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Photoluminescence in crystalline silicon quantum wells

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Crystalline silicon single quantum wells (QWs) with a minimum Si layer thickness of around 1 nm were fabricated by high temperature thermal oxidation of separation by implantation of oxygen (SIMOX) and epitaxial layer transfer (ELTRAN®) silicon-on-insulator (SOI) wafers. Not only Si thickness but also defect-free SOI materials may be important factors for observation of quantum-confined transition in the Si QWs. Si QWs fabricated from SIMOX SOI wafers showed strong interface-mediated luminescence, which is independent of Si thickness, at 1.63 and 1.49 eV in the Si thickness range from 1 to 7 nm. On the other hand, Si QWs fabricated from ELTRAN SOI wafers showed very strong thickness dependent luminescence in the range of 1.36–1.77 eV without interface-mediated luminescence, where the Si thickness range was 3–1 nm. The ability to detect quantum-confined luminescence seems to arise from the use of high-quality defect-free ELTRAN SOI wafers, from suppressed interface state luminescence by high temperature oxidation, and, possibly, from interface matching by crystalline silicon oxide. Hydrogen passivation suggests luminescence from a weak Si═O state at around 1.59 eV, but luminescence due to quantum confinement is more predominant in the ELTRAN Si QWs. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2430919]

I. INTRODUCTION

Light emission from silicon has been demonstrated not only in three-dimensional crystals[1,2] but also when the silicon is in the form of low dimensional structures such as in porous silicon,[3] superlattices,[4] quantum wells (QWs),[5–8] and quantum dots.[9] Among these, monocrystalline single Si QWs are the most fundamental silicon-based nanostructures for understanding quantum confinement features. Si QWs have been fabricated by thermal oxidation and oxide etch-back processing of SOI wafers, previously, separation by implantation of oxygen[5,6] (SIMOX) and epitaxial layer transfer (ELTRAN) silicon-on-insulator (SOI) wafers.[7,8] Quantum confinement effects in these structures are expected when the silicon well thickness is comparable to the Bohr radius of bulk crystalline silicon (around 5 nm).

Photoluminescence (PL) from crystalline Si QWs can be classified into two categories: (a) interface-mediated transitions, dominated either by a peak at 1.65 eV for Si QWs from SIMOX SOI wafers[5,6] and at 1.80 eV for Si QWs from ELTRAN SOI wafers,[7] and (b) a thickness dependent luminescence shift with Si layer thickness reduction.[8] Possible origins of PL spectrum in case (a) is the localized $Si-SiO_2$ interface states, and in case (b) it relies on the quantum confinement effect in the QWs. In previously reported Si QWs,[5–7] luminescence intensity from an interface-mediated transition was high compared to luminescence intensity from a quantum confinement transition. However, the present authors reported clear quantum-confined luminescence from Si QWs fabricated by single step thermal oxidation of ELTRAN SOI wafers.[8] The present paper explores these differences in more details.

In the interface-mediated transition model, electrons and holes migrate to localized interface states where radiative recombination takes place, leading to light emission. This is the model used to explain PL from porous silicon[9] and Si QWs.[5,6,10] One possible $Si-SiO_2$ interface model involves an oxygen double bond to silicon at the interface, but many structural models have been used to explain the nature and role of the $Si-SiO_2$ interface states. The interface-mediated emission is explained by radiative recombination of trapped carriers at localized interface states, arising from lattice mismatch between crystalline silicon and amorphous thermal SiO_2 or located in a crystalline oxide layer near the interface.[6,10] Crystalline silicon oxide, i.e., cristobalite, at the a-SiO_2–Si (100) interface has been proposed to reduce interface states.[11] The proposed direct band gap energy of cristobalite of 1.5 eV at the Γ point has been considered as a possible origin of the observed strong interface-mediated transitions at 1.65 eV observed from Si QWs fabricated from SIMOX SOI wafers.[5–7,9] However, it is difficult to explain the interface-mediated transitions observed at 1.8 eV for Si QWs fabricated from ELTRAN SOI wafers with this model.[7]

