

Growth of Carbon Nanotube Using Microwave Plasma Chemical Vapor Deposition and Its Application to Thermal Dissipation of High-Brightness Light Emitting Diode

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Abstract—Microwave plasma chemical vapor deposition was used to synthesize the carbon nanotube (CNT) on silicon wafers. The catalyst was used the mixture of Ni and Co alloys. The suitable weight percentage of Co content for growing the CNT was found to be 1.6% in this work. Due to the excellent high thermal conductivity, we mixed the CNT with epoxy to serve as the adhesive joining element of high-brightness light emitting diode (HB-LED). Compared to the commercial epoxy, we had found that the junction temperature was decreased from 120°C to 103°C, and the thermal resistance was decreased from 81 C/W to 67 C/W. These results show that the mixture of CNT and epoxy could be a promising candidate for applying to the thermal dissipation of the HB-LED package.

Keywords: carbon nanotube, microwave plasma chemical vapor deposition, high-brightness light emitting diode, junction temperature.

I. INTRODUCTION

Since carbon nanotube (CNT) was observed by Iijima in 1991 [1], it has attracted much attention due to its unique physics and chemical properties; such as high aspect ratio, high chemical stability, high mechanical strength, high electrical conductivity, and excellent thermal conductivity. Therefore, the CNTs have opened up a wide range of research and their potential applications such as emission display [2], gas sensor [3], CNT-FET [4], and hydrogen storage [5].

Several methods such as arc discharge [6], laser ablation [7], and different forms of chemical vapor deposition (CVD) [8]- [9] have been used to synthesize the CNTs. The manufacturing equipments used in arc discharge and laser

Manuscript received March 5, 2011; revised April 8, 2011. This work was financially supported by the Technology Development Program for Academia (TDP) under the contract no. 97-EC-17-A-07-S1-105.

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ablation method are more complicated, but the growth parameters are easy to control. Conversely, the growth parameters of the CVD method are not easy to control but are reliable. Furthermore, this method is considered to be the most popular way to generate the great number, good reproducibility, and high quality CNTs with low temperature processing. Therefore, the multiwall CNTs (MWCNTs) were grown using the microwave plasma CVD (MPCVD) in this work. The catalyst was used the mixture of nickel (Ni) and cobalt (Co) alloys. We discussed the effect of various Co contents on the characteristics of the CNTs.

Because the CNTs show excellent characteristics in thermal conductivity, it is attractive for researchers to study the thermal conducting applications using the CNTs. Theory predicts the thermal conductivity of CNTs at room temperature is as high as 6600 W/(m·K) [10]. The measured thermal conductivity of MWCNT is about 3000 W/(m·K) [11]. This value is higher than that of known thermal conducting materials of diamond or graphite. Therefore, the CNT might be a popular choice in the next generation for applying to the thermal dissipation of high-power devices.

In recent years, the solid state lighting using a high-brightness light emitting diode (HB-LED) has been an attractive candidate for general illumination applications. The HB-LED can be used to produce high luminosity, but there exists an increasing heat effect in the P-N junction. The thermal dissipation is very important to the HB-LED because the luminescence will reduce linearly and the life will reduce exponentially with the increasing junction temperature. Therefore, it draws many scholars to investigate the proper thermal conduction design to keep the HB-LED operating safely under the critical temperature. The CNT might be one of the possible materials used to enhance the thermal dissipation of HB-LED due to its high thermal conductivity

In this paper, the CNTs were grown using the MPCVD system. We mixed the CNTs with the epoxy to serve as the adhesive joining element of the HB-LED. The results show that the junction temperature and thermal resistance can be greatly improved. Therefore, the mixture of CNTs and epoxy could be a promising candidate for the thermal dissipation design for the HB-LED package.

II. EXPERIMENT

The CNTs were produced using a MPCVD system [12]. It was known that using the Fe, Co and Ni as the catalyst in various growth processes lead to the formation of CNT.

However, we used the Ni and Co mixtures as the catalyst in this work. The substrate was used a n-type Si (100) substrate on which the catalyst layer of the alloy film of the Co and Ni of thickness 20 nm were co-deposited by a RF sputtering system. An RF power of 50 W at 13.56 MHz was supplied to a Ni target along with Co tablet through an impedance matching box. We controlled different numbers of Co tablet to obtain the various weight contents in the mixture. The qualities of growing MWCNTs were controlled by some parameters including the gas flow rate, the microwave power, the pressure, the temperature, and the deposition time.

