

**INFLUENCE OF A Cr LAYER ON THE GLASS SUBSTRATE
ON THE GROWTH OF CARBON NANOTUBES
BY CHEMICAL VAPOR DEPOSITION**

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We report the effect of a Cr layer on the glass substrate during the growth of carbon nanotubes (CNTs) by chemical vapor deposition. When Fe was used as a catalyst in the CNT growth, longer CNTs were obtained by increasing the thickness of the Cr layer. However, CNTs were not grown on the surface with a thick Cr film and Co or Ni catalyst. These results arise from a difference in the mechanism of CNT formation when using different catalyst metals.

Keywords: Carbon nanotubes; CVD; Cr layer; SEM; Glass substrate

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1. Introduction

Carbon nanotubes (CNTs) have attracted much attention as promising materials for application in nanotechnology and nano-devices because of their superior structural, mechanical, chemical, thermal, and electrical properties.¹⁻³ CNT formation has been carried out using various techniques, such as plasma-enhanced or thermal chemical vapor deposition (CVD),⁴⁻⁶ SiC surface decomposition,^{7,8} arc discharge,^{9,10} laser vaporization¹¹ and more. The different methods form CNTs with a variety of shapes and features.

For the application of CNTs to field emission displays, it would be necessary to grow CNTs directly on the electrode for use as cathodes. Therefore, obtaining CNT films with controllable growth and good emission properties is important.

In CNT formation by CVD, it is well-known that the catalyst is one of the most important parameters. CNTs have been grown using transition metal catalysts at relatively low temperature. Because the density and diameter of the CNTs is dependent on the size of the catalyst particles, it is also important to investigate the interaction between the catalyst and the buffer layer, which is generally used in CNT growth. The buffer layer may act as a diffusion barrier between the catalyst and the substrate,¹² affecting the CNT properties. To control the detailed characteristics of CNT growth, it is necessary to understand the role of metal catalysts at a fundamental level.

In the present paper, we investigated the influence of a Cr layer in the growth of CNTs on a glass substrate by CVD. We will show that the Cr layer affected the size of the fine catalyst particles deposited upon it.

2. Experimental

The substrate was made of glass (MATSUNAMI Inc., Micro Cover Glass), which was cleaned in acetone and rinsed in deionized water before being inserted into a vacuum chamber. A pure Cr buffer layer and Fe, Co, or Ni catalyst were deposited by RF-sputtering (ANELVA, SPF-210H). The thickness of the catalyst layer, measured by a surface texture measuring

instrument (SURFCOM, 1400D), was about 3 nm. The sample was introduced into the reaction chamber under a base pressure of 2×10^{-5} Pa. The surface was annealed at 550°C using an infrared lamp in Ar gas (1.3×10^3 Pa) to form fine catalyst particles for CNT formation, with temperatures measured using an optical pyrometer. The annealing time in making particulate Fe, Co, or Ni was 40 min, 15 min, and 12.5 min, respectively. CNT growth was performed in a CVD chamber for 15 min in C_2H_2 , H_2 , and Ar gases at a total pressure of 1.3×10^3 Pa. We observed several structures on the CNT-grown surfaces by scanning electron microscopy (SEM).

3. Results and discussion

Figure 1 shows SEM images taken after CVD formation of CNTs on a glass substrate with each catalyst (Fe, Co or Ni), with varying thickness of the Cr buffer layer (about 3, 35, or 100 nm).

At first, no CNT growth could be confirmed for a Cr thickness of 3 nm with Fe catalyst, as shown in Fig. 1(a). However, we observed very short CNTs with a length of about ~ 0.1 μm and diameters of 80~100 nm for Cr thicknesses of 35 and 100 nm, as shown in Figs. 1(b) and 1(c), respectively.

Next, we observed long CNTs with random orientation in Fig. 1(d). CNTs with a length of about ~ 1.3 μm and diameter of about 70~100 nm were formed on the substrate surface. The features of the CNTs in Fig. 1(e) coincide approximately with those in Fig. 1(d). The density of CNTs decreased slightly with increasing thickness of the Cr buffer layer. When the thickness of the Cr buffer layer was about 100 nm, we could confirm no CNT growth.