In previous Si QW devices reported by others, an oxide etch-back process was always used to reduce thick superficial Si layers, resulting in Si surface passivation by only a

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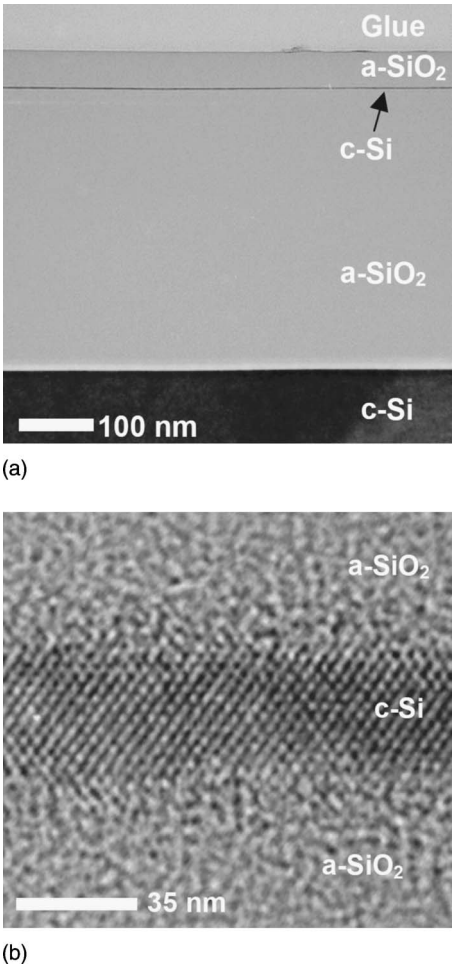

FIG. 1. Dark field TEM images of the oxidized SIMOX wafer: (a) $SiO_2/Si/SiO_2$ and (b) Si lattice image of crystalline region enclosed in SiO_2.

thin oxide layer. The highest surface passivation in Si photovoltaics can be achieved by high temperature thermal oxidation with a thick oxide layer (around 110 nm thick) followed by annealing with an Alneal processing (thick Al under 4% H_2 forming gas atmosphere).

In this paper, we fabricate single Si QWs by the thermal oxidation of SIMOX SOI wafers, using the etch-back process to reduce the relatively thick Si layer, and by one-step thermal oxidation of ELTRAN wafers. The luminescence properties of the fabricated single Si QWs were investigated and compared. Hydrogen treatment by an Alneal process was applied for the Si QWs and the luminescence properties were studied.

II. SI QW FABRICATION

SIMOX SOI wafers are fabricated by oxygen ion implantation, resulting in a relatively thick superficial Si layer of 180 nm in our case, while the superficial Si thickness of the ELTRAN wafers, fabricated by epitaxial Si growth on the porous silicon, was 52 nm. The superficial silicon layers in both the SIMOX and ELTRAN wafers are crystalline, (100) oriented, and *p* type (doped with 10^{16} boron atoms/cm^3). Cleaning in piranha solution (3:1 $H_2SO_4:H_2O_2$) for 10 min

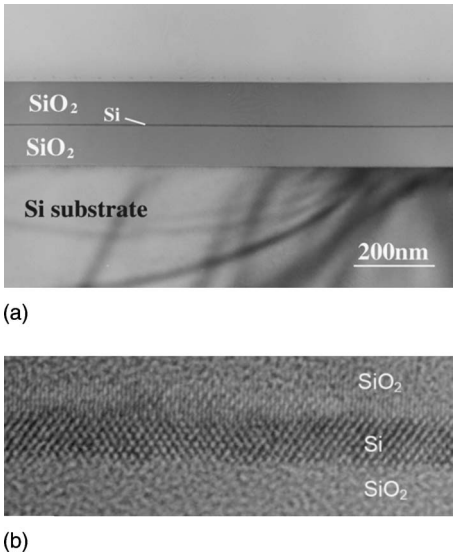

FIG. 2. Dark field TEM images of the oxidized ELTRAN wafer: (a) $SiO_2/Si/SiO_2$ and (b) Si lattice image of crystalline region enclosed in SiO_2. The HRTEM image shows five to seven atomic Si layers (1.36–1.90 nm total thickness) with an apparent ordered transition layer on the upper SiO_2–Si interface.

and RCA2 (7 H_2O:1HCl:1:H_2O_2) cleaning for 10 min were used to remove the organic and metallic impurities throughout all experiments.

