Stacked Ge islands for photovoltaic applications

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Abstract

Stacked Ge islands formed via the Stranski–Krastanov growth mode were incorporated into the intrinsic layer of Si-based pin diode to improve the performance of the solar cells in the near-infrared regime. The onset of the external quantum efficiency was extended up to around 1.4 µm for the solar cells with stacked Ge islands. The quantum efficiency was found to increase with increasing number of stacking, and the onset of the photocurrent response was in good agreement with room-temperature photoluminescence energy of the Ge islands. These results manifest that the Ge islands did play a role to increase the quantum efficiency. Furthermore, a part of electron-hole pairs generated within Ge islands was separated by the internal electric field and contribute to the photocurrent.

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1. Introduction

Self-assembled Ge islands on Si have been intensively investigated during recent years for future electronic and optical applications based on Si technology [1–5]. The island is known to be spontaneously formed during epitaxial growth of Ge on Si via the Stranski–Krastanov (SK) growth mode. The SK growth mode is driven by the minimization of free energy where the increased surface energy due to the island formation is overcompensated by the gain of the strain energy. Since the islands can be formed without introducing misfit dislocations and complicated lithography techniques, the SK growth mode is regarded as a promising route towards the fabrication of nanoscale islands, which might act as quantum dots (QDs). The most possible electronic applications of QDs include quantum cellular automata [6] and single electron transistors require precise control of the size and the position of QDs. Notwithstanding several approaches such as growth on patterned substrates [7–15] have been carried out to accomplish the requirement, it still remains a critical issue. On the other hand, there are several applications of Ge islands where the control of the size and the position as well as the occurrence of the quantum size effect are not critical. For example, light detection in the near-infrared regime utilizing narrower bandgap compared with that of Si. This is a promising technique since the bandgap can be tuned between 1.3 and 1.55 µm, which is important for optical communication. In this particular application, Ge islands are more advantageous than Ge thin film with equivalent volume in terms of the crystal quality. Especially, the total volume of Ge is important for light absorption and this can be increased by stacking Ge islands without introducing misfit dislocations. In fact, normal incident response of Si-based pin diodes with Ge islands [16] and enhancement of response in heterojunction phototransistors with Ge islands [17] have been successfully demonstrated. Another possible application is to incorporate Ge islands into Si-based solar cells for more efficient light absorption. Although an attempt has been already done by Konle and his coworkers [18], nevertheless improved performance of the solar cells with Ge islands has not been clearly observed. In fact, only quantized states near the Si-valence band edge contributed to the photocurrent, and the ground states in the Ge islands did not play a role in increasing the current owing to fast recombination. As a result, small increase of the short-circuit current in the solar...
cells with Ge islands was compensated by the decrease of the open-circuit voltage, and the overall efficiency was not improved but instead it was reduced.

In this paper, we report on photovoltaic application of Ge islands for an improved performance of quantum efficiency in the near-infrared regime. Vertically stacked Ge islands with 50–150 repetitions grown by gas-source molecular beam epitaxy (MBE) were inserted into the intrinsic region of Si pin diode. Furthermore, photoluminescence (PL) measurement confirmed that the extended response of quantum efficiency originates from the ground states of Ge islands.

2. Experiments

The basic sample structure contains stacked Ge islands in the intrinsic region sandwiched by n-Si layer and p-Si substrate as illustrated in Fig. 1. Epitaxial growth was carried out using a gas-source MBE system (AirWater VCE S2020). The source materials for Si and Ge were chosen as disilane and germane, respectively. The starting material was boron-doped p-type Si(100) substrate with 3-inch diameter and resistivity of 1–10 $\Omega$ cm. A standard chemical treatment with a final process of hydrogen termination by diluted HF was done before the substrate was loaded into the growth chamber. After thermal treatment at 820 $^\circ$C to obtain a clean surface, the solar cell structure was grown at 700 $^\circ$C in the following sequence: a 100 nm-thick Si buffer layer was first grown, and subsequently 8 monolayers (ML) of Ge and 39 nm-thick Si spacer layers were grown. The Ge coverage of 8 ML was chosen to be larger than the critical coverage of 3.7 ML in the growth mode changeover from Frank-van der Merwe to the SK mode [3]. Therefore, Ge islands are expected to be formed with leaving wetting layer. The spacer width of 39 nm was chosen to allow the stacking of Ge islands through the strain field of buried islands but not to drastically change the growth mode [19,20]. The unit of Ge islands and the Si spacer was repeated 50–150 times followed by a 600 nm-thick Si cap layer. After MBE growth, the cap layer was converted to n-type by thermal diffusion of P from a spin-coated diffusion source. The solar cells were completed by evaporating Al back contact and Ag front fingers to characterize device performance. It is noted that antireflection coating, surface texturing, and back surface field were not employed in this study.

