Self-assembled growth of nanostructural Ge islands on bromine-passivated Si(111) surfaces at room temperature

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Abstract. We have deposited relatively thick (∼60 nm) Ge layers on Br-passivated Si(111) substrates by thermal evaporation under high vacuum conditions at room temperature. Ge has grown in a layer-plus-island mode although it is different from the Stranski–Krastanov growth mode observed in epitaxial growth. Both the islands and the layer are nanocrystalline. This appears to be a consequence of reduction of surface free energy of the Si(111) substrate by Br-passivation. The size distribution of the Ge nanoislands has been determined. The Br–Si(111) substrates were prepared by a liquid treatment, which may not produce exactly reproducible surfaces. Nevertheless, some basic features of the nanostructural island growth are reasonably reproducible, while there are variations in the details of the island size distribution.

1. Introduction

Spontaneous formation of small Ge islands during deposition of Ge on Si has been the subject of many recent studies. Technologically, one of the major advantages of Ge is its compatibility with conventional Si integrated technology with the potential for incorporation of low dimensional self-assembled Ge islands. However, such applications require that the islands are of the size needed for a specific device and that the size of the islands is uniform. Ge growth on Si has been studied very extensively as a classic case of Stranski–Krastanov (SK) growth [1,2], which also provides a straightforward route for producing self-assembled quantum dots [1]. Formation of self-assembled Ge islands of various shapes like hut, pyramid and dome and their shape transitions have been fascinating [2–4]. A variety of methods, such as molecular beam epitaxy (MBE) [2,5,6], chemical

vapor deposition (CVD) [7–9] at atmospheric pressure and below, liquid phase epitaxy [10] and solid phase epitaxy [11] have been used for sample preparations. Most of the studies have been performed on Si(001) surfaces and some on Si(111) [11,12]. Some of these studies concentrated only on the size distribution of the Ge islands [3,4,8]. Here we report on the size distribution of Ge nanoislands obtained in vacuum deposition of Ge on bromine-passivated Si surfaces.

Passivation of silicon surfaces by adsorbed bromine, observed in experiments on samples prepared by a wet chemical method [13–17] and theoretical calculations [18], has raised a number of possibilities of both scientific and technological importance. These include the possibility that such passivated surfaces might permit epitaxy of thin overlayer films and growth of self-assembled structures without the expensive and, from production standpoint, unacceptable need for ultra high vacuum (UHV) processing. The Br-passivated Si surface has proven to be an extremely stable system for non-UHV analysis [13,14,19].

Growth under high vacuum conditions on chemically prepared bromine-passivated Si(111) [denoted hereafter Br–Si(111)] surfaces has already shown many interesting features − many of them comparable to UHV growth. In room temperature vacuum deposition, epitaxial Ag layers have been grown on Br–Si(111) surfaces [20]. Epitaxial gold silicide islands have been grown on Br–Si(111) surfaces in a self-assembled process [21] and the phenomenon of shape transition of islands in heteroepitaxial system [22], which might be a route to form quantum wires, has been observed and quantitatively analyzed [23]. Not only Si(111), but also Si(110) surfaces can be passivated by bromine in a bromine–methanol treatment. Growth of a large number of straight parallel self-assembled gold silicide wire-like islands with aspect ratio as large as 200 : 1 on Br–Si(110) substrates has been observed [24]. This growth behavior reflects the two-fold symmetry of the Si(110) surface. As Ge growth on Si is an important topic, we considered it worthwhile to explore the growth of Ge on Br–Si(111) substrates.

In the growth of Ge layers on Br–Si(111) surfaces, spontaneous formation of Ge nanostructural islands on a compact nanostructural layer was observed [12]. The process of mass transport from the Ge layer to Ge islands was studied and the activation energy for this process was determined from the Arrheneous behavior of the mass transport process [12]. Although the growth occurs in a layer-plus-island mode, it is basically different from the layer-plus-island growth in the SK mode, which occurs in epitaxial growth due to an interplay between surface and interface free energies and strain energy. The Ge layers on Br–Si(111) substrates are not epitaxial. Yet a layer-plus-island growth is observed. In the present study we are concerned with the size distribution of the Ge islands. The growth mechanism, which is different from the case of epitaxial growth, will be discussed. Secondly, the preparation of the bromine-passivated Si substrates involves a wet chemical treatment. Since in liquid treatment, surfaces are prone to being difficult to reproduce exactly, it is a natural question whether various aspects of the nanostructures grown on Br-passivated Si surfaces are reproducible. We also explore the aspect of reproducibility of the size distribution of nanostructural Ge islands on the as-deposited Ge layers on Br–Si(111) surfaces at room temperature.