The initial 180 nm superficial Si thickness of the SIMOX wafers was reduced by 1,1,1-trichoroethane (TCA) based thermal dry oxidation at 1000–1050 °C followed by oxide etch-back processing in a dilute HF solution. This procedure was repeated several times to obtain a final Si thickness of less than 5 nm. A SIMOX wafer is prepared by the formation of a buried layer of SiO_2 by implantation of oxygen ions beneath the surface of a single crystalline silicon wafer.[12] The standard dose used is 1.8×10^{18} cm^{-2} at 200 keV, which produces a 400 nm thick buried oxide layer upon a high temperature anneal at 1310 °C for 6 h in a nitrogen atmosphere with 0.5% oxygen and subsequently at 1350 °C for 40 h.[13] The interfaces between the buried oxide and the Si substrate as well as the interface between the superficial Si layer and buried oxide layer are ideally smooth. Figure 1 shows, for an oxidized SIMOX wafer, a transmission electron micrography (TEM) of the superficial layers and a high resolution TEM (HRTEM) of the ultrathin Si layer. The Si thickness embedded in the oxide layers is estimated as 3.2 nm by counting the Si lattice fringes along the (100) direction, where the fringe distance is 0.271 nm.

The thinner initial superficial Si layer of ELTRAN wafers was allowed reduction to less than 5 nm thickness by a single step dry oxidation at 1050 °C, producing a 115 nm thick oxide, without any oxide etch-back process. Figure 2 shows the TEM images of an oxidized ELTRAN wafer and a HRTEM image of the ultrathin Si layer. An apparently ordered structure of silicon oxide was observed in the upper thermal SiO_2–Si interface of the samples in cases where the thin monocrystalline Si layers were less than 3 nm thick.[14] The ordered SiO_2 layer has 1.9 Å atomic spacing along the (110) direction and a thickness of up to 17 Å along the (100) direction. Candidate structures, based on the observed spac-

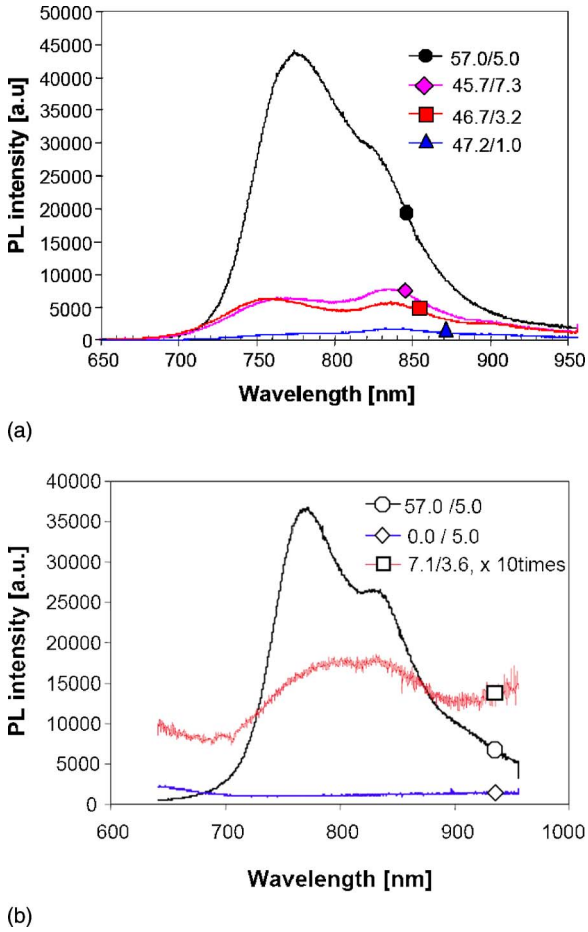

FIG. 3. (Color online) PL spectra from the $SiO_2/Si/SiO_2$ quantum well fabricated on the SIMOX wafers at 10 K. Top oxide and Si thicknesses (in nm) are shown in the symbol legends.

