Fabrication of nanopores utilizing SiC/Si(001) heteroepitaxial growth on SOI substrates: Nanopore density control

Hafizal Yahaya\textsuperscript{a,b}, Yoshifumi Ikoma\textsuperscript{a}, Keiji Kuriyama\textsuperscript{a}, Teruaki Motooka\textsuperscript{c}
\textsuperscript{a}Dept. of Materials Science and Engineering, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan;
\textsuperscript{b}Dept. of Science, Universiti Teknologi Malaysia, International Campus, 54100 Jalan Semarak, Kuala Lumpur, Malaysia;
\textsuperscript{c}Kyushu University Cleanroom Laboratory Facility, 8-7 Yayoigaoka, Tosu, Saga 841-0005, Japan

ABSTRACT

We have investigated the nanopore formation utilizing SiC/Si (001) heteroepitaxial growth. Inverse pyramidal pits were produced by [111] faceted on the top of Si layer of Silicon on Insulator (001) substrate after SiC growth by using CH\textsubscript{3}SiH\textsubscript{3} pulse jet chemical vapor deposition. Randomly distributed nanopores with the size of \~{}10 nm were obtained after dipped into BHF solution for etching the buried oxide layer through the top of the pit. It was found that the densities of the pits and the nanopores strongly depend on the initial SiC nucleation density which can be controlled by the pulse frequency and number of CH\textsubscript{3}SiH\textsubscript{3} pulse jets.

Keywords: Nanopore, SOI, SIMOX, Supersonic jet CVD, SiC, Si, Heteroepitaxial growth, Pit formation.

1. INTRODUCTION

Nanopore DNA sequencing is one of the most promising technologies being developed as a cheap and fast alternative\textsuperscript{1}. Mainly there are two kind of nanopores are being fabricated. They are biomaterial where a-hemolysin, a transmembrane protein inserted in a lipid bilayer\textsuperscript{2} and solid-state domain such as silicon nitride\textsuperscript{3,4}, SiO\textsubscript{2}\textsuperscript{5}, multiwall carbon nanotube\textsuperscript{6} and aluminum oxide\textsuperscript{7}. For silicon nitride ion beam sculpting is used\textsuperscript{3,4} while high energy electron beam is for SiO\textsubscript{2}\textsuperscript{5}. However, these techniques are not suitable for mass production. Chemical vapor deposition (CVD) is widely used in the semiconductor industry to produce thin films. It is suitable for fabricating samples in mass production. We have previously developed a new CVD technique using pulsed supersonic free jets\textsuperscript{8}. Since this method makes it possible to control the film thickness by adjusting the pulse width and frequency\textsuperscript{9}, it is suitable for growing very thin SiC/Si multilayer structures\textsuperscript{10,13}. During the formation thin SiC, Si atoms are consumed from the Si substrate\textsuperscript{14}. The SiC/Si interface has been plagued with the concurrent formation of voids in the Si substrate. The voids or interfacial pits are randomly formed in hollow inverted pyramids surrounded by [111] facet lying just beneath the film\textsuperscript{14,15}. Recently, we reported that the nanopore can be obtained by using these [111] faceted pits in the top Si layer of Silicon on Insulator (SOI) substrates during the SiC/Si(100) heteroepitaxial growths utilizing CH\textsubscript{3}SiH\textsubscript{3} pulse jet CVD\textsuperscript{16}. In this paper, we further investigated the influence on CH\textsubscript{3}SiH\textsubscript{3} pulse jet numbers and frequencies of the nanopore formation.

2. EXPERIMENTAL PROCEDURES

We used Separation by IMplanted OXygen (SIMOX) (001) substrates with the top Si and buried oxide (BOX) layer of 180 nm and 100 nm, respectively as shown in Figure 1(a). They were cut into 25x25 mm\textsuperscript{2} pieces. Conventional RCA cleaning\textsuperscript{17} was carried out in order to remove metal and organic contamination on the substrate surface and then the substrates were introduced into the chamber immediately after being dipped in aqueous 5\% buffered HF (BHF) solution to remove the native oxide. The SiC growth on SIMOX (001) was carried out utilizing pulse jet CVD system which described elsewhere\textsuperscript{8}.

