. Hence, this wafer was not exposed to atmospheric conditions, but rather annealed in the same vacuum cycle after the growth. Subsequent inspection of the films on wafer No. 2 demonstrated the formation of islands in the regions where the selective growth had taken place. The islands were characterized by an AFM (Digital Instruments Nanoscope III Dimension 5000). Figure 4 shows an AFM image of the islands formed in region A of wafer No. 2. These islands are larger than the previously reported dots formed by SK growth of Ge on silicon substrates, which were 20–75 nm wide.[6,7] The root mean square (rms) rough-

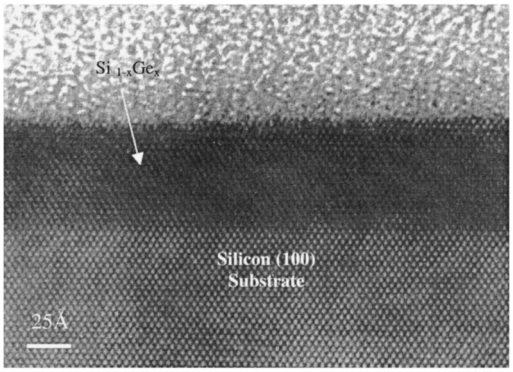

FIG. 3. TEM of as-grown selective SiGe film in region A in wafer No. 1 showing a 55 Å film.

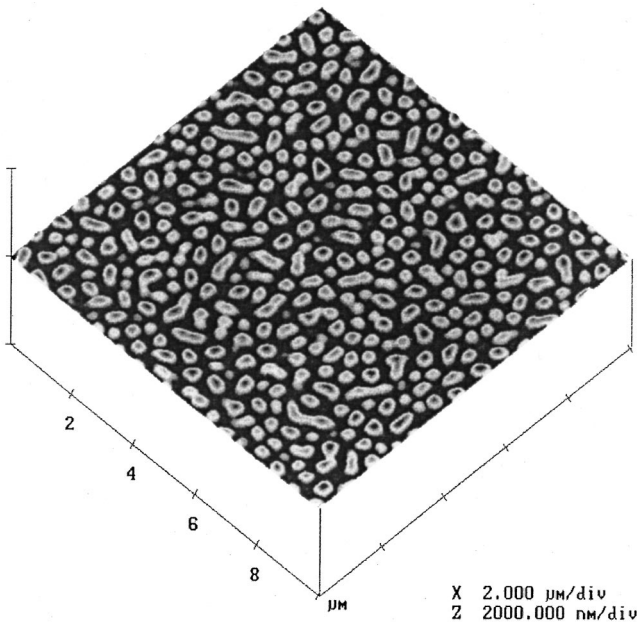

FIG. 4. AFM scan of the islands in region A.

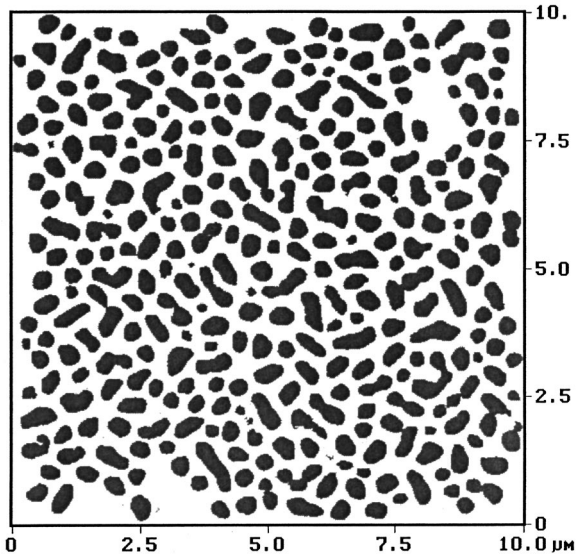

FIG. 6. AFM scan for the grain size analysis in region A.

ness of a $10\,\mu m \times 10\,\mu m$ area in region A of wafer No. 2 was 23.6 nm. The island density was found to be about 3.2 μm^{-2}. From the roughness scans, the maximum height of the islands was found to be 102.5 nm also confirmed by a cross-sectional scan. Region B in wafer No. 2 showed islands which were most uniform in size when compared to regions A and C. The rms roughness of the silicon germanium islands in between the oxide squares in region B was found to be 20.7 nm, and the island density was increased to about 6 μm^{-2} as compared to 3.2 μm^{-2} in region A. From the roughness scans, the maximum height of the islands in region B was found to be 127 nm.

