Germanium nanoislands grown by radio frequency magnetron sputtering: Annealing time dependent surface morphology and photoluminescence*

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Structural and optical properties of ∼ 20 nm Ge nanoislands grown on Si(100) by radio frequency (rf) magnetron sputtering under varying annealing conditions are reported. Rapid thermal annealing at a temperature of 600 °C for 30 s, 90 s, and 120 s are performed to examine the influence of annealing time on the surface morphology and photoluminescence properties. X-ray diffraction spectra reveal prominent Ge and GeO_2 peaks highly sensitive to the annealing time. Atomic force microscope micrographs of the as-grown sample show pyramidal nanoislands with relatively high-density (∼ 10^{11} cm^{-2}). The nanoislands become dome-shaped upon annealing through a coarsening process mediated by Oswald ripening. The room temperature photoluminescence peaks for both as-grown (∼ 3.29 eV) and annealed (∼ 3.19 eV) samples consist of high intensity and broad emission, attributed to the effect of quantum confinement. The red shift (∼ 0.10 eV) of the emission peak is attributed to the change in the size of the Ge nanoislands caused by annealing. Our easy fabrication method may contribute to the development of Ge nanostructure-based optoelectronics.

Keywords: germanium nanoislands, radio frequency magnetron sputtering, photoluminescence, surface morphology

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1. Introduction

Controlled growth and characterization of germanium (Ge) nanostructures are key issues for optoelectronic device fabrication. In particular, Ge/Si(100) self-assembled nanostructures have generated intense interest because of their simplicity, and they have opened up new possibilities for optoelectronic and microelectronic applications. Understanding the growth of Ge nanoislands using the Stranski–Krastanov mechanism is topically important and fundamentally challenging for device functionality.[1] Transforming an indirect band gap material (such as bulk Ge) to a direct gap material (nanosized Ge) gives rise to light emission, which is very attractive for full-color display as well as integrated optoelectronics technology. Among the techniques used to fabricate low-dimensional semiconductor structures, radio-frequency (rf) magnetron sputtering has several advantages, including low deposition temperature, higher film purity when compared to existing melting techniques,[2,3] easy fabrication, and low cost.[4] In recent years, the sputtering method has been widely exploited with the intent of making high-density nanostructures and showed tremendous promise.[5,6] However, only a few studies have been focused on the effect of annealing time on the surface morphology and the optical behavior of nanostructures.[7,8]

It has been established that quantum confinement (QC) modifies the energy band gap of low-dimensional semiconductor materials and strongly influences the electronic structure properties.[9,10] Despite the numerous models that have been proposed to explain the QC-triggered change in photoluminescence (PL), attributing it to surface states, defects in the oxides, core-shell structures, or chemical complexes, the mechanism is still under debate. Mestanza *et al.* recorded room temperature PL spectra from a Ge nanostructure prepared by an ion implantation technique and observed a broad blue band at around 3.2 eV (400 nm) in addition to a weak violet peak around 4 eV (310 nm). The authors suggested that the peaks originated from Ge-oxygen-deficient centers.[11] Sun *et al.* grew Ge QDs via molecular beam epitaxy (MBE), which showed a temperature dependent PL peak at ∼ 2.05 eV.[12] Despite extensive studies of synthesis and characterization, few efforts have been made to explore the dependence of surface morphology and optical behavior on annealing time and temperature. Wan *et al.* produced ultra-high-density (∼ 10^{11} cm^2) Ge QDs with a mean size of ∼ 14 nm by high vacuum electron beam evaporation, in which the density decreased as the annealing temperature was increased.[13] The exact nature of the structure, density, roughness, and grain size are not clearly understood, nor is their control mechanism.