First the MPCVD system pumps down to a vacuum of 5×10^{-3} Torr. Then the pressure is increased to 26 Torr by introducing H_2 gas at a flow rate of 90 sccm to the chamber and the temperature is set to the growth temperature $500^\circ C$. The microwave power is turned to get stable plasma inside the chamber. The H_2 plasma pre-treatment on the substrates breaks the Ni-Co alloy film into nanoparticles.

After we have pre-treated the substrate for 12 minutes, the methane (CH_4) is introduced to the chamber for 10 minutes for CNTs growth at a flow rate of 10 sccm. The CH_4 provides the carbon for nanotube growth. The microwave power is set to 700 W. The growth of CNTs terminates when the methane gas supply turns off and the system allows cooling down to room temperature. The properties of the plasma-treated catalyst and the prepared CNTs are evaluated by scanning electron microscopy (SEM), transmission electron microscope (TEM), and Raman microscope (RM).

III. RESULTS AND DISCUSSIONS

As-deposited Ni-Co alloy films on Si substrates using RF sputtering system are continuous and smooth. However, after H_2 plasma treatment, they change to randomly distributed quasi-spherical particles. Breaking of Ni-Co alloy films into nanoparticles is attributed to the continuous collisions by active ions in the plasma with the film. The heating process will result in the stress caused by the mismatch of thermal expansion coefficients of the Ni-Co alloy film and Si substrate contributed to the formation of nanoparticles. The catalytic particles with diameters in a similar range can act as the nucleation seeds for the growth of CNTs.

Figure 1 shows the SEM images of the surface morphologies of Ni-Co catalytic particles on Si substrate after H_2 plasma treatment under different Co weight percentages; (a) 0.7%, (b) 1.6%, (c) 4.3%, and (d) 5.2%, respectively. Figs. 1 (a) and (b) show high density and the diameters distributed in the range of 20-120 nm. However, the particles sizes increases with the increase of the weight ratio of the Co component, as shown in Figs. 1 (c) and (d). The particle size is estimated to be around 40-200 nm, and the distribution density is low. The catalytic particles play a crucial role at the tip of the CNTs in the growth. Some large catalytic particles with a diameter of several hundred nm probably can not contribute to the CNT growth. As shown, the better particles size and distribution density occur at 1.6% wt of Co content here.

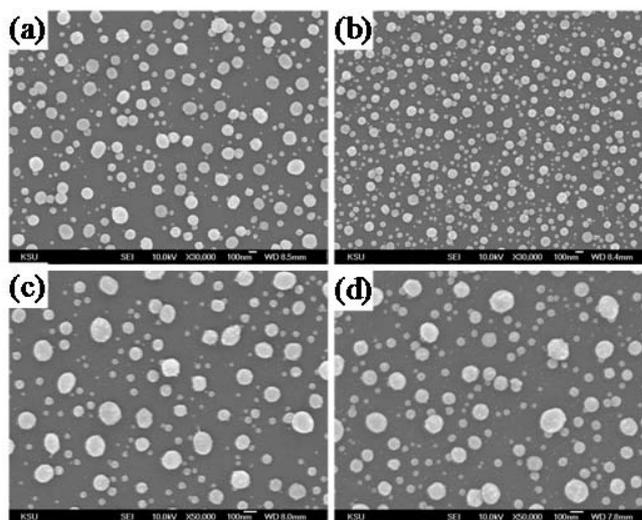


Fig. 1. SEM images of the surface morphologies of Ni-Co catalytic particles on Si substrate with different Co weight percentages; (a) 0.7%, (b) 1.6%, (c) 4.3%, and (d) 5.2%, respectively

Fig. 2 shows the corresponding SEM image of the grown CNTs with respect to the Fig. 1. Synthesized CNTs are uniformly distributed with a relatively high density, as shown in Fig. 2 (b). For the other cases, the densities of the CNTs are reduced significantly, especially in Figs. 2 (c) and (d). The amplified image of Fig. 2 (b) is shown in Fig. 2 (e), which demonstrates that synthesized CNTs are uniformly distributed and the average diameter of the CNTs is about 45 nm. All CNTs are laid down on the substrate in long noodle-like shapes. The height of the CNTs is ranged from $4 \mu m$ to $6 \mu m$. Based on the SEM analysis, we estimate the suitable weight percentage for the Co component in the Ni-Co mixture catalyst for growing the CNTs is about 1.6%.

