

Chapter 5 Conclusions

The process to fabricate the alloy-capped CNTs (including catalyst sputtering, H-plasma pretreatment, CNTs deposition, H-plasma post-treatment, chemical etching, alloy sputtering and high temperature heat trimming in vacuum) and analyses for each processing step were carried out. From the experimental results, the following conclusions can be drawn.

- 1 The diameter of CNTs is closely associated with the size of the catalyst particles. The diameter and tube number density can be manipulated by adjusting the catalyst thickness.
- 2 CH₄ and H₂ concentrations play a crucial role to determine the carbon nanostructures, which act as the carbon source and etchant. An overabounding carbon concentration in the gas phase is a more favor condition for continuously depositing on the sides of catalysts to form rattan-like CNTs. The formation of rattan-like CNTs can be suppressed by decreasing CH₄ or increasing H₂ flow rate.
- 3 During CNTs growth, amorphous carbon can be preferentially etched off and the CNTs are left under higher H₂ concentration. Therefore, the higher H₂ concentration can result in a lower Raman I_D/I_G ratio and more tubule-like CNTs left.
- 3 The post-treatment for fabricating the open-ended CNTs can be considered as a two-step treatment, i.e. H-plasma etching and chemical etching. It can provide a remedial method to change CNTs morphology from rattan-like to tubule-like, or further from tubule-like to the opened-tips CNTs.
- 4 Under the present conditions, to open caps of tubule-like CNTs, the best conditions of this two-step post-treatment are 1-min H-plasma etching and followed by 3-min 0.25 M HNO₃ etching step, which is capable to maintain the structure integrity of CNTs and to remove the catalysts completely.

- 5 On anisotropic reaction under H-plasma atmosphere, the strained regions with the greatest curvature on the as-grown CNTs tips are the preferred etching sites.
- 6 The purpose of capping open-ended CNTs tips with phase-change alloy can be carried out by alloy sputtering process (200 nm) and followed by proper heating (420°C for 30 min). However, it may suffer the drawback of composition alternation.
- 8 Using H-plasma and chemical etching post-treatment, the field emission ability of the as-grown CNTs can be enhanced by opening their tips and maintaining their structure integrity. On the other hand, oxidation of the exposed catalysts on carbon layer-stripped CNTs can lead to a decline of field emission ability.
- 9 I would like to propose a mechanism for the post-treatment process to indicate the corresponding structure changes from the as-grown CNTs to the alloy-capped CNTs, as shown schematically in Figs. 5-1 (a) ~ (e). Under the as-grown CNTs state (Fig. 5-1 (a)), Co catalyst is covered with an ultra-thin carbon layer on tip of the tube. After 1 min H-plasma post-treatment, the carbon layer is removed (Fig. 5-1 (b)). Then, it is chemically etched for 3 min to remove the catalyst completely (Fig. 5-1 (c)). Subsequently, 200 nm phase-change alloy is sputtered on the open-ended CNTs (Fig. 5-1 (d)), where the opened-tip is a favor site to deposit thicker alloy film than the side wall of tube. Finally, sample is heated at 420°C for 30 min in vacuum, the thinner alloy film around the side wall of tube will be evaporated away more easily. Therefore, the alloy-capped CNTs can be finally obtained (Fig. 5-1 (e)).

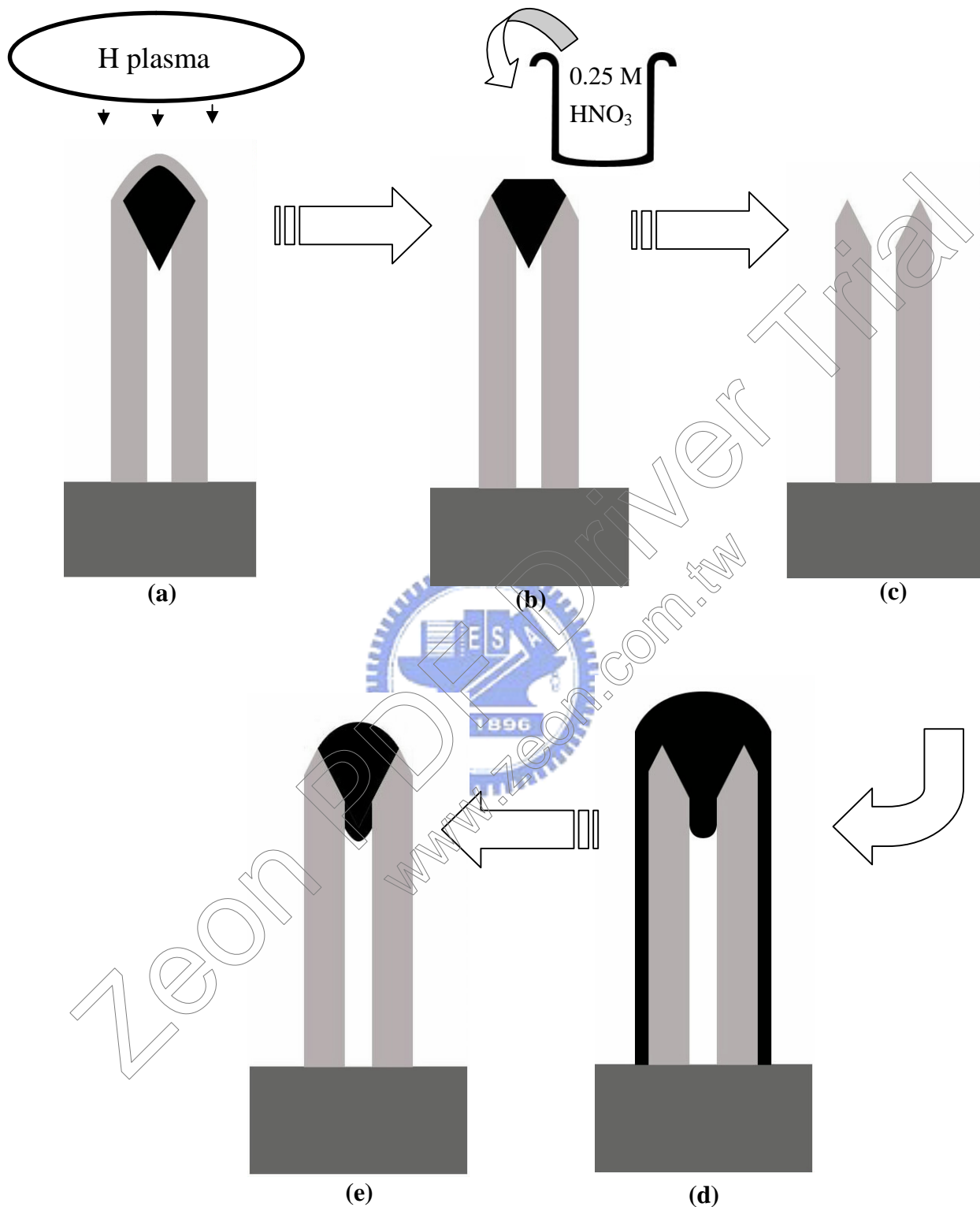


Fig. 5-1 My proposed post-treatment mechanism to show changes in CNTs morphologies in each post-treatment step: (a) As-grown CNTs, (b) H-plasma post-treated CNTs, (c) Chemically etched CNTs, (d) Open-ended CNTs covered with phase-change alloy film and (e) Heat treated CNTs.