2. Experimental

Commercial Si(111) wafers (*n*-type, P-doped, 10–20 Ω cm) were used as substrates. The method of preparation of the Br–Si(111) substrate is described hereafter. The Si(111) sub-

strates were thoroughly cleaned in deionized distilled water, methanol, trichloroethylene, again in methanol and finally etched in 48% hydrofluoric acid (HF) for five minutes. A bromine–methanol solution (0.05% bromine by volume) was squirted onto the sample while the sample was taken out of HF, taking care that the sample was not exposed to air prior to being wet by the bromine–methanol solution. The sample was then rinsed in methanol and dried by blowing dry Ar gas. This sample is described as Br–Si(111) sub-strate. These type of substrates were used in many growth studies including those in refs [12,20,21,23,24]. Ge was deposited by thermal evaporation at the rate of 0.5 nm/s on Br–Si(111) substrates kept at room temperature (RT) under high vacuum ($\sim$3 $\times$ 10^{-6} torr). Besides using the quartz microbalance, we used Rutherford backscattering spectrometry (RBS) and X-ray reflectometry (XRR) to determine the film thickness. We report results for a film thickness of $\sim$60 nm. RBS measurements were performed using 1.0 MeV He$^+$ ions from the 3 MV Pelletron accelerator at the Institute of Physics (IOP), Bhubaneswar. XRR and X-ray diffraction (XRD) measurements were made with the X-ray facility at IOP, Bhubaneswar. Micrographs using atomic force microscopy (AFM) were obtained in air with a Digital Instruments Nanoscope III equipment at the Chinese University of Hong Kong.

3. Results and discussions

Let us first discuss the case of epitaxial growth of Ge on Si substrates. Surface free energy of Ge is slightly smaller than that of Si, i.e., $\sigma_{Ge} < \sigma_{Si}$. This is the wetting condition and layer-by-layer growth would be expected. However, the lattice constant of Ge is 4% larger than that of Si. In epitaxial growth, Ge lattice shrinks in the interface plane in order to adapt to the Si lattice. This leads to an expansion of the Ge lattice in the direction normal to the surface. The strain thus introduced in the Ge layer alters the layer-by-layer growth and layer-plus-island or SK growth takes place. In fact, growth proceeds as a uniform layer up to 3–4 monolayers (1 monolayer corresponds to 7.83×10^{14} atoms/cm^2 and 6.78×10^{14} atoms/cm^2 on Si(111) and Si(100) surfaces respectively) and then islands grow on this thin ($\sim$1 nm) wetting layer [1–11].

In our case the Ge layer is not epitaxial. This is confirmed by high resolution XRD and RBS/channeling measurements. Typical RBS/channeling spectra are shown in figure 1. While a reduction in the backscattering yield from Si is observed, there is no reduction in yield from the Ge layer when the incident ion beam is aligned along the [111] crystallographic direction normal to the Si(111) surface. An epitaxial Ge layer would have shown a reduction in the backscattering yield under this condition. As detected by Raman spectroscopy, the layer is actually nanocrystalline and upon annealing the layer transforms into a microcrystalline structure [12]. It may be noted that RBS/channeling is a very powerful technique for the analysis of epitaxial structures. This technique has been extensively used for the study of Ge layers on Si, where minimum backscattering yield in Si under channeling condition corresponds to a minimum yield in the Ge layer [25]. However, in our case since the Ge layer is not single crystalline, we cannot extract further insight from RBS/channeling measurements.