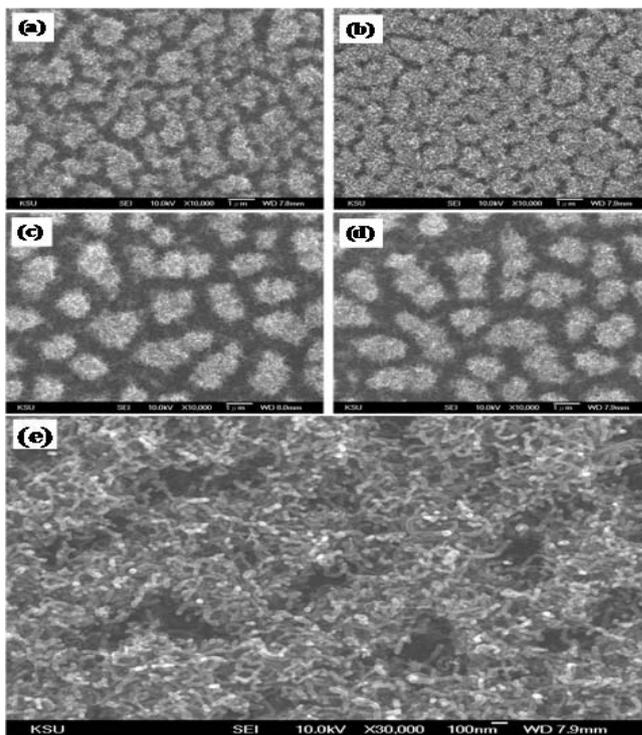


Fig. 2. SEM image of CNTs under different Co weight percentages; (a) 0.7%, (b) 1.6%, (c) 4.3%, (d) 5.2%, and (e) amplified image of (b).

Fig. 3 shows the corresponding TEM image of the CNTs. An important feature is that the CNTs consist of hollow compartments. The TEM image taken at a higher magnification clearly shows that the average outer diameter is about 40-45 nm. This value is similar to that shown in the SEM result.

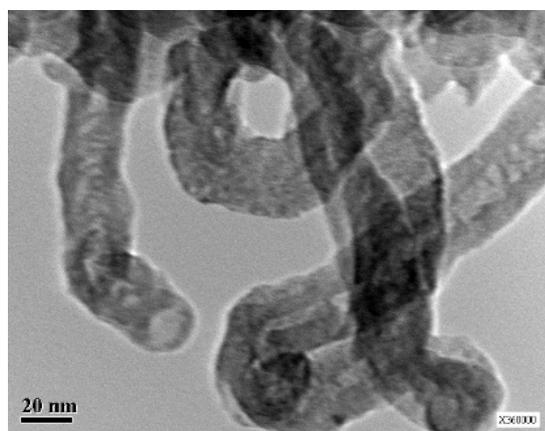


Fig. 3. The TEM image of the CNTs.

The RM has proved to be a popular non-destructive technique successfully used in the characteristics of carbon-based materials. Fig. 4 shows the micro-RM of the CNTs grown on the Si substrate with different contents of Ni-Co catalyst. The excitation laser is a 632.8 nm He-Ne laser. The CNT is identified by a clear G-line at 1590 cm^{-1} [13].

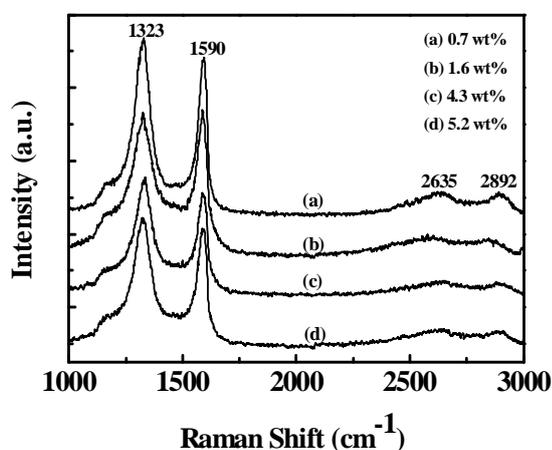


Fig. 4. Micro-Raman spectrums of the CNTs grown on the Co-Ni co-deposited Si substrate.

The G-band corresponds to a phonon high-frequency E_{2g} first-order mode of graphite and is related to the vibration of sp^2 -bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer [14]. It is known that the D band corresponding to 1323 cm^{-1} is related to the defects in graphitic sheets or carbonaceous particles on the surface of CNTs. The D-band is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite, defects in the curved grapheme sheets, and the turbostratic structure of grapheme structure. We also obtain the second order peak of D band; occurring at 2635

cm^{-1} , which is attributed to the possible presence of amorphous carbonaceous products, disordered carbon, defects in curved graphite sheets, tube ends, and surviving impurities [15]-[16]. Another weak broad band at 2892 cm^{-1} is the combination of the D and G bands.

