Control of geometry in Si-based photonic nanostructures formed by maskless wet etching process and its impact on optical properties

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We demonstrate that maskless wet etching of self-assembled Ge quantum dot (QD) multilayers can create large-area photonic nanostructures, and the geometry can be tuned by changing wet etching conditions. It is found that the reflectance in the near-infrared wavelength can be decreased by controlling geometry, and an increase in the depth of the photonic nanostructures results in enhancement of photoluminescence intensity from Ge QDs. These results show that control of geometry in photonic nanostructures is useful for enhancement of optical absorption in the Ge QD multilayers.

1. Introduction

It is well recognized that quantum dot (QD) has become one of the essential technologies due to their unique properties such as control of photon energy based on quantum size effect, formation of intermediate band, longer carrier relaxation time compared with bulk material, and so on [1-3]. Among a variety of QD materials, self-assembled Ge QDs sandwiched between Si spacer layers are extensively studied in order to improve optical properties [4-6]. It is reported that introduction of Ge QDs in solar cells enhances optical absorption of incident photons in near-infrared wavelength and electron-hole pairs generated in Ge QDs brings an increase in photocurrent [7]. We recently reported that carrier extraction from Ge QDs increases superlinearly with an increase in excitation intensity under strong photoexcitation [8]. Therefore, the combination of Ge QDs with photonic nanostructures is expected to improve the solar cell properties by efficient trap of incident photons into a solar cell structure [9-12]. However, in the case of QD solar cells, textured substrates cannot be employed as a template to grow self-assembled Ge QD multilayers in order to maximize utilization of incident photons because crystal quality in Ge QD multilayers will be degraded by growing on tilted surfaces. In recent work, we developed a technology to fabricate photonic nanostructures coupled with self-assembled Ge QDs multilayers based on

simple maskless wet etching, and demonstrated that a solar cell with the photonic nanostructure coupled with Ge QD multilayers has a high potential for enhancement of conversion efficiency [13,14]. It should be therefore critical to enhance optical absorption in Ge QDs based on control of geometry in the photonic nanostructures for realization of highly efficient solar cells.

In this study, we demonstrate that geometry of photonic nanostructures can be tuned by changing the wet etching process. Furthermore, we investigate the effect of geometry in the photonic nanostructures on optical properties. These results show that wet etching conditions and structural parameters in Ge QD multilayers are very crucial to control optical properties of the photonic nanostructures formed by maskless wet etching.

2. Sample fabrication process

50 layers of Ge QDs with Si spacer layers were grown on Si (100) substrates by gas source molecular beam epitaxy system (AirWater VCE S2020) using disilane (Si_2H_6) and germane (GeH_4) as source gases at 700 °C. The flow rates of Si_2H_6 and GeH_4 were fixed at 4.0 and 2.5 sccm, respectively, and source gases were alternatively introduced to the growth chamber. A 10 sec growth interruption was employed at the heterointerface in order to prevent intermixing of residual gases. The Ge QD layers with

coverage of 8 monolayers were grown via the Stranski-Krastanov growth mode. They were separated by Si spacer layers with a constant nominal thickness, and the topmost Ge QD layer was covered with a Si capping layer of the same thickness as spacer layers. A series of samples with 5-nm and 20-nm-thick Si spacer layer were prepared. Subsequently, the Ge QDs multilayers were chemically etched in a HF/HNO₃ (HF:HNO₃=1:100) or a 4 mol/liter KOH solution without any mask patterns. By the wet etching, photonic nanostructures are formed around the vicinity of surface in the Ge QD multilayers since preferential wet etching occurs owing to modulation of internal stress and material composition. The shape of the photonic nanostructures was observed by transmission electron microscope (TEM; JEM-ARM200F; JEOL Ltd. Japan) operated at 200 kV and scanning electron microscope (SEM; JEOL JSM-7001FA) and the depth in the photonic nanostructures was estimated from cross-sectional profile by atomic force microscope (Digital Instruments Nano-scope IIIa). TEM samples were prepared using an ion milling method: mechanical grinding and polishing (MA-200e, Musashino denshi, Japan), dimple grinding and polishing (dimple grinder model 659; Gatan Inc., U.S.A.), and low-energy Ar ion milling under the conditions of 50.2 kV (PIPS model 691; Gatan Inc., U.S.A.). For Photoluminescence (PL) measurements, wavelength-tunable picosecond laser pulses, obtained from an optical parametric

oscillator system based on a Ti:sapphire laser, were used as the excitation source. The excitation wavelength was set at 1200 nm.