Grain size analysis software from Digital Instruments was used to determine the size distribution of the islands in wafer No. 2 and the grain size was found to vary with the initial exposed silicon area. The AFM scan of islands in region A and B are shown in Figs. 6 and 7, respectively. Within the $10\,\mu m \times 10\,\mu m$ area in region A, the mean grain size was found to be $1.29 \times 10^5\,nm^2$ ($\sim$359 nm diameter assuming a circular shape) with a standard deviation of $6.62 \times 10^4\,nm^2$ ($\sim$257 nm), as tabulated in Fig. 8(a). As can be seen from the pictures in Fig. 8, and numerically demonstrated by the grain size analysis, there is a large variation in island size. In particular, a few of the islands are large and oblong which increases the standard deviation. Of course, it is desirable to have the island size as uniform as possible.

Between the oxide patterns in region B, the mean grain size of silicon–germanium islands was found to be $4.83 \times 10^4\,nm^2$ ($\sim$245 nm diameter assuming a circular shape) with a standard deviation of $1.67 \times 10^4\,nm^2$ ($\sim$139 nm).

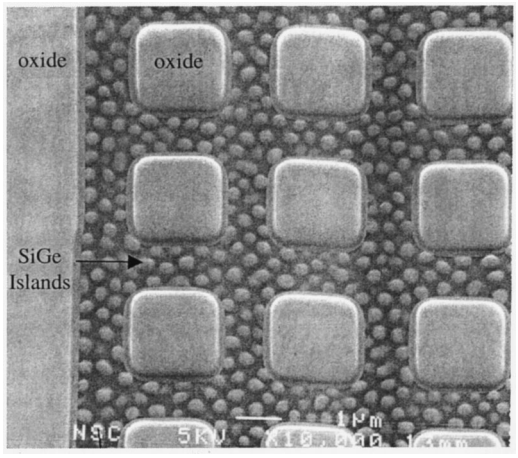

FIG. 5. Angled scanning electron microscope picture of region B. Islands are formed in the regions between the oxide where the film was initially grown selectively.

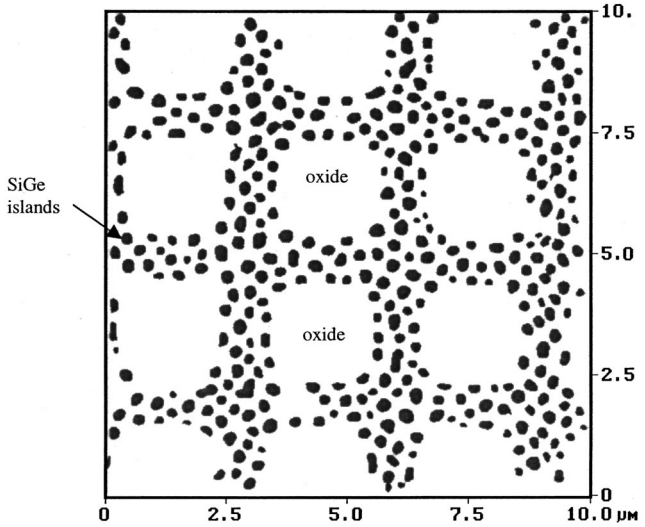

FIG. 7. AFM scan for the grain size analysis in region B. The oxide regions were subtracted from the analysis.

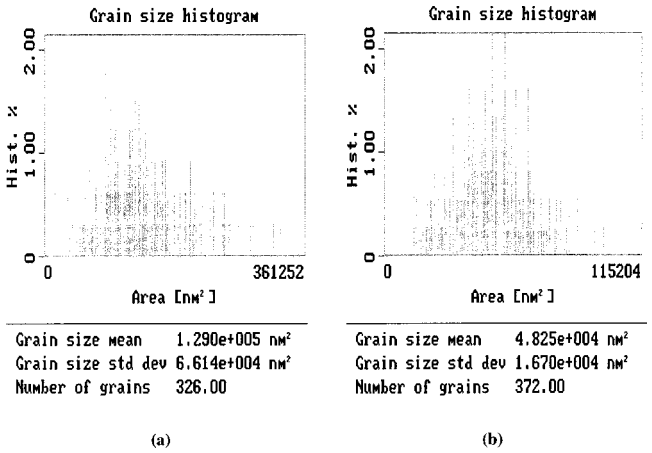

FIG. 8. (a) Histogram of device island size from grain analysis of region A. (b) Histogram of device island size from grain analysis of region B (excluding the oxide regions).

histogram of the island size in region B is shown in Fig. 8(b). The island size and the standard deviation are reduced compared to what was observed in region A.

