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MBE-grown $Ge_{1-x}C_x$ nanocrystals by using a novel bio-nanoprocess due to protein "ferritin"

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1. Introduction

The research for Si-based optoelectronic devices has been an important subject, especially for such an application to Si-based optoelectronic IC (OEIC) or Si photonics. As for the Si-based optoelectronic materials, Si nanocrystals, β-$FeSi_2$, SiGe superlattices and $Ge_{1-x}C_x$ epilayers are known. We have studied on $Ge_{1-x}C_x$ epilayers, which with a C content of 4%<x<11% are considered likely to have a direct-transition-type band structure [1] and little lattice mismatch with a Si substrate [2]. Until now, $Ge_{1-x}C_x$ of x=3% was realized using an arc-plasma gun as a new C source. However, the remarkable bandboring occurs [3]. In this work, a development of high-density and very small diameter (< ϕ 10 nm) $Ge_{1-x}C_x$ nanocrystals on a Si(100) substrate is carried out by using a novel bio-nanoprocess and a solid source MBE technique. As a final object, $Ge_{1-x}C_x$ nanocrystals with a direct-transition-type band and/or a quantum confinement effect are aiming to realize new strongly light-emitting devices.

2. Experiments

Fig. 1 shows a schematic of bio-nanoprocess with self-arranged ferritins and subsequent MBE growth process of $Ge_{1-x}C_x$ nanocrystals using a Si thin film nanomask.

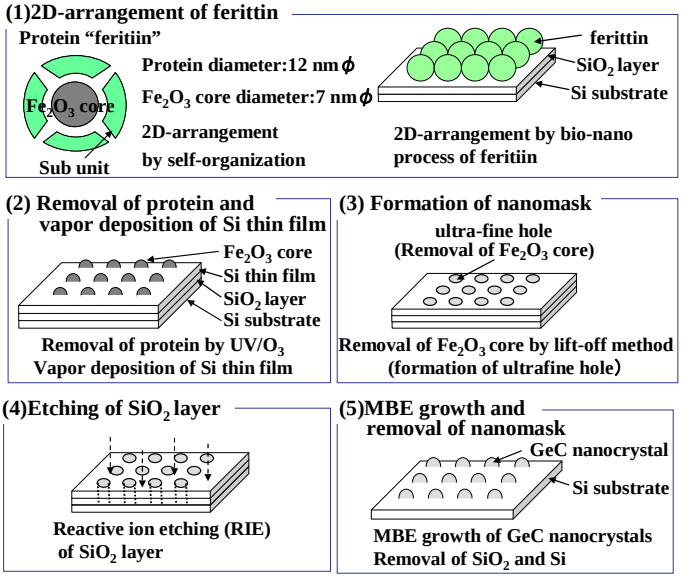

Fig.1 Schematic of process flow of fabricating $Ge_{1-x}C_x$ nanocrystals using bio-nanoprocess and MBE growth technique

An n-type Si(100) wafer with a thermally grown SiO_2 layer (thickness 10 nm) was used as the substrate. The substrate was cleaned using an UV dry cleaner (Fig. 1(1)). 2-D arrangement of ferritins was fabricated on the surface of substrate by the so-called bio-nanoprocess. The ferritins have a diameter of 12 nm, and their inside iron-oxide (Fe_2O_3) core of a diameter of 7 nm. The detail of bio-nanoprocess was reported elsewhere [4]. Then, the proteins were removed at 300℃, for 10 min in the IR furnace (O_2 flow-rate 1 l/min and programming rate 5℃/ min).

