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Vertically aligned carbon nanotube growth from Ni nanoparticles prepared by ion implantation

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Abstract

Vertically aligned carbon nanotubes (CNTs) were synthesized from Ni nanoparticles prepared by ion implantation. Ni ions were implanted at 30 keV into thermally grown SiO_2 substrates using a focused-ion-beam. High-density nanoparticle formation was investigated with high doses up to 5.0×10^{17} ions/cm^2. Dense Ni nanoparticles in the order of 10^{11}–10^{12} cm^{-2} were obtained on a SiO_2 substrate, and the particle density and diameter were controlled by post-implantation annealing. Particles annealed at 700 °C led to vertically aligned CNTs. Interestingly, catalysts were longer along the vertical axis and the lower half of the Ni particle was buried in SiO_2.

Keywords: Ion implantation; Carbon nanotube; Vertically aligned; Nanoparticle

1. Introduction

Carbon nanotubes (CNTs) have attracted attention for electronic applications, such as field effect transistors (FETs) [1] and interconnect [2], due to their large allowable current density [3], ballistic transport [4], and high thermal conductivity [5]. With scaling down of the interconnect size in LSI, the current density passing through the metal increases, resulting in electromigration of metal atoms and circuit failure. CNTs can be used to replace Cu interconnects because they allow a current density 3–4 orders of magnitude higher than Cu. To use CNTs for multi-layer interconnects and vertical FET applications [6], catalysts for CNT growth should be prepared in nano-sized dielectric holes. However, it is difficult to deposit catalysts in a controlled amount at the bottom of the high aspect ratio via holes by electron-beam deposition or sputtering [7].

Ion implantation is a very interesting method for this purpose. Ion implantation can be applied easily in LSI processes and catalysts can be implanted at the bottom of via holes in precisely controlled amounts. Recently, growth of carbon nanofibers, MWCNTs and SWCNTs has been demonstrated by Ni and Fe ion implantation [8–12]. Adhikari [10] obtained catalyst particles with a density of 1.6×10^{11} cm^{-2}. However, the resultant CNTs were not aligned. Although vertically aligned CNTs were shown at a dose in the order of 10^{16} ions/cm^2, catalyst particles and grown CNTs had very low densities [12]. The microelectronic applications described above require a high-density of vertically aligned CNTs. Thus, high-density catalyst particles must be prepared by ion implantation.

In this study, a focused-ion-beam (FIB) system was used to investigate formation of high-density nanoparticles in high doses up to 5.0×10^{17} ions/cm^2. The particle diameter and density were studied with different doses and post-implantation annealing temperatures. Finally, we succeeded in growth of vertically aligned and dense CNTs from implanted Ni catalysts.

2. Experimental

The growth process of vertically aligned CNTs by implanted catalysts is shown in Fig. 1. (a) First, we separated Ni ions from Ni–P–Pt liquid metal ion sources (LMIS) using a mass separator, and then Ni^+ ions were implanted into a SiO_2 layer 500 nm thick

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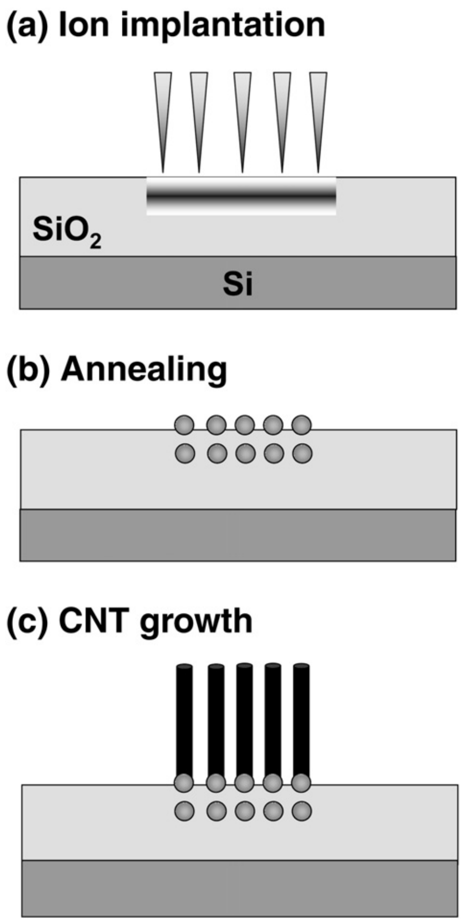

Fig. 1. Schematic of the growth process of vertically aligned CNTs on catalysts prepared by ion implantation.