From the SEM image of the glass surface with Ni catalyst shown in Fig. 1(g), we found that the length of the CNTs was about ~ 0.6 μm and the diameter was about 60~80 nm. In Figs. 1(h-i), we observe no CNTs, but fine catalyst particles on the surface with a diameter of about 60~80 nm.

SEM images of the fine particles of several different catalysts adsorbed on the glass surface

with a Cr buffer layer are shown in Fig. 2. We did not observe the formation of fine particles in Fig. 2(a), which corresponds to Fe catalyst and a Cr film of 3 nm. The density and size of the fine particles increased slightly as the thickness of Cr films increased. In the case of Co catalyst (Figs. 2(d-f)), fine particles were formed even on surfaces with thin Cr layers. The density and size of the fine particles did not change over the range of Cr layer thickness from 3-100 nm. With a Ni catalyst (Figs. 2(g-i)), the density and size of the fine particles on a Cr-35 nm film were nearly equal to those on a Cr-100 nm film. However, fine particles did not form on the Cr-3 nm adsorbed surface. We found that the density and size of the fine particles depended on the thickness of the Cr films. Therefore, we believe that the interactions between the catalysts and the glass substrate were restricted by the Cr films. According to the experiments by Wang *et al.*, a Cr film on glass acts as a diffusion barrier for Cu atoms.¹³ We suggest that Cr layers can prevent catalyst atoms from diffusing into the glass substrate. The size of the fine particles thus depended upon the thickness of the Cr films.

For a Co or Ni catalyst, we found that CNT growth was suppressed with increasing Cr film thickness. Chuang *et al.* reported that there is a strong adhesion force between Ni nanoparticles and a Ti film surface for CNT growth in a Ti/Si system.¹⁴ Because of this force, Ni nanoparticles could not be pushed up in the CNT growth. We suppose that there are also strong adhesion forces between Co or Ni catalysts and a Cr film. CNT growth using a Ni catalyst adopted a “through-tip” mechanism in general. We believe that the Ni could contribute sufficient catalytic activity while trapped on the Cr buffer layer.

Moreover, we noticed when using a Co catalyst that the diameter of the CNTs became large and the length shortened when we increased the Cr film thickness from 3 nm to 35 nm. H. Liu *et al.* reported that the diameter of CNTs depends on that of the fine particles used as a catalyst.¹⁵ The diameters of the CNTs in Figs. 1(d-e) correspond to those of the fine particles in Figs. 2(d-e). Therefore, we confirmed that the formation of fine particles is one of the most important requirements to forming desirable CNTs by CVD.

The formation of CrSi and CrSi₂ was previously reported after annealing a Cr film on a

Si(111) surface at high temperature.¹⁶ In constructing a field emission display device, it is necessary to examine the influence of the Cr film on the CNT growth in detail. If the size and density of the fine particles can be controlled simply by changing of thickness of the buffer layer, it will become possible to make CNTs with desirable characteristics.

4. Conclusions

The influence of Cr layer thickness on a glass substrate in CNT growth by CVD was investigated using SEM. When using a Co or Ni catalyst, the lengths and densities of CNTs grown on the surfaces decreased with increasing thickness of the Cr layers. The thickness of the Cr layer affects the formation of fine catalyst particles and the adhesion force between the catalyst and Cr layers. Thus, the Cr layer thickness is an important parameter in the growth of CNTs by CVD.

Acknowledgments

This work was partially supported by the Nippon Sheet Glass Foundation for Materials Science and Engineering.

