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Effects of hydrogen pretreatment on physical-vapor-deposited nickel catalyst for multi-walled carbon nanotube growth

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Abstract. Physical vapor deposited nickel catalyst layers of 10, 50, 100, 200, 350, and 500 Å were granulated using hydrogen plasma for varying times to determine an effective carbon nanotube (CNT) growth process using microwave plasma enhanced CVD (MPECVD). Nickel was deposited via sputtering or evaporation. The catalyst granule size, density, and resulting CNTs were analyzed. Sputtered nickel of 50 Å with 5 minutes of hydrogen plasma pretreatment resulted in the most effective CNT growth.

Keywords: carbon nanotube growth, hydrogen plasma, physical vapor deposition.

1 INTRODUCTION

In 1991 Iijima published transmission electron microscope (TEM) images of multi-walled carbon nanotubes (MWCNT) [1]. The unique electrical and mechanical properties of carbon nanotubes (CNTs) has resulted in an explosion of research into CNT fabrication and applications that continues today. In 1995, de Heer et al. demonstrated the field emission capabilities of carbon nanotubes with the fabrication of a small electron gun using MWCNT [2]. Research into the development of effective and efficient CNT field emission devices has thrived since this seminal publication. The most financially lucrative application for a CNT field emission device is in field emission displays (FED). Currently, the technology for displays includes cathode ray tubes (CRTs), plasma displays, liquid crystal displays (LCD), and organic light emitting diode (OLED) displays. CRT displays are usually extremely heavy compared to all other displays and they are also limited in size. Plasma displays offer larger sizes, wide viewing angles and flat screens but they require a significant amount of power, suffer from burn-in and have a relatively short life span. OLED displays are the newcomers to the market boasting low power consumption and wide viewing angles. However, current OLED displays suffer from stability problems and have short life spans. CNT FEDs in comparison have the potential to out perform the other display technologies by reaping the benefits in contrast, color, and viewing angle of CRTs without the typical drawbacks in weight, size, and power.

This research effort investigated the effects of a hydrogen plasma pretreatment on nickel (Ni) catalyst layers deposited via DC magnetron sputtering and e-beam evaporation with varying thicknesses on a silicon (Si) substrate. The results were used to determine an effective catalyst deposition method, thickness, and pretreatment time for successful CNT growth using microwave plasma enhanced chemical vapor deposition (MPECVD).

2 PHYSICAL VAPOR DEPOSITION

Physical vapor deposition (PVD) is the process of creating a vapor via physical means and depositing the vapor to form a thin film. There are a number of methods of physically

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creating a vapor. E-beam evaporation and DC sputtering were used for depositions in this research. Evaporation uses a thermal source to heat the target material to its melting point. The resulting vapor impinges on the substrate and, after reaching a condition of supersaturation, condenses forming a thin film [3]. Sputtering uses ions from a gas discharge plasma in an electric field. The electric field accelerates the ions towards the target material, the cathode. The resulting collision and transfer of kinetic energy dislodges atoms from the target which then impinge on the substrate, the anode, forming the desired thin film [3].

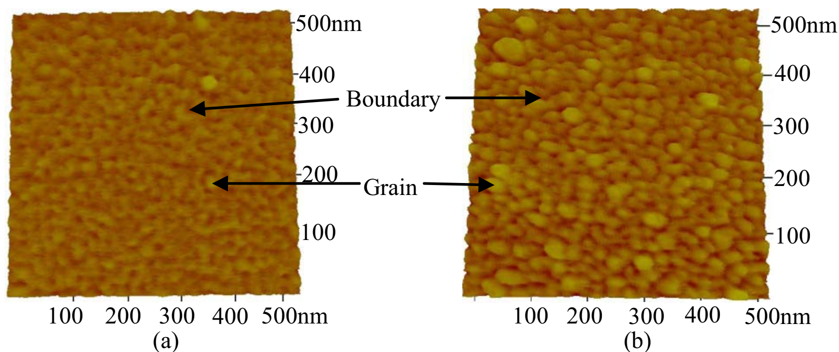


Fig. 1. AFM image of as-deposited 100 Å of (a) evaporated Ni and (b) sputtered Ni.

