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Influence of growth and annealing conditions on photoluminescence of Ge/Si layers grown on oxidized Si surfaces

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Abstract

Ge/Si structures with a layer of Ge islands grown on oxidized Si surfaces and covered with Si were recently found to exhibit intense photoluminescence (PL) in the D1 region ($\sim$0.8 eV) after annealing at high temperatures. We show that this PL is a property of the Ge/Si structures grown at low temperatures from about 400 to 500 °C, at which crystal defects are introduced through the coalescence of strained three-dimensional islands. PL features are found to be independent of Ge thickness over a wide range from 0.7 to 3 nm. A monotonic increase in PL with annealing temperature is observed up to 1000 °C, but PL completely vanishes after annealing at higher temperatures. The transmission electron microscopy data show the presence of dense arrays of crystal defects in the Si layer capping the layer of Ge islands.

1. Introduction

Recent investigations demonstrate progress in the development of Si-based light emitters for the 1.5–1.6 μm wavelength region [1]. Si structures emit light in this region due to optical transitions through defect states in the Si band gap, which can occur with higher efficiency than indirect band-to-band optical transitions. These defects are usually introduced into Si crystals by plastic deformation [2–4]. They exhibit several bands in photoluminescence (PL) spectra. The most important one has been labelled D1 [2]. Over the last decade, considerable effort has been directed toward finding methods that form defects in Si that produce intense light emission in the D1 region with a reduced efficiency of nonradiative recombination processes.

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It was found that defects can be introduced in a Si surface layer up to about 1 μm thick by Si wafer direct bonding [5]. The nonradiative recombination can be effectively reduced by using a combination of gettering and passivation [6].

Defects in Si for the purpose of light emission are commonly formed by their introduction into already grown Si crystals. We recently reported a method that creates dense arrays of crystal defects in Si during its growth. This method is based on the use of an array of three-dimensional (3D) Ge islands grown on oxidized Si surfaces. The defect formation occurs due to the mechanism of Si overgrowth on the array of Ge islands. After high-temperature annealing, the grown Ge/Si structures can exhibit intense PL in the D1 region. Another effect of annealing is the reduction of nonradiative recombination [7]. Defect structures and hence the PL intensity are essentially dependent on the growth and annealing conditions. In this paper we explore the influence of technological parameters such as the growth temperatures of both the array of Ge islands on oxidized Si surfaces and the Si capping layer, the annealing temperature and time, and the amount of Ge in the array of Ge islands on the PL properties of these Ge/Si structures.

2. Experimental details

The structures were grown by solid-source molecular-beam epitaxy on p-type FZ-grown Si(100) wafers with a resistivity of 20–100 Ω cm. The natural oxide was removed from the wafer surface by decomposition at 830 °C in an ultrahigh-vacuum growth chamber. Si buffer layers about 100 nm thick were grown at 550 °C and annealed at 750 °C for a few minutes. Then the Si surface was oxidized at 500 °C in oxygen at a pressure of 2×10^{-6} Torr for 10 min to grow a silicon oxide film about 0.5 nm thick [8, 9]. Deposition of Ge on the oxidized Si surface results in the formation of hemispherical Ge islands with an areal density of about 2×10^{12} cm^{-2} in a wide range of parameters such as growth temperature, deposition rate, and coverage used [10, 11]. The layer of Ge islands were covered with a Si capping layer usually about 100 nm thick. The deposition rates were about 1×10^{-2} nm s^{-1} for Si and 3×10^{-3} nm s^{-1} for Ge. The pressure in the growth chamber did not exceed 2×10^{-9} and 5×10^{-10} Torr during Si and Ge deposition, respectively. Reflection high-energy electron diffraction (RHEED) was used to control the three-dimensional (3D) surface morphology after the different growth stages. The post-growth annealing was performed in a separate lamp furnace at temperatures from 700 to 1100 °C for times between 1 s and 30 min in a dry oxygen or nitrogen atmosphere.