The ratio of the intensity of D peak (I_D) to the intensity of G peak (I_G) is a measurement of the amount of disorder in the CNTs. The I_D/I_G band intensity ratio increases when covalent bonds are formed. Among the four Raman spectrums, we have found that the intensity of peak at the G band is slightly stronger than that of the D band for curve (b). The I_D/I_G ratio of the CNT in this measurement is smaller than 1, which suggests less defect content in the CNT. This indicates that the quality of the CNTs under this growth condition is better than the other conditions. Based on the RM analysis, we confirm the fact that the CNTs have the multiwall structure, but there might be some defects or carbonaceous particles on the wall surface.

IV. APPLICATION

The solid state lighting using a HB-LED is an attractive candidate for general illumination applications. The thermal dissipation is very important to HB-LED because the luminescence will reduce linearly and the life will reduce exponentially with the increasing junction temperature. Therefore, it draws many scholars to investigate the proper thermal design to keep the HB-LED operating safely under the critical temperature.

The CNT is a promising candidate to improve the thermal dissipation of HB-LED due to its excellent thermal conductivity. Recently, K. Zhang et al. demonstrated the application of CNTs array as a thermal interface material (TIM) of HB-LED [17]. They found that the CNT-TIM can greatly reduce the thermal interfacial resistance significantly compared to the commercial TIM. However in this work, we mix the CNTs with the epoxy, which is often used as a conductive adhesive layer for mounting the LED chip on the surface of the conductive structure. The thermal conductivity of epoxy is less than 0.5 W/(m·K). Therefore, we expect this mixture could be an effective adhesive joining element.

For a uniform dispersion of the CNTs in the epoxy, it is important to put high energy into the system because the nanoparticles tend to agglomerate in the epoxy. Therefore, it is very important to overcome these van der Waals-forces for a good dispersion. First the CNTs are immersed in acetone for several hours in an ultrasonic bath. Then the epoxy is added into this solution. Finally we use the high-speed mixer to mix this solvent.

The GaN-based epilayer is grown on a (0001)-oriented sapphire substrate by a metal-organic chemical vapor deposition (MOCVD) system. The LED comprise a 30-nm-thick GaN nucleation layer, a 2- μm -thick undoped GaN layer, a 2- μm -thick Si-doped n-GaN layer, an InGaN/GaN multiple-quantum wells (MQWs) active region of 457 nm emitting wavelength, and a 300-nm-thick Mg-doped p-GaN layer. After standard etching and electrode evaporating process, the LED wafer with thickness of substrate grinded to 150 μm is cleaved into thousands of 45 \times 45 mil^2 chips. The LED chips are then die bonded in a

lead frame of surface-mount type by epoxy mixed with the CNT. After wire bonding and encapsulation, the LED lamps are finished.

Figure 5 shows the cross-section SEM image of the CNTs along with the epoxy. We can see that the CNTs are suitably mixed with the epoxy. The weight percentage of the CNTs in the mixture is about 10 %. Two different average diameters of the CNTs with respect to 15 nm and 45 nm, which are grown using the MPCVD system under different process conditions, are used in this application. In addition, the CNT/epoxy composites are compared to a common commercial epoxy for the HB-LED measurements.

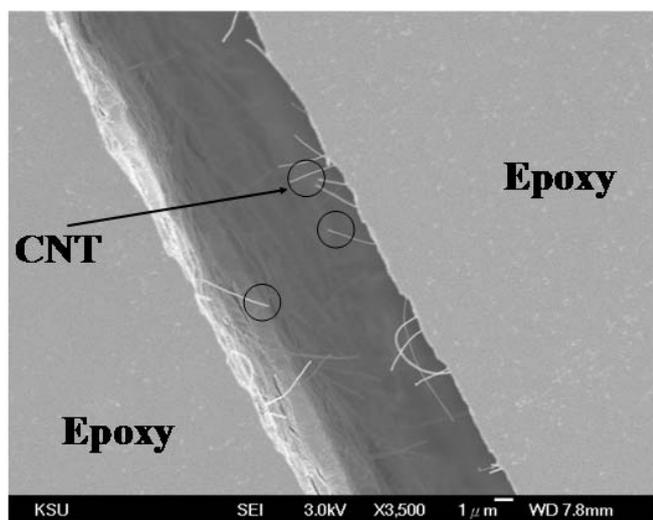


Fig. 5. Cross-section SEM image where the CNTs are mixed with the epoxy.