Figure 1 shows AFM phase measurements of as-deposited sputtered and evaporated 100 Å Ni catalyst layers. The sputtered Ni clearly has larger grain size and more defined grain boundaries. Both evaporated and sputtered thin films are deposited in a condition of supersaturation which typically results in small grain sizes due to a high rate of nucleation [4]. With the exception of impurities which can cause compressive stress, evaporated films generally have tensile intrinsic stress [5]. Sputtered films, on the other hand, have been shown to have both compressive and tensile intrinsic stresses with stress reversal occurring through control of many parameters such as ion mass, substrate temperature, target-plasma separation, and especially gas pressure. Sputtering at lower pressures typically results in compressive stress with tensile stress occurring at higher pressures. The reversal occurs between 1 and 10 mTorr [4]. The compressive stress has been attributed to shot-peening effects and possibly sputter gas incorporation. Radic et al. demonstrated some control of the grain size of sputtered nanocrytalline nickel thin films. Average grain size was varied from 11 nm to 150 nm by changing the substrate temperature during deposition [6]. Sputtered catalyst layers offer more control over the thin film properties.

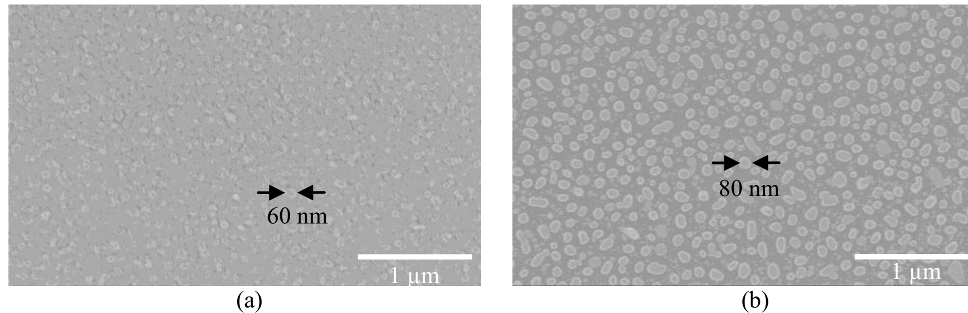
Samples were prepared with a titanium (Ti) layer 200 Å thick sputtered or evaporated onto an n-type silicon wafer [100] to act as an adhesion and diffusion barrier for the Ni catalyst layer and the subsequent CNTs. The Ni catalyst layers had thicknesses of 10, 50, 100, 200, 350, and 500 Å with samples of each thickness deposited by both e-beam evaporation and DC sputtering. For the hydrogen plasma pretreatment and CNT growth, an ASTeX 1.5 kW MPECVD system consisting of a 1.5 kW microwave plasma generator and 3.5 kW RF induction heater was used.

3 SAMPLE PRETREATMENT

CNT growth via MPECVD requires a catalyst for the CNT to nucleate around. The transition metals Fe, Ni, Co, and alloys composed of one or more of these transition metals are typically used as the catalyst materials. Before CNT growth is possible; it is necessary to pretreat the catalyst layer, a process that granulates the catalyst into nano-size islands. The catalyst nanoparticles are necessary for CNT growth and it has been shown that the diameter of the Ni nanoparticle corresponds to the diameter of the resulting CNT [7]. When hydrogen plasma is

used to granulate the Ni, it results in dispersed nanoparticle diameters. However, multi-walled CNTs can vary in diameter from less than 10 nm to 100 nm in diameter. The nominal goal for MWCNT growth is nanoparticles distributed around 50 nm or less.

