Parallelization of carbon nanowalls synthesized by MPECVD: application for anisotropic conductive films

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Abstract: In this work, results on the synthesis and parallelization of carbon nanowalls (CNW) are presented. The CNWs were deposited from a mixture of CO/H2 using microwave plasma-enhanced chemical vapor deposition (MPECVD). A comparison was carried out for the effect of electrode shape to modulate the plasma sheath and parallelize CNW. SEM images showed that a large area of up to 400 µm could be parallelized using a metal wire compared to a metal film or plate. The measured sheet resistance reveals the anisotropic characteristic of CNW film after parallelization making it a potentially functional coating for application as an anisotropic conductive film.

Keywords: CNW, Parallelization, ACFs, Microwaves PECVD

1. Introduction

Carbon nanowalls (CNW) are interconnected stacks of graphene sheets vertically grown on a substrate; each sheet is composed of a few layers of graphene with length and height ranging from a few nanometers to microns [1]. Thanks to their unique properties, such as large surface area, and high active graphene edges, CNW have attracted significant attention for many applications [2, 3]. To expand its applicability as an anisotropic conductive film (ACF), controlling CNW shape and growth parallel direction during its synthesis is essential. So far, few studies have examined the effect of localized electrical field on the growth of CNW, showing that the plasma sheath allows the control of CNW's growth direction, and its random distribution can be partially parallelized [4, 5]. However, the parallelized area remains very small, restricting their use. In this study, we demonstrate that the CNW parallel area can be enlarged up to a few hundred microns by using floating metal wire electrode to excite the surface plasmon and control the horizontal growth direction of CNW. The electrical resistance of CNW was examined after alignment suggesting its anisotropy, making it a potentially functional coating for application as an ACF.

2. Experimental and analysis

The growth and parallelization of carbon nanowalls were carried out simultaneously in the same reactor. The apparatus is a microwave plasma-enhanced chemical vapor deposition (MPECVD) fed by a mixture of CO/H2. Fig. 1 depicts a schematic of the instrument used, and Table 1 summarizes the deposition conditions for CNW. Three metal electrode configurations were compared to modulate the plasma sheath and parallelize the CNW. First, a metal film deposited by sputtering with a thickness of 2µm; second, a metal plate of 300µm height; in both cases electrode was in contact with the cathode; and third, a metal wire with a diameter of 100µm floating from the substrate surface as shown in Fig. 1.

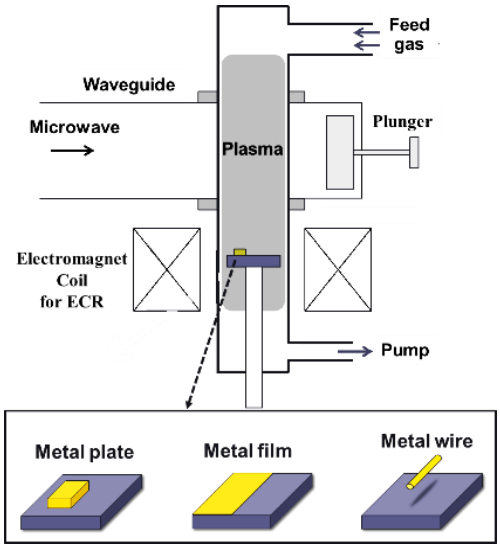

Fig.1: Experimental set-up for CNW growth and parallelization

Table 1: Growth conditions of the CNW

Substrate	Si
Total feed rate	10 sccm
CO: H_2 ratio	2:8~8:2
Pressure	50 Pa
Deposition time	45~60 s

The random and parallelized CNWs were observed by Scanning Electron Microscopy (SEM). The anisotropy of CNWs films was evaluated by measuring their conductivity using a four-point probe. Furthermore, the transparency of CNW to visible light was examined using optic microscopy. The influence of the CO: H2 ratio and pressure deposition on CNW parallelization and anisotropy was evaluated.

3. Results and discussion

Fig. 2 depicts the SEM images of parallel CNW; It can be seen that in the case of a metal film electrode (Fig. 2a), the parallel area is negligible, less than 5µm, compared to the metal plate where an area of about 200µm in the vicinity of the metal electrode was parallelized (Fig. 2b). Thus, indicating that a thicker metal plate is better for the parallelization; however, the deposition rate becomes slow due to the shadowing effect. Despite increasing the thickness of the metal plate to over 300µm, we note that the parallel area remains the same. For the metal wire system with a diameter of 100µm floating at about 100µm from the surface substrate (Fig. 2c), the parallel area could be increased up to 400µm, signifying that the metal wire is the best system to enlarge the parallelization of CNW. The aligned area remains unchanged with a large wire diameter. These results indicate that we successfully enlarged the parallel area of CNW using an additional wire metal, to a few hundred microns compared to a few tens microns, reported in [5].