Formation of nanostructural Ge islands are also observed on the as-deposited nanocrystalline Ge layers on Br–Si(111) substrates. Ge islands are seen in the AFM micrographs of figure 2. Size distribution of the Ge islands have been obtained from the AFM results. Various aspects of the size distribution will be discussed later. Let us first try to understand the growth mechanism in comparison to the epitaxial growth.
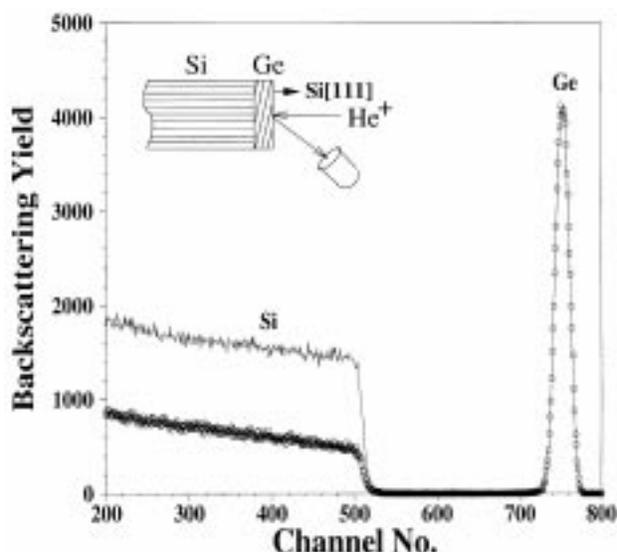
Figure 1. Typical RBS/channeling spectra from an as-deposited Ge/Br–Si(111) sample. When the incident ion beam is aligned with the [111] crystallographic axis of substrate Si, there is a reduction in ion backscattering yield (∘ ∘ ∘) from Si due to channeling of ions into it. When the incident direction is slightly misaligned, the yield is higher (−) due to lack of channeling. No change in yield is observed from the Ge layer under these aligned (∘ ∘ ∘) and random (−) incidence conditions. The spectra are normalized to the same number of incident ions. Channel number indicates the energy of the backscattered He$^+$ ions. The experimental geometry is schematically shown in the inset.

In view of the fact that the wetting layer is only 3−4 monolayers or about 1 nm in the epitaxial growth of Ge on Si, all earlier studies on the growth of Ge nanostructural islands involved deposition of only a few additional monolayers of Ge on Si surfaces at an elevated temperature. In such cases the wetting Ge layer is coherent with the substrate and the Ge islands grow on this coherent wetting layer. In our case the island growth occurred on relatively thick Ge layers deposited on Br-passivated Si substrates at room temperature. Our growth conditions are quite different from those in earlier studies [1–11] and the growth mechanism is also different. When dangling bonds on a Si(111) surface are passivated by Br, it reduces the free energy of the surface. When substrate surface free energy, σ_s, is significantly lower than that of deposited film, σ_f, it is a case of non-wetting and it is likely to have island growth provided the deposited atoms have enough mobility. Surface free energies of Ge and Si are 1100 erg/cm^2 and 1200 erg/cm^2 respectively [26] (although it depends on surface orientation). This wetting condition $\sigma_{Ge} < \sigma_{Si}$ ensures the initial layer-by-layer growth in the case of epitaxial growth. A Br-passivated silicon substrate would have significantly lower surface free energy compared to Ge. Thus, under this non-wetting condition the Ge growth on Br–Si(111) surface is likely to be in the form of islands. (In fact we have used this non-wetting condition ($\sigma_f \gg \sigma_s$) to grow nanocrystalline Ge islands (∼25 nm height, ∼100 nm base diameter) directly on a polymer layer by depositing a relatively thin Ge layer (equivalent to 5 nm) [27,28]). When more Ge is deposited, coalescence of islands leads to a nanocrystalline compact layer as revealed from
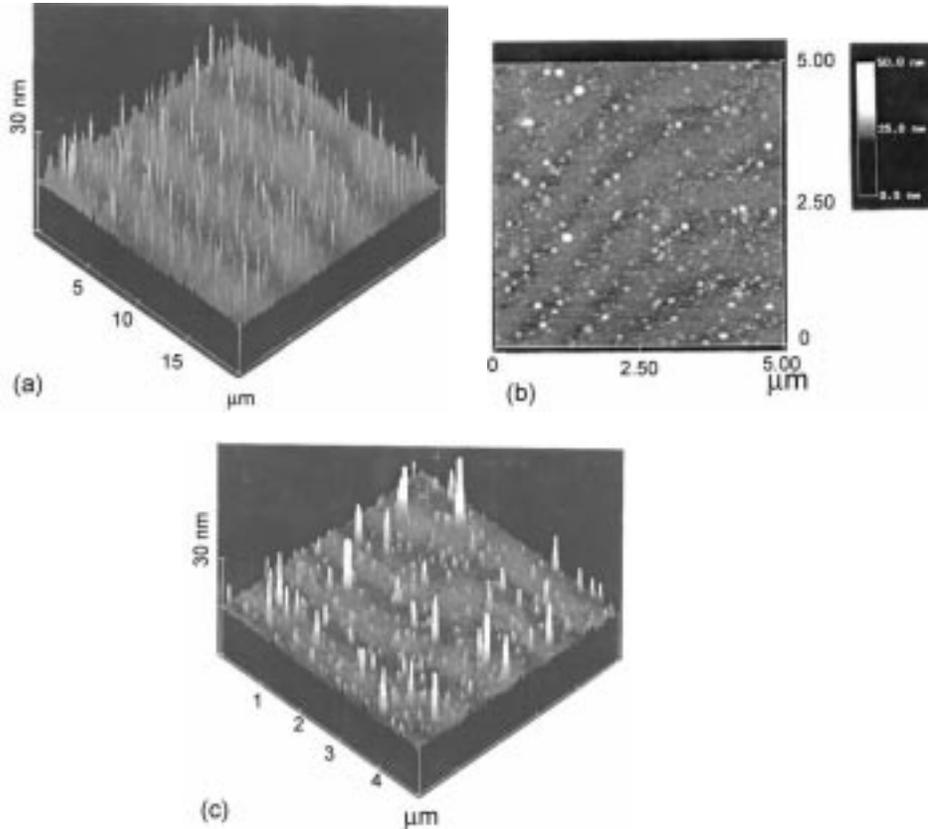
Figure 2. AFM images from an as-deposited sample. (**a**) A 3-D image of a large area (20 μm $\times$ 20 μm) where tall islands are visible. (**b**) A 2-D image of a smaller area (5 μm $\times$ 5 μm) shows the diameter of the islands. (**c**) A 3-D scan corresponding to the image in (**b**) shows that shorter islands have higher number density compared to that of the taller islands.