External quantum efficiency of the solar cells was measured using monochromatic light with a fixed photon number of $1 \times 10^{14}$/cm$^2$. The photocurrent without external bias was measured with a computer interfaced Keithley digital multimeter and converted to the external quantum efficiency. PL measurements were carried out using a standard lock-in technique with a liquid-nitrogen-cooled Ge photodetector (North Coast EO-817L). The samples were mounted on a cold finger of a closed-cycle cryostat. The 532 nm line of a second harmonics of Nd:YAG laser was used as an excitation source. Atomic force microscopy (AFM) was carried out to observe the surface morphology of uncapped samples.

3. Results and discussions

Fig. 2 shows low-temperature PL spectra taken at 20–40 K from as-grown sample with 100 times stacked Ge islands. At lower energies of the Si-related peak at around 1100 meV, several additional lines can be seen. These peaks are assigned as no-phonon (NP) and transverse optical (TO) phonon lines from the wetting layer and PL from the Ge islands (L). From this spectral feature, it can be confirmed that Ge islands were grown with leaving wetting layer, that is, the SK growth mode took place. This was further confirmed by AFM as shown in Fig. 3, which displays a 5 $\times$ 5 $\mu$m image of uncapped 8 ML-Ge grown on Si. As is well known, the bimodal islands of domes and pyramids are clearly observed. The density of the islands is in the order of $10^{10}$/cm$^2$. With increasing temperature, it is seen that PL from the wetting layer drastically decreases. On the other hand, PL from the Ge islands remains almost unchanged but the intensity slightly increases with...
increasing temperature. These results show that thermal escape of excitons from the wetting layer occurred, and they were captured by the Ge islands and radiatively recombined there. Therefore, the Ge islands were confirmed to effectively confine excitons and their crystal quality is good enough to give PL without considerable loss by nonradiative recombinations. However, in terms of photovoltaic applications, not only nonradiative but also radiative recombinations of photogenerated electron-hole pairs must be avoided otherwise they cannot contribute to the photocurrent. Therefore, we inserted stacked Ge islands in the intrinsic layer of pin diode to enhance the separation of electron-hole pairs with the aid of built-in electric field.

Fig. 4 compares external quantum efficiency of the solar cells with stacked Ge islands with different number of repetitions. As a reference, the quantum efficiency of control sample without Ge islands is also displayed. Enhanced quantum efficiency is clearly observed for the solar cells with stacked Ge islands, and the efficiency increases with increasing number of stacking. Room-temperature PL spectrum of as-grown stacked Ge islands, and the external quantum efficiency of the solar cell are compared in Fig. 5. The onset of the photocurrent response of the solar cell is seen to be in good agreement with broad PL line from the Ge islands. These results manifest that the improvement of the quantum efficiency in the near-infrared regime was undoubtedly contributed by the presence of the Ge islands. It is considered that a part of electron-hole pairs generated within the Ge islands was separated by the internal electric field, and contributed to the current without recombination within Ge islands or at Ge/Si interfaces. Owing to the narrower bandgap of Ge compared with that of Si, the response is expected to extend in the longer wavelengths. The agreement with PL and the onset of the photo response suggests that not only the excited states but also the ground states will contribute to the current. This phenomena was not observed in the previous experiments [18].

Fig. 6 illustrates two possible transport mechanisms of carriers generated in Ge islands through vertical stacking. The schematic was drawn for the valence band owing to much larger band discontinuity compared with the conduction band in Ge/Si system. One possibility is
a sequential transport including thermal escape from an island to the Si spacer, diffusion toward neighboring islands and recapture. Another possibility is wire-like transport of carriers within Ge islands through electronic coupling owing to the thin spacer width. In order to increase the current by minimizing the recombination within Ge islands, the latter mechanism is preferable. However, it is not clear which mechanism is dominant. To clarify this, more experiments are obviously necessary to systematically change the structural parameters. Especially, the amount of electronic coupling is considered to be tuned by Si spacer width and/or the strength of the internal electric field. Another strategy is to utilize SiGe alloy for the spacer layer to facilitate the carrier escape from the islands.

Finally, it should be remarked that the absolute value of the external quantum efficiency of the present device in the near infrared regime is less than 2%, and more improvement is required to realize large short-circuit current to overcompensate the reduction of the open-circuit voltage. Possible reasons for the small external quantum efficiency would be the recombination of electron-hole pairs and/or insufficient absorption of the incoming light. The former would be avoided by controlling the structural parameters as mentioned already. The latter would be improved by further increase of the number of stacking and incorporation of the advanced processing such as surface texturing for efficient light trapping. However, high-temperature process that can deform the Ge islands must be avoided since this results in the increase of the effective bandgap and the photo response in the near infrared regime will be lost [21].

4. Summary

In summary, we tried to utilize stacked Ge islands formed via the SK growth mode to improve the performance of the Si-based solar cell in the near-infrared regime, and demonstrated the appearance of external quantum efficiency up to around 1.4 μm. With increasing number of stacking, the quantum efficiency was found to systematically increase. In addition, the onset of the photocurrent response was in good agreement with PL energy of the Ge islands. From these results, the Ge islands are concluded to contribute to the increase of the quantum efficiency in the near-infrared regime. Strategies for further improvements of the solar cell performance are also discussed.

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