Enhanced quantum efficiency of solar cells with self-assembled Ge dots stacked in multilayer structure

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We report on the performance of solar cells with stacked self-assembled Ge dots in the intrinsic region of Si-based p-i-n diode. These dots were epitaxially grown on p-type Si(100) substrate via the Stranski–Krastanov growth mode by gas-source molecular beam epitaxy. Enhanced external quantum efficiency (EQE) in the infrared region up to 1.45 μm was observed for the solar cells with stacked self-assembled Ge dots compared with that without Ge dots. Furthermore, the EQE was found to increase with increasing number of stacking. These results show that electron-hole pairs generated in Ge dots can be efficiently separated by the internal electric field, and can contribute to the photocurrent without considerable recombination in Ge dots or at Ge/Si interfaces. [DOI: 10.1063/1.1600838]

Self-assembled Ge dots on Si have attracted much interest as a promising direction for the application of Si-based quantum electronic and optoelectronic devices. Growth of multilayer arrays,[1] growth kinetics, and various growth modification[2,3] of Ge dots were extensively studied. One of the noticeable applications of Ge dots is photodetectors for mid- and near-infrared detection.[4–6]

A decade ago, low-dimensional structure, such as quantum well (p-i-n) solar cells, was first proposed to improve the overall conversion efficiency as an alternative approach to the conventional tandem solar cells.[7] In quantum well solar cells, the short-circuit current and the open-circuit voltage can be independently optimized because the absorption edge and spectral characteristics can be modified by the width and the depth of the well. Moreover, to provide direction to high-efficiency solar cells, quantum dots were theoretically proposed to offer innovative approach to enhance the performance of solar cells.[8] In the intrinsic region of the p-i-n solar cell, a quantum dot layer is inserted for photon absorption in the longer wavelengths of the solar spectrum. In addition, vertical alignment[9] and electronic coupling[10] of quantum dots triggered by the strain fields of the buried quantum dot layers occurred. Consequently, possible channeling of electrons and holes can easily take place in the vertically aligned and electronically coupled dots and they probably contribute to the enhancement of quantum efficiency. However, these expectations were not observed in the previous experiment that utilized ten layers of Ge dots with Sb surfactant for solar cells application.[11] Spectral response in the infrared region was not enhanced instead it was suggested that more stacked layers of Ge dots will be inserted in the space charge region to improve the performance of the solar cells.

On the other hand, functional crystals as base material for the design of high efficiency solar cells that enhanced absorption performance are also developed, i.e., SiGe multicrystalline with microscopic compositional distribution[12,13] and many others.[14] However, it is difficult to grow defect-free and dislocation-free SiGe bulk crystal since precise control of various growth parameters is highly needed.

To overcome this difficulty, a molecular beam epitaxy (MBE) system was introduced to grow high-quality crystals and dislocation-free self-assembled Ge dots. The theoretical model previously mentioned is realized in our present work that utilized self-assembled Ge dots stacked in multilayer structure for solar cells application. It is expected that inclusion of Ge dots in the intrinsic region would increase the short circuit current without considerable loss of open-circuit voltage due to band gap engineering.

In this letter, we present a result on the performance of solar cells with self-assembled Ge dots stacked in multilayer structure that exhibit improved external quantum efficiency (EQE) in the infrared region compared with the conventional Si-based solar cells. Spectroscopic response in the longer wavelengths up to 1.45 μm was observed owing to the presence of Ge dots and an increase of the EQE with increasing number of stacking was confirmed. A possible reason for the decrease of the response in the infrared region with increasing annealing temperature is discussed based on the results of photoluminescence (PL) spectroscopy.

The samples were grown using a gas-source MBE (Air-Water VCE S2020) system utilizing disilane (Si_2H_6) and germane (GeH_4) as gas sources on p-type Si(100) substrate with a resistivity of 1–10 Ω cm. All samples underwent thermal cleaning for 10 min at 820 °C. The base pressure and temperature in the growth chamber were kept at around 1×10^{-10} Torr and 700 °C, respectively. A 100 nm Si buffer layer was first grown to achieve an epitaxial surface. Subsequently, self-assembled Ge dots stacked in multilayer (50 and 100 layers) structure was grown via the Stranski–

