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Visible photoluminescence from Ge quantum dots

K.W. Sun[a,*], S.H. Sue[a], C.W. Liu[b]

[a]Department of Physics, National Dong Hwa University, Hualien, Taiwan, ROC
[b]Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, ROC

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Abstract

Spectroscopic analyses on stacked Ge quantum dots (QDs) on Si (1 0 0) substrates are presented. Strong and visible photoluminescence around 620 nm from stacked Ge QDs is observed. The luminescence is intense and clearly visible to the naked eye at both room temperature and low temperature. We have investigated the temperature dependence of the luminescence, as well as the composition of Ge dots via transmission electron microscopy and the Raman spectroscopy. Possible causes of the visible luminescence are also speculated in this report.

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Keywords: Photoluminescence; Ge quantum dot; Raman spectroscopy

1. Introduction

Optical and electronic properties of semiconductor quantum dots (QDs) have attracted much attention, because they exhibit new quantum phenomena and have potentials for becoming novel and future photonic devices. Studies on nanocrystals or QDs made from direct-gap semiconductors such as InAs, GaAs, CdS, CdSe, etc. have been reported experimentally and theoretically. More recently, self-assembled Ge QDs grown by the Stranski-Krastanov mode have been studied for their potential applications for Si-based electronic and optoelectronic devices [1–8]. There is also a wide list of recipes for realizing QDs [9–13]. Ge overlayers on Si(0 0 1) are subjected to strain originating from the lattice mismatch between Si and Ge and led to the formation of spontaneously grown islands. Such a low dimensional structure can be an alternative to overcome the inherent electronic property of indirect bandgap semiconductors by exploiting the overlap of carrier wave functions due to quantum confinement, so that radiative recombination can be greatly increased compared to that in the bulk crystals.

*Corresponding author. Tel.: +886 3 866 2500; fax: +886 3 866 2303.
E-mail address: kwsun@mail.ndhu.edu.tw (K.W. Sun).

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Most of the photoluminescence (PL) studies on Ge QDs were focused in the photon energies near the infrared regions. In this letter, we present investigations on multi-layer Ge QD structures grown by UHVCVD. We have observed visible light luminescence from indirect bandgap Ge QDs excited with an argon ion laser. Experimental results from atomic force microscopy (AFM), transmission electron microscopy (TEM), temperature dependent Raman and PL techniques are provided. The possible mechanisms of the visible light luminescence are speculated.

The Ge QD samples in this work were prepared in a standard UHVCVD system. Epitaxial layers were deposited on blanket 200 mm (0 0 1) Si wafers (p type, 1–10 Ω-cm). Silane (SiH_4) were used as silicon source gases and germane (Ge H_4, 1% diluted in H_2) as the germanium source gas. Before deposition, Si wafer is dipped in 10% diluted HF solution to produce H-termination. The wafer was sent to the loading chamber after spin dry. The wafer was then placed at the reactor chamber at a pressure of 10^{-6} Torr for 20 min to ensure thermal stability. A 60 nm Si buffer layer was deposited to smooth out the Si surface and to clean the contamination. The quantity of deposited Ge atoms is measured by equivalent-monolayer (eq-ML, $1\,\text{eq-ML} = 6.24 \times 10^{14}\,\text{atoms/cm}^2$). At growth temperature of 600 °C, 13.1 eq-ML of Ge were deposited on Si surface at a rate of 5.5 eq-ML/min. Samples of multi-layer QD structures with periods from five to 10 were grown with 30 nm Si spacers. At the end of growth the samples were capped with Si.