AFM scans and grain size analysis was also performed in region C, which were the 4 μm$\times$3 μm initial silicon openings, as shown in Fig. 9. The islands are clearly smaller in size than those in region A. However, the distribution is dense, similar to those observed in region B (Fig. 7). The data from Figs. 9 and 10 clearly show that island size is a function of the size of the initial silicon open areas on which the selective SiGe film was grown. When the openings are small, the size of the SiGe islands formed after annealing is also small. Comparatively, the islands are larger when they are grown on larger areas of silicon. Cross-sectional TEM was also used to characterize region C, and a representative image is shown in Figs. 11(a) and 11(b). The previously smooth film has clearly coarsened into islands. There are

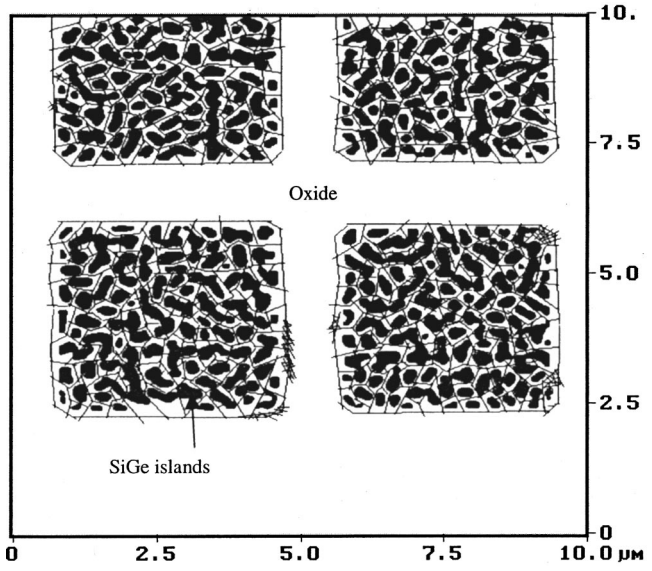

FIG. 9. AFM scan for the grain size analysis in region C.

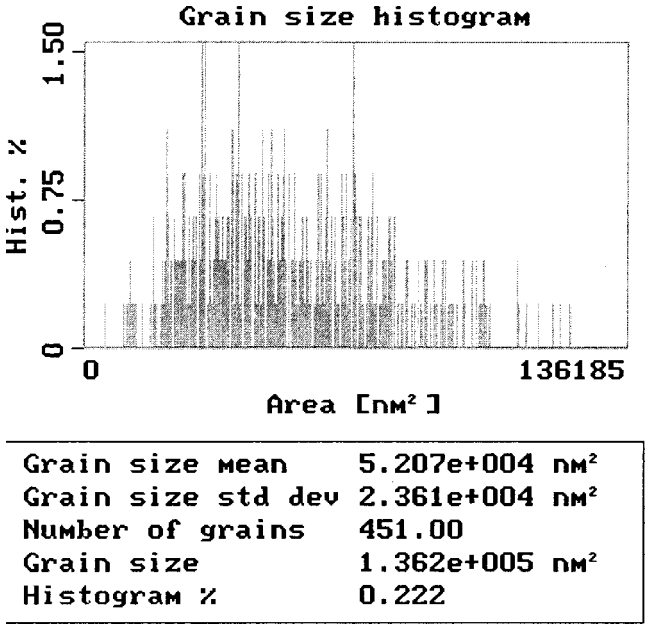

FIG. 10. Histogram of device island size from grain analysis of region C.

defects and stacking faults within the islands originating from the interface. The region adjacent to the islands is depressed and it appears that migration of silicon atoms has taken place from these regions to the islands. Micro-Auger studies were performed with a spot size which was smaller than one of the islands in region C. The germanium concentration in the unannealed, strained film was found to be 41.05% (50 Å deep into the surface), whereas the germanium concentration in the annealed film was found to be 18% (at