Figure 6 shows the measurement of junction temperature in this HB-LED. As shown, the smallest junction temperature is occurred at the condition with the CNT/epoxy composites having 15 nm diameters of the CNTs. That is because the specific surface area of 15 nm diameters of the CNTs is larger than that of 45 nm diameters of the CNTs under the same weight condition. Therefore, the junction temperature is decreased from 120 °C to 103 °C. The degradation percentage is about 14%.

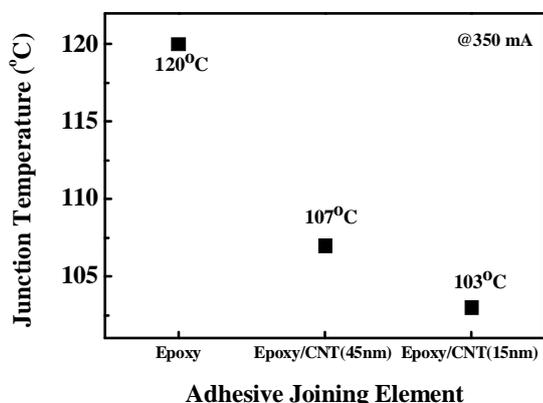


Fig. 6. Measurement of the junction temperature of the HB-LED under different conditions.

Thermal resistance is the object of impeding the effect of heat conduction. From the HB-LED junction to the thermal contact at the bottom of package, the thermal resistance can

be calculated from the difference of junction temperature (T_j) and ambient temperature (T_a), and the forward voltage (V_f), and forward current (I_f). The formula is expressed as:

$$R_{th} = (T_j - T_a) / (V_f * I_f) \quad (1)$$

The test current is 350 mA with the corresponding voltage 3.3 V. Under the composite with 15 nm diameter of CNTs condition, we can obtain the thermal resistance is decreased from 81 °C/W to 67 °C/W. The degradation percentage is about 17%.

Figure 7 shows luminous intensity versus injection current (L-I) characteristics of the LEDs with/without CNTs mixed in the die-bonding epoxy. The saturation current of LED without the CNTs mixed in the die-bonding epoxy is 1100 mA, and those of LEDs with diameter 50 nm and 15 nm MWCNT mixed in the die-bonding epoxy are 1200 mA and 1340 mA, respectively. The thermal conductivity of pure die bonding epoxy is lower than that of the CNTs mixed die bonding epoxy, and the saturation current of the LED with diameter 15 nm CNTs mixed in the die-bonding epoxy has increased 21.8% compared with that of LED without the CNTs mixed in the die-bonding epoxy. Therefore, it is demonstrated that the epoxy/CNT could be used as a good adhesive joining element, which can effectively decrease the junction temperature and thermal resistance in the HB-LED applications.

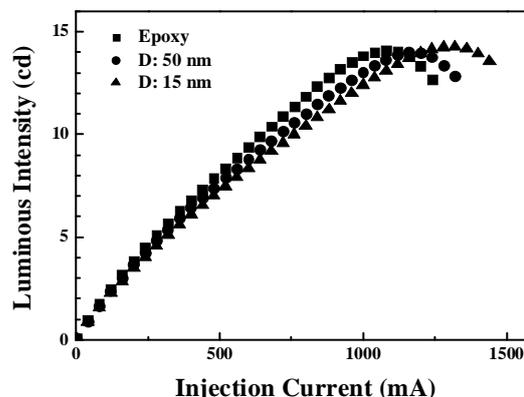


Fig. 7. Measurement of luminous intensity versus injection current (L-I) characteristics of the HB-LED under different conditions.

V. CONCLUSION

We have grown the CNTs on a Co/Ni co-deposited n-type Si substrate using the MPCVD method. We have found that the suitable weight percentage of the Co in the mixture of Co/Ni catalyst for growing the CNTs is about 1.6%. The CNT is a promising candidate to improve the thermal dissipation of high power devices because its thermal conductivity is high. Therefore, we demonstrate the application of the CNTs to the HB-LED package. Under the epoxy/CNTs composite with 15 nm diameter of CNTs condition, we have concluded that the junction temperature is decreased from 120 °C to 103 °C, and the thermal resistance is decreased from 81 °C/W to 67 °C/W compared to the commercial epoxy. The saturation current is increased from 1100 mA to 1340 mA. Based on the experimental results, we

can conclude that the epoxy/CNT is a promising adhesive joining element in the HB-LED package.

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