The hydrogen-plasma pretreatment was performed at 20 Torr with a substrate temperature of 400 °C and microwave power at 400 W. The granulation and CNT growth processes were adapted from Wong et al. [7]. A set of samples of each thickness and deposition method were pretreated for 3.5, 5, and 7 minutes. The results were analyzed using SEM images and AFM measurements collected from three different locations across each sample.



(a) (b)

Fig. 2. 100 Å Ni Layer after 5-minute pretreatment. SEM image shows good nanoparticle formation: (a) evaporated Ni and (b) sputtered Ni.

Ni layers of 10, 350, and 500 Å were processed; however, 10 Å proved to be too thin and no Ni was present after even the shortest pretreatment time. The thicker Ni layers (350 and 500 Å) were too thick, resulting in Ni islands much too large to facilitate CNT growth. Both evaporated and sputtered samples showed clearly that as the nickel thickness increases, so does the size of the granules. The sputtered films consistently have larger granules than the evaporated films of the same thickness. This is attributed to the larger grain sizes of the as-deposited sputtered films. In normal grain growth, the average grain size increases because larger grains tend to grow while smaller grains tend to shrink and be absorbed by the larger grains [4]. Thin films seldom experience completely normal grain growth due to interactions with the larger substrate at grain boundaries and the almost always prevalent conditions that favor certain grain orientations. For example, Ni nanocrystals show a preference for the <111> direction to be out of plane which indicates grains of this orientation grow faster than other orientations [6]. The results, represented in Fig. 2, show the sputtered nanoparticles remain slightly larger than the initially smaller evaporated nanoparticles, indicating that the general trend of normal grain growth applies.

The hydrogen plasma is expected to be a vapor etchant, which is considered beneficial during CNT growth where the H_2 removes amorphous carbon [8]. When hydrogen plasma is used to granulate the catalyst layer during pretreatment, etching also occurs. If the pretreatment process is too long and the catalyst layer too thin, it can be completely etched away, as was the case with the 50 and 100 Å evaporated Ni layers after 7 minutes of pretreatment. The 50 and 100 Å sputtered Ni layers were not removed during the 7-minute pretreatment.

Oddly enough, if the Ni catalyst is pretreated for too long, the nickel nanoislands will begin to conglomerate into larger islands not suitable for CNT growth. The average diameter of nanoparticles of the 50 Å sputtered Ni increased from 25 nm to 40 nm from the 5-minute pretreatment to the 7-minute pretreatment. This phenomenon has been documented and attributed to Ostwald ripening [9]. Thus, determining the optimum pretreatment time is a crucial step in the CNT growth process.

Apart from the size of the catalyst, the areal density of the Ni catalyst is another important consideration. A high areal density will result in a dense CNT carpet which will aid in the

growth of vertically aligned CNTs. Figure 2 clearly illustrates that the evaporated samples have smaller-diameter particles with a higher areal density compared to the sputtered samples. The 5-minute pretreatment resulted in granulation closest to the nominal goal of 50 nm nanoparticles. The 50 Å evaporated and sputtered Ni catalyst was granulated into nanoparticles averaging 20 nm and 25 nm, respectively; and the 100 Å evaporated and sputtered Ni was granulated into nanoparticles averaging, respectively, 45 nm and 58 nm. The 200 Å Ni samples had average particle sizes of more than 100 nm, but due to the dispersive nature of the process there were many nanoparticles less than 100 nm as well.

AFM measurements were used to determine the surface morphology of the catalyst nanoparticles, specifically the boundaries or separation between granules. A representative AFM measurement comparing the 100 Å sputtered and evaporated samples is shown in Fig. 3. The evaporated sample has smaller diameter granules with a higher areal density than the sputtered sample. For CNT growth, the pretreatment process must transform the Ni catalyst layer into Ni nano-islands and Fig. 3(a) shows that the evaporated samples have little to no spacing between their granules. CNT growth requires the hydrocarbon gas to completely surround the Ni catalyst for nucleation. The evaporated samples have many nanoparticles not completely separated, which may impede CNT growth.

