

PARAMETRIC STUDIES OF THIN FILM NICKEL CATALYST FOR THE GROWTH OF CARBON NANOTUBES

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Abstract. The thickness and morphology of the catalyst film significantly affect the properties of carbon nanotubes (CNTs). The catalyst size and shape are the key factors for the controlling of CNT diameter. The objectives of this study are to develop a thin catalyst film for CNTs growth application by varying the time of deposition and investigate the effect of radio frequency (rf) plasma power. The thin catalyst film was developed using physical sputtering method with an rf power between 20 to 100 watt at varying deposition time with nickel as a catalyst. The Ni/Cr film in this study was fabricated on corning glass substrates. The thin film nickel catalyst was obtained with a thickness of 12 nm using surface profiler and was characterized using field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) to determine the morphologies and particle size of the catalyst. The rf power and deposition time is found remarkably influence the catalyst morphology. Higher power supply are found to be more effective for scattering the catalyst thin film, homogeneous and uniform thin film on the substrate.

Keywords: Carbon nanotubes (CNTs); catalyst; nickel; plasma bombardment; plasma breaking

Abstrak. Ketebalan dan morfologi bagi filem pemangkin mempengaruhi sifat nanotub karbon (CNT). Saiz dan bentuk lapisan mangkin adalah faktor utama bagi pengawalan diameter CNT. Objektif bagi kajian ini adalah untuk menghasilkan satu filem pemangkin nipis untuk aplikasi pertumbuhan CNT dengan mempelbagaikan masa pemendapan dan menyiasat kesan kuasa plasma frekuensi radio (rf). Filem pemangkin nipis ini disediakan menggunakan kaedah *physical sputtering* dengan kuasa rf di antara 20 hingga 100 watt dengan mempelbagaikan masa pemendapan dengan menggunakan pemangkin nikel. Filem Ni/Cr dalam kajian ini telah disediakan pada substrat kaca *corning*. Filem pemangkin nipis nikel telah diperolehi dengan ketebalan 12 nm menggunakan *surface profiler* dan telah digambarkan sifat fizikalnya menggunakan *field emission scanning electron microscopy* (FESEM) dan *atomic force microscopy* (AFM) bagi menentukan morfologi dan saiz zarah bagi pemangkin. Kuasa rf dan masa pemendapan didapati dengan luar biasanya mempengaruhi morfologi mangkin. Bekalan kuasa lebih tinggi telah didapati lebih berkesan bagi penyerakan pemangkin filem nipis, filem nipis homogen dan seragam pada substrat.

Kata kunci: Nanotub karbon (CNT); mangkin; nikel; hentaman plasma; pemecahan plasma

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1.0 INTRODUCTION

Since their discovery in 1991 by Iijima [1], carbon nanotubes (CNT) have attracted great interest among researchers due to their high mechanical strength [2], high hydrogen storage [3], and electrical properties [4]. CNT is considered to be of technological importance due to its numerous applications, such as field emission display [5], potential molecular quantum wire [6], tip of microscope [7], etc.

The growth of CNT requires the use of a catalyst. The most commonly used catalysts are transition metals or alloys in the form of thin films or nanoparticles. All CNT synthesis methods relied on syntheses on catalysts, sizes and densities of CNTs are decided by those of the catalysts. Thus, various methods of catalyst deposition have been developed, such as sputter deposition technique [8], ion beam deposition technique, pulse-laser deposition technique and electron beam deposition technique. Among these, sputter deposition technique has been oftenly used for catalyst formation, due to a high deposition rate at low substrate temperature.

The microstructure and properties of CNT are influenced by the nature and preparation of catalyst. The dimensions of the catalyst particles determine the diameter and structure of nanotubes grown in a CVD process. Ni thin films are deposited using sputter deposition radio frequency (rf) plasma power, and examined by surface profiler, atomic force microscope (AFM), and field emission scanning electron microscopy (FESEM). Thus, the main interest of this study are to develop a thin catalyst film for CNTs growth application by varying the time of deposition and investigate the effect of radio frequency (rf) plasma power.