on a Si substrate at an acceleration voltage of 30 kV with doses of 1.0–5.0 × 10^{17} ions/cm^2 using FIB. Using the mass separator, not only the valence of Ni ions but also the isotopes of ^{58}Ni and ^{60}Ni could be separated. We confirmed that there were no differences in catalysts and resultant CNTs using the isotopes. Note that Ni has isotopes other than those mentioned above, but the others were not used because of their very low fractions. Implantation was performed at room temperature and the implanted region was 30 × 30 µm–100 × 100 µm. The implanted Ni was analyzed using secondary ion mass spectrometry (SIMS). (b) After Ni implantation, the substrate was annealed at 460–700 °C for 30min in H_2 gas to control the density and the diameter of Ni particles on the surface. The SiO_2 was not etched after ion implantation and Ni catalysts formed on the substrate surface were used. (c) The substrates were then introduced into a remote-plasma CVD apparatus [13] for CNT growth. CNTs were grown at 600 °C in a mixture of H_2 (45sccm) and CH_4 (5sccm) at 60Torr for 2 h.

SIMS techniques were used to measure Ni concentrations as a function of depth from the surface. Although it is difficult to evaluate the Ni concentration quantitatively by SIMS at the high doses used in this study, the tendencies of shifts in peak positions can be determined. The position of the peak Ni concentration shifted close to the surface as the dose increased. It is well known that the higher the dose amount, the larger the sputtered depth [14]. Sputtered depths measured by atomic force microscopy (AFM) after ion implantation were in agreement with this tendency. As a result, the Ni concentration at the surface increased with increasing the dose.

3. Results and discussion

Ni nanoparticles were formed on the SiO_2 surface after ion implantation without annealing the substrates. The density was 8.6 × 10^{11} and 5.4 × 10^{11} cm^{-2} at doses of 2.5 × 10^{17} and 5.0 × 10^{17} ions/cm^2, respectively (Fig. 2(a)). The particle density and diameter were controlled by post-implantation annealing. Fig. 2(b)–(d) show Ni particles on the surface at a dose of 5.0 × 10^{17} ions/cm^2 after annealing at 460–700 °C. The particle density and the mean diameter variation with annealing temperature are shown in Fig. 2(e). The plots at room temperature indicate as-implanted states. Although the density increased to 9.2 × 10^{11} cm^{-2} after annealing at 460 °C, it decreased at higher temperatures and was 3.0 × 10^{11}cm^{-2} with annealing at 700 °C, which was lower than that of as-implanted (5.4 × 10^{11}cm^{-2}). The diameter showed the opposite tendency. This phenomenon occurred due to Ostwald ripening [15]. Ni

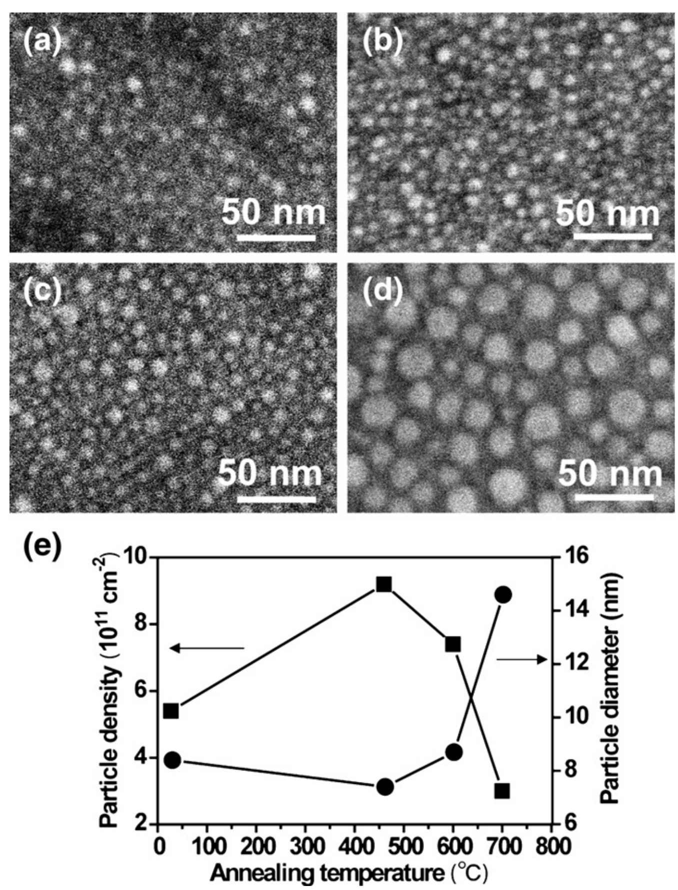

Fig. 2. SEM images of Ni nanoparticles at a dose of 5.0 × 10^{17} ions/cm^2 (a) without annealing, after annealing at (b) 460 °C, (c) 600 °C and (d) 700 °C. (e) Particle density and mean diameter variation with annealing temperature at a dose of 5.0 × 10^{17} ions/cm^2.