ing in HRTEM images, are either quartz or cristobalite, but it is not possible to determine the exact phase of the apparently crystalline oxide using our available experimental techniques.[14] Another crystalline oxide, tridymite, has an atomic spacing of 3.8 Å along the (110) direction, making it an unlikely candidate.

III. LUMINESCENCE PROPERTIES OF SI QWS

The PL measurements were performed using an argon ion laser operating at 514.5 nm and a SPEX spectrometer with 200 μm slit width. A silicon photodiode was used as the detector for visible light and a liquid nitrogen cooled Ge detector for near-IR wavelengths, followed by a lock-in amplifier. The laser powers were set to 10 and 20 mW for the Si QWs fabricated from the SIMOX and ELTRAN SOI wafers.

A. SIMOX SOI wafers

Low temperature PL spectra of the Si QWs fabricated from the SIMOX wafers are independent of the Si layer thickness, as shown in Fig. 3. To compare the PL spectra directly, excitation power and detector exposure time were set to 10 mW and 4 s, respectively. The Si layer thickness was measured from the HRTEM images, typically as shown in Fig. 1(a). Two luminescence bands located at 760 nm (1.63 eV) and 836 nm (1.48 eV) are observed for Si thickness in the range from 3.2 to 7.3 nm, as shown in Fig. 3(a). The main difference between the cases is luminescence intensity. The luminescence located at 1.63 and 1.48 eV may relate to Si thickness in Si QWs, but also oxide properties such as oxide thickness and passivation of the silicon are influential factors for the optical transitions.

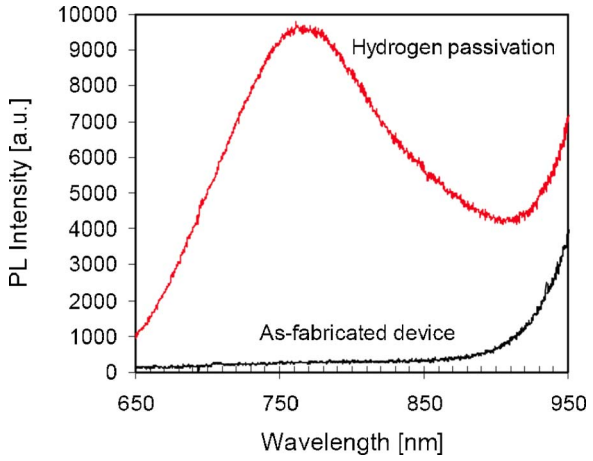

FIG. 4. (Color online) Luminescence from hydrogen treated 2.5 nm thick Si QW at 300 K. Hydrogen treatment reveals luminescence at 1.63 eV.

The strong luminescence peaks from 5 nm thick Si QWs disappear, as shown in Fig. 3(b), when the top oxide layer was removed by a dilute HF solution. The boundary condition in this case could be either an abruptly terminated or a fluorene-terminated surface. An abrupt surface may give high nonradiative recombination. A fluorene-terminated surface, after dipping in 4.9% HF solution, has been reported to have surface recombination velocity of around 300 cm/s,[15] which may not be sufficient to passivate an ultrathin Si (100) layer. The disappearance of luminescence by oxide removal can be explained either by the luminescence originating from the oxide layer or by enhanced nonradiative recombination at the exposed interface. When a thin oxide layer (7 nm oxide resulting in 3.6 nm Si) was regrown, a very weak PL spectrum was observed.

A nominally 2.5 nm thick Si QW device was subjected to hydrogen treatment using an Alneal process. The Alneal consisted of thermal evaporation of a 100 nm Al layer onto the device prior to furnace annealing under a forming gas consisting of 4% H_2 in N_2 atmosphere. The device was annealed at a temperature of 450 °C for 30 min. Atomic hydrogen is generated through reactions between a deposited Al layer and adsorbed water vapor or OH radicals in the oxide surface and effectively passivates the $Si-SiO_2$ interface.[16] The Al layer was subsequently removed by cleaning in piranha solution. Figure 4 shows the effectiveness of the hydrogen treatment. The nominal 2.5 nm thick Si QW device was hard to observe as a PL spectrum at room temperature (300 K) in this particular case. However, the hydrogen treated device clearly reveals the luminescent intensity at 1.63 eV more significantly.

Figure 5 shows the PL spectra of 5 nm Si QW, which has the highest luminescence, at elevated temperature. The strongest luminescence peak at 760 nm showed temperature quenching and the luminescence peak at 1000 nm (i.e.,

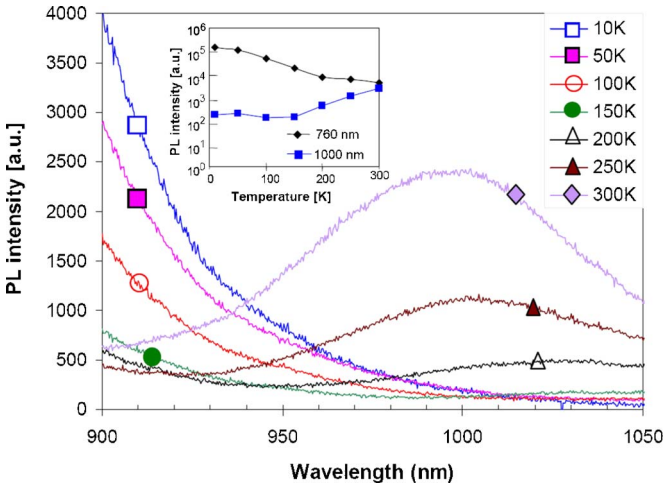

FIG. 5. (Color online) Luminescence from a defect-mediated transition at 1000 nm and interface-mediated transition at 760 nm measured from 5 nm thick Si QW. Inserted figure shows the peak intensity dependence on the measurement temperature.

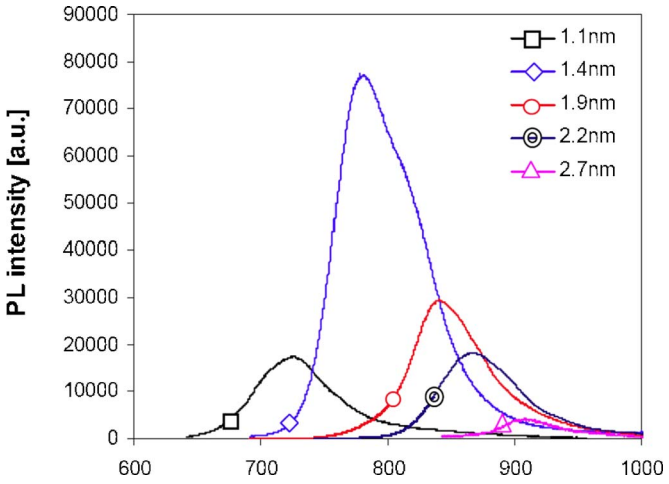

FIG. 6. (Color online) PL spectra of the Si QWs fabricated from ELTRAN SOI wafers. Substrate temperature was 10 K.

1.24 eV) appeared as a result of increasing the measurement temperature, as indicated by the inset in Fig. 5. The luminescence at a wavelength of 1000 nm is assigned as a thermally activated transition, which is indicative of defects in the Si layer. Defect photoluminescence is often observed in amorphous silicon. In amorphous silicon, one usually considers mostly delocalized states (extended states) and weakly localized states (the band tail states) in the light absorption and emission processes.[17] Defects in the amorphous silicon layers provide the dominant recombination path when their density is above about 10^{17} cm^{-3} or when the temperature is higher than about 100 K.[17] Rapid activation of photogenerated carriers occurs in the extended state, and the recombination occurs after the carriers are trapped into the band tail states. The origin of the thermally activated transition observed at 1000 nm may be implantation defects or precipitates in the SIMOX wafers.

B. ELTRAN SOI wafers

ELTRAN SOI wafers have uniform Si thickness and an atomically flat SiO_2–Si interface with low defect density. Defect density in the superficial Si layer is reported to be of the order of 50 cm^{-2} and is mentioned as 10 cm^{-2} in the product homepage.[18]

Owing to a relatively thin (~52 nm) and uniform superficial Si layer, thermal oxide thickness after oxidation of the superficial Si layer remained around 111±3 nm through all samples. Also 110 nm thick thermal oxide is known to produce a low density of electronic defects at the Si–SiO_2 surface of the underlying silicon and therefore has been used, for example, for surface passivation of high efficiency crystalline silicon solar cells.[19]

The PL spectra are shown in Fig. 6, without any curve fitting, for a substrate temperature of 10 K. The Si thicknesses are again taken from the HRTEM images because HRTEM appears to give the most reliable results. PL whose wavelength depends on the Si layer thickness is clearly observed, without evidence of strong PL from interface states. Interface-mediated transitions have been previously observed in Si QWs fabricated from ELTRAN wafers.[7] As a result of the suppression of the interface-mediated transitions using high-quality thick oxide (~110 nm), quantum confinement effects may be more apparent. The blueshift of the PL and its rapidly increasing intensity with decreasing Si thickness in the samples ranging from 1.4 to 2.7 nm thickness are indicative of quantum confinement effects. Decreasing intensity for 1.1 nm thick Si is indicative of a boundary effect. With decreasing thickness of the Si layers, nonradiative recombination via the Si/SiO_2 interface dominates and results in the PL intensity decreasing. Emission is directly related to the absorption from the principle of detailed balance.[20] Decreasing thickness would weaken absorption were it not for quantum confinement. The PL spectrum from the nominal Si thickness of 1.1 nm in Fig. 6 has an obvious shoulder and was explained as Si thickness fluctuation by the present authors.[8]

Figure 7 shows luminescence spectra from different positions of samples of nominally 1.1 and 2.2 nm thick Si

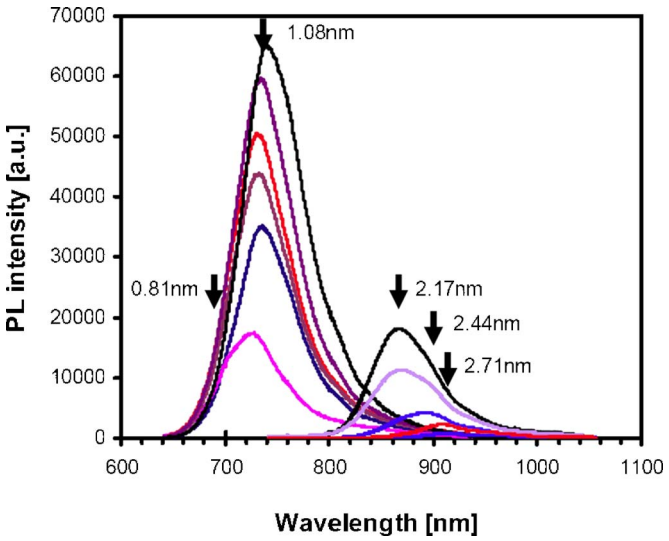

FIG. 7. (Color online) Luminescence spectra from different positions on two individual samples (5×5 mm^2) of nominally 1.1 and 2.2 nm thickness at 10 K.