2.0 MATERIALS AND METHODS

Glass substrate covered with 100 nm thick chromium (Cr) layer was used as substrates. In order to investigate the impact of a thin catalyst layer on carbon nanotube growth, the thickness of Ni layer was manipulated from 5 to 20 nm. Ni was deposited by physical vapor deposition (PVD) on the top of the stack.

Ni with purity higher than 99.9% was used as starting material in this work to prepare stacked Ni film structure. A thin Ni layer was deposited on glass by rf sputtering deposition process, high vacuum coater (HVC) as shown in Figure 1 (a). For the deposition of the Ni film, the base pressure was kept below 1.2×10^{-2} torr. The film was sputtered in the constant voltage mode at a frequency of 13.56 MHz with the operating power changed from 20 to 100 Watt and the deposition time was changed from 20 to 600 second. The HVC deposition conditions, such as pressure, temperature and gas flow rate, were the same for all samples: pressure: 1.6 Pa, temperature T : 25 °C, and Ar gas flow rate: 10 sccm.

Prior to catalyst deposition, the original glass slide was cut into a suitable size. These substrates were then cleaned in acetone, methanol and distilled water for 10 mins and heat drying with iso-propanol. Firstly, the cleaned glass substrate was

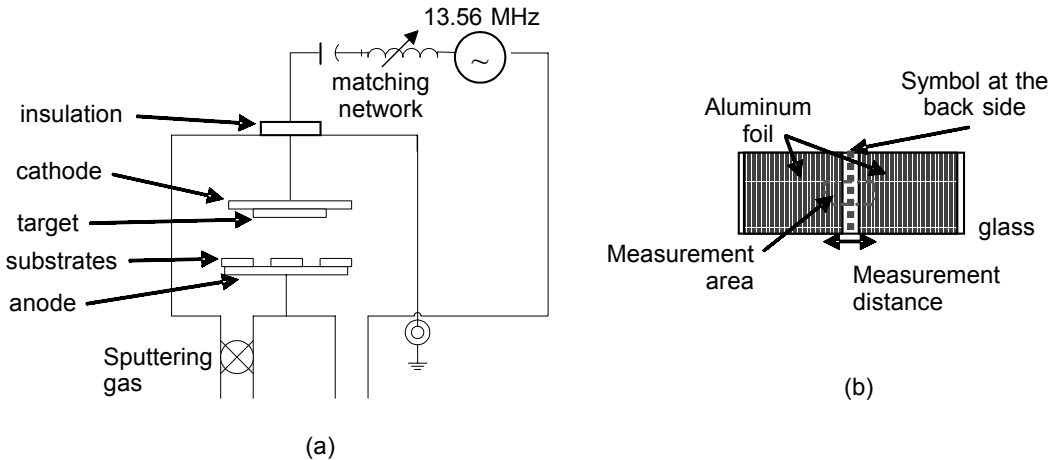


Figure 1 (a) Schematic cross-section of rf sputtering system, (b) The straight line that was used for thickness measurement

protected with aluminum foil with the exposed area at the centre of the glass to produce a gap between the aluminum foil as shown in Figure 1(b). The substrate were transferred to a HVC chamber and pumped to pressure below 2.5×10^{-5} torr. The vacuum pumping system in HVC consists of both Seiko Seiki turbo pump, and Edwards E2M18 rotary pump. At the initial stage, the rotary pump was pumped down the pressure of HVC chamber to 1.9×10^{-2} torr. The turbo pump was then operated in order to pump down the pressure to approximately 9.0×10^{-7} torr.

After the working pressure has been stabilized, ion gun pre-clean was carried out in the presence of argon gas for 5 mins followed by pre-sputtering process for 5 min. Deposition of the Ni was carried out under various conditions to investigate the effect of plasma power and process time on the deposition characteristics. Thickness of the film can be determined by measuring the vertical side of the film using Dektak³ surface profiler. Scan distance and speed for this measurement was set at 2000 μm and 80 $\mu\text{m}/\text{s}$ respectively. As the stylus moves vertically from the reference point, the vertical difference between the sample and the symbol was detected. The thicknesses of the film were then measured. The evaluations of the samples were performed using FESEM and AFM.

3.0 RESULTS AND DISCUSSION

Dektak³ surface profiler was used to measure the thickness of the post deposition sample. Results of sample no. 2 are shown in Figure 2.

