Formation and Characterization of Si Quantum Dots with Ge Core for Functional Devices

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Abstract

High density formation of Si quantum dots with Ge core on thermally-grown SiO₂ has been demonstrated with control of highly-selective CVD. And characteristic carrier confinement and recombination properties in the Ge core and an impact of P delta-doping to the Ge core on the properties have been studied systematically.

1. Introduction

Semiconducting quantum dots (QDs) have been intensively studied because of their unique physical properties related to well-defined discrete energy states in QDs caused by 3-dimentional carrier confinement and distinct Coulomb blockade phenomena [1, 2]. Such unique properties will open up novel functionalities in their device application. For example, the floating gate application of quantum dots will lead us to multivalued capability in charge Currently, light emission from Si-based storage [3, 4]. nanostructures including Si- and Ge-QDs has stimulated considerable interest in the field of silicon-based photonics because of its potential to combine photonic processing with electronic processing on a single chip [5, 6]. Much effort to improve light emission efficiency and its stability has been devoted with deliberate approaches which include not only the confinement of injected carriers but also the use of strained structures and impurity doping. So far, we have reported the formation of Si-QDs with Ge core on ultrathin SiO₂ by controlling the thermal decomposition of pure SiH₄ and 5% GeH4 diluted with He alternately, and demonstrated unique charged storage characteristics of an individual Si-QD with a Ge core, and confirmed type II energy band alignment between Si clad and Ge core, that is, electrons are stored in the Si clad and holes in the Ge core, from the surface potential measurements before and after electron injection and emission by means of AFM/Kelvin probe force microscopy [7, 8]. In this paper, we have reviewed briefly our recent achievement on high-density formation and characterization of Si-QDs with Ge cores on SiO2 and then focused on how light emission properties from Si-QDs are changed with embedding Ge core and P-delta doping to Ge core.

2. Formation of Si-QDs with Ge core

Si-QDs with an areal density as high as $\sim 1x10^{11}$ cm⁻² were formed on thermally-grown SiO₂/c-Si(100) by controlling the early stages of LPCVD using pure SiH₄ at 560°C and subsequently highly selective depositions for Ge core and Si cap on pre-grown Si-QDs were carried by thermal decomposition of 5% GeH₄ diluted with He and of pure SiH₄, respectively, with keeping a gas pressure as low as 2.7Pa. Under such a low pressure, no new nucleation occurs and, as a result, quantum dots consisting of Si clad and Ge core were prepared with the same areal density as pre-grown Si-QDs. In phosphorus delta-doping to Ge core, a pulse injection of 1% PH₃ diluted with He was performed during the Ge deposition. For surface passivation of QDs so prepared, ~2nm-thick SiO₂ was formed by exposing the dot surface to remote O₂ plasma at 560°C.

AFM images show that, with progression of deposition step, the areal dot density remains unchanged at $\sim 1.0 \times 10^{11}$ cm⁻² while the dot height increases step by step. The result indicates the selective deposition of Ge on the pre-grown Si-QDs and subsequent selective Si-capping of the dots. Such highly selective depositions of Ge and subsequent Si on the dots were also verified by XPS measurements. Moreover, AFM measurements confirmed no significant change in the dot size and the areal density with P delta-doping to the Ge core. The existence of P-donors in QDs was also verified by surface potential measurements after sweeping the electrically-biased AFM tip as a function of tip bias with respect to the substrate.