References

1. J. Jang, S. J. Chung, H. S. Kim, S. H. Lim and C. H. Lee, *Appl. Phys. Lett.* **79** (2001) 1682.
2. Y. Zhang, K. Suenaga, C. Colliex and S. Iijima, *Science* **281** (1998) 973.
3. K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, U. G. Hasko, G. Pirio, P. Legagneux and F. Wyczisk, *Appl. Phys. Lett.* **79** (2001) 1534.
4. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal and P. N. Provencio, *Science* **282** (1998) 1105.
5. W. Z. Li, S. S. Xie, L. X. Qain, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao and G. Wang, *Science* **274** (1996) 1701.
6. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tomblor, A. M. Cassell and H. Dai, *Science* **283** (1999) 512.
7. M. Kusunoki, T. Suzuki, T. Hirayama, N. Shibata and K. Kaneko, *Appl. Phys. Lett.* **77** (2000) 531.
8. G. Zhang, Y. Hashimoto, A. Nakamura, A. Tanaka, J. Temmyo and Y. Matsui, *Jpn. J. Appl. Phys.* **46** (2007) L53.
9. E. G. Gamaly and T. W. Ebbesen, *Phys. Rev. B* **52** (1995) 2083.
10. D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, *Nature* **363** (1993) 605.
11. A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, U. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fisher and R. E. Smalley, *Science* **273** (1996) 605.
12. I. T. Han, B. K. Kim, H. J. Kim, M. Yang, Y. W. Jin, S. Jung, N. Lee, S. K. Kim and J. M. Kim, *Chem. Phys. Lett.* **400** (2004) 139.
13. L. Wang, T. Chen, T. Feng, Y. Chen, W. Que, L. Lin and Z. Sun, *Appl. Phys. A* **90** (2008) 701.
14. C. -C. Chuang, W. -L. Liu, W. -J. Chen and J. -H. Huang, *Appl. Surf. Sci.* **254** (2008) 4681.
15. H. Liu, G. -A. Cheng, R. Zheng, Y. Zhao and C. Liang, *Surf. Coat. Tech.* **202** (2008) 3157.
16. P. Wetzel, C. Pirri, J. C. Peruchetti, D. Bolmont and G. Gewinner, *Phys. Rev. B* **35** (1987) 5880.

Figure Captions

Fig. 1: SEM images taken after CNT formation on glass substrates with (a, d, g) 3 nm, (b, e, h) 35 nm, and (c, f, i) 100 nm thick Cr layers by CVD using (a-c) Fe, (d-f) Co, and (g-i) Ni catalysts, respectively.

Fig. 2: SEM images of fine particles of (a-c) Fe, (d-f) Co, and (g-i) Ni catalysts on glass substrates with (a, d, g) 3 nm, (b, e, h) 35 nm, and (c, f, i) 100 nm thick Cr layers.