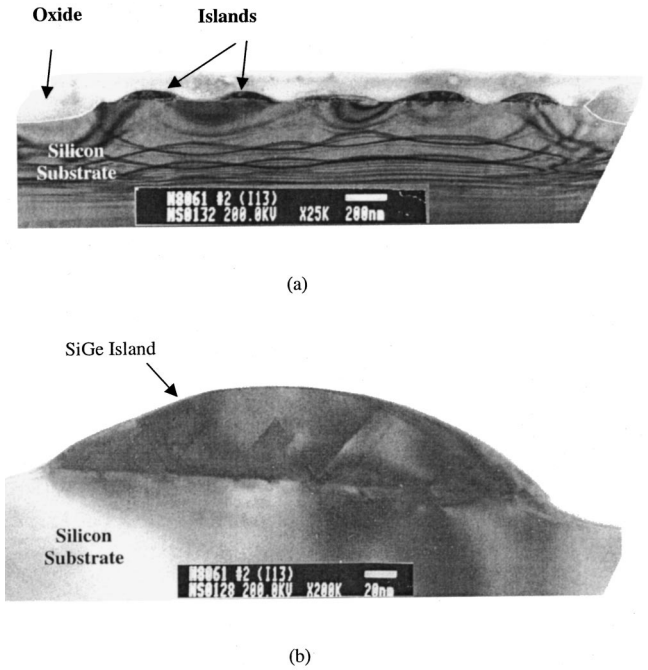

FIG. 11. (a) Cross-sectional TEM through the islands. The oxide edges have been highlighted. (b) Close up TEM through one of the islands showing stacking faults within the islands.

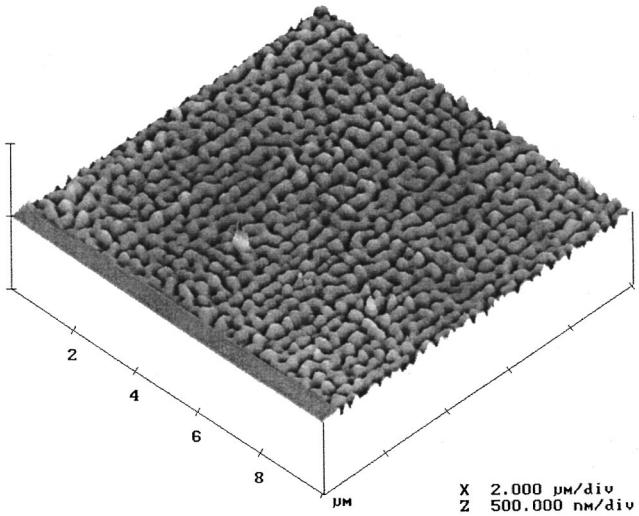

FIG. 12. AFM scans in region A after the thermal annealing (subsequent to the growth). Anneal was performed at 650 °C for 25 min at 20 Torr in hydrogen. Order is clearly visible.

the same depth of 50 Å). Hence, it appears that additional silicon species were incorporated into the islands as the film relaxed and formed islands resulting in a net lower germanium concentration in the islands and a depletion of the silicon surface around the islands.

IV. EFFECT OF ANNEAL CONDITIONS AND DISCUSSION

Various annealing conditions were explored in order to produce uniformly sized islands and to improve our understanding of the underlying physical phenomena occurring in this system. An additional sample was grown as described in the section above, however, the temperature of the *in situ* anneal was reduced to 650 °C for 25 min in hydrogen at 40 T. The resulting film was still highly strained and had not relaxed, i.e., SEM micrograph images revealed a lack of any island formation. AFM analysis of this particular sample showed a rms roughness of only 1.17 nm. This indicated that the initiation of island formation is certainly thermally driven and annealing at a lower temperature (for a longer duration of time) did not form islands as did the sample that was annealed at 750 °C for 6 min at 40 T. The relaxation mechanisms of such a system have also recently been studied where wave and island formation was observed as function of annealing conditions.[15] It has been confirmed that hydrogen acts a surfactant in silicon growth and thought to reduce surface mobility. The same might also be true in the SiGe system. The formation of these islands is related to the surface migration and lateral movement of the atoms to adjacent sites. The diffusion of the atoms is related to their mean free path, which is known to be a function of pressure. Hence, an anneal was performed on an additional wafer at 650 °C for 25 min in hydrogen at 20 T to examine the effect on island shape and form. Figure 12 shows an AFM image of this region. As clearly evident, the island density, shape, and size are different than the sample annealed at the previous conditions. The surface undulations and waves are also spatially reduced. These samples and conditions show the most ordered arrangement of submicron sized islands. When Fig. 12 is compared to Fig. 4, the islands in Fig. 12 are smaller, have a higher area density, and are ordered. The grain size analysis was not performed since the islands are not isolated and are still connected. The rms roughness of islands in Fig. 12 (region A) was found to be 19.8 nm, and the island density was increased to about 11 μm^{-2} clearly indicating an increased packing. From the roughness scans, the maximum height of the islands was found to be 142 nm. The connection between the islands can possibly be removed either by an etching step or by a sacrificial oxidation step. It can also be conjectured that given the proper thickness of the film and anneal conditions, the islands can be made perfectly ordered.