The shapes and sizes of the dots have been determined by means of AFM and TEM. The AFM image of the Ge island sample is shown in Fig. 1. Under above growth conditions, the Ge islands form dome-like shapes and the mean widths and heights of the dots are ~80 nm and ~6 nm, respectively. TEM measurements (see Fig. 2) of the dots indicate good uniformity of each QD layer, especially the initial one. By using Si spacers of appropriate thickness during the growth, a strain-mediated interaction energy between Ge islands on top and below the Si interlayer favors nucleation of a new island nucleus on top of a buried island. Our TEM

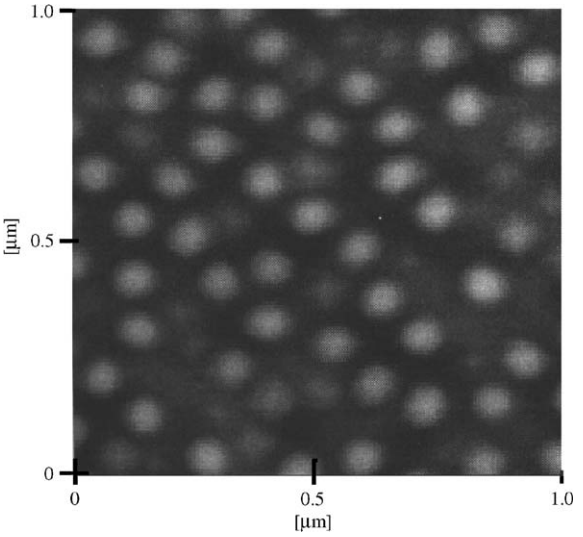

Fig. 1. 1 μm × 1 μm AFM image of the Ge island sample.

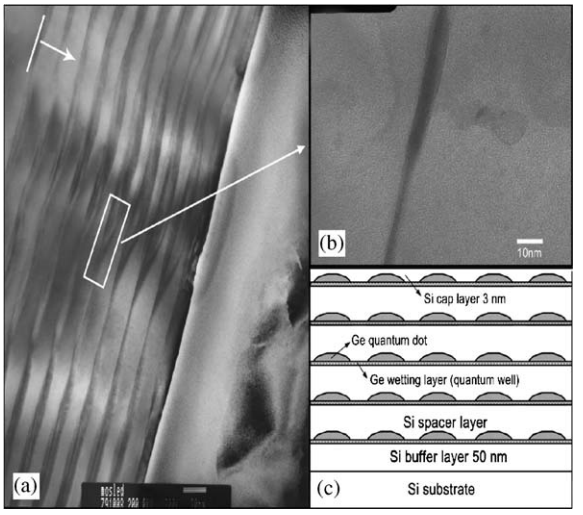

Fig. 2. (a) Cross-section TEM image of multi-layer Ge quantum dot structures. The white arrow in upper left corner indicates the growth direction. (b) Close up image of a single dot (c) schematics of the multi-layer Ge quantum dots on (0 0 1) Si substrates.

images show good vertical alignment of QDs in multi-layer structures and the structures are dislocation free. The vertically ordering of dots can also enhance the optical properties of the dots. In our experiment, the best thickness of Si spacer is 25 nm.The activation energy extracted by integral

intensity with various temperatures can reaches 180 meV.The Raman scattering measurements were performed at both low and room temperatures using a SPEX triplemate spectrometer with a charge-coupled device detector. The spectra were recorded in the $z(x, y)\bar{z}$ back scattering geometry. The spectra were excited with the 514.5 nm line of an argon ion laser or with the 532.5 nm line of a diode pump solid state laser. Fig. 3 shows the Raman spectra of the QDs. The sharp peak at $520\,cm^{-1}$ has the same frequency as that of the optical phonon peak in bulk Si. The peak at $302\,cm^{-1}$ is attributed to the Ge–Ge vibration mode in the QDs. The peak at $418\,cm^{-1}$ is identified with Si–Ge interface phonon mode localized at the surfaces of Ge quantum structures.