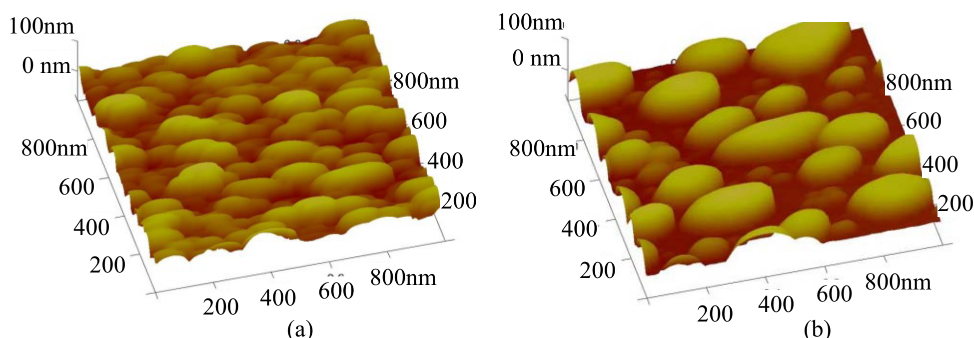


Fig. 3. AFM measurement of 5-minute pretreatment (a) 100 Å evaporated Ni and (b) 100 Å sputtered Ni.

3 CNT GROWTH

After the granulation of the catalyst has been accomplished the MPECVD system is adjusted to promote the growth of CNTs. Van der Waals forces between closely packed CNTs combined with the plasma from the microwave plasma generator system creates an environment that promotes vertical CNT growth. CNT growth is achieved by increasing the substrate temperature to 650 °C, increasing microwave power to 1000 W, and maintaining the pressure at 20 Torr while introducing the carbon feedstock gas, methane (CH_4), at a ratio of 1:8 with the hydrogen gas. The samples used above to analyze the pretreatment process were not used for CNT growth. Instead, samples with the same parameters were pretreated for the specified time and then subjected to the 2-minute growth process without being removed from the MPECVD chamber.

A CNT growth time of 2 minutes was used with a goal of 1.5 µm CNTs. The 10, 350, and 500 Å Ni samples were completely unsuccessful showing no CNT growth. This was expected, due to the lack of any Ni after pretreatment on the 10 Å samples and the lack of granulation of the 350 and 500 Å Ni samples. The 50, 100, and 200 Å Ni samples all had some CNT growth. The 200 Å Ni samples, evaporated and sputtered, only showed sporadic CNT growth between the large granulated Ni particles. From Figs. 4(a) and (c), it is very clear CNT growth was minimal on the evaporated 50 and 100 Å samples, while the sputtered samples, Figs. 4(b) and (d), had significant CNT growth. As noted above, the AFM measurements indicated evaporated films tend to result in granules that are closely packed

together and may not be completely separated which would prevent the growth of CNTs. The sputtered films in comparison showed complete granulation in the AFM measurements, see Fig. 3 (b), and resulted in successful CNT growth. Comparing Figs. 4(b) and (d), we see that the 50 Å sputtered Ni samples which had smaller average nanoparticle diameters with greater areal density resulted in denser growth with smaller diameter CNTs than the 100 Å sputtered Ni samples.

