

## Self-assembled Ge nanostructures on polymer-coated silicon: Growth and characterization

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Self-assembled Ge nanoparticles have been grown on polymer-coated Si substrates by thermal evaporation under high vacuum utilizing the nonwetting condition given by the surface free-energy relation  $\sigma_{\text{Ge}} \gg \sigma_{\text{polymer}}$ . The nanostructures have been characterized by Raman spectroscopy, atomic-force microscopy (AFM), and optical microscopy. Raman spectrum shows a prominent Ge–Ge vibration peak at  $302 \text{ cm}^{-1}$ . AFM and optical microscopy show the formation of isolated Ge islands ( $\approx 100 \text{ nm}$  base,  $\approx 25 \text{ nm}$  height), nanowires (160 nm base, 25 nm height), and islands in linear chains. The possibility of embedding such nanostructures in waveguide structures are discussed. © 2000 American Institute of Physics. [S0003-6951(00)00333-8]

Nanometer-sized crystals of semiconductor materials are of great importance due to the possibility of developing electronic devices and studying quantum-confinement effects, which are opening the opportunities for quantum lasers, single electron transistors, and a host of other applications.<sup>1</sup>

Thin polymer layers have various applications. Spin-coated polymer layers are routinely used in the semiconductor industry.<sup>2</sup> Polymers, in general, have a low electron density. So a polymer layer, sandwiched between two layers of other materials with higher electron densities may be used to fabricate x-ray waveguides.<sup>3</sup> While nanoparticles and polymers are individually important, their combinations, e.g., nanoparticle/polymer composites, may open the way for applications such as tunable optoelectronic and dual-function hybrid devices.<sup>4–7</sup>

Ge nanoparticles have been grown, usually on silicon substrates, by molecular-beam epitaxy (MBE) and other methods. The lattice mismatch between Ge and Si and the consequent strain leads to a layer-plus-island growth process in which Ge islands grow on a uniform Ge layer. This method does not provide isolated Ge dots.

In standard MBE growth there are three possible modes of growth depending on the surface free energy of the substrate ( $\sigma_s$ ), that of the deposited material ( $\sigma_f$ ), and the interface free energy ( $\sigma_i$ ). Three-dimensional (3D) island growth or Volmer–Weber (VM) growth is the usual mode when  $\sigma_f + \sigma_i > \sigma_s$ . Layer-by-layer or Frank van der Merwe (FM) growth occurs when  $\sigma_f + \sigma_i < \sigma_s$ . An intermediate growth mode—layer-plus-island or Stranski-Krastanov (SK) growth—occurs when  $\sigma_f + \sigma_i \approx \sigma_s$  and a lattice mismatch is involved.<sup>8</sup> Ge on Si, with a 4% lattice mismatch, grows in the SK mode. When growth on polymer substrates is consid-

ered, there is no question of lattice mismatch and SK growth is not expected. In the absence of any definite lattice structure of the substrate (polymer) FM growth simply corresponds to wetting and VM growth to nonwetting. We have used this nonwetting criterion to grow Ge nanoclusters on polymer surfaces as  $\sigma_{\text{Ge}} \gg \sigma_{\text{polymer}}$ . Raman spectra from this system is comparable to that for Ge nanoclusters grown by MBE showing a distinct crystalline Ge–Ge vibration peak. Growth of Ge nanostructural islands—dots and wires—are also revealed in atomic-force microscopy (AFM). Optical microscopy additionally shows self-assembled linear arrangements of Ge islands on defects on the polymer layer leading to a quasiperiodic one-dimensional lattice or wire-like structures.

A polymer blend [15% polystyrene (PS), 85% poly(*p*-bromostyrene-stat-styrene) (PBr<sub>0.06</sub>S)] layer of 35 nm nominal thickness was deposited on a silicon wafer by spin coating. Earlier, we used such a polymer blend layer on a Au-coated Si substrate to demonstrate x-ray resonance enhancement (waveguide behavior) in such a layer.<sup>9</sup> For the study of growth on this polymer blend layer, 5 nm Ge was deposited (0.08–0.09 nm/s) by thermal evaporation under high-vacuum condition with the substrate at room temperature.

A Raman spectrum from such a sample is shown in Fig. 1. The spectrum is strikingly similar to that for Ge nanostructural islands grown on Si by molecular-beam epitaxy,<sup>10</sup> except that we do not observe the Raman line due to the Si–Ge vibration mode. This is expected as the Ge nanocrystals in our case are on the polymer layer and not in direct contact with underlying Si. The peak at  $302 \text{ cm}^{-1}$  is due to Ge–Ge vibration and has practically no shift from the Ge–Ge peak for bulk crystalline Ge. Raman spectra from nanostructures are expected to show phonon-confinement effects, namely, a frequency shift of the Raman peak with respect to the bulk

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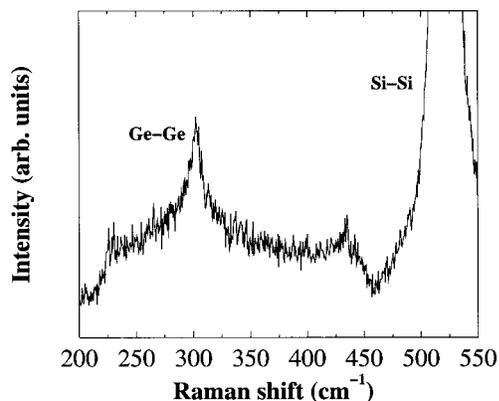


FIG. 1. Raman spectrum from the sample excited by the 514.5 nm line of an Ar<sup>+</sup> laser.

value and an asymmetry of the peak shape.<sup>11</sup> As the size of the islands becomes larger, the Raman peak position and shape tend to be that for the bulk crystals. The size over which the confinement effect is observable depends on the phonon dispersion curve  $\omega(q)$  of the material. For Ge,

$$\omega(q) = \omega_p - A \left( \frac{q}{q_0} \right)^2,$$

where  $q_0 = 2\pi/a_0$ ,  $a_0$  being the Ge lattice constant,  $\omega_p$  corresponds to the phonon energy at  $q=0$ , and  $A = 104 \text{ cm}^{-1}$ . It turns out that the Raman peak shape is not too sensitive to size variation, and peak shift and peak asymmetry are hardly detectable for a crystalline size of  $>20 \text{ nm}$ .<sup>12</sup> In the Raman shift region,  $400\text{--}450 \text{ cm}^{-1}$ , we observe a background peak. In the MBE-grown Ge dots on Si, a Si-Ge alloy peak at  $\sim 413 \text{ cm}^{-1}$  rises on this broad background.<sup>10</sup> The absence of a Si-Ge alloy peak in our spectra indicates that Ge islands are not in contact with Si under the polymer layer. Our micro-Raman studies involve a beam spot of  $50 \mu\text{m}$ . In spectra obtained from different regions of the sample, although showing some variation in the details, the overall features are identical.

Optical and atomic-force microscopy reveal the nanostructural Ge directly. The AFM micrograph shown in Fig. 2(a) shows the formation of scattered Ge islands as well as an array of islands arranged on a line (shown by an arrow). Islands forming a continuous line in a quasi-one-dimensional structure are also observed [Fig. 2(b)]. A higher-magnification micrograph showing individual Ge islands in the structures is shown in Fig. 2(c).

The islands have a size distribution. The large islands in Fig. 2(a) have typical base diameters of  $\sim 100 \text{ nm}$  and heights of  $\sim 25 \text{ nm}$ . The Ge wire seen in Fig. 2(b) has a base width of  $\sim 200 \text{ nm}$  and a height of  $\sim 25 \text{ nm}$ . These sizes of the Ge islands, along with their Raman mode at  $302 \text{ cm}^{-1}$ , confirm that the nanostructures are actually nanocrystalline structures.