Raman spectroscopy [12]. However, we also observe islands on top of the layer as seen in the AFM micrographs (figure 2). We have used Raman spectroscopy measurements on our as-deposited samples. The details of the analysis of the Raman spectra have been presented elsewhere [12]. The results of Raman studies may be summarized as follows: (i) The Ge islands are nanocrystalline, (ii) the Ge layer on which the Ge islands have grown is also nanocrystalline and (iii) the layer has non-zero average strain with a strain distribution while the islands are relaxed. Apparently, the system reduces its total energy by partial strain relaxation via the formation of self-assembled relaxed islands on the layer.

Since the mobility of the deposited atoms is a requirement for island growth, one may wonder if island growth is possible at all at room temperature. On a silicon surface there is observable diffusion at a temperature as low as 25°C with an activation energy of 0.94 eV [29]. For the layer-plus-island or SK growth of Ge on Si(100) surfaces under UHV condition, a previous study provided an activation energy of (0.84 $\pm$ 0.14) eV for sur-

face diffusion [30]. Molecular dynamics simulation [31,32] for Ge self-diffusion of Ge adatoms on Si(100) surface obtained an activation energy of 0.73 eV. Ronald and Gilmer [33] obtained anisotropic activation energies of 0.64 eV and 0.80 eV for the fast-diffusion and slow-diffusion direction respectively, for the $Ge_n/Si(100)$ system, where n denotes the number of Ge monolayers deposited. For Ge/Si(111) the activation energy is expected to be $\sim$0.6 eV [31,32]. By scanning tunneling microscopy (STM) experiments, Lagally and coworkers estimated an activation energy of 0.59 ± 0.1 eV for Ge diffusion on Si(100) and 0.45 eV for Ge diffusion on the $Ge_n/Si(100)$ system [34]. It appears that the activation barrier for surface diffusion is expected to be in the range 0.45–0.85 eV even for this UHV growth cases. This is a small fraction of the bulk activation barrier (2.97 eV). In our high vacuum growth, both partial contamination and polycrystallinity can enhance diffusion. It has been shown for the growth of Ge on Br–Si(111) substrates that there is significant diffusion on the Ge layer at room temperature with an activation energy as low as 0.45 ± 0.04 eV and at higher annealing temperatures, increased diffusion leads to an increased number density of the islands and the growth of taller islands in a layer-to-island mass transport process [12].

Let us discuss the island size distribution now. In figure 2a, a three-dimensional (3-D) AFM image of a large area (20 μm $\times$ 20 μm) is shown. In this figure, we see many islands (appearing like spikes) and that they are more or less uniformly distributed over the surface. Mainly the taller islands are noticeable in figure 2a. The shorter islands and the diameter of the islands are not resolved in this figure. Scans over a smaller area (5 μm $\times$ 5 μm) are shown in figures 2b and 2c. We see that the number density of shorter islands is much larger than that of taller islands. The size distribution of these islands is shown in figure 3.