The mechanisms behind the formation of these islands can be postulated as follows. The initiation of the island formation is due to the relaxation of the metastable grown film once thermal energy is provided to the system. The mechanisms could be similar in nature to ones governing the SK growth processes. Initially, the unannealed film is strained and in a metastable state. When thermal energy is provided to the system, the film relaxes and the surface drives to attain the lowest energy, i.e., the islands. A modified form of Ostwald ripening could be taking place that assists in the formation of the islands.[5,8,11] Ostwald ripening occurs in various materials, where second phase particles grow in a matrix to form clusters and reduce the total energy of the system. The initiation can take place from kink sites either at the edges of the oxide/SiGe or from sites of imperfection at the SiGe/Si interface. Lower temperature reduces the formation of the islands due to the reduction in the thermal energy provided to initiate the relaxation. The lateral diffusion, migration of atoms, and surface undulations of the film are expected to be dependent on the ambient pressure and the hydrogen surface coverage. This was found in our case since reducing the pressure increases the diffusion and the ''mean free path'' of the atoms and enhances the formation smaller size islands.

V. CONCLUSIONS

In conclusion, we have examined a new technique to form ordered self-assembled device islands using annealing of thin SiGe films, which were selectively grown within oxide windows. The novel two-step process includes the growth of the film and an *in situ* thermal anneal which relaxes the metastable film into self-assembled islands. The island distribution and size were examined using AFM and the highest density and smallest size islands were formed in the smallest size oxide windows. The size of the islands was smaller when the ambient hydrogen pressure was reduced. Using the approach presented in this article, evidence has been presented which shows that ordered self-assembled device islands can be formed with proper optimization of the annealing conditions.

ACKNOWLEDGMENTS

The authors would like to thank C. Weitzsacker of Charles Evans and Associates for micro-Auger analysis and National Semiconductor Corporation, Sunnyvale, CA, where the films were grown.

Presented at the ICAMPM Conference, Santa Clara, CA, 7–11 February 2000.

[1]N. P. Kobayashi, T. R. Ramachandran, P. Chen, and A. Madhukar, Appl. Phys. Lett. **68**, 3299 (1996).
[2]J. M. Moison, F. Houzay, F. Barthe, and L. Leprince, Appl. Phys. Lett. **64**, 197 (1994).
[3]B. R. Bennet, R. Magno, and B. V. Shanabrook, Appl. Phys. Lett. **68**, 505 (1996).
[4]Y. Peng, B. Wang, W. Chen, and S. Liu, Opt. Quantum Electron. **29**, 985 (1997).
[5]T. I. Kamins, E. C. Carr, R. S. Williams, and S. J. Rosner, J. Appl. Phys. **81**, 211 (1997).
[6]T. I. Kamins and R. S. Williams, Appl. Phys. Lett. **71**, 1201 (1997).
[7]T. I. Kamins and R. S. Williams, Surf. Sci. **405**, L580 (1998).
[8]G. Rosenfeld, K. Morgenstern, I. Beckmann, W. Wulfhekel, E. Laegsgaard, F. Besenbacher, and G. Comsa, Surf. Sci. **402–404**, 401 (1998).
[9]T. I. Kamins, D. A. A. Ohlberg, R. Stanley Williams, W. Zhang, and S. Y. Chou, Appl. Phys. Lett. **74**, 1773 (1999).
[10]R. Bashir, A. E. Kabir, and K. Chao, Appl. Surf. Sci. **152**, 99 (1999).
[11]J. Moller, K. I. Jacob, and J. Schmelzer, J. Phys. Chem. Solids **59**, 1097 (1998).
[12]L. Vescan, M. Goryll, K. Grimm, and C. Dieker, Proceedings of the Topical Meeting on Silicon Monolithic Integrated Circuits in RF Systems, Ann Arbor, MI, 17–18 September 1998, p. 38.
[13]A. Balandin, G. Jin, and K. L. Wang, J. Electron. Mater. **29**, 549 (2000).
[14]J. W. Mathews and A. E. Blakeslee, J. Cryst. Growth **32**, 265 (1974).
[15]K. Grimm, L. Vescan, C. Visser, L. K. Nanver, and H. Luth, Mater. Sci. Eng., B **69–70**, 261 (2000).