In optical microscopy, where we have a larger field of view, we have observed many interesting features. These are shown in Fig. 3. Figures 3(a) and 3(b) show Ge dots arranged on straight lines in quasiperiodic one-dimensional structures. These have grown perhaps on defect lines on the polymer layer. The defect lines can be mechanical defects or phase boundaries between the two components (PS and

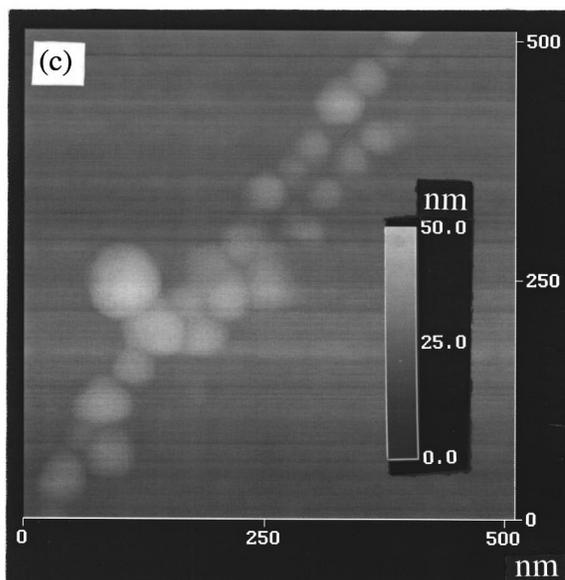
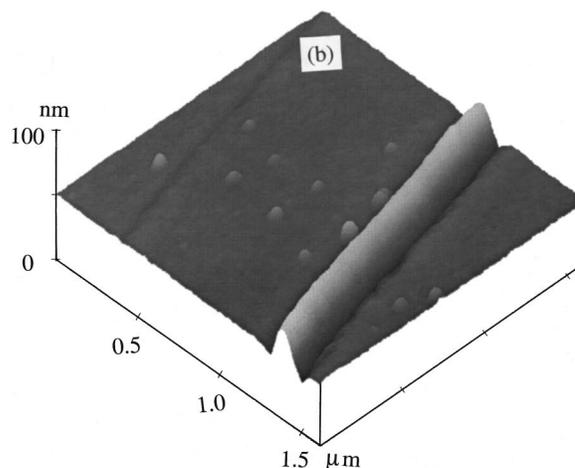
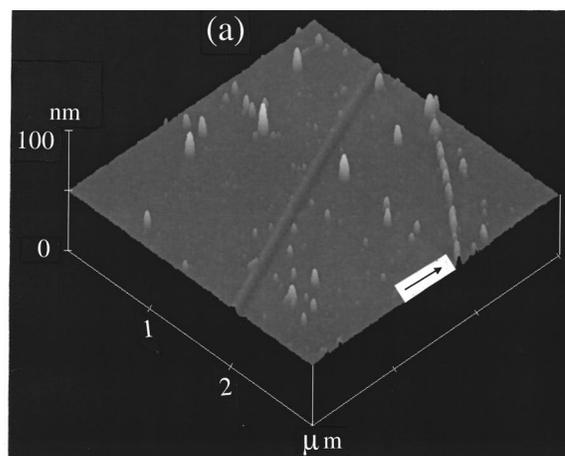


FIG. 2. Atomic-force microscopic images of Ge nanostructures: (a) 3D image showing isolated islands and an array of islands (shown by the arrow), (b) 3D image showing a Ge wire, and (c) plan-view showing groups of Ge islands in a quasilinear structure.

PBr<sub>x</sub>S) of the polymer blend. Figure 3(c) shows the formation of a continuous (dots in contact) linear chain of islands. Figure 3(d) shows the formation of a complex structure—a continuous chain of islands with a superimposed larger quasiperiodic feature and a discrete set of islands arranged on a parallel line. Larger structures appear to be composed of agglomerated smaller islands. Figure 3(e) also shows a quasi-