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In this article, the surface morphology, and the structural and optical properties of Ge nanoislands grown on Si(100) by rf magnetron sputtering under varying rapid thermal annealing conditions are reported. The samples are characterized using atomic force microscopy (AFM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and PL. The evolution of the nanoislands is studied as a function of the annealing time. AFM is used to extract root mean square (RMS) roughness, nanoisland number density, volume, and the ratio of the grain area. The room temperature PL as a function of the annealing time is also examined, and a mechanism is presented.

2. Experimental procedure

Ge nanoislands were deposited on a (100) oriented P-type silicon substrate by rf magnetron sputtering. Prior to deposition, the Si substrate was dipped in 5% hydrofluoric acid to remove the surface native oxide followed by rinsing in deionized water and drying in a flux of nitrogen. The chamber was first evacuated to a base pressure of 2×10^{-5} torr. The deposition was carried out at 300 °C substrate temperature, 100 W rf power, and 10 sccm Ar flow, the deposition time was 350 s. The estimated Ge layer thickness was 50 nm, as measured by spectroscopic reflectometry (Filmetrics). The sample was then subjected to rapid thermal annealing (RTA) in nitrogen ambience at 600 °C for 30 s (sample B), 90 s (sample C), and 120 s (sample D). The as-grown sample was labeled A. A Bruker D8 advance diffractometer was used to study the structural characteristics of Ge nanoislands using Cu-$K\alpha$ radiations (1.54 Å) at 40 kV and 100 mA. The 2θ range was set to 0°–90° with a step size of 0.021° and a resolution of 0.011°. An AFM built by Seiko Instrument Inc. (SPI3800) was used to study the surface morphology, whereas a Perkin Elmer Ls 55 luminescence spectrometer probed the photoluminescence characteristics of the nanoislands.

3. Results and discussion

3.1. Surface morphology

The AFM micrographs in Fig. 1 show the annealing time-dependent evolution of the shape and size distribution of the Ge nanoislands. The growth of nanoislands follows the Stranski–Krastanov mode, in which a wetting layer first covers the substrate. A lattice misfit $\sim 4.2\%$ between the deposited Ge material and the Si substrate hinders the growth of over-layers on the strained structure. Consequently, the growth process changes from layer-by-layer to spontaneous formation of three-dimensional nanoislands.[14] The line scan profiles of the as-grown and annealed samples (120 s) are presented in Fig. 2. The baseline sample consists of a distribution of pyramid-shaped islands that become dome-shaped upon annealing for 120 s. The aspect ratio of islands has been defined by various groups in different manners.[15–17] When defined as the ratio of the height to the length of the base of the island, the average aspect ratios measured from the line profile scans are 0.35 for the baseline sample and 0.23 for the annealed samples. It is important to note that the size of nanoislands determined using the AFM observation is slightly overestimated because of a tip artifact. The sample annealed for 120 s in Fig. 2 has noticeably larger dome-shaped islands.