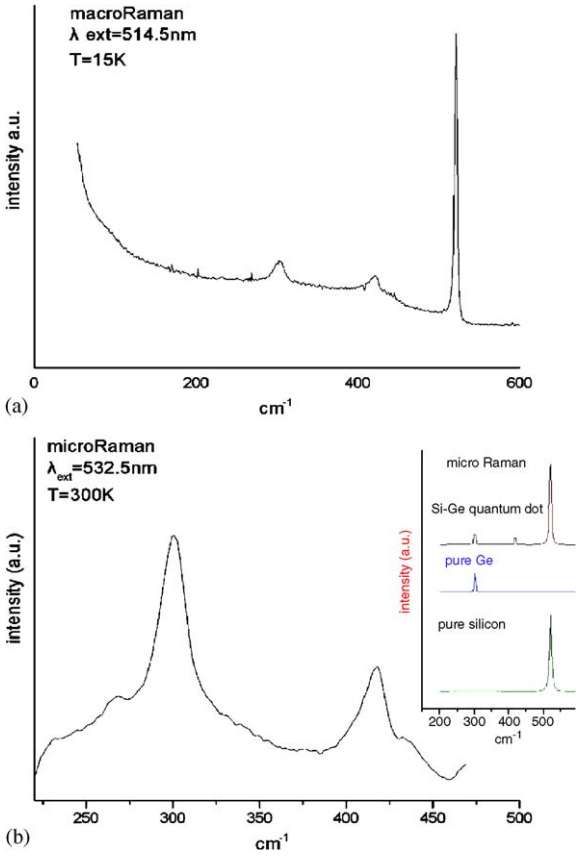

Fig. 3. Macro- and micro-Raman spectra of the stacked Ge quantum dots at $T = 15\,K$ and 300 K, respectively. Micro-Raman spectra of the bulk Ge and Si sample are also placed in the inset of (b) for comparison.

To determine the compositions in the strained-induced self-assembled Ge dots, we use the Raman characterization methods reported in Refs. [14,15]. From the Raman spectral features we find that a certain amount of intermixing takes place between Si spacer layers and Ge QDs in multilayer structures and the average Ge content in the dots is about 0.917. Additional measurements were performed, using a micro-Raman setup with spatial resolution of about 1 μm. The micro-Raman spectra of the QDs as well as the Raman spectra of bulk Si and Ge are also shown in Fig. 3 for comparison. Despite the high sensitivity of the probe, neither Ge-related signal (resulted from the very thin wetting layer) nor signals resulted from motion of Si atoms in specific local environments [16] (Si local mode) were detected.

The low temperature PL spectra from the stacked QDs are shown in Fig. 4(a). These dots emit a PL signal centered around 0.87 eV, which was recently shown to originate from spatially indirect, phononless carrier recombination between holes confined in the Ge dots and electrons confined in surrounding tensile-strained Si [17]. The peak at about 0.76 eV is attributed to deep transition of C–O complex. In comparing to PL intensity of samples with only a single layer of Ge QDs (as shown in Fig. 4(b)), the stacked QDs indeed show improvement on the PL intensity of the fundamental transition by orders of magnitude. Surprisingly, for the stacked QD samples, an unexpected broad luminescence signal centered around 2 eV with a large linewidth (full-width at half-maximum (FWHM) of about 67 nm at 100 K) was also detected when the PL measurements were performed with a spectrometer equipped with a liquid-nitrogen cooled CCD detector. However, for samples which a single layer of QDs was deposited, we have only observed the fundamental transitions and the visible light emission was absent. In Fig. 5 we show the temperature dependence of the visible PL spectra and the integrated continuous-wave PL intensity. The PL spectrum does not dependent on the temperature, but the intensity does vary at different temperatures. The strongest PL intensity was observed at the temperature of about 100 K and the intensity started to quench toward both the

