Electrodeposition of carbon nanofibers on Si electrode from alcohol electrolytes at room temperature

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Introduction

In recent years, more attention has been paid to electrochemical deposition technique for preparing thin carbon film, such as DLC film, because of low capital equipment cost, simplicity and low temperature synthesis. The carbon film is composed of C-H bonds and carbon atoms with sp^2 and sp^3 orbitals, and the physical property depends strongly on the composition of the film. Various carbon films have been prepared by electrochemical deposition with different experimental conditions [1, 2]. The effect of hydroxyl groups in the molecules of electrolyte played important roles in deposition of carbon films. Fibrous carbons have also been produced by an electrochemical deposition method from organic solutions using transition metal catalysts, such as iron and nickel nanoparticles [3]. In the present study, we tried to prepare carbon nanofibers by an electrochemical deposition method from alcoholic solutions and Si electrodes using Ni nitrite as a catalyst.

Experimental

n-type Si wafer with the resistivity below 0.02 Ωcm was cut into sizes of 1.5×1.5 cm^2. The surfaces were washed by acetone and then treated the square of wafer with HF. The wafers thus treated were used as electrodes, and each of those was covered with insulator except the center area with 3 mm in diameter. The space between the cathode and anode was kept at 5 mm. The potential difference applied between the anode and cathode was kept at 1000 V. 0.3 mg of Ni nitrate was dissolved in 20 ml of ethanol, and 0.2 ml of the solution was mixed with 50~80ml ethanol or benzyl alcohol. Ni deposition on the electrode surface was expected to be 5nm. During the experiments, the electrolytes were stirred 100ppm and the temperature was maintained around 20°C. The electrochemical deposition of carbons was carried out for 8 - 60h.

Results and Discussion

Figure 1 shows the XPS spectra for Si cathode and anode using ethanol electrolyte under 1000 V for 20 h with Ni nitrate.

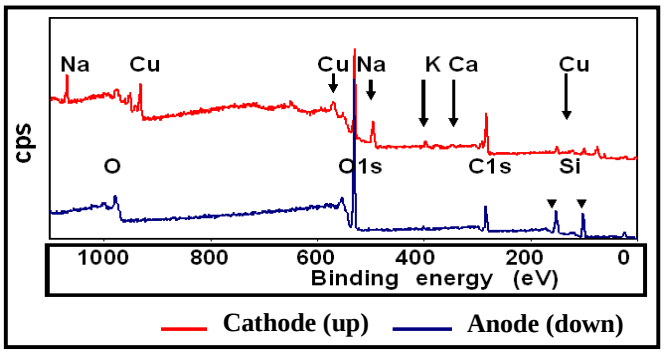

Fig. 1 XPS spectra for Si electrodes using ethanol electrolyte under 1000 V for 20 h with Ni nitrate.

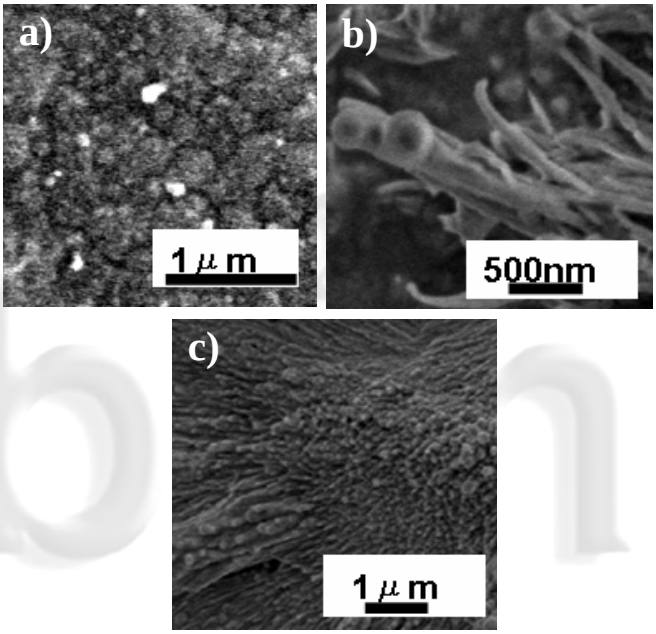

Fig. 2 SEM images of carbonaceous materials deposited on Si cathode using benzyl alcohol electrolyte under 1000 V for 20 h without Ni nitrate (a), 20 h with Ni nitrate (b) and 60 h with Ni nitrate (c).