3. Results and discussion

3.1. Control of geometry in photonic nanostructures

Figure 1(a) shows plan-view SEM image for Ge QD multilayers consisting of 10-nm-thick Si spacer layer. For the sample before wet etching, the Ge QDs with various lateral sizes less than 150 nm and densities of $2.6 \times 10^9 \text{ cm}^{-2}$ are randomly distributed. The cross-sectional TEM image for the sample after etching with HF/HNO₃ solution for 30 sec is shown in Fig. 1(b). Ge QDs are clearly seen as white regions along vertical direction due to QD formation by self-alignment. In addition, the dips of the dimple shape are seen around the surface region due to preferential wet etching around stacked Ge QD areas. Plan-view SEM images of the samples formed by HF/HNO₃ and KOH etching are shown in Fig. 1(c) and 1(d). For both the samples, the sizes and densities of the surface dips and the pillars are almost the same as those of Ge QDs before wet etching in Fig. 1(a). For Ge QD multilayers, internal stress accumulated in the Si spacer layer is modulated since the stress is locally induced in the Si spacer layer just above the Ge QDs because of lattice mismatch between Si and Ge. In addition,

materials composition is also periodically modulated since Ge composition of stacked Ge QD areas is larger than that of the surrounding area. The modulated strain and materials composition lead to a modulated wet etching rate. Therefore, in case of HF/HNO₃ etchant surface dips are formed due to larger wet etching rate of Ge QDs and strained Si while in case of KOH etchant Ge QD pillars are created owing to lower etching rate of Ge QDs. These results clearly manifest that photonic nanostructures are formed by preferential wet etching, and moreover, their geometry can be tuned by changing an etchant.

In order to control geometry in photonic nanostructures, we investigate the dependence of wet etching time on the depth of photonic nanostructures. Figure 2 shows the depth plotted as a function of wet etching time for samples with 5-nm and 20-nm-thick Si spacer layers etched with (a) HF/HNO₃ and (b) KOH solution. For all the samples, we can find the relatively large dispersion for the depth of photonic nanostructures. As is mentioned above, photonic nanostructures are created by preferential wet etching of the stacked Ge QD areas or the surrounding areas of Ge QDs. It is therefore thought that the dispersion is brought by fluctuation of the sizes for the as-grown Ge QDs. This means that improvement of the uniformity of the diameter and height in Ge QDs may result in reduction of the dispersion. In both cases, the depth of

photonic nanostructures firstly increases by increasing wet etching time, and the further increase of etching time results in decrease of the depth. In the case of HF/HNO₃ etching, the reduction of the depth is caused by disappearance of Ge QD multilayers as confirmed by energy dispersive x-ray spectroscopy. On the other hand, in the case of KOH etching at long wet etching time, we found that the top region of the Ge QD pillars is tilted as indicated by white arrows in the inset of Fig. 2(b). Therefore, we can say that the reduction of the depth in photonic nanostructures is related with lift-off of Ge QDs based on side-etching of Si spacer layers just below the Ge QDs. When the Si spacer thickness is decreased, the depth is seen to increase for both samples etched with HF/HNO₃ and KOH. This is provided by larger modulation of the strain and materials composition [15]. These results imply that there is an optimal condition of wet etching and structural parameters in Ge QD multilayers for formation of the photonic nanostructures with larger depth.

3.2. Optical properties of photonic nanostructures

Figure 3(a) shows reflectance spectra for Ge QD multilayers with 5-nm-thick Si spacer layers before wet etching and photonic nanostructures with the similar depth around 100 nm formed by HF/HNO₃ etching for 10 sec and KOH etching for 12 min.

An abrupt increase in the reflectance around 1000-1200 nm region is clearly seen for all the samples due to the light reflection from the backside surface based on the onset of the optical transparency [16]. By photonic nanostructure formation, the reflectance is seen to reduce in the entire wavelength for both HF/HNO₃ and KOH etching. This result indicates that the amount of incident photons incorporated into the Ge QD multilayers is increased. Also, we can clearly see the difference for reduction of the reflectance in these spectra. For the sample etched with HF/HNO₃ solution the reflectance uniformly decreases in the wavelength from 300 nm to 1600 nm while for the sample etched with KOH solution, the reflectance is largely reduced in the visible wavelength. In the case of HF/HNO₃ etching, the stacked Ge QDs are preferentially etched as is seen in Fig. 1(c). On the other hand, the etching rate of Si is faster in the case of KOH etching. Therefore, the amount of Si around the surface is larger for the sample etched by HF/HNO₃, leading to the larger change of effective refractive index around the surface compared with the sample etched by KOH. This would explain the smaller reflectance in the visible wavelength for the sample etched by KOH based on different geometry in the photonic nanostructures [17]. This result implies that formation of photonic nanostructures by KOH etching contributes to reduction of the reflectance in visible wavelength effectively. Figures 3(b) and 3(c) show the reflectance at the wavelength of

1300 nm plotted as a function of wet etching time for samples etched with HF/HNO₃ and KOH solution, respectively. In both cases, the reflectance is firstly decreased by increasing wet etching time, and the change of reflectance becomes small at longer wet etching time. This tendency corresponds to the dependence of wet etching time on depth of photonic nanostructures as seen in Figs. 2. This manifests that the amount of reflectance is related to the depth of photonic nanostructures. In near-infrared wavelength, the reflectance of the sample etched with HF/HNO₃ is smaller than that of the sample etched with KOH due to the larger depth formed by the HF/HNO₃ etching as seen in Fig. 2(a). These results indicate that the photonic nanostructure formation by HF/HNO₃ etching is effective for reduction of reflectance in the near-infrared wavelength.

To verify enhancement of optical absorption in Ge QD multilayers in near-infrared wavelength based on photonic nanostructure formation, we investigated PL intensities at a temperature of 10 K by using excitation source of 1200 nm wavelength. Figure 4 shows the PL intensities at a 1600 nm wavelength, which corresponds to radiative recombination in Ge QDs, plotted as a function of wet etching time for samples etched with HF/HNO₃. An increase in the PL intensities can be clearly seen by increasing wet etching time. It is well known that the photonic nanostructure formation results in

extension of optical pass length in the Ge QD multilayers owing to surface scattering of incident photons. It is therefore thought that radiative recombination is enhanced due to an increase in optical absorption in the Ge QD multilayers by light trapping and an increase in depth of photonic nanostructures brings improvement of the effect. On the other hand, the PL intensity does not increase monotonically with increasing wet etching time. This is attributed to reduction of Ge volume by wet etching of the Ge QD multilayers presumably. These results imply that condition of wet etching and structural parameters in Ge QD multilayers should be optimized for significant enhancement of optical absorption. We can conclude that the cost-effective formation of photonic nanostructures fabricated by simple maskless wet etching is considered to be a promising tool to realize large-area optical devices with an advantage of light trapping, which could be utilized for mass production of quantum dot solar cells.

4. Summary

We demonstrated that geometry in photonic nanostructures formed by simple maskless wet etching could be tuned by changing etchant and controlling structural parameters in Ge QD multilayers. For both samples etched with HF/HNO₃ and KOH solution the depth of photonic nanostructures increased with increasing wet etching time

owing to preferential wet etching. However, at longer wet etching time, in the case of KOH etchant reduction of the depth was observed due to lift-off of Ge QDs while in the case of HF/HNO₃ etchant the depth dropped because of disappearance of stacked Ge QDs areas. Moreover, we found that geometry in photonic nanostructures influenced the reflectance significantly. For photonic nanostructures formed with HF/HNO₃ etching, PL intensity at the 1600 nm wavelength, which corresponds to radiative recombination in Ge QDs, was enhanced by increasing depth of photonic nanostructures. This means that optical absorption in Ge QD multilayers is strongly related to geometry in photonic nanostructures. We can therefore conclude that maskless wet etching of self-assembled Ge QD multilayers is effective for mass production of solar cells with photonic nanostructures coupled with QDs owing to anti-reflection properties, large-area fabrication process and low fabrication cost.

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Figure captions

Figure 1

(a) Cross-sectional TEM image and (b) Plane-view SEM images for Ge QDs multilayers with 10-nm-thick Si spacer layers. The geometry in photonic nanostructures is changed by (c) HF/HNO₃ etching for 30 sec and (d) KOH etching for 7min, respectively.

Figure 2

The depth of photonic nanostructures plotted as a function of wet etching time with (a) HF/HNO₃ and (b) KOH etchant. The circular and triangular symbols represent the depth of the photonic nanostructures obtained from samples with 5-nm and 20-nm-thick Si spacer layers, respectively. The inset of Fig. 2(b) shows a cross-sectional SEM image for a photonic nanostructure obtained from Ge QD multilayers with 5-nm-thick Si spacer layers

Figure 3

(a) The reflectance spectra for Ge QDs multilayers and photonic nanostructures formed

by HF/HNO₃ etching for 10 sec and KOH etching for 12 min. The amount of reflectance at a wavelength of 1300 nm is plotted as a function of wet etching time for samples etched with (b) HF/HNO₃ and (c) KOH solution.

Figure 4

Dependence of wet etching time with HF/HNO₃ etchant on PL intensity at a 1600 nm wavelength, which corresponds to radiative recombination in Ge QDs.

Figure 1

Figures 2

Figures 3

Figure 4