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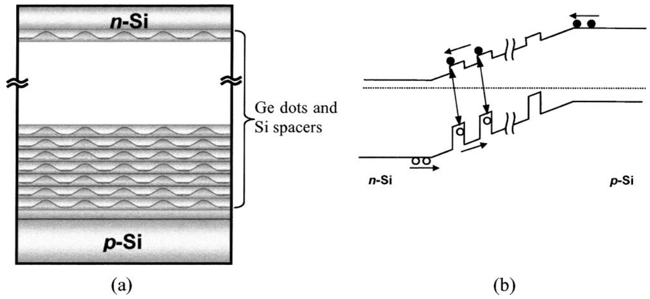

FIG. 1. Schematic diagram of Ge dots in multilayer structure (a) and the corresponding energy band structure (b) for solar cells application.

Krastanov growth mode separated by 39 nm thick of Si spacer layer and finally capped with 0.6 μm of Si. The $p-n$ junction was formed through thermal diffusion of phosphorous from spin-coated Ohka coat diffusion source at 800, 900, and 1020 °C. Al and Ag were evaporated for backcontact and front fingers, respectively.

PL measurements were carried out using a standard lock-in technique with a liquid-nitrogen-cooled Ge photodetector (North Coast EO-817L). The 532 nm line of a second harmonics of Nd:yttritium–aluminum–garnet laser was used as an excitation source. Atomic force microscopy (AFM) measurement was performed in a tapping mode to observe the surface morphology of the uncapped sample. EQE was measured using tungsten and xenon lamps as light sources that pass through a monochromator. The short circuit (no bias) photocurrent was directly measured with a computer interfaced Keithley digital multimeter.

Figure 1(a) shows the schematic diagram of self-assembled Ge dots stacked in multilayer structure in the intrinsic region to enhance the absorption performance in the longer wavelengths whose energy band structure is shown in Fig. 1(b). It is speculated that vertical alignment and electronic coupling between dots probably occur due to stacking effects[9,10] and channeling of electrons and holes might contribute to the enhancement of spectral response.

Figure 2 shows a 2×2 μm^2 AFM image of the self-assembled Ge dots with 8 monolayers (ML) coverage grown at 700 °C. At this growth temperature, appearance of bimodal islands, domes, and pyramids, are usually observed.[15] The pyramids have rectangular bases along {100} directions and

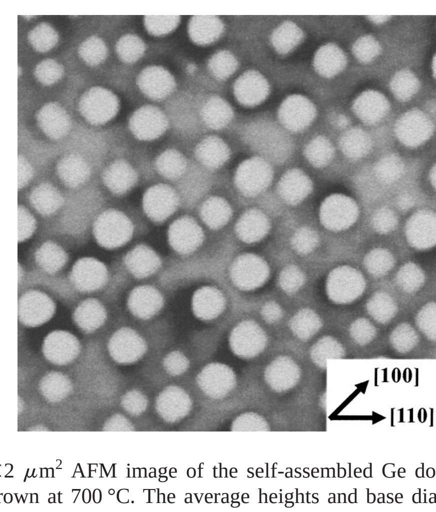

FIG. 2. 2×2 μm^2 AFM image of the self-assembled Ge dots with 8 ML coverage grown at 700 °C. The average heights and base diameter of dots are about 17 and 81 nm, respectively.

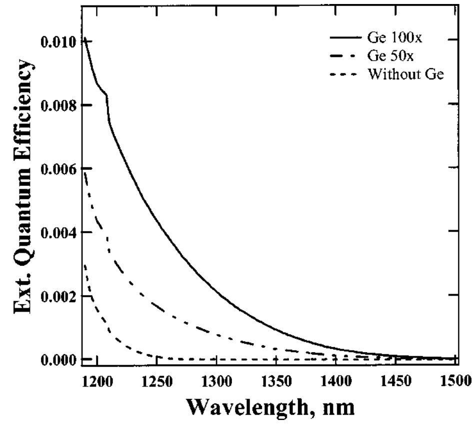

FIG. 3. Comparison of external quantum efficiency of the solar cells with different stacked layers and without self-assembled Ge dots in the intrinsic region annealed at 900 °C.

four facets directed along {105} directions while the round shaped domes have multifaceted surfaces. The average height and average base diameter of the Ge dots were about 17 and 81 nm, respectively. The area density was in the order of 10^{10} cm^{-2}.