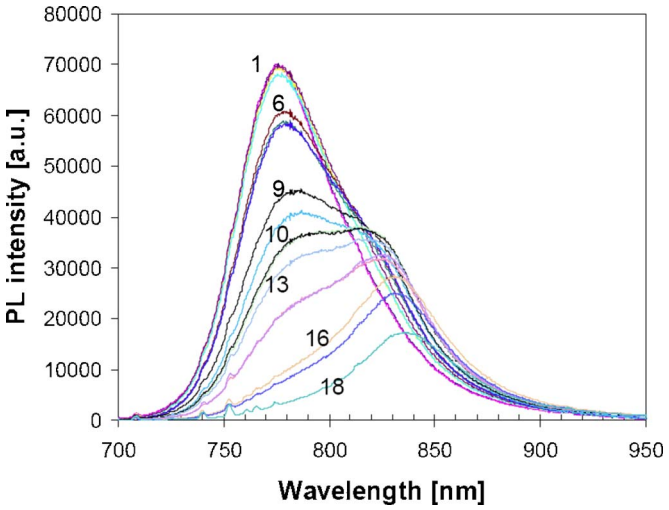

FIG. 8. (Color online) Luminescence spectra from the sample with tapered Si thickness. The numbers correspond to position spaced 1 mm apart along the taper.

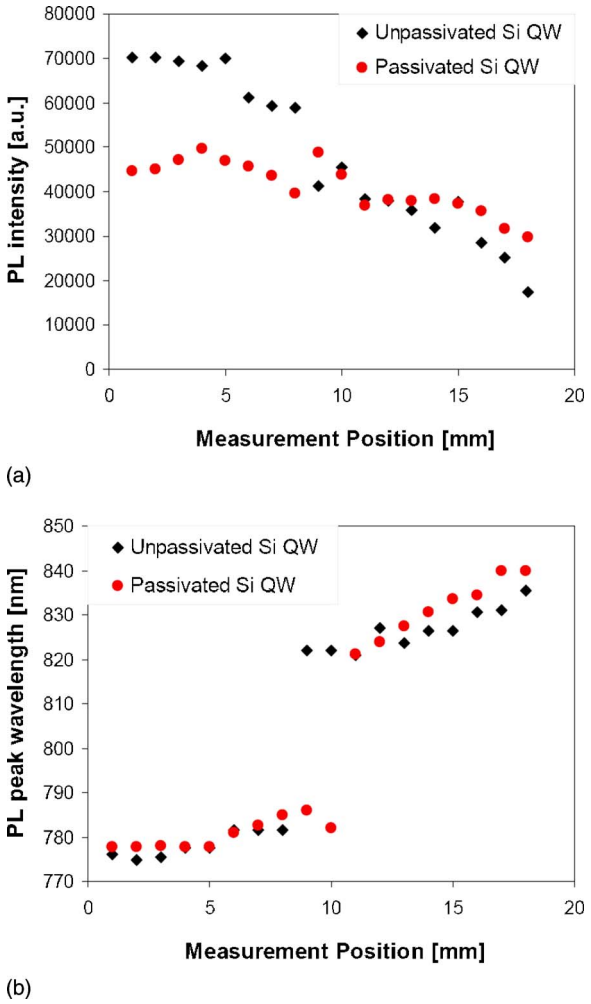

FIG. 9. (Color online) Comparison of (a) luminescence peak wavelength and (b) luminescence peak intensity before and after hydrogen treatment.

thickness. For the 1.1 nm sample, strong peaks at 730–740 nm (1.68–1.70 eV) and shoulder peaks at 700 nm (1.77 eV) are apparent. Some points on this sample do not produce luminescence. They are attributed to stop changes in the sample thickness equal to an atomic layer thickness as indicated. The interface luminescence mechanism could not explain the luminescence spectra from 2.2 nm thick Si QW (seven dot layers in the HRTEM image); the strongest spectrum in Fig. 6 has its peak at a wavelength of 871 nm (1.42 eV). The second strongest spectrum has a shoulder peak at 895 nm (1.39 eV), with its main peak also at 871 nm wavelength. The third strongest spectrum has one peak at 897 nm (1.39 eV) and a shoulder peak at ~916 nm. The final two luminescence spectra have their peak energy at ~916 nm (1.35 eV), comparable in both peak position and intensity with the 2.7 nm thick QW (ten dot layers in the HRTEM image) shown in Fig. 6. The emission wavelengths of 871, 895, and 916 nm correspond to three different Si thicknesses, i.e., 2.2, 2.4, and 2.7 nm. Other samples with different average Si thickness also show similar behavior.