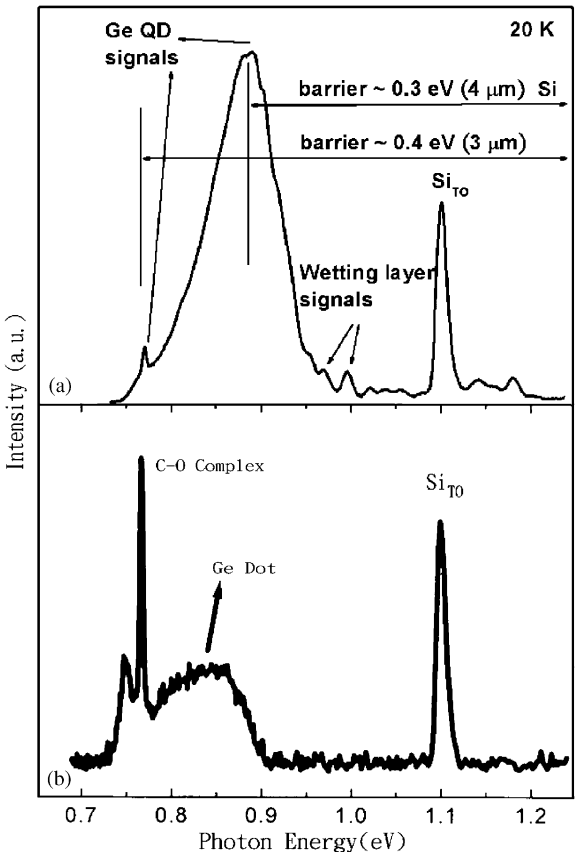

Fig. 4. PL spectra of (a) the multi-layer and (b) a single layer Ge quantum dot samples measured at 20 K. The excitation wavelength is at 514.5 nm.

high- and low-temperature end. The temperature dependence of the luminescence intensity suggests that the emission around 2 eV possibly originates from transitions between bands with multi-level structures. This is also in consistent with the broad linewidth observed in the PL spectra. The multi-level band structures provide high enough density of states for the photoexcited carriers to scatter into and make the "2 eV" transitions become favorable in addition to the fundamental one. Dependence of the integrated luminescence intensity on pumping power is also shown in Fig. 6. The integrated intensity shows almost linear dependence on the pumping power. Although the PL intensity varies from one place to the other, however, it can be observed through out the whole wafer. The PL intensity was so strong that it can

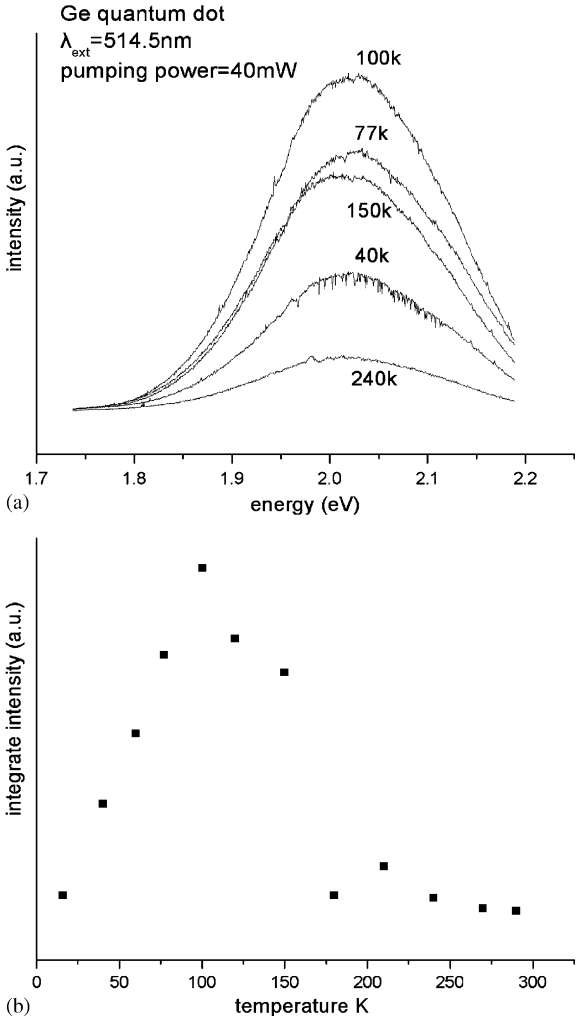

Fig. 5. PL spectra and integrated PL intensity as a function of temperature. The luminescence spectra as well as the integrated intensity are measured in a CW experiment with pumping power = 90 W/cm^2 and excitation wavelength of 514.5 nm.

be seen with naked eyes even at room temperature. Fig. 7 shows the video image of the yellowish luminescence spot on the wafer taken at room temperature by filtering out the scattering light from the pump laser (514.5 nm) with a notch filter. All of the above experimental results can be reproduced even after the samples were exposed in the air for months.

