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Fabrication of vertically-aligned CNT electrodes using plasma-enhanced CVD for chemical sensors.

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Carbon nanotubes (CNTs) have attracted considerable interest for applications to interconnects and via-holes [1] due to their potential for high current density. In addition to that, the CNTs are expected to be suitable for chemical sensors because of their chemical stability [2]. However, there are little reports which study the possibility of CNTs as electrodes for chemical sensors. In this report, we have clarified the effects of diffuse layer in the CNT-immersed electrolyte on the electrode characteristics. We also have shown that CNT electrodes were more sensitive than Pt electrodes.

The vertically-aligned CNT electrodes were fabricated by using grid-inserted plasma-enhanced chemical vapor deposition (PECVD) [3]. Figure 1 shows a SEM image of the vertically-aligned CNTs and schematic structure of the CNT electrodes. The CNTs were grown by PECVD using the Fe/Ti double-layer catalyst formed in the SiO_2 opening. The size of the catalyst pattern was 80×80 μm^2 and CNT height was 5 μm. Double-layer catalyst was effective in growing high-density vertically-aligned CNTs [4]. Here, we define the area of the catalyst S_c as the area of the CNT electrodes. A Pt electrode formed by EB evaporation was also fabricated as a reference. In order to investigate the effect of the structure of the CNT electrodes, different electrode patterns with equal area shown in Fig. 2(a) was also prepared.

Fig. 3 shows the result of voltammetry. We used phosphate buffered saline (PBS) with potassium ferricyanide (1 mmol/l) as electrolyte. Pt was used as a counter electrode and AgCl/Ag as a reference electrode. The voltage was swept from 0 V via 0.6 V back to 0 V at sweep rate of 100 mV/s. A current of upward convex corresponds to oxidation, and a current of downward convex corresponds to reduction. It is notable that the peak current is dependent on the electrode shape in spite of the same S_c as shown in Fig. 3. Figure 4 shows a difference in peak currents of oxidation and reduction (I_{pp}) as a function of the total surface area of the CNT electrode, S_t. Here we define the S_t as a sum of the area of S_c and the side surface of the CNT electrode objectifying it as a rectangular solid as shown in Fig. 2(b). I_{pp} is proportional to S_t as shown in Fig. 4. This fact suggests that the inside of the CNT forrest doesn't contribute to oxidation/reduction. That is, reactant does not diffuse into the CNT forrest. This suggests that the width of the diffuse layer formed on the CNT surface is wider than the distance between CNTs.

We estimated the width of the diffuse layer by using a pattern with different electrode spacings. The CNT electrodes with a catalyst diameter of 2 μm was arranged as a 23×45 array at spacings of 2~40 μm as shown in Fig. 5(a). Figure 5(b) shows I_{pp} as a function of the electrode spacing. While I_{pp} increased in proportion to the electrode spacing at first, it increased abruptly at 20 μm spacing and did not change after that. This result can be explained by taking the diffuse layer into account as schematically shown in Fig. 6. When the electrode spacing is small, diffuse layer at each electrode surface overlaps each other. In this case, the effective total electrode surface area S_t increases with increase of electrode spacing because of the decrease of overlapped area resulting in an increase of the I_{pp}. In contrast, when the electrode spacing is larger than the diffuse layer, there is no overlap of diffuse layer resulting in no I_{pp} change. Based on this result, the width of the diffuse layer can be estimated to be 7.5~10 μm as a half of the electrode spacing.

Figure 7 shows the comparison between CNTs and the Pt as an working electrode. A larger I_{pp} was obtained in CNT electrode than Pt electrode. The current density including the effect of side surface was 3.32 A/m^2 in the case of CNT electrode. This value is about two times larger than that of the Pt electrode (1.55 A/m^2). This result indicates that the CNTs are suitable for electrode in chemical sensors with high current density.

The vertically-aligned CNT electrode was fabricated by using grid-inserted PECVD. It has been demonstrated that each CNTs do not work as independent electrodes because of the diffuse layer formed on the CNT surface. The width of the diffuse layer was estimated to be 7.5~10 μm based on the voltammetry using electrode array with different electrode spacings. It has also been shown that the CNT electrode is better than Pt electrode having higher current density.

References

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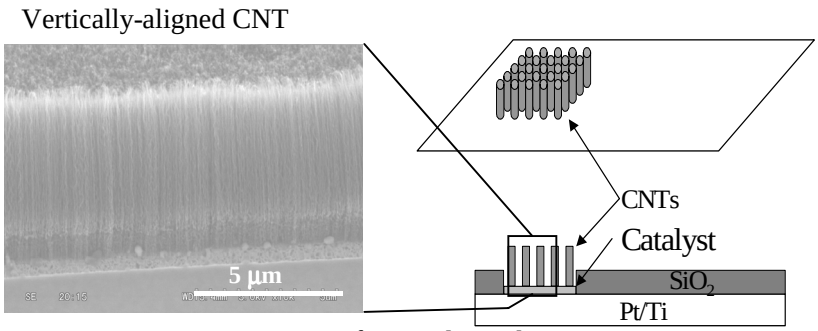

Fig.1 Structure of CNT electrode.