The sample was conveyed by molecular beam epitaxial growth chamber (2-chamber MBE:Eiko EV-100), and then a 2 nm-thick Si ultra-thin film was deposited on the substrate at 28℃ in a vacuum ($1x10^{-9}$ Torr) by using an electron-beam evaporating cell(Fig. 1(2)). The sample was taken out of the chamber, and the Fe_2O_3 cores were removed by dipping in hydrochloric acid at room temperature for 30 minutes (Fig. 1(3)). As the result of this process, the Si nanomask with the ultra-fine holes 7 nm in diameter was fabricated. Through this nanomask, the 10 nm-thick SiO_2 layer on the Si substrate was etched away for 2 sec by reactive ion etching (RIE) using etching gas CF_4 (20 sccm) + H_2 (10 sccm) at a pressure of 1 Pa under the conditions of ICP electric power 125W, bias power 10W (Fig. 1(4)). The sample was again conveyed into the same MBE growth chamber, where the natural SiO_2 film was removed at 900℃ for 30 min in a vacuum ($1x10^{-9}$ Torr). All $Ge_{1-x}C_x$ compound layers were grown at a substrate temperature T_s of 500℃ in a vacuum ($5x10^{-9}$ Torr) by supplying Ge flux from a K-cell and pulsed C molecular beam from a vacuum-type arc-plasma gun (ULVAC APG-1000) as described in detail elsewhere [3]. The substitutional C composition x of $Ge_{1-x}C_x$ epilayer was controlled by the supplied amount of C. Without the nanomask, $Ge_{1-x}C_x$ nanocrystals due to the S-K mode were formed at random to have diameters of 10 to 20 nm. With the nanomask, a 1nm thick C film was first deposited at *Ts*=500℃ and $5x10^{-9}$ Torr, and subsequently a 3 nm thick $Ge_{1-x}C_x$ epilayer with x=1.5% was grown under the same conditions. The sample taken out of the chamber was dipped in hydrofluoric acid at room temperature for 30 min to remove the SiO_2 layer and to lift-off the Si nanomask and $Ge_{1-x}C_x$ film. As a result, the $Ge_{1-x}C_x$ nanocrystals of high density and uniform size were fabricated (Fig. 1(5)).

Photoluminescence (PL) spectra were measured by Ar^+ laser (wavelength 488 nm and laser power 2.5 kW/cm^2). The samples were cooled down in a cryostat and their PL spectra were detected by a liquid-nitrogen cooled Ge pho-

todiode through a monochromator in the standard lock-in technique.

3. Results

Fig. 2 shows the SEM image of a high-density ferritin-arrangement adsorbed on a Si substrate. Each of the observed spherical dots is a Fe_2O_3 core inside a ferritin. After removing the proteins in the IR furnace, it is obvious by SEM observation that neither condensation nor deformation of Fe_2O_3 cores takes place. The core diameter is 7 nm and the density is $5x10^{11}$ cm^{-2}. Removing the proteins was verified by XPS, consequently the N_{1s} peak of proteins cannot be detected below the XPS sensitivity.

Fig.3 shows the SEM image of Si nanomask with nano-size (diameter:7 nm) and high-density holes. Every dark spot corresponds to an ultra-fine hole. The hole diameter is 7 to 20 nm, and large-diameter holes are observed at places, because the lift-off process is not optimized yet.

Through the Si nanomask, the $Ge_{1-x}C_x$ compound was grown by MBE and then the Si nanomask and the SiO_2 layer were removed by the hydrofluoric acid to form the $Ge_{1-x}C_x$ nanocrystals. Fig. 4 and Fig.5 show the XRD profile and the SEM image of the sample, respectively. The $Ge_{1-x}C_x$ (004) peak of XRD was observed as shown in Fig. 4, as compared with that of a 110 nm thick $Ge_{1-x}C_x$ epilayer. This result made clear that the $Ge_{1-x}C_x$ nanocrystals grew epitaxially on the Si(100) substrate. From this peak position, the substitutional C composition x is calculated to be x=1.5% according to Vegard's law. From Fig.5, the average diameter and density of $Ge_{1-x}C_x$ nanocrystals are 8 ± 4 nm and $1x10^{11}$ cm^{-2}, respectively.