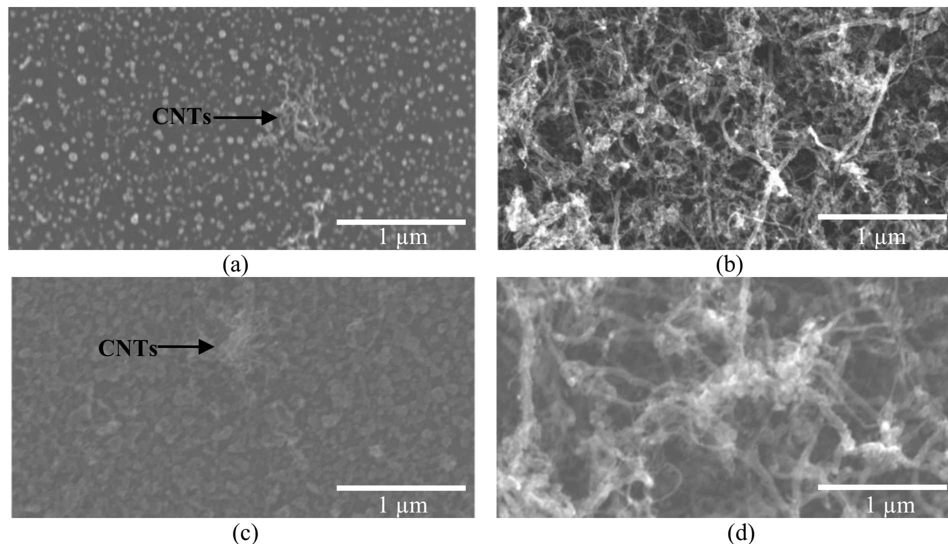


Fig. 4. SEM image after 5-minute pretreatment and 2-minute CNT growth for (a) 50 Å evaporated Ni, (b) 50 Å sputtered Ni, (c) 100 Å evaporated Ni, and (d) 100 Å sputtered Ni.

AFM measurements and patterned CNT growth experiments were used to determine a CNT growth rate for this process of approximately 1 μm per minute. The growth time begins with the introduction of the carbon feedstock gas. MWCNTs approximately 2 μm in length were achieved with a growth time of two minutes. A CNT carpet of approximately 13 μm was achieved with a growth time of 15 minutes. It should be noted that the lower portion of the CNTs tend to have some vertical alignment, however, the free ends do not.

4 CONCLUSIONS

In this phase of a continuing research effort to develop CNTs, a study of hydrogen pretreatment of Ni catalyst layers deposited on a Ti diffusion barrier has been used to determine an optimum pretreatment time, catalyst deposition method, and thickness for CNT growth via MPECVD. As expected, thicker catalyst layers resulted in larger nanoparticles after pretreatment. Most significantly, it was shown that sputtered catalyst films facilitate CNT growth much better than evaporated films despite SEM imaging indicating better granulation with the evaporated films. The lack of CNT synthesis with evaporated catalyst layers was attributed to incomplete separation of the Ni nanoparticles shown through AFM measurements and the larger grain size and more defined grain boundaries of the initial sputtered Ni. While the thicknesses of the evaporated and sputtered layers were identical, there are clearly significant differences in the films. The sputtered Ni was deposited at a pressure of 3.2 mTorr which is within the intrinsic stress transition range of 1-10 mTorr. The sputtered film may have compressive stress, while the evaporated film is most likely under tension. Evaporated catalysts are often used successfully in CNT synthesis. The results of this effort have demonstrated a significant difference in the properties of sputtered and evaporated films in the same process conditions. Thus, sputtered and evaporated catalysts should not be

considered interchangeable in a CNT fabrication process. Further research will be conducted to determine the intrinsic stress of the sputtered films and how changing the sputtering parameters, especially pressure, affect the pretreatment granulation and subsequent CNT growth. It should be noted that further testing has shown that a change in the barrier layer material can significantly influence the necessary pretreatment time for effective granulation.

Variations of the pretreatment time, catalyst layer deposition and thickness were used to achieve desired catalyst nanoparticle diameters while maintaining a relatively high areal density for the growth of CNTs. The results of this study, as demonstrated with AFM measurements and SEM images, show a 50 Å sputtered Ni catalyst layer granulated for 5 minutes in a hydrogen plasma was the most effective recipe for growing dense CNTs via MPECVD. This recipe has proven reliable, achieving dense CNT growth in continued research efforts into gated CNT field emission arrays.

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