* hafizal@zaiko8.zaiko.kyushu-u.ac.jp; phone +81-92-802-2966; fax +81-92-802-2990;
Electronic grade CH₃SiH₃ was introduced into the CVD chamber by utilizing a Parker Hannifin Corporation General Valve with a nozzle diameter of 0.8 mm. The distance between the substrate and the valve was approximately 20 cm. During the SiC growth and pit formation [Figure 1(b)], the substrate temperature and the pulse CH₃SiH₃ pulse width were set at 900 °C and 100 μs, respectively. It should be noted that a pulse beam produced by the valve nozzle is 1.7 x 10¹⁷ molecules and the total number of molecules arriving on the substrate is estimated to be ~1.4 x 10¹⁴ molecules / cm². The pulse frequency and pulse number were changed at 1~10 Hz and 600~18000 pulses respectively. After the SiC growth, the nanopores were formed by dipping into BHF solution for 10 min in order to remove BOX layer under the {111} faceted pits [Figure 1(c)]. Then the films were characterized by using scanning electron microscopy (SEM).

### 3. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the SEM images of samples of as-grown and after being dipped into BHF solution, respectively. Square pits with the <011> oriented sides with the density of 2.1x10⁸ cm⁻² are homogeneously distributed over the surface as shown in Figure 2(a). On the other hand, pits with shadow of circular patterns are clearly observed after being dipped into BHF solution for 10 min [Figure 2(b)]. The circular patterns have ~1 μm in diameter and the density of 6 x10⁵ cm⁻². This is due to the BHF etching process where BOX layer was partly removed from the top of the pits to form an air gap. This air gap corresponds to circular patterns which are indicating the formation of nanopore.
In order to investigate the dependence of nanopore formation on CH$_3$SiH$_3$ pulse numbers, we carried out the SiC growths by introducing various pulse numbers at frequency of 5 Hz. Figure 3 shows the SEM image samples of as SiC growth [Figures 3(a), 3(c) and 3(e)] and after BHF dipped [Figures 3(b), 3(d) and 3(f)]. When the pulse number is increased from 6000 pulses to 18000, randomly distributed pits was formed with constant density at ~3x10$^8$ cm$^{-2}$ [Figure 3(a), 3(c) and 3(e)]. On the other hand, nanopore was formed with significantly increased in density from 0 to 4.2x10$^6$/cm$^2$ respectively on the Si surface after dipped into BHF solution [Figures 3(b), 3(d) and 3(f)]. The result can be explained through pit formation and SiC nucleation mechanism reported by Li et al.$^{14}$ Pits were named as voids or trenches and their formation strongly depends on the SiC nucleation density. When high pulse number is introduced into the sample surface, SiC nucleation exhibit significantly higher density on the top Si surface and the size of the produced pits becomes deep enough to reach the top of BOX layer. This result shows that the pit density remains constant, while the density of nanopore increases with increasing of pulse number.

Figure 3. SEM surface of pits (SiC growth) and nanopores (after BHF dipped) at frequency of 5 Hz with different pulse numbers. 6000 pulses for (a) and (b), 9000 pulses for (c) and (d), 18000 pulses for (e) and (f).

It should be noted that the influences of pulse frequency on nanopore formation can be investigated by the samples with pulse irradiation numbers at 18000 pulses for 10 Hz and 5 Hz as shown in Figures 2(b) and 3(f). At 18000 irradiation pulses where the frequency was dropped from 10 Hz to 5 Hz, we found that the pit density was increased from 2.1x10$^8$ cm$^{-2}$ to 3.1x10$^8$ cm$^{-2}$, respectively [see Figures 2(a) and 3(e)], while the nanopore density was shown the same increasing pattern from 6x10$^5$ cm$^{-2}$ to 4.2x10$^6$ cm$^{-2}$, respectively [see Figures 2(b) and 3(f)]. This result shows that the pit and nanopore densities are remarkably increased as the frequency of pulses decreased.

4. CONCLUSIONS

We have investigated the SEM images surface of nanopores formation on SOI substrates utilizing SiC/Si(001) heteroepitaxial growth by using supersonic jet CVD. It was found that nanopores can be obtained in the top Si layer by etching the BOX layer under the pits. We have shown that the density of nanopore can be increased by decreasing the pulse frequency and increasing the number of pulse jet. The results indicate that the density of the nanopore formation can be controlled by utilizing pulse frequency and number of CH$_3$SiH$_3$ pulse jets.
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