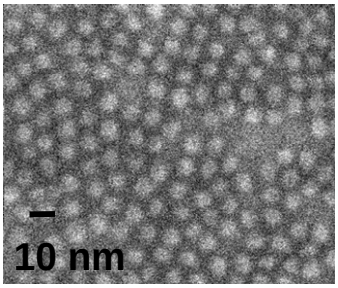

Fig.2 SEM image of ferritin arrangement adsorbed on Si(100) substrate

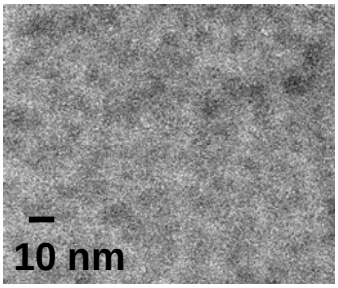

Fig.3 SEM image of Si nanomask with nano-size holes

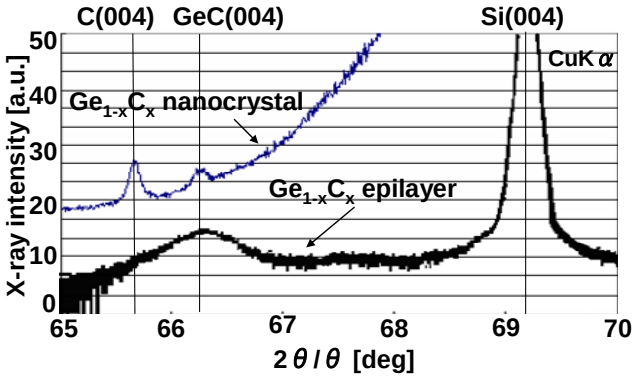

Fig.4 XRD profile of $Ge_{1-x}C_x$ nanocrystals

Fig.6 shows the PL spectrum of the $Ge_{1-x}C_x$ nanocrystals capped by a 100 nm-thick Si MBE film (550℃,20 min). The PL intensity is very weak, but the PL peak observed around 1300 nm is speculated to originate due to quantum confinement in $Ge_{1-x}C_x$ nanocrystals.

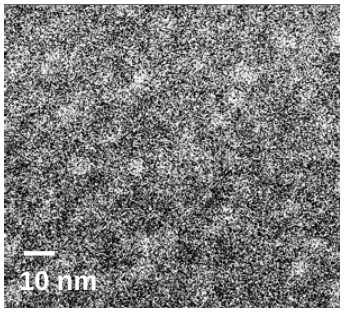

Fig.5 SEM image of $Ge_{1-x}C_x$ nanocrystals on Si(100)

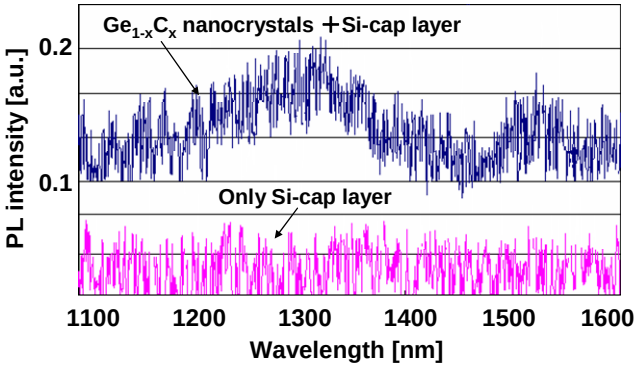

Fig.6 PL spectrum of $Ge_{1-x}C_x$ nanocrystals

4. Conclusion

High-density (≧$1x10^{11}$ cm^{-2}) and very small and uniform diameter (8±4 nm) $Ge_{1-x}C_x$ nanocrystals on a Si(100) substrate was developed by using a novel bio-nanoprocess (Si thin film nanomask) with self-assembled ferritins and a solid-source MBE growth technique with a new C source due to an arc-plasma gun. From the position of observed XRD peak of $Ge_{1-x}C_x$ (004), the substitutional C composition x is calculated to be x=1.5% by Vegard's low. From the $Ge_{1-x}C_x$ nanocrystals, the PL peak around 1300nm was observed. Hence, the uniform size $Ge_{1-x}C_x$ nanocrystals will be fabricated by optimizing process conditions, and the future-aim is to develop Si-based light emitting devices.

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