The spectroscopic response in the infrared region of the solar cells with and without stacked self-assembled Ge dots in the intrinsic region is shown in Fig. 3. It is clearly observed that quantum efficiency is enhanced in the infrared region up to 1.45 μm for the solar cells with stacked Ge dots compared with that without stacked Ge dots in the intrinsic region. On the other hand, the solar cells without stacked Ge dots in the intrinsic region exhibit an EQE up to around 1.2 μm only. This enhanced spectral response in the infrared regime results from the absorption of solar spectrum by Ge dots with narrower effective band gap compared with that of Si.

The solar cells with 100 layers of stacked self-assembled Ge dots have reasonable enhanced performance compared with the 50 layers. The obvious reason for this dependence of spectral response is attributed to the number of layers in the confinement structures that could make more effective light absorption. In addition, the excited carriers within the Ge dots improved the EQE of the solar cells in the infrared region. Importantly, these results show that electron-hole pairs generated in Ge dots can be efficiently separated by the internal electric field, and can contribute to the photocurrent without considerable recombination in Ge dots or at Ge/Si interfaces.

Figure 4 shows the temperature dependence of EQE of solar cells with 100 layers of stacked Ge dots. It is noted that EQE drastically decreases with increasing annealing temperature. The solar cells annealed at lower temperatures exhibit a spectral response up to 1.45 μm. In contrast, the solar cells annealed at 1020 °C demonstrate a spectral response up to 1.25 μm only.

Results of 10 K PL measurements from 100 layers of stacked self-assembled Ge dots with 8 ML coverage grown at 700 °C and annealed at different temperatures are shown in Fig. 5. The PL spectrum of the as-grown sample in the energy range between 800 and 900 meV obviously correspond to the Ge dots. Existence of double-peak structure can be seen. These broad peaks might be ascribed to the appear-

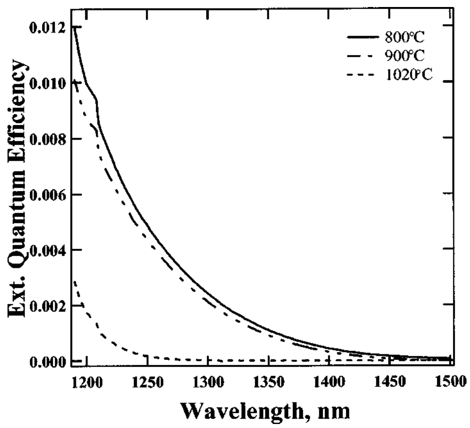

FIG. 4. External quantum efficiency of solar cells with 100 layers of self-assembled Ge dots at different annealing temperatures.

ance of the islands containing point defects and might be assigned as no-phonon (NP) and TO phonon energy.[16] Furthermore, these might be attributed to a bimodal island size distribution[17] that we observed in the AFM image (Fig. 1). The PL lines around 1041 and 983 meV originate from the Ge wetting layer. These can be assigned as NP and TO phonon lines by their energy difference. When the solar cells are annealed at 800 °C, almost no changes of peaks compared from the as grown samples. When annealing temperature was further increased to 900 °C, a blueshift of photon energy was observed. This suggests that deformation of Ge dots and alloying with the Si spacer occurred. Furthermore, pronounced blueshift of photon energies can be seen after annealing at 1020 °C. This implies that disappearance of Ge dots probably occurs and they possibly transform to inhomogeneous SiGe quantum well.

Finally, the spectroscopic response of the solar cells close to 1.45 μm should be commented. This response corresponds to the PL lines of Ge dots whose energy range is between 800 and 900 meV. Thus, this is a manifestation that Ge dots indeed contribute to the enhancement of EQE. Decrease of EQE can be observed after annealing (Fig. 4). The possible reason for this decrease might be the interdiffusion of Ge dots with the Si spacer after annealing as shown in the blueshift of photon energies (Fig. 5). Consequently, alloying takes place and band gap increases, leading to the decrease in spectroscopic response. On the other hand, after annealing at 1020 °C, possible transformation of Ge dots to inhomogeneous SiGe quantum well takes place as indicated in Fig. 5. This pronounced blueshift of PL peaks is consistent with the decrease of EQE close to 1.2 μm only (Fig. 4). This strongly indicates that the presence of Ge dots in the space charge region significantly improve the EQE of the solar cells. Deformation and alloying complexities can be avoided if the formation of $p-n$ junction is carried out at lower annealing temperature. As a result, an increase in spectral response at further longer wavelengths is expected.