3. Photoluminescence (PL) properties

High density Si-QDs with Ge core, in which the average dot height was ~7nm including a Ge core height of ~2.5nm, shows PL signals in hump-shaped spectrum in the energy region from 0.64 to 0.8eV and a distinct blue shift from phonon-assisted PL from c-Ge(100) substrate. The observed blue shift and spectral shape are associated with radiative recombination related to the quantized states of the Ge core. In fact, with an increase in the Ge core size, a red shift in PL spectrum was observed. On the other hand, coreless Si-QDs, which were fabricated in the same process steps except a selective deposition for Ge core, shows PL signals in the energy region from 1 to 1.6eV and no PL signals in the lower energy region. Notice that in the energy region over 0.8eV, no PL signals from Si-QDs with Ge core were detectable, which means that radiative recombination in the Si clad is suppressed significantly. Namely the result implies that the radiative recombination in Ge core is promoted as a results of hole confinement in deep potential well of Ge core as predicted from the type II energy band alignment between Si clad and Ge core. In addition, we

confirmed that, by N_2 anneal at 700°C, PL signals below 0.8eV from Si-QDs with Ge core were completely eliminated with no changes in dot size and areal density while new PL signals were generated in the region of 1.0-1.4eV as a result of compositional intermixing between Si clad and Ge core. Thus, it is concluded that, in as-prepared Si-QDs with Ge core, radiative recombination in the Ge core is the major origin of room temperature luminescence.

To gain a better understanding of the radiative recombination in the Ge core, an impact of p-doping to Ge core on PL properties were examined in the temperature range from 72 to 300K. Obviously, one can see a significant difference in PL spectral shape between undoped and Pdoped QDs (Fig. 1). As demonstrated in Fig. 1, from the analysis of each observed PL spectrum using Gaussian components, it is found that the PL spectrum from pure Si-QDs with Ge core consists of 4 components and that, in the P-doped case, another component, Comp. 5, peaked at ~0.69eV is needed in addition to the 4 components derived from the undoped case to reproduce the measured PL spectrum. As for each of the 4 common components, there are no appreciable differences in both the spectral width and the peak energy between undoped and P-doped cases, irrespective of temperature in PL measurements. Hence, the Comp. 5 with a spectral width narrower than other components is a characteristic emission of P-doped QDs. Notice that a fairly weak temperature dependence of the peak energy of individual components, in comparison to the temperature dependence of energy band gaps of bulk Ge and Si, is attributable to encapsulation of QDs with SiO₂ having a small thermal expansion coefficient which is lower over one digit than bulk Ge and Si (Fig. 2(a)). The analysis of the temperature dependence of the integrated PL intensity of each component represents that the activation energy in thermal quenching process of the Comp. 5 is smaller than those of the other components and is very close to the activation energy of P-donors in Ge (Fig. 2 (b)). The result indicates that the Comp. 5 can be assigned to the recombination related to the transition from P donor levels to the 1st quantized state in the valence band of the Ge core. Considering the fact that the energy separation between the Comps. 5 and 1 is the same as the energy position of the donor level measured from the conduction band edge of bulk Ge, the Comp. 1 is likely to be attributed to the recombination through the 1st quantized states between valence band and conduction band of Ge core. And the radiative transitions between the higher order quantized states in the conduction and the valence bands of Ge core are likely to be responsible for the higher energy components, Comps. 2 and 3. Since the Si clad acts as a shallow potential well for electrons in type II band alignment so that electron wave function in Si clad can penetrate into Ge core, the Comp. 4 is attributable to the radiative recombination caused by coupling between the electron quantized state in Si clad and the hole quantized state in Ge Furthermore, from the slope of log-log plot in core. power dependence of each deconvoluted excitation component, all the component showing a power index below

unity suggests bound exciton like emission rather than free exciton emission presumably reflecting strong carrier confinement system especially for holes in Ge core.



Fig. 1 Room temperature PL spectra for (a) Si-QDs with undoped Ge core and (b) with P-doped Ge core. In each case, the result of spectral deconvolution is also shown.



Fig. 2 Temperature dependences of (a) PL peak energy and (b) integrated intensity of each deconvoluted component for Si-QDs with P-doped Ge core. In (a), temperature dependences of energy bandgaps of bulk Ge and Si are also shown as references.

4. Conclusions

The hole confinement in Ge core plays an important role on radiative recombination in Si-QDs with Ge core. And it is confirmed that P-doping to Ge core can open a new pathway for radiative recombination between the quantized stats and donor levels.

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