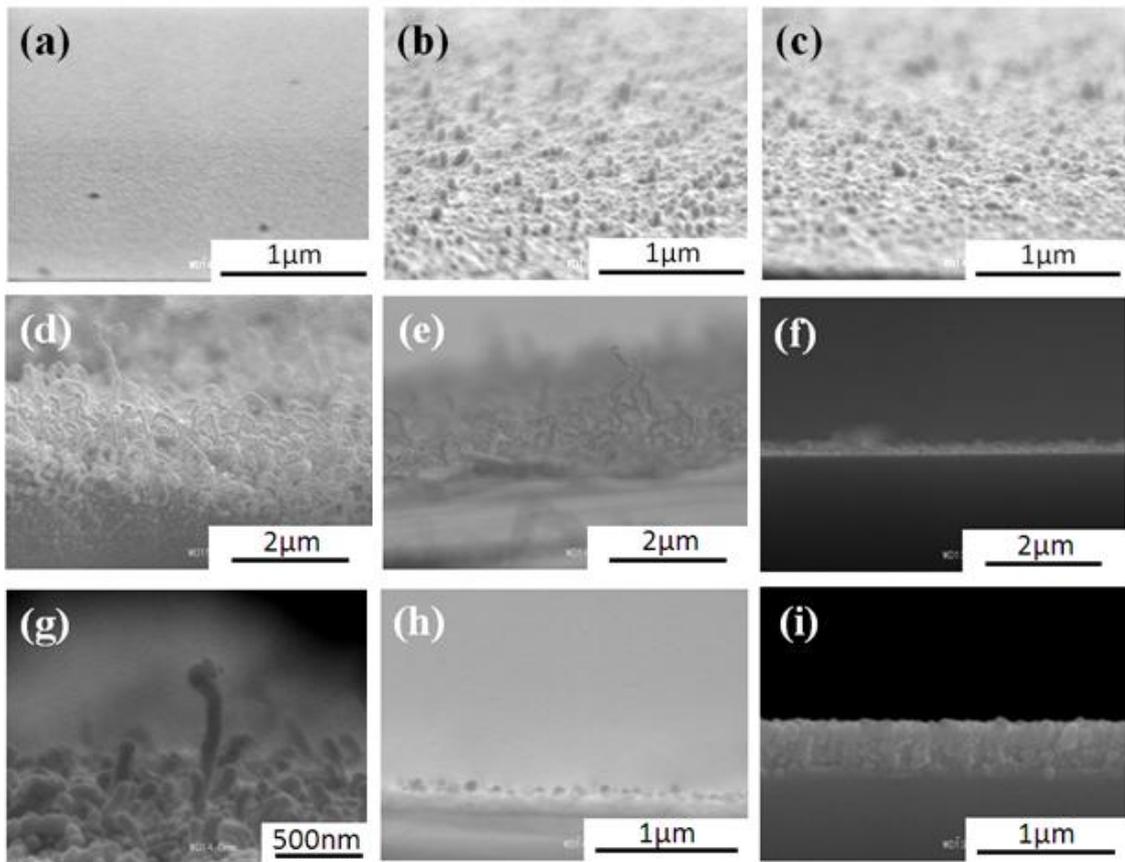


Fig. 1:

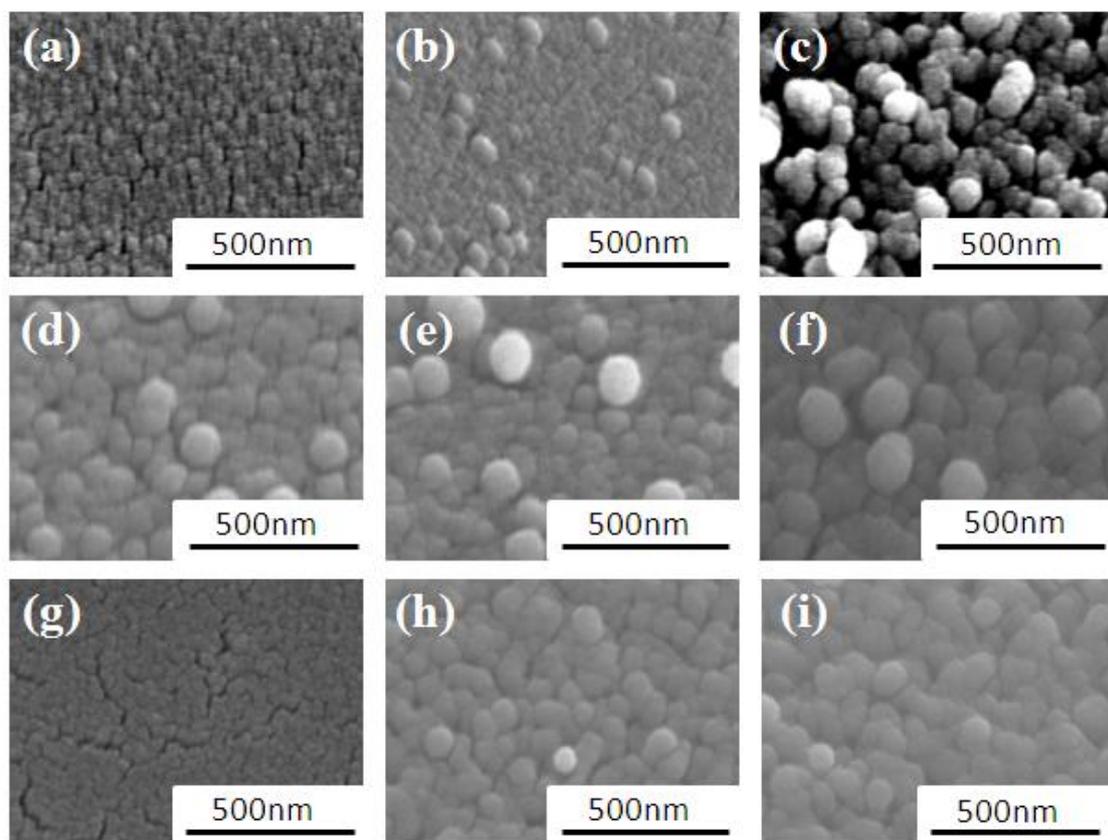


Fig. 2: