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

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ABSTRACT

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 bring 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 QD 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 s 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 QD multilayers were chemically etched in a HF/HNO_3 ($HF:HNO_3 = 1:100$) or a 4 mol/l 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

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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

Fig. 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 2.6×10^9 cm^{-2} are randomly distributed. The cross-sectional TEM image for the sample after etching with HF/HNO_3 solution for 30 s 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/HNO_3 and KOH etching are shown in Fig. 1(c) and (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, material 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 material composition lead to a modulated wet etching rate. Therefore, in case of HF/HNO_3 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. Fig. 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/HNO_3 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/HNO_3 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/HNO_3 and KOH. This is provided by larger modulation of the strain and material 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.

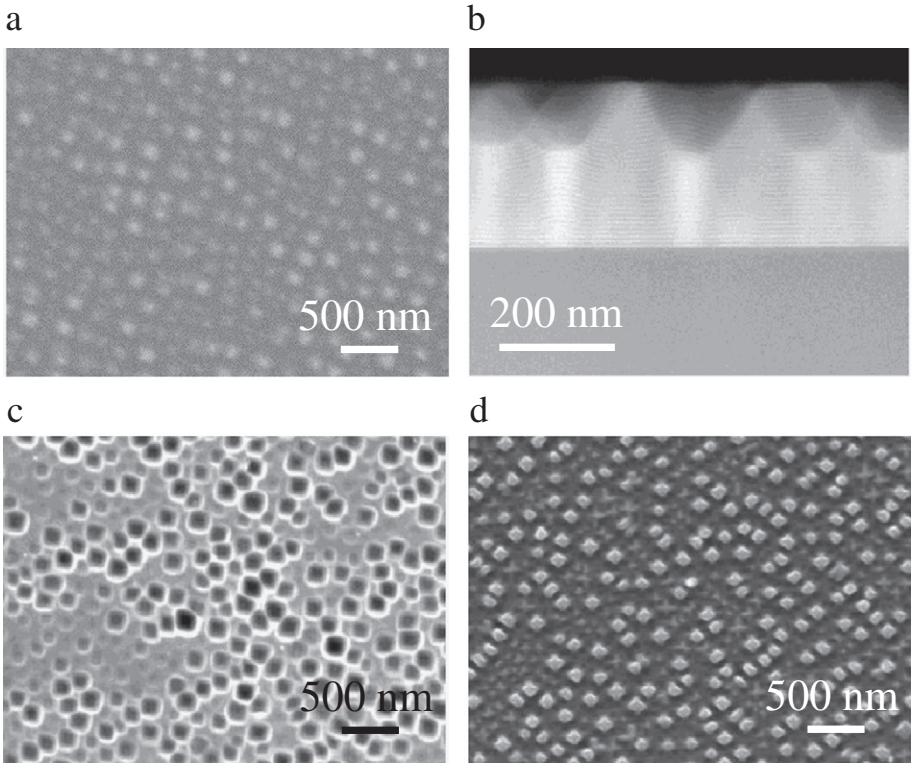

Fig. 1. (a) Cross-sectional TEM image and (b) Plane-view SEM images for Ge QD multilayers with 10-nm-thick Si spacer layers. The geometry in photonic nanostructures is changed by (c) HF/HNO_3 etching for 30 s and (d) KOH etching for 7 min, respectively.