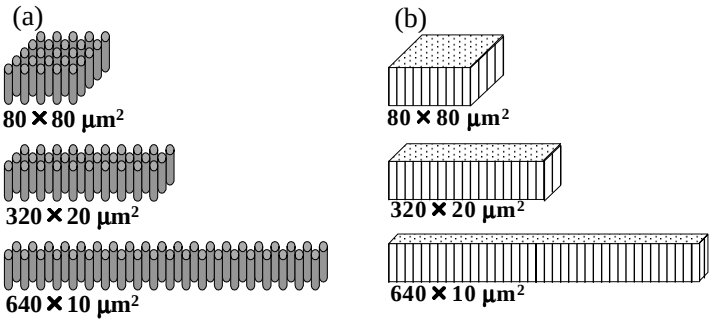

Fig.2 Electrode pattern with different shape;
(a)CNT electrode,
(b)Electrode objectifying as a rectangular solid.

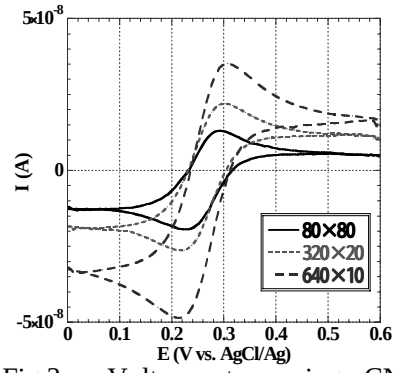

Fig.3 Voltammetry using CNT electrode with different shape.

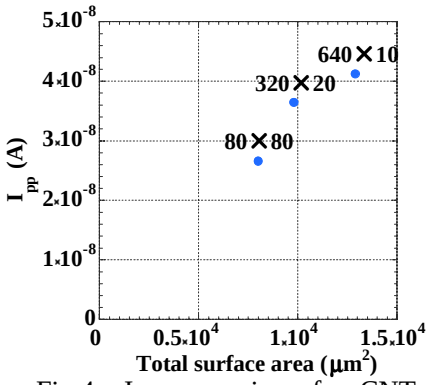

Fig.4 I_{pp} comparison for CNT electrodes with different shape.

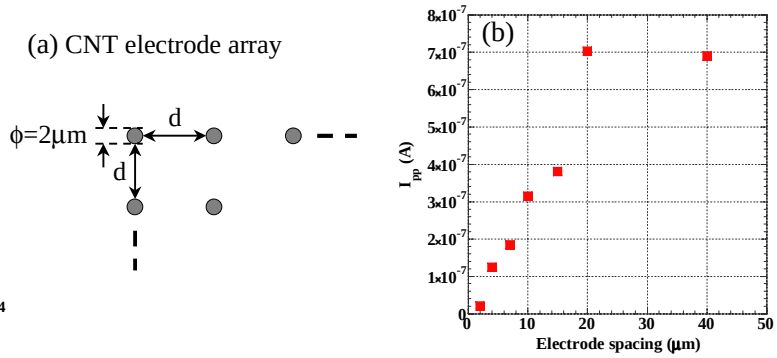

Fig.5 I_{pp} for different electrode spacing;
(a)Electrode array, (b) electrode spacing dependence.

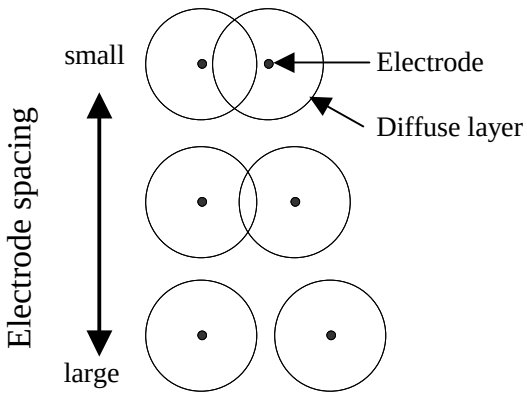

Fig.6 Schematic illustration of the effect of the diffuse layer.

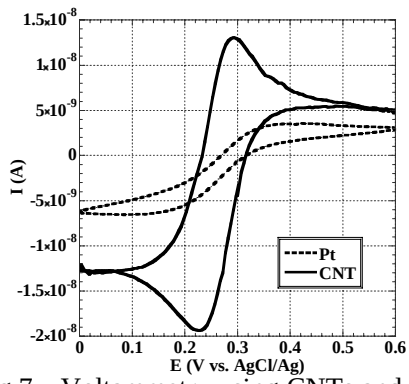

Fig.7 Voltammetry using CNTs and Pt as a working electrode.