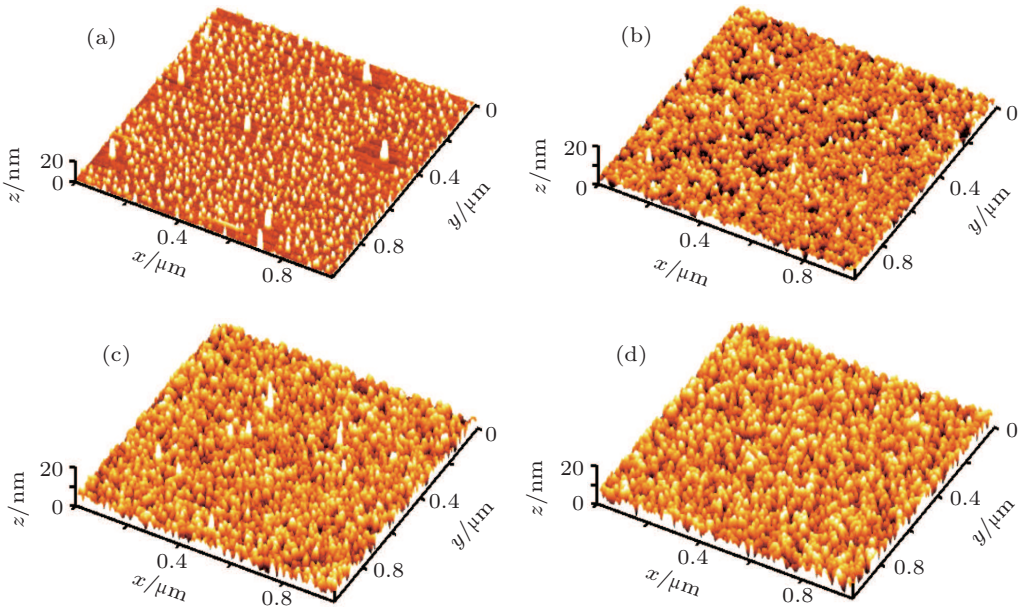


Fig. 1. (color online) The 2D AFM images of (a) as-grown sample and those annealed for (b) 30 s, (c) 90 s, and (d) 120 s.

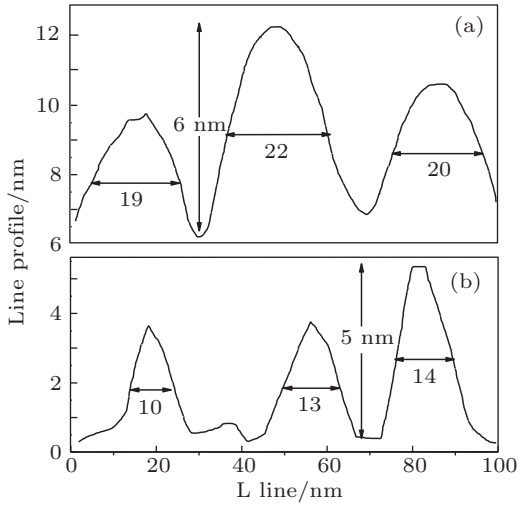


Fig. 2. Line scan profiles of (a) sample annealed for 120 s and (b) as-grown sample.

Due to the heat treatment, islands are found to coarsen via structural and compositional changes through continuous strain relaxation. Coarsening is a competitive growth process where some islands grow at the expense of others in order to minimize the total surface energy.[18] This leads to an increase in the mean island volume with time, which results in a simultaneous decrease in the mean areal island density. In a system of pure Ge clusters, coarsening can occur by a combination of different mechanisms, such as Oswald ripening mediated by adatom diffusion between islands or Si inter-diffusion.[19,20]

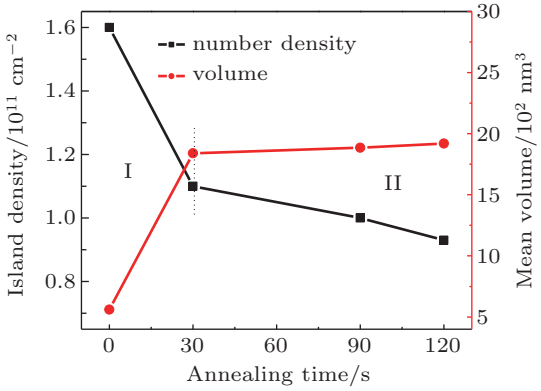


Fig. 3. (color online) Island number density and mean island volume with respect to annealing time. The data are calculated from AFM topographic images. The regions marked in the figure are discussed in the text.

The mean island density and volume obtained from AFM micrographs are plotted with respect to annealing time in Fig. 3. In the sample annealed for 30 s, the Si inter-diffusion is a dominant coarsening mechanism, allowing the pyramid-shaped islands to re-equilibrate to larger alloyed pyramid-shaped islands.[21] The incorporation of Si via inter-diffusion into the Ge islands changes the lattice constant of the islands, reducing the lattice misfit with respect to the Si substrate, as shown in region I of Fig. 3. Beyond 30 s of annealing, Oswald ripening is more dominant (marked as region II). Larger dome-shaped islands act as sinks and grow at the expense of smaller ones. In addition, the larger islands release their strain very fast via misfit dislocations at the islands' edges.

The root mean square roughness and ratio of grain area obtained from AFM are presented in Fig. 4. The observed ratio of grain area shows a continuous decrease as a function of increasing annealing time, which is consistent with the number density trend.

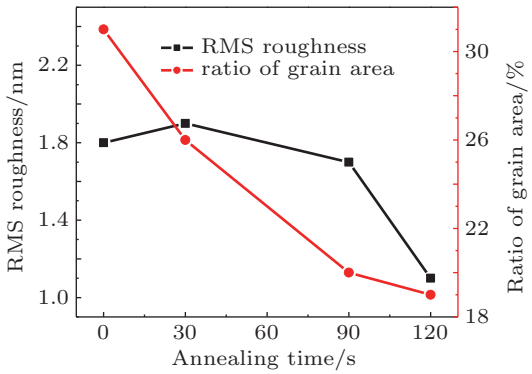


Fig. 4. (color online) Plot of RMS roughness and grain area surface coverage with respect to annealing time.

Furthermore, the RMS roughness of a baseline sample increases slightly after annealing for 30 s due to the formation of larger nanoislands and highly irregular distributions of height and width. Beyond the threshold of 30 s, the roughness decreases rapidly as the annealing time is increased. In addition, the islands' morphology changes gradually to a dome-like form with less than 1.2 nm roughness.

3.2. Structural analysis

The EDX spectra of the baseline and the 120 s-annealed samples (Fig. 5) confirm the presence of Ge in addition to silicon, oxygen, and carbon. The Ge peaks indicate the existence of nanoislands composed purely of Ge, as observed in the AFM. By annealing the sample, the Ge content is decreased, indicating that some of the Ge vaporizes, diffuses further inside the Si substrate, and intermixes with the Si.

The XRD spectra of samples A, C, and D shown in Fig. 6 confirm the existence of Ge nanoislands on the Si substrate. The noticeable peaks indexed as Ge (111) and (311) clearly indicate the diamond cubic structure of Ge. The most intense peak of Ge appears at (111), a fact which can be used to estimate the size of Ge islands. The peak present at 29° for all the samples can be indexed to the (111) reflection of the hexagonal symmetry of GeO_2. Because silicon has the same crystal structure as Ge, the peak from the Si(100) plane occurs at 69°.[22] It can be inferred from the XRD line shapes that increasing the annealing time causes a substantial change in the Ge (111) peak intensity and the corresponding full width at half maximum (FWHM), attributed to the growth of the islands' size.