The differences between the thicknesses of the samples were shown in Table 1 as the rf power and deposition time were varied. In order to investigate effect of time on the deposition process, catalyst was prepared with three different times, *i.e.* 20, 60 and 600 second with the deposition power kept at 20 Watt. Figure 3(a) depicts the

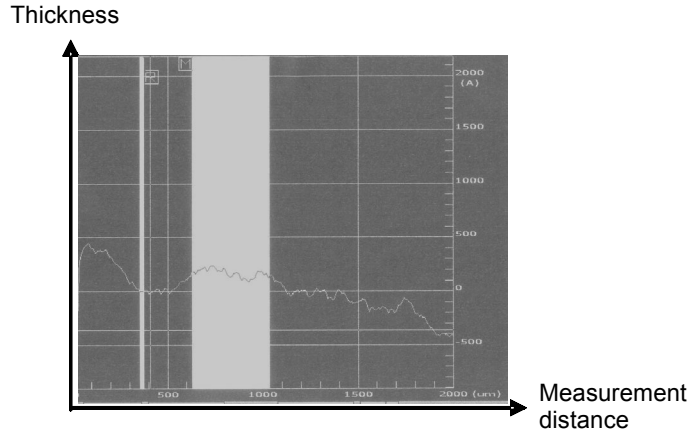


Figure 2 Thickness of sample 2 measured by Dektak³ surface profiler

Table 1 Thickness of Ni deposited on the glass substrate detected using Dektak³ surface profiler

Sample no.	Substrate T (°C), rotation speed	RF Power (Watt)	Deposition Time (sec.)	Dektak ³ Surface Profiler (nm)
1	25, 25 rpm	20	20	5.00
2	25, 25 rpm	20	60	18.07
3	25, 25 rpm	20	600	19.89
4	25, 25 rpm	30	50	11.00
5	25, 25 rpm	50	60	13.33
6	25, no rotation	80	120	16.65
7	25, 25 rpm	80	120	12.20
8	25, 25 rpm	100	180	12.90

thickness of Ni deposited with different time. It is noticed that a large peak in thickness occurred between samples number 1 and 2 with an increasing trend. The sample thickness increased significantly from 5 to 18.07 nm when the deposition time was increased from 20 to 60 second. However, the increasing of the thickness tend to be slow as deposition time was increased to 600 second. Further investigation using FESEM revealed that nickel was not uniformly distributed on the substrate surface for sample 1, but for sample 2, the as-deposited films are relatively smooth (Figure 3(c)).

The rf system requires minimum power supply to ensure maximum effective power delivered to the target surface, and sputtering can be achieved. Thus, deposition time between 60 to 600 second seemed to be the optimum working time to produce Ni thin catalyst film. Figure 3(b) and (c) shows the surface of sample number 1 at the rf power 20 Watt and the deposition time of 20 second with the surface of sample number 2 at the rf power 20 Watt and the deposition time of 60 second, respectively.

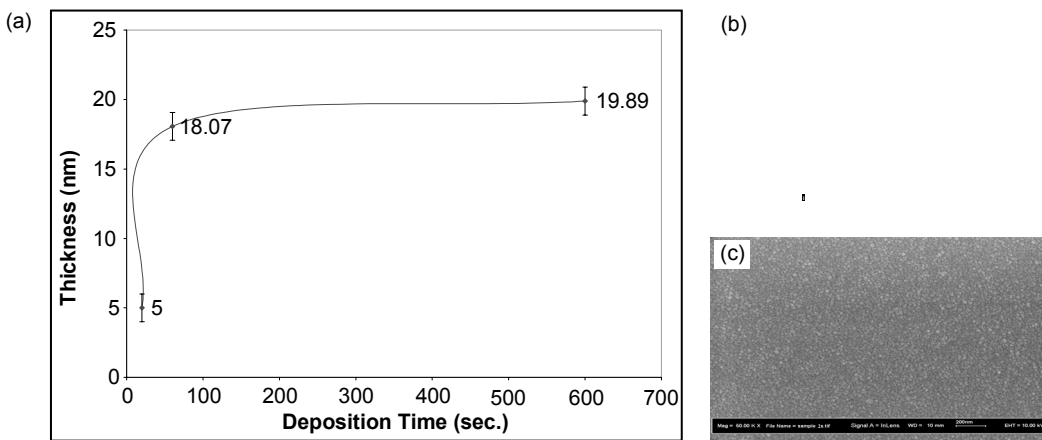


Figure 3 (a) Effect of deposition time on thickness of Ni at rf power at 20 Watt. FESEM image of nano-sized nickel particles deposited on glass for sample 1 (b), and for sample 2 (c)