Figures 3a and 3b show the distributions of islands in diameter and height respectively. Figure 3c shows the scatter plot of diameter vs. height. About 80% of the islands are distributed over the height range 0.5–3.0 nm with an average height of $\sim$1.6 nm. About 20% of the islands have heights greater than 3 nm in a wide distribution. From figure 3a, we see that the diameter of the islands are distributed over the range $\sim$100–240 nm with average diameter $\sim$165 nm. Only 6% of the islands are in the larger diameter (> 240 nm) tail. The scatter plot of diameter vs. height (figure 3c) shows that taller islands have larger diameter, the diameter variation with height being slower for islands taller than $\sim$3 nm. The distribution is monomodal unlike that obtained in epitaxial growth, where a bimodal distribution is observed.

Usually with liquid treatment of surfaces it is difficult to reproduce the results. Since our Br–Si(111) substrates are prepared by a liquid chemical treatment, in order to check the reproducibility of the size distribution of the Ge islands we made measurements on several samples. In the present series of experiments, the size distribution of islands which differs the most from that in figure 3 is shown in figure 4. We notice that the overall distributions of the shorter islands are very similar except that there is a shift in average diameter and average height in opposite directions. Here we observe a larger proportion of taller (> 4 nm) islands. 44% of the islands are taller than 4 nm although their diameters do not change appreciably. We have not observed any clear bimodal distribution like those observed in the epitaxial growth of Ge on Si [3,4,8,9]. This is not surprising since the growth mechanism is completely different in our case. In CVD growth in the pressure range from 10 torr to atmospheric pressure at 550°C and 600°C, Kamins *et al* [8] obtained a bimodal distribution of Ge islands – one group around 4–5 nm ($\sim$2–3 nm for thin layers)
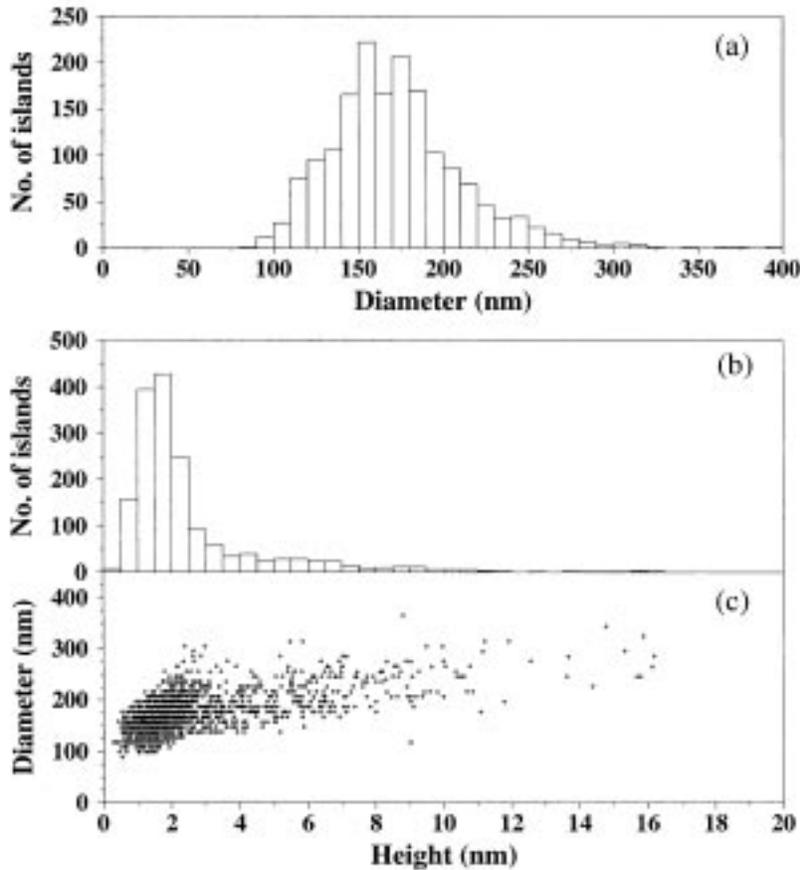
Figure 3. (**a**, **b**) The size distributions of islands corresponding to figure 2. (**c**) The diameter vs. height scatter plot of the islands.