PL spectra were measured using a standard lock-in technique in conjunction with an InGaAs photomultiplier detector or a Ge detector, a grating monochromator, and the 325 nm line of a He–Cd laser or the 532 nm line of a frequency-doubled diode-pumped Nd:YAG laser. The laser beams, focused on the sample, were about 1 mm in diameter with power of 6 and 0.4 mW for the 325 and 532 nm lines, respectively, to measure PL spectra at 4 K.

3. Experimental results

The Si overgrowth on a layer of Ge islands occurs in a fashion in which deposited Si adatoms predominantly attach to the surface of Ge islands, and not to the surface of the rest of the Si oxide film in the areas between the islands [11]. As a result, elastically strained 3D Si islands with Ge islands in their core appear at the initial stage of Si growth. The array of Si islands has an ultrahigh density of about 2×10^{12} cm^{-2}, the same as the initial array of Ge islands. Further Si deposition leads to the formation of a Si layer with a high concentration of crystal defects appearing through the coalescence of elastically strained Si islands.

It was recently found that such Ge/Si structures exhibit intense PL in the D1 region after high-temperature annealing. This PL was shown to originate from crystal defects in the Si

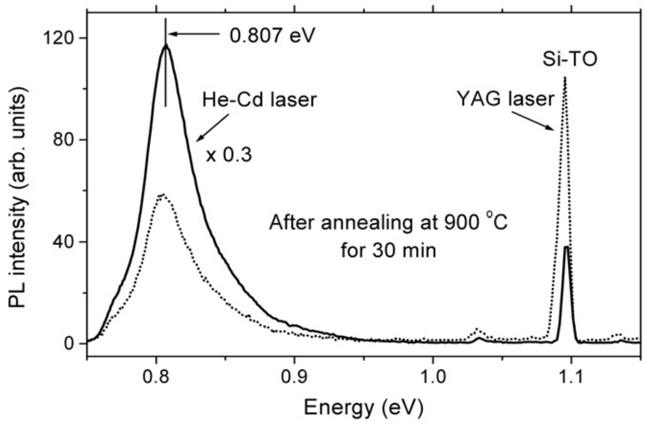

Figure 1. Low-temperature ($T = 4$ K) PL spectra of the Ge/Si structure after annealing at 900 °C for 30 min in O_2. Spectra were measured using excitation photon wavelengths of (solid line) 325 nm and (dotted line) 532 nm. The structure contains one layer of Ge islands (1.1 nm) grown on the oxidized Si surface at 500 °C and covered with a Si capping layer (100 nm) at 470 °C.

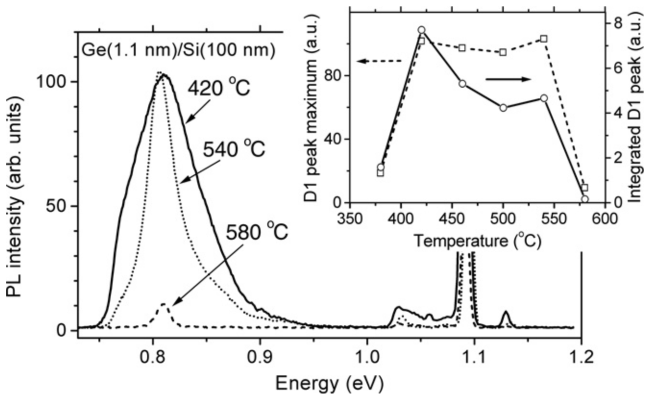

Figure 2. PL spectra (4 K, $\lambda_{exc} = 532$ nm) of Ge/Si structures after annealing at 1000 °C for 10 s in N_2. The structures contain one layer of Ge islands (1.1 nm) grown on oxidized Si surfaces at T and covered with a Si capping layer (100 nm) at 470 °C, where T is the temperature marked on the figure at the corresponding spectra. The inset shows the dependence of (a) the D1 peak maximum and (b) its integrated intensity on the temperature of Ge growth.

capping layer, but was not from the substrate [7]. This conclusion is also reached by comparison of the PL spectra measured using excitation photon wavelengths of 325 and 532 nm (figure 1). Because the penetration depth in Si is about two orders of magnitude longer for a 532 nm laser beam than for a 325 nm laser beam, the contribution to the PL signal from the surface layer is higher than that from the bulk when the 325 nm laser is used. This relationship produces a greater ratio between the intensities of the D1 peak and the Si transverse optical (TO) phonon peak, as is seen in the PL spectra presented in figure 1. Comparison with PL spectra of Ge/Si structures grown using the Stranski–Krastanov growth mode have shown that PL in the D1 region in our case is not caused by radiative recombination through Ge quantum dots [7].

The structural properties of Ge islands grown on oxidized Si surfaces depend on the growth temperature. Figure 2 is presented to show how this growth temperature influences the PL spectra of whole Ge/Si structures. The most intense PL was observed from the Ge/Si structures

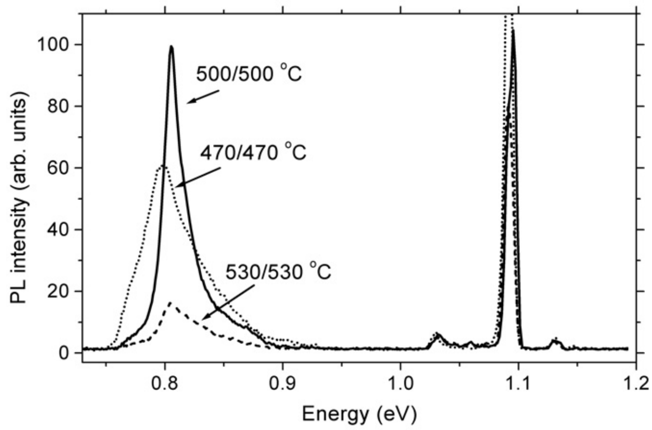

Figure 3. PL spectra (4 K, $\lambda_{exc} = 532$ nm) of Ge/Si structures after annealing at 900 °C for 30 min in O_2. The structures contain one layer of Ge islands (1.1 nm) grown on oxidized Si surfaces at T_1 and covered with a Si capping layer (100 nm) at T_2, where T_1 and T_2 are the temperatures marked as T_1/T_2 in the figure.

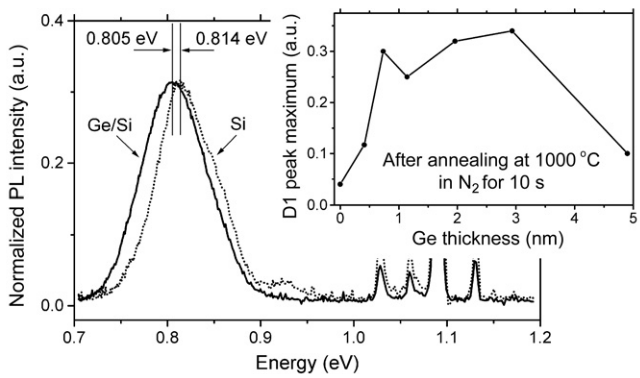

Figure 4. Normalized PL spectra (4 K, $\lambda_{exc} = 532$ nm) of Ge/Si and Si structures after annealing at 1000 °C for 10 s in N_2. The Ge/Si structure was grown by Ge deposition (0.7 nm) on the oxidized Si surface at 420 °C, followed by covering with a Si layer 100 nm thick at 470 °C. The Si structure was grown by Si deposition (100 nm) on the oxidized Si surface at 470 °C. The inset shows the dependence of the peak maximum in the D1 region on the nominal thickness of Ge layers.

with Ge islands grown in the range from 400 to 540 °C. The difference between the temperature dependences of the D1 peak maximum and the integrated intensity of the D1 peak shows that structures grown at lower temperatures exhibit wider D1 peaks. A similar temperature dependence was observed when the growth temperature of the Si capping layer was examined as a variable parameter (figure 3). A range from 400 to 500 °C was found to be most favourable for obtaining intense PL as a function of the Si growth temperature.

Another parameter that can affect PL in the D1 region is the nominal thickness of deposited Ge. The experimental results show that the D1 peak shape and its energy position are almost independent of this parameter, as illustrated in figure 4. The maximum of the D1 peak has a plateau for its dependence on the Ge thickness in the range from about 0.7 to 3 nm and decreases at larger and smaller thicknesses. Because the size of Ge islands is determined by the thickness

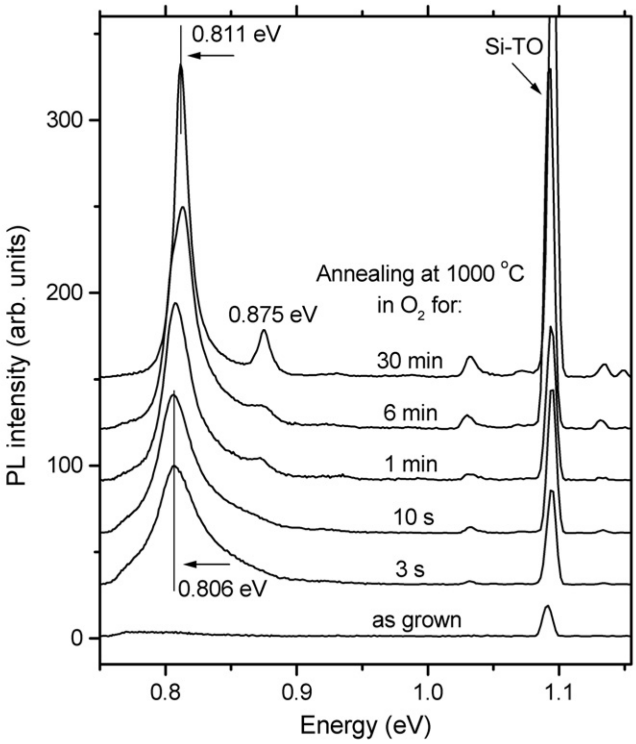

Figure 5. PL spectra (4 K, $\lambda_{exc} = 532$ nm) of the structure after annealing at 1000 °C for the time marked in the figure at each spectrum. The structure contains one layer of Ge islands (1.1 nm) grown on an oxidized Si surface at 540 °C and a covering Si layer (100 nm) grown at 470 °C.

of Ge deposited, these data are in accordance with the previously made conclusion that the radiative recombination producing the D1 band takes place outside the layer of Ge islands. At coverages above 3 nm, Ge islands coalesce and cover the surface almost completely. The obtained results show that Si layers grown on such a surface are not favourable for producing intense PL after annealing.

The intensity of both D1 and Si–TO bands increases as the annealing time increases (figure 5). This simultaneous increase is a result of a reduction in nonradiative recombination. At the same time, the appearance of the intense D1 band also evidences the formation of dense arrays of radiative defects. Longer annealing makes the D1 band narrower and induces a shift in its position from 0.806 to 0.811 eV. Similar, but less pronounced, annealing time dependences were observed for 900 and 950 °C. A long period of annealing at 1000 °C causes the appearance of the D2 line (figure 5). The D2 line is not observed after annealing at temperatures below 1000 °C. The emission in the D2 region is likely to come from the substrate, because it was not observed in PL spectra measured using excitation at 325 nm wavelengths.

The Ge/Si structures do not exhibit PL in the D1 region after annealing at temperatures higher than 1000 °C, as shown in figure 6. Recently, we found conditions for growing Si layers on oxidized Si surfaces, which can also produce PL in the D1 region [12]. However, to exhibit intense PL, the Si structures require annealing at temperatures higher than that for the Ge/Si structures. Si structures thus differ from Ge/Si structures in that they have the ability to keep and enhance PL in the D1 region after annealing at temperatures higher than 1000 °C (figure 6(b)).

The Ge/Si structures contain a high concentration of crystal defects that propagate from the layer of Ge islands through the whole deposited Si layer. The concentration of defects is higher at the Ge/Si interface (figure 7(a)). After annealing at 700 °C, arrays of crystal defects are seen more clearly in high-resolution transmission electron microscope (HRTEM) images

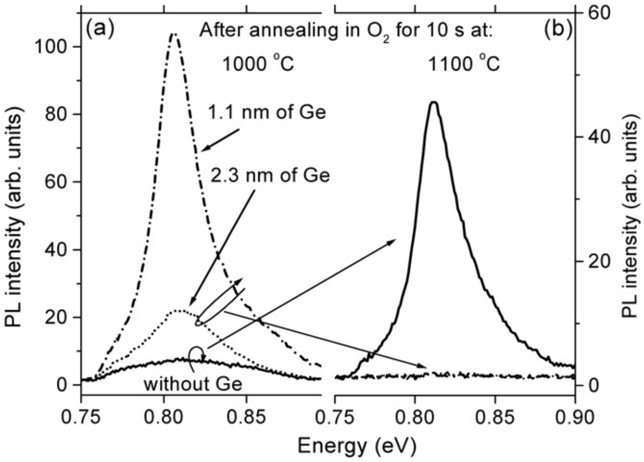

Figure 6. PL spectra (4 K, $\lambda_{exc} = 532$ nm) of structures after annealing at (a) 1000 °C and (b) 1100 °C for 10 s in O_2. The Ge/Si structures contain one layer of Ge islands (1.1 nm and 2.3 nm of Ge deposition, marked in the figure at the corresponding spectrum) grown on oxidized Si surfaces at 540 °C covered with a Si capping layer (100 nm) grown at 470 °C. The Si structure consists of only a Si layer (100 nm) grown on the oxidized Si surface at 470 °C.

(figure 7(b)). Annealing at 900 °C causes the defects to be distributed homogeneously through the whole Si capping layer.

4. Discussion

Structures of Ge quantum dots embedded in Si matrices usually exhibit PL at energies from about 0.7–0.9 eV, depending on the growth temperature. The ability to exhibit this PL vanishes after annealing of the structures at temperatures higher than 700 °C [7, 13, 14]. It was suggested that this behaviour is a result of strain relaxation by means of partial decay of Ge dots into surrounding Si by diffusion. Therefore, the PL generated by our structures after high-temperature annealing cannot be attributed to Ge quantum dots, but it can definitely originate from crystal defects in Si layers capping the layer of Ge islands [7]. These defects form due to the growth mechanisms of both Ge islands on oxidized Si surfaces and Si capping layers on the layer of Ge islands. The Ge growth on an oxidized Si surface starts with the nucleation of 3D islands without the formation of a two-dimensional Ge wetting layer [10]. The Ge islands appear to have a spherical-like shape, which changes to hemispherical as the growth temperature increases. The subsequent Si growth proceeds with Si atom attachment mainly to Ge islands [11]. At growth temperatures of about 400–500 °C, crystal defects are introduced into the growing Si layer at the stage of coalescence of elastically strained epitaxial and nonepitaxial Si islands. These defects can dominate over Ge quantum dots in the efficiency of light emission, as shown here by PL measurements. The Ge/Si structures grown at higher temperatures contain a reduced concentration of crystal defects. These structures are the subject of studies of the properties of Ge quantum dots in Si matrices [15–17].

The Ge/Si structures grown at the lower temperatures contain crystal defects such as stacking faults which were observed by RHEED [7]. These structures produce rather weak PL in the broad spectral region from 0.7 to 1.0 eV. The HRTEM data show that high-temperature annealing causes the formation of a homogeneous defect structure in the whole Si capping layer. However, the identification of defects is difficult because of their high concentration.