Experimental results for sample 1 to 3 showed that deposition time around 60 second is the optimum time for nickel deposition, which can affect the sample condition and produce better catalyst adhesion on the surface of substrate. In order to study the effect of operating power on the deposition process, four different parameters were prepared (sample 4, 5, 7 and 8) and the results are shown in Figure 4. Both the rf power and deposition time were increased to investigate the scattering of catalyst on the surface of the substrate. If the plasma power and deposition period were made longer, the thicknesses of the catalyst were increased and the depositions were uniformly distributed over the surface. It is also noted that, samples 4 and 5 were characterized by relatively large roughness with grain heights in the range of 11 – 13 nm. In contrast, for sample 7, the catalyst was more uniformly distributed over the surface, and the feature heights were much smaller in the range of 12 – 12.5 nm.

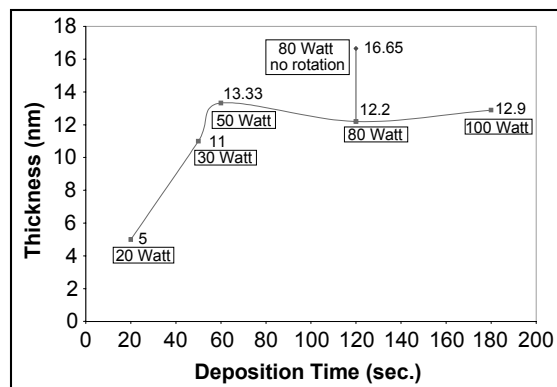


Figure 4 Effect of rf power and deposition time on thickness of Ni

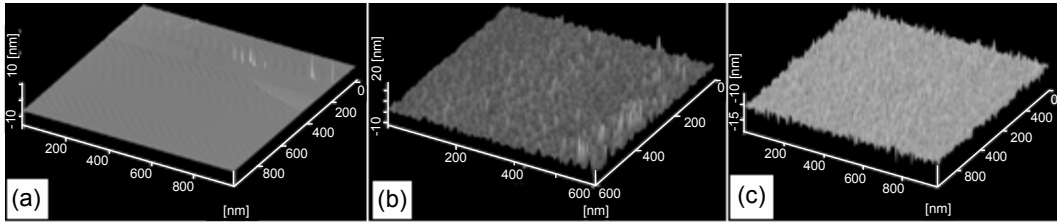


Figure 5 AFM image of (a) glass surface without any deposition (b) Ni deposited for 120 second and rf power 80 Watt, without rotation (c) Ni deposited for 120 second and rf power 80 Watt, rotation at 25 rpm

The AFM images of the surface topography are presented in Figure 5. In order to investigate the effect of sample rotation during deposition process on the dispersion of catalyst on the substrate surface, nickel catalyst was deposited without any rotation for sample 6. It can be seen that the deposition process itself created relatively rough surfaces, resulting in large grains with low density being non-uniformly distributed over the surface. In contrast, for the sample 7 with a sample rotation during the deposition process, the catalyst was more uniformly distributed, and the feature height was much smaller due to the sample rotation that can help in uniform film formation during the deposition process.

From these observations, we conclude that rf power of 80 watt and the deposition time of 120 seconds to be the optimum condition for the deposition of uniform nickel thin film. It is to be noted that the optimum plasma power condition might be different for different thicknesses of nickel catalysts and/or different species of catalysts other than nickel.

4.0 CONCLUSIONS

The rf power and deposition time is found remarkably influence the catalyst morphology. Higher power supply are found to be more effective for scattering the catalyst thin film, homogeneous and uniform thin film on the substrate. Sample rotation helps to get more uniform film during the deposition process. The detailed investigation of the catalyst behavior prior to deposition is helpful in explaining its influence on the nanostructures obtained and it can be extended for carbon nanotubes synthesis.

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