Now we discuss the possible mechanisms of the visible PL as follows. In the bulk crystal of indirect-gap materials, the electron–hole recombi-

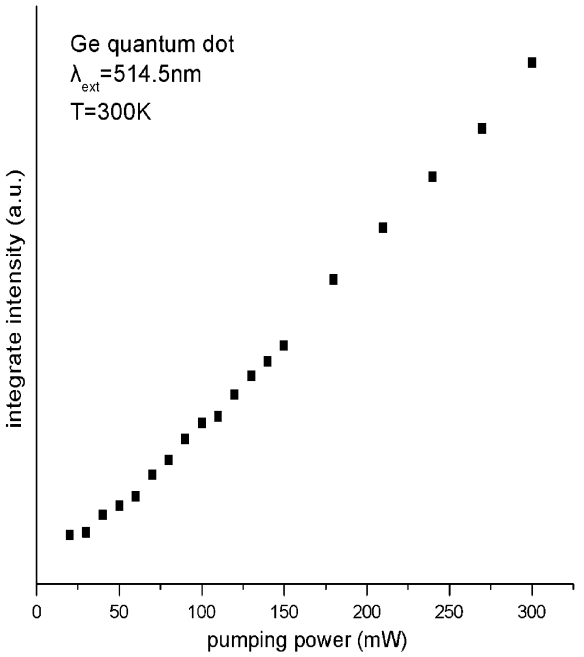

Fig. 6. Integrated luminescence intensity of the stacked Ge quantum dots as a function of pumping power at room temperature. The excitation wavelength is at 514.5 nm.

Fig. 7. Video image of the yellowish luminescence spot.

nation is possible only through phonon emission or absorption because the wave vector difference between the conduction band bottom and the valence band top must be compensated. It is expected that the blue shift of the L–Γ indirect transition occurs as size decreases. In a theoretical work by Takagahara et al. [18] the quantum confinement effect on the L–Γ excitonic transition using the effective mass approximation and the Luttinger Hamiltonian in Ge QDs was calculated. They show that blue shift of the peak of PL spectrum from infrared to visible region occurs as the diameter decreases. Visible luminescence was indeed observed in ultrafine Si particles at room temperature by Takagi et al. [19]. Their results indicate that carrier confinement in the Si microcrystallites causes its PL phenomenon. However, our Ge QDs are relatively large in size (in the x–y plane) and results from the PL spectrum (we can still observed the fundamental indirect transition at 0.87 eV) as well as the temperature dependence of spectra do not favor the model of the visible luminescence due to the confinement-induced blue shift of the L–Γ transition.

On the other hand, it is possible to convert an indirect optical transition into a direct one by forming a superlattice structure [20,21] by which the size of the Brillouin zone is reduced and the conduction band minimum is folded onto the Γ point, resulting in a direct gap material. In nanostructures such as a QD, the periodicity due to a superstructure is absent and the idea of zone-folding cannot be applied.

However, be noted that, direct transition from valence band to conduction band can occur at almost all points in momentum space (except those forbidden by selection rules). These transitions have energies greater than the energy gap. Furthermore, there are subbands in both conduction and valence bands which still allow higher transitions. Earlier studies on higher energy transitions on Ge thin films via transmission and reflectance measurements have observed absorption singularities and reflectivity peaks around photon energies of 2 eV [22]. In QD nanostructures, the electronic states become complete discrete as in the atoms and molecules and the state mixing also occurs for different k states. The transition acquires some allowed character from the k state admixture and k is not a good quantum number. We speculate that the geometry and the

strong confinement (keep in mind that our dots have an average height of only a few nanometers) in the growth direction of the Ge QDs result in the spreading of wave functions among photoexcited electrons in the higher conduction bands. Together with the high density of states provided by the multi-level band structures, the direct high-energy optical transitions now have much larger oscillation strength and they become faster than phonon emission processes. Furthermore, the absence of the "2 eV" emission in the PL spectra of samples with a single layer of Ge dots also provides supporting evidence to our speculation.

In conclusion, we report our observation of strong PL spectra at visible light wavelengths from Ge QDs grown on Si (1 0 0) substrates. The possible mechanism of this visible PL is speculated and it is possibly due to the geometry and strong quantum confinement in the growth direction. This quantum confinement has led to spreading of photoexcited electrons' wave functions in the higher conduction bands so that the direct high-energy optical transitions become allowed in the dots.

Acknowledgments

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