and the other around 15 nm height. Growth at higher temperatures apparently tends to produce islands with higher average diameter and higher average height [6,8] (shorter group: ∼3.5 nm (550°C); ∼5 nm (600°C); taller group: ∼11 nm (550°C); ∼15 nm (600°C); ∼24 nm (700°C)). The average height of (shorter) islands in our case is somewhat smaller. However, post-deposition annealing, in general, increases average island height [12]. In the epitaxial growth Ge deposition is performed at an elevated substrate temperature; although a bimodal distribution is energetically favorable [3], for high deposition rate even at 550 °C substrate temperature, no clear bimodal distribution is observed. A bimodal distribution is achieved by post-deposition annealing [4]. During annealing the nanocrystalline islands grow further by drawing additional Ge from the wetting layer [4]. This layer-to-island mass transport has also been observed upon annealing for the Ge on Br–Si(111) system [12]. Although our deposition conditions are quite different – namely, deposition under high vacuum (10^{-6} torr pressure) on chemically passivated substrates at room temperature,
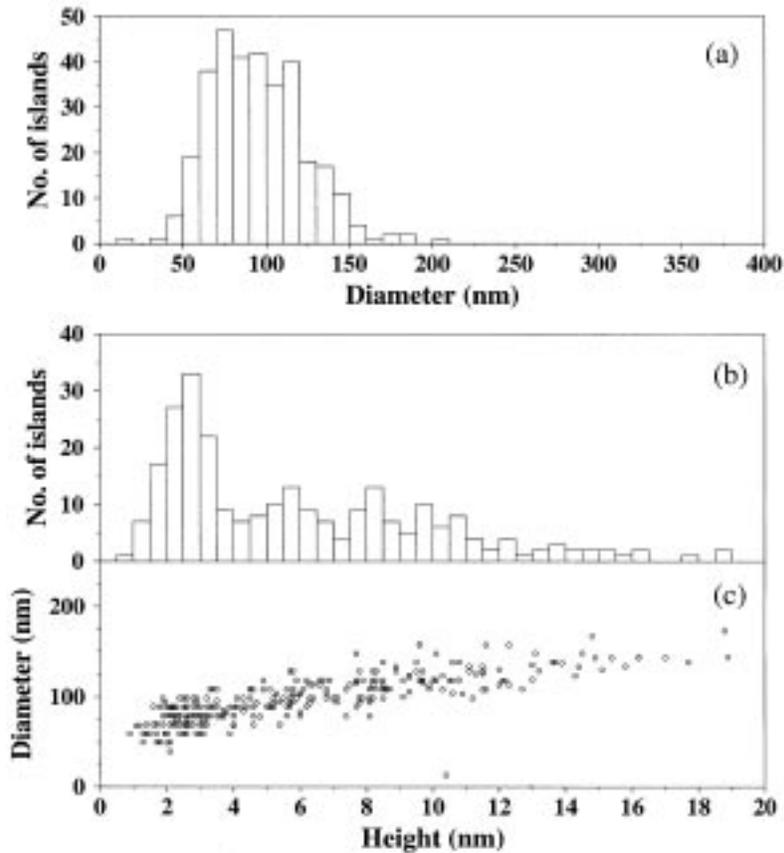
Figure 4. Size distribution plots (**a**, **b**) and the scatter plot (**c**) of islands for another identically prepared sample.

it is striking that the island growth features have some similarities to those in epitaxial growth [4,8]. The fact that monomodal island growth, as seen in figure 3, can be obtained is encouraging as a uniform size of islands is suitable in technological applications.

On the question of reproducibility of the island size distribution, we find that the shorter group of islands is reasonably reproducible with slight variations in average height. The taller group of islands do not seem to have a very well-defined distribution.

4. Conclusion

We have obtained self-assembled growth of nanostructural Ge islands on thin ($\sim$60 nm) nanocrystalline Ge layers deposited under high vacuum conditions at room temperature on Br–Si(111) surfaces, prepared by a wet chemical method. The islands are almost uniformly distributed over the surface. The heights of the major group of islands are in the range

0.5–4 nm. The average diameters range from 90 to 165 nm. The taller group of islands are mainly between 4 and 15 nm. Some variations are observed in the details of the island size distributions for several samples. This variation in the island size distribution might be attributed partly to the problem of reproducibility in liquid treatment of the substrate. Although a monomodal island distribution can be obtained, its reproducibility aspect needs to be explored further.

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