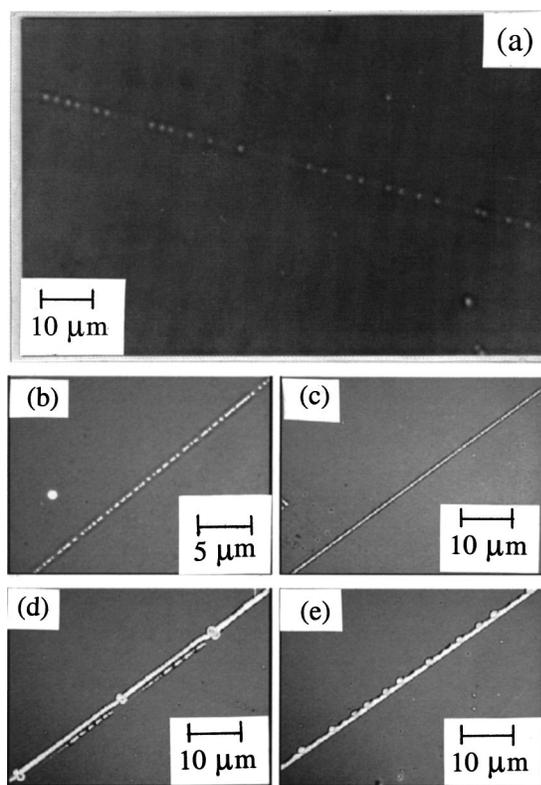


FIG. 3. Optical microscopic images showing Ge nanostructures in different morphologies: (a) isolated islands on a line defect; (b) and (c) linear chains of islands; (d) a complex structure with a superimposed quasiperiodic larger structure; and (e) a quasiperiodic asymmetric structure with preferential growth on one side, some isolated islands are also seen in the micrograph.

periodic structure with an asymmetric growth pattern. While a detailed understanding of these intriguing morphologies in a self-assembled growth process would require further investigations, this method of nanocrystalline growth reveals remarkable possibilities. With optimized growth conditions, suitable choice of polymers and patterned modification of polymer properties by lithography, it may be possible to grow one- or two-dimensional lattice with controlled dot size and lattice parameter for tailor-made properties.

The formation of these nanostructures from Ge deposited by thermal evaporation requires significant Ge diffusion. One may wonder whether such a significant diffusion of Ge on a polymer surface at room temperature (25 °C) is possible. Apparently, it is possible. Ge nanostructural island formation on a Ge surface has been observed at room temperature. For Ge diffusion on a Ge surface, the diffusion activation barrier has been found to be quite small, 0.45 eV.<sup>12</sup> Even diffusion of Si on a Si surface was observed at 25 °C. By direct atom tracking in the temperature range as low as 25–128 °C, Swartzentruber obtained a diffusion barrier of 0.94 eV for Si-dimer diffusion on silicon surfaces. For Si-monomer diffusion, this value is even lower, 0.7 eV.<sup>13</sup> These activation barriers for diffusion on surfaces are significantly smaller compared to activation barriers for bulk diffusion: 2.97 eV for Ge in germanium<sup>14</sup> and 4.76 eV for Si in

silicon.<sup>14,15</sup> For Ge diffusion on a polymer surface, the activation barrier is expected to be smaller than 0.45 eV, the value obtained for Ge diffusion on a germanium surface, and thus at room temperature a significant diffusion would be expected. This would enable Ge nanostructural island formation.

In conclusion, we have demonstrated the formation of Ge nanocrystalline structures on a polymer layer under standard high-vacuum deposition by thermal evaporation. Self-assembled nanostructural dots, isolated or coalesced on the line defects into lattice-like or continuous structure, have been found to form. We believe that by lithographic techniques, patterns of modified properties on the polymer layer can be produced which would act like defect structures. Deposition of materials (like Ge) on this modified polymer layer would lead to formation of a nanostructural lattice or grating, which could again be protected by another layer of polymer on them for further studies on these tailored lattices of nanostructural dots. The top polymer layer, besides providing protection from environmental degradation, would also be useful for dual-function hybrid polymer–nanoparticle devices.<sup>6</sup> Moreover, it can also act as an enhancer of incident electromagnetic field on such nanostructures. It has been shown for x rays incident on a 100 nm polymer-coated substrate that the x-ray intensity, under suitable conditions, can increase as much as 25 times of the incident intensity at the middle of the film.<sup>9</sup> This would certainly facilitate various kinds of studies, even on tiny volumes of materials in these embedded structures.

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