In the deposit on the cathode, Cu, Na, K, Ca were found, while those were not found in the anode. Therefore, all metal ions were seemed to move to cathode, and the observations and measurements were made only for the depositions on cathode. The SEM images of carbonaceous materials deposited on Si cathode using benzyl alcohol electrolyte under 1000 V for 20 h without and with Ni nitrate are shown in Fig. 2 (a) and (b), respectively. In the case of without Ni nitrate, a granular texture was observed for the deposition on Si cathode as shown in Fig. 2 (a), while carbon nanofibers with 100 – 160 nm in diameter were formed on the Si cathode under 1000 V for 20 h by using Ni nitrate as shown in Fig. 2 (b). Spherule can be seen on the top of some nanofibers. However, isolated

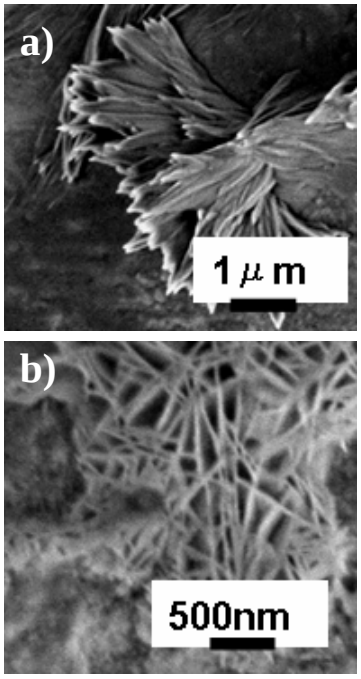

Fig. 3 SEM images of carbonaceous materials deposited on Si cathode using ethanol electrolyte under 1000 V for 12 h with Ni nitrate.

carbon nanofibers were not observed for the deposition of carbons on the 60 h-loaded cathode as shown in Fig. 2 (c). It can be assumed that the deposition became dense and the spaces between the nanofibers were covered with carbonaceous materials as the deposition time increased. In Fig. 3, the SEM images of carbonaceous materials deposited on Si cathode using ethanol electrolyte under 1000 V for 12 h with Ni nitrate were shown. A plate-like texture (Fig. 2 (a)) or fibrous nanotexture (Fig. 2 (b)) was observed for several parts of the deposition on Si cathode and these texture were also observed for the depositions obtained for longer deposition times.

Figure 4 shows the Raman spectra for carbonaceous materials deposited on Si cathode using ethanol (a) and benzyl alcohol (b) electrolyte under 1000 V for 20 h with Ni nitrate. The deposition obtained using ethanol electrolyte exhibits two types of Raman spectra as shown in Fig. 4 (a). The area corresponding to the fibrous nanotexture observed by SEM, such as Fig. 3 (b), showed the lower part of the spectra in Fig. 4 (a). In the spectrum, there are three peaks, two of them originate from amorphous carbon with sp^2 (1350 cm^{-1}, 1580 cm^{-1}) and the other is due to C-H bond close to 1450 cm^{-1}. The area without the fibrous nanotexture of the deposition obtained using ethanol electrolyte showed the upper part of the spectra in Fig. 4 (a). The deposition of the area can be regarded as organic substance.

On the other hand, the deposition obtained using benzyl alcohol electrolyte exhibits the Raman spectra as shown in Fig.

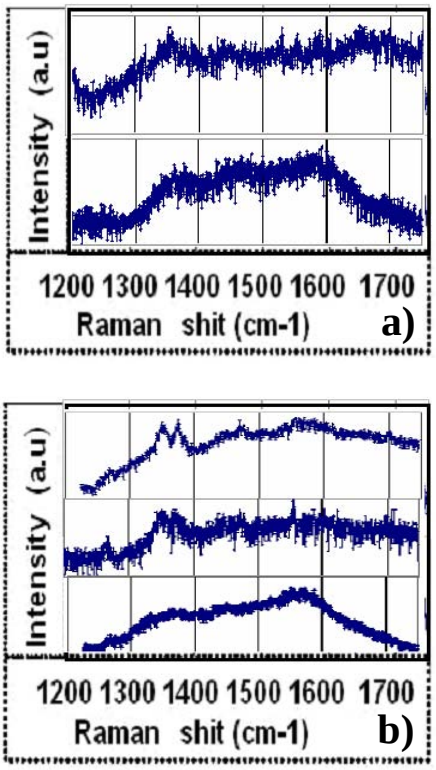

Fig. 4 Raman spectra for carbonaceous materials deposited on Si cathode using ethanol (a) and benzyl alcohol (b) electrolyte under 1000 V for 20 h with Ni nitrate.

4 (b). The area corresponding to the fibrous nanotexture observed by SEM, such as Fig. 2 (b), showed the lower part of the spectra in Fig. 4 (b). The area without the fibrous nanotexture of the deposition obtained using benzyl alcohol electrolyte showed the upper and middle spectra in Fig. 4 (b). The deposition of these areas can also be regarded as organic substance.

Conclusions

Carbon nanofibers were deposited on a Si electrode in ethanol and benzyl alcohol electrolytes with a small amount of nickel nitrate under a high voltage of 1000V at room temperature. The texture and structure of the nanofibers were examined by SEM observations and Raman spectroscopy. The nanofibers were found to be amorphous carbons with about 100∽150nm in diameter.

References

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