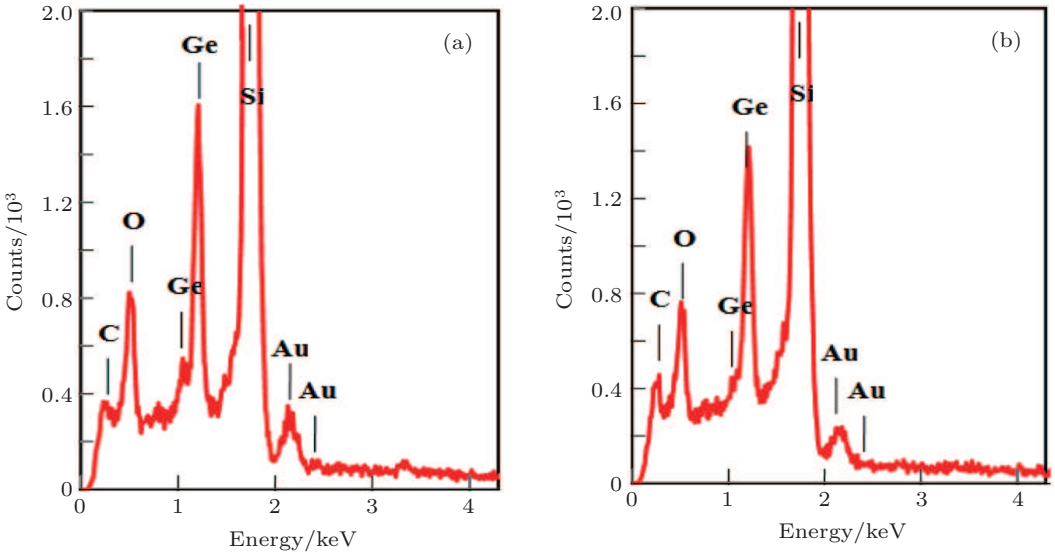


Fig. 5. (color online) EDX spectra of (a) as-grown and (b) 120 s-annealed samples. The presence of oxygen is due to surface oxidation during the sample preparation and the post-annealed analyses.

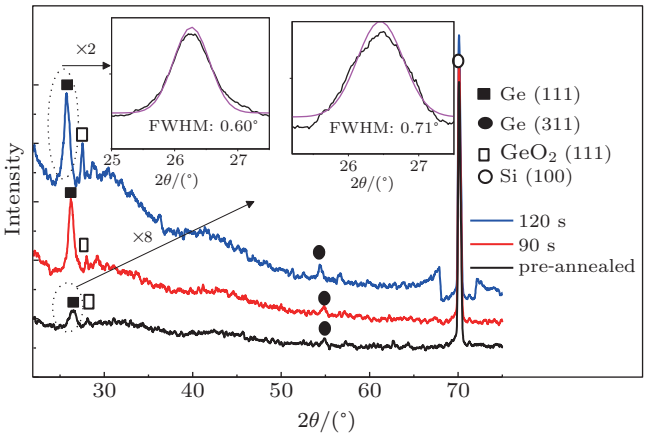


Fig. 6. (color online) X-ray diffraction patterns of as-grown and annealed (90 s and 120 s) samples. Insets: Ge(111) peaks are magnified and fitted with a Gaussian curve to extract the FWHM value.

Interestingly, the small FWHM signifies a big grain size because there are only a small number of grains in one X-ray beam spot. The Scherrer FWHM analysis indicates that the island growth is highly sensitive to the annealing time. The estimated size for the as-grown sample is $\sim$ 13 nm. The size of the islands in the sample annealed for 120 s is $\sim$ 16 nm. The saturation of the Ge (111) peak beyond 90 s implies there is no further increase in the grain size with further annealing. This saturation may be attributed to the accumulation of the large number of homogeneous nuclei of increasing size formed by the mechanism of annealing time-dependent agglomeration.

3.3. Optical behavior

The room temperature photoluminescence emission spectra of the as-grown and annealed samples recorded using a 239 nm laser are illustrated in Fig. 7. The PL intensity patterns of all the samples exhibit high intensities and broad peaks in the energy range from 3.19 eV to 3.29 eV. The broadening of the peaks for the annealed samples fitted to the Gaussian distribution clearly shows the increase in nanoisland size distribution. The peaks are located at 3.19 eV, 3.21 eV, 3.23 eV, and 3.29 eV. The PL red shift of $\sim$ 0.10 eV, caused by the increasing size of nanoislands due to heat treatment, confirms quantum confinement. Furthermore, the silicon inter-diffusion is the dominant coarsening mechanism for the longer annealing time, and it decreases the compressive stress, shifting the peak to a lower energy value.[23,24]