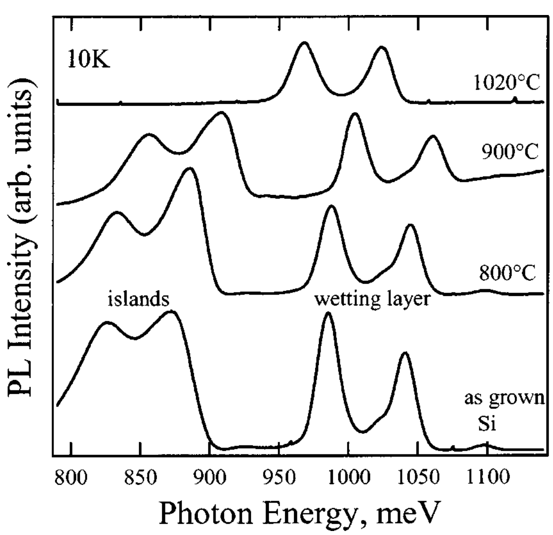

FIG. 5. 10 K PL spectra of 100 layers of self-assembled Ge dots with 8 ML coverage grown at 700 °C showing the blueshift of photon energies after annealing at different temperatures.

In summary, we reported the enhanced EQE of solar cells in the infrared region with self-assembled Ge dots stacked in multilayer structure. It was revealed that electron-hole pairs generated in Ge dots can be efficiently separated by the internal electric field, and can contribute to the photocurrent without considerable recombination in Ge dots or at Ge/Si interfaces.

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[1] J. Tersoff, C. Teichert, and M. G. Lagally, Phys. Rev. Lett. **76**, 1675 (1996).
[2] N. Usami, M. Miura, Y. Ito, and Y. Shiraki, Appl. Phys. Lett. **77**, 217 (2000), and references therein.
[3] N. Usami, Y. Araki, M. Miura, Y. Ito, and Y. Shiraki, Appl. Phys. Lett. **76**, 3723 (2000), and references therein.
[4] H. Presting, Thin Solid Films **321**, 186 (1998).
[5] S. Tong, J. L. Liu, J. Wang, and K. L. Wang, Appl. Phys. Lett. **80**, 1189 (2002).
[6] C. Miesner, K. Brunner, and G. Abstreiter, Infrared Phys. Technol. **42**, 461–465 (2001).
[7] K. W. J. Barnham and G. Duggan, J. Appl. Phys. **67**, 3490 (1990).
[8] A. V. Aroutiounian, S. Petrosyan, A. Khachatryan, and K. Touryan, J. Appl. Phys. **89**, 2268 (2001).
[9] A. A. Darhuber, V. Holy, J. Stangl, G. Bauer, A. Krost, F. Heinrichsdorff, M. Grundmann, D. Bimberg, V. M. Ustinov, P. S. Kop'ev, A. O. Kosogov, and P. Werner, Appl. Phys. Lett. **70**, 955 (1997).
[10] G. S. Solomon, J. A. Trezza, A. F. Marshall, and J. S. Harris, Jr., Phys. Rev. Lett. **76**, 952 (1996).
[11] J. Konle, H. Presting, H. Kibbel, and F. Banhart, Mater. Sci. Eng., B **89**, 160 (2002).
[12] K. Nakajima, N. Usami, K. Fujiwara, Y. Murakami, T. Ujihara, G. Sazaki, and T. Shishido, Sol. Energy Mater. Sol. Cells **73**, 305 (2002).
[13] K. Nakajima, N. Usami, K. Fujiwara, Y. Murakami, T. Ujihara, G. Sazaki, and T. Shishido, Sol. Energy Mater. Sol. Cells **72**, 93 (2002).
[14] M. Isomura, K. Nakahata, M. Shima, S. Taira, K. Wakisaka, M. Tanaka, and S. Kiyama, Sol. Energy Mater. Sol. Cells **74**, 519 (2002).
[15] G. Medeiros-Ribeiro, A. M. Bratovski, T. I. Kamins, D. A. A. Ohlberg, and R. S. Williams, Science **279**, 353 (1998).
[16] M. Gorykk, L. Vescan, and H. Lüth, Thin Solid Films **336**, 244 (1998).
[17] O. G. Schmidt and K. Eberl, Phys. Rev. B **61**, 13721 (2000).