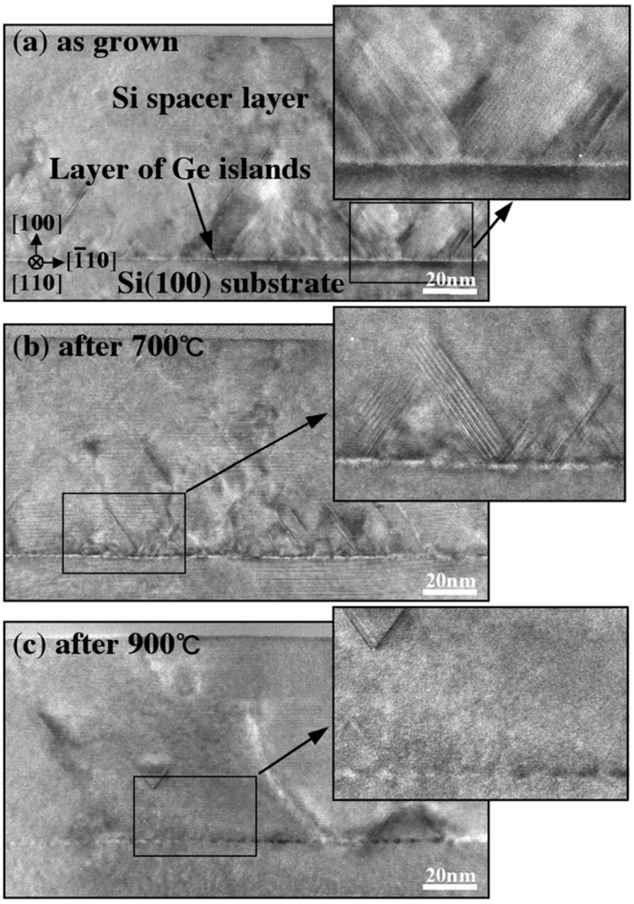

Figure 7. HRTEM images of the structure (a) as grown and after annealing at (b) 700 °C and (c) 900 °C for 30 min in O_2. The structure consists of one layer of Ge islands (1.0 nm) grown on the oxidized Si surface at 540 °C, covered with a Si capping layer (100 nm) grown at 470 °C.

The intense PL in the D1 region associated with these defects is also a result of a reduction in the efficiency of nonradiative recombination processes.

A scheme of the optical transitions in the D1 region has not yet been finally established. Light emission with an energy of around 0.8 eV can come either from transitions between one of the Si bands (conduction or valence) and a deep level of defect states in the Si bandgap or from transitions between two sub-bands created by defects. It is known that two types of defects, namely, dislocations and self-interstitial Si clusters, are the most thermally stable. The first ones do not posses a sufficiently deep energy level in the Si band gap to produce 0.8 eV transitions between a band and a subband, according to both theoretical calculations [18, 19] and experimental results [20]. However, these transitions are possible between a dislocation-related sub-band which is located near the valence band edge (a shallow level) and a deep level near the conduction band edge [21]. At the same time, the self-interstitial Si clusters alone are able to produce sufficiently deep energy levels in the Si band gap [22]. However, it is not possible to establish the predominant recombination scheme through our experimental results.

Our structures also contain defects such as clusters of the rest of the Si oxide films. For samples with high concentrations of oxygen, radiative recombination centres were described in terms of donor–acceptor pairs in which oxygen complexes and dislocations create, respectively, donor and acceptor energy levels in the Si band gap [23]. The amounts of the rest of the Si oxide films in our structures decrease considerably when the growth temperature increases from 400 to 500 °C, but the PL does not change. This implies that the role of Si oxide clusters in PL is negligible, and the origin of PL can therefore be associated with dislocations and interstitial clusters. The role of Si oxide films is, however, essential in the formation of specific conditions for the initial growth stages of Ge and Si layers.

5. Conclusions

We have determined conditions for the growth of Ge/Si nanostructures on oxidized Si surfaces and for subsequent annealing, at which crystal defects dominate over quantum dots in photoluminescence. These conditions consist of relatively low growth temperatures of about 400–500 °C and high annealing temperatures of 800 to 1000 °C. Dense arrays of Ge islands grown on oxidized Si surfaces create a unique substrate for subsequent growth of Si layers with a high concentration of crystal defects. These defects, under annealing, become transformed into a homogeneous Si structure that exhibits intense PL in the D1 region. High thermal stability makes this structure interesting for the fabrication of light emitters by using conventional processes of Si technology.

Acknowledgments

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