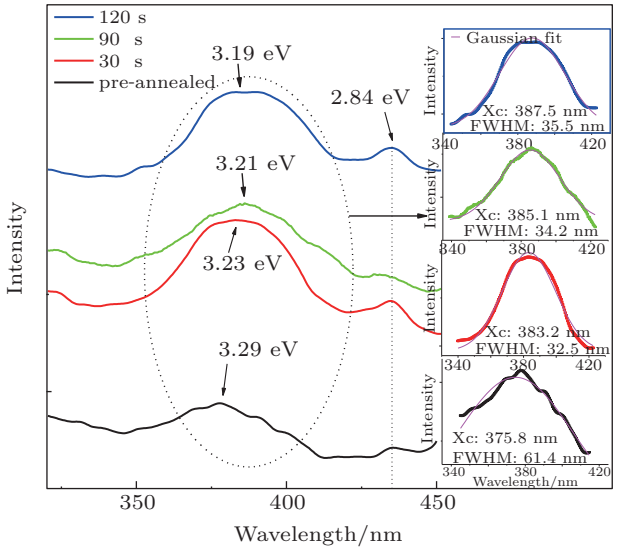


Fig. 7. (color online) PL spectra of the samples under 239 nm excitation wavelength. Gaussian de-convolution of the intense peak for each sample is presented in insets.

The observed intense blue band centered at 3.29 eV differs from the PL peak at 3.1 eV under longer-wavelength excitation reported by others.[25,26] Since the photon-absorption and photo-excitation take place inside the Ge nanoislands[25] and the observed blue emission shows a significant size de-

pendence, it is reasonable to exclude the possibility of direct exciton radiative recombination responsible for this emission. However, there may be other mechanisms responsible for the weak peak around ~ 2.84 eV, such as defect-related luminescent centers in the matrix and at the interface. The PL band at ~ 3.29 eV shows a significant shift upon annealing, however the ~ 2.84 eV peak remains unchanged. This observation clearly indicates their different origins. It is important to note that Ge is uniformly deposited on the silicon substrate, and that the larger Ge nanoislands formed during annealing may have some effect on the observed PL spectra.

During nanoisland growth, the oxygen-deficiency defects formed in the silicon and Ge oxide matrix may contribute to the emission process. The oxidation of Ge nanoisland surfaces is confirmed by the presence of the oxygen peak in the EDX spectra and GeO_2 in the XRD pattern (Fig. 5), which supports the possibility of the formation of a core-shell like structure. GeO_2 defects have been reported to contain two nonbonding electrons by Ginzburg *et al*. Moreover, Gallagher and Osterberg made the same observation in Ge doped silica glass fibers.[27,28] Such defects form a ground-state singlet level (S0), an excited singlet level (S1), and a triplet level (T1). In this energy scheme, the blue luminescence of ~ 3.29 eV may be attributed to a T1 $\rightarrow$ S0 transition. Furthermore, the orange–green PL band centered at ~ 2.84 eV probably originates from the oxygen-deficiency-related defects in the silicon oxide matrix because no amount of annealing is found to influence this emission.

The appearance of the microstructure in the PL spectra may be due to oxygen-passivated nanoislands having a broad size distribution. In addition, the near band-edge transition of the wide band gap, especially the radiative recombination of the free excitons through an exciton–exciton collision process, may contribute to this microstructure.[10]

4. Conclusion

Ge nanoislands were deposited on Si (100) substrates by rf magnetron sputtering and characterized. The influence of rapid thermal annealing on the surface morphology and photoluminescence properties was studied. The size and shape evolution, RMS roughness, number density, volume of islands, and the ratio of grain area were quantified by AFM. The Schereer equation was used to estimate the size of the islands using XRD spectra. The increase of the island size was attributed to a coarsening mechanism in the Ge/Si (100) system and was found to be highly sensitive to the heat treatment. The room temperature PL spectra of the baseline sample exhibited strong and broad peaks that were found to shift as the annealing time was increased. This observation was attributed to quantum confinement of carriers in the Ge nanoislands. Our experimental methodology provides a process to control the size and morphology of the Ge nanoislands and hence tune the band gap energy of the material. This is valuable for the development of high quality nanophotonics based on these structures.

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