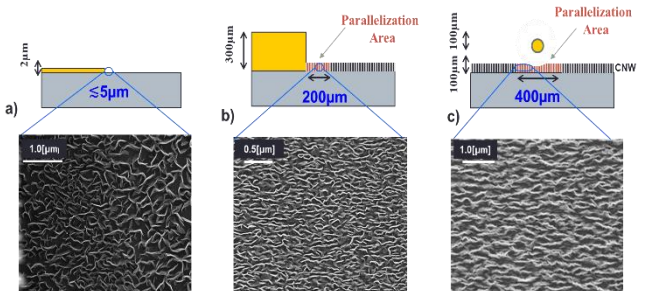

Fig. 2: Parallelized CNW using system; a) metal film, b) metal plate, and c) metal wire.

Besides the electrical field, perpendicular to the substrate resulting from the plasma discharge, an additional horizontal electrical field is induced by the extra metal electrode placed/floating on the substrate giving rise to a moment dipole on the CNW surface. Thus, causing the CNW polarization in the horizontal direction by the plasma sheath resulting in its parallelization as the growth progresses [5, 6, 7]. The induced plasma sheath is proportional to the electrode thickness, Hence, in the case of the thin metal film electrode, the induced electric field is very weak, resulting in a small parallel area, whilst, in the case of a plate electrode, the parallel area could be expanded up to 200 µm.

Transparency and surface resistance of random and parallel CNW by a metal wire system was evaluated. The results indicate that the resistance value of parallel CNW decreases in the parallel direction, while it increases in the perpendicular direction. A minor change was observed in CNW transparency following their parallelization. Fig. 3a shows SEM images of parallel CNW by metal wire electrode under two pressure, 50 Pa and 100 Pa. It can be seen that the spacing between the CNW increases with pressure while maintaining CNWs parallel. Fig. 3b shows the transparency versus sheet resistance for the same sample. For both operating pressures, the resistance value in the parallel direction remains slightly the same. However, a significant increase is noticed in the perpendicular direction with the rise in pressure. This can be explained by the increase in wall spacing with the operating pressure, as shown in fig. 3a. The average anisotropy value obtained for parallel CNW formed at 100 Pa was 1.75 compared to 1.52 at 50 P.

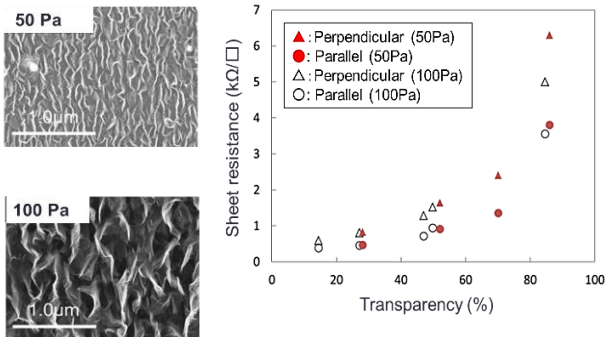

Fig. 3: a) SEM Images, b) Sheet resistance versus transparency in parallel and perpendicular directions at different pressures.

The effect of the CO:H2 ratio on CNW structure and its parallelization was evaluated. Fig. 4a proposes a reaction mechanism for CNW growth; a low CO:H2 ratio results in a relatively large flake size than a high ratio, owning to the etching ability of hydrogen. However, with a high CO:H_2 ratio, the branching of CNW is significant due to the abundant lattice defects. Thus, preventing its orientation control by an electrical field, as can be seen in the SEM images of fig. 4b.

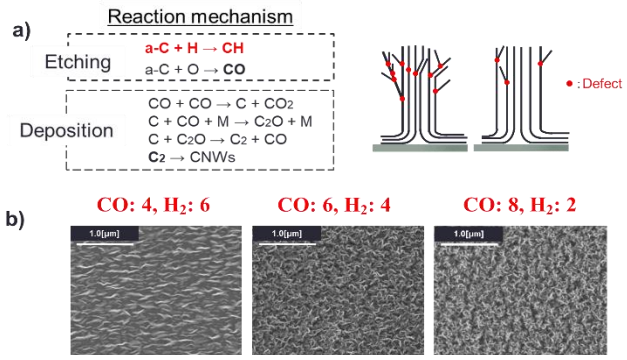

Fig. 4: a) Reaction mechanism of CNW growth, and b) SEM images of CO:H_2 ratio on CNW parallelization

4. Conclusion

Catalyst-free and parallel carbon nanowalls were successfully grown by the MPECVD system with an additional metal electrode. Three metal electrode

configurations were compared to modulate the plasma sheath and parallelize CNW. The metal wire electrode floating above the substrate would be the best configuration for a large-area deposition system with substrate scanning. The anisotropy of parallel CNW was confirmed by film surface resistance measurement. it was shown that increasing the operating pressure enhances the anisotropy of parallel CNW. Furthermore, a lower $CO:H_2$ ratio for CNW growth provides a lattice with fewer defects and less branching, which promotes its parallelization by an electrical field.

References

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