To investigate this monolayer fluctuation in thickness more systematically, a sample was specially fabricated with a tapered Si layer thickness over a large area about 15 $\times 20$ mm^2. The tapered Si region was chosen after a careful Si thickness mapping of available wafers using spectrophotometry.[21] The thermal oxidation resulted in a processed Si taper from a thick region to a thinner region, and finally a region of zero Si thickness as determined by spectrophotometer (reflection) measurement.[21] HRTEM results, however, show that zero Si thickness as deduced from the measurement by spectrophotometer actually could correspond to layers containing up to three or four monolayers of silicon pairs. PL was measured at 18 positions on the sample spaced 1 mm apart. The peak PL wavelengths in Fig. 8 from the first eight points are in the wavelength range from 776 to 781.5 nm. The next PL peak appears at ~825 nm from the 9th point to the 12th point. From the 13th point onward, the peak intensity at ~780 nm is smaller than the second luminescence peak at ~825 nm. Finally, the PL peak at ~780 nm disappears, and only one PL peak appears at ~840 nm from point 16 and onward. PL peaks at 780, 825, and 840 nm are believed to correspond to luminescence from five, six, and seven Si monolayers.

The tapered sample was performed in an Alneal process to modify the SiO_2–Si interface and PL measured at the same positions. In Si QWs, the hydrogen saturation of dangling bonds largely eliminates surface states and provides a smooth termination of atomic orbits similar to the boundary condition at an interface with wide-band-gap material. The PL peak position of a hydrogen treated sample is almost the same (3–9 nm wavelength shift), as shown in Fig. 9(a). The difference in peak intensity is shown in Fig. 9(b). Hydrogen treatment reduces PL intensity at around 780 nm and enhances PL intensity at the wavelength higher than 820 nm. This PL dependence implies the presence of two possibly independent processes. For example, direct luminescence from electronic states located at around 780 nm (~1.59 eV), which could be associated with the interface state,[6,9,10] may be reduced, decreasing the signal at this wavelength. However, nonradiative recombination through their or related states may increase after hydrogen treatment.

IV. CONCLUSIONS

Photoluminescence properties in single Si quantum wells were studied using SIMOX and ELTRAN SOI wafers. We fabricated Si QWs in a $SiO_2/Si/SiO_2$ structure by a high temperature thermal oxidation until the Si thickness was on the order of 1 nm.

The PL spectra from the QWs fabricated using SIMOX wafers showed two peaks at 1.49 and 1.63 eV, independent of Si layer thickness. The observed PL intensity of the SIMOX Si QWs strongly depends on the oxide thickness. The two PL bands (1.49 and 1.63 eV) disappeared when the top oxide layer was etched in dilute HF solution. As an oxide layer grew, PL started to be observed. Hydrogen treatment intensively enhances the PL band at 1.63 eV by eliminating interface states. A defect-mediated transition band at emission wavelength of 1.24 eV becomes active at temperatures above 200 K. Not only Si thickness but also oxide properties are important factors for the observation of quantum-confined transition in Si QWs fabricated using SIMOX wafers.

In contrast to the SIMOX wafers, the Si QWs fabricated from ELTRAN wafers show Si thickness dependent luminescence in the energy range from 1.36 to 1.77 eV. In this case, there was no evidence for interface-mediated luminescence as was observed from the SIMOX Si QWs in this paper and previously reported for other QWs fabricated from both SIMOX (Refs. 5, 6, and 10) and ELTRAN SOI wafers.[7] A crystalline silicon oxide was easily observed in samples in which the Si thicknesses were less than 3 nm, as reported elsewhere.[14] Hydrogen passivation suppresses luminescence at around 1.59 eV, which could be associated with interface states[6,10] and enhances the radiative recombination emission at energies lower than 1.51 eV. Interface luminescence may exist in ELTRAN Si QWs, but the quantum confinement is believed to be a more predominant luminescence mechanism for the devices.

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