"Diamond/CNT Film Interface for Heat Dissipation in Electronic Devices"

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Summary:

The project AOARD-08-4056 was supported by the Asian Office of Aerospace Research and Development on the "*Diamond/CNT film interface for heat dissipation in electronic devices*". We have carried out the following works:

1. We have made multi-wall Carbon nanotube (CNTs) by thermal CVD technique and diamond material by MP-CVD technique.
2. We have developed simple techniques for functionalizing the CNTs materials to form CNT-COOH and CNT-$C_6H_4NH_2$.
3. We have made the advanced thermal dissipation materials by adding the functionalized CNTs and diamond into commercial thermal glue
4. The material was successfully applied in a micro-processor of a personal computer. The materials could reduce the maximum temperature of the processor and stabilize for longtime operation in full load 100% usage CPU mode. The CPU can work in over locking mode up to 125% the default speed of the CPU without over the safety temperature.
5. A simple model and calculations for the thermal response were carried out and the calculation was well suited with the experiment measurement.
6. The results related to the project was published and presented at 01 Invited talk and 01 presentation at the International Conference the APCTP-ASEAN Workshop on Advanced Materials Science and Nanotechnology, September 15-20, 2008, NhaTrang-Vietnam, 01 book chapter published in "Nanotechnology R&D and Business Trends in the Asia Pacific Rim", World Scientific Publisher, Singapore, 2009, and a manuscript submitted to the Journal of Diamond and Related Materials Journal.
7. The project confirmed and opened up a way to apply the CNT material in other high power laser system, high power LED for lightings and other civil application.

I. Introduction:

Carbon nanotube (CNT) is a new type of carbon material that was found in 1991. One of the most valuable properties of the CNT is its extremely high thermal conductivity (3000 W/m.K compared to thermal conductivity of Ag 419 W/m.K). The CNTs is a conductive material with high aspect ratio structure. It suggested an approach in applying the CNTs in thermal dissipation media to improve the performance of computer processor and other high power electronic devices.

The commercial thermal matching media is normally basing on silver. By adding a suitable amount of the CNTs into the commercial silver paste, it is expected to reduce the temperature and strongly improve the capacity density, the performance of any high power electronic components such as micro-processor, high power laser, high power LED for lighting, an so on. The materials can also be applied in other civil application such as in high voltage transformers.

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The results related to this project was published and presented at the International Conference the APCTP-ASEAN Workshop on Advanced Materials Science and Nanotechnology, September 15-20, 2008, NhaTrang-Vietnam; a book chapter published in ?Nanotechnology R&D and Business Trends in the Asia Pacific Rim?, World Scientific Publisher, Singapore, 2009, and a manuscript submitted to the Journal of Diamond and Related Materials Journal.

14. ABSTRACT
Commercial thermal matching media such as thermal grease are normally basing on silver. By adding a suitable amount of the CNTs into the commercial silver paste, it is expected to improve the conductivity and the performance of any high power electronic components such as micro-processor, high power laser, high power LED for lighting, and so on. In this research, CNT materials were successfully functionalized to form CNT-COOH and CNT-C6H4NH2. The functionalized CNTs material was added to a commercially available thermal paste up to 2% and still keeping the sticking properties of the paste. This 2% CNT-thermal paste was shown to reduce the temperature of the micro processor down to 65oC, prolong the thermal rise time and work without reducing the CPU performance for more than 10 days in full load and even up to 125% CPU usage mode without exceeding the safe operating temperature. Analytical calculations were carried out and verified with experiment data.

15. SUBJECT TERMS
Thermophysics, Carbon nano tubes, Electronic Devices, Thermodynamics

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To realize the idea, it is important to do the fictionalization of the CNT materials in order to improve the separation and contribution of the CNTs into the based material. In this project we:

- Utilize multi-wall CNTs made by thermal CVD and diamond made by MPCVD techniques
- Develop techniques for functionalize the CNTs materials to improve the solubility in the solution
- Make advanced thermal dissipation materials by adding the functionalized CNTs and diamond into commercial thermal glue by mechanical methods
- Compare the thermal dissipation efficiency of the CNTs and the commercial silver base materials by directly measure the temperature of the micro-processor of a computer

II. Results

1. Result of synthesis and functionalizing

We have developed a thermal CVD to produce multi-wall CNTs. The technique indeed was already existed in our laboratory. However, the purity of the material is needed to be improved. We have developed an *insitu* purifying technique by oxidation in oxygen at 400^oC. The material is multi-wall CNTs with diameter: 10-50 nm; length: several tens μm; purity can be increased up to 95%. Fig. 1 is typical SEM and TEM images of the grown CNTs. Due to the geometric structure and the hydrophobic nature, the CNTs materials is tend to stick together and the CNTs materials are not soluble in water and other solution. As seen in Fig. 2 (B0) the CNTs were accumulated rightly in water.

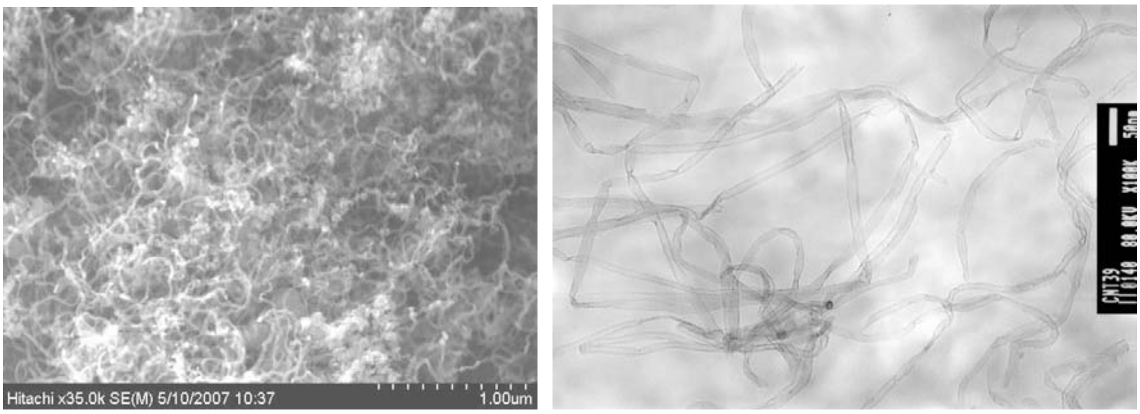

Fig. 1. Typical SEM and TEM images of the CNTs

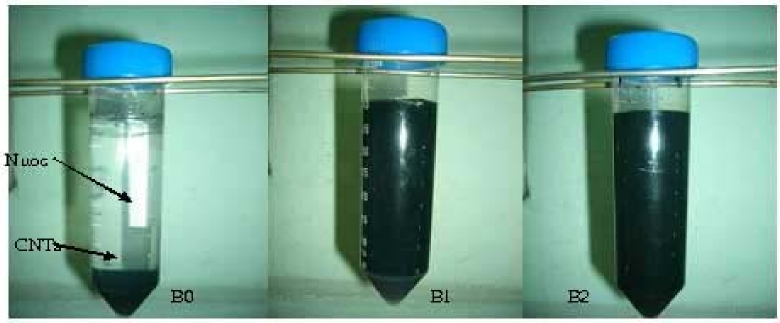

Fig. 2. Original CNT (B0) and functionalized CNT-COOH (B1) and CNT-$C_6H_4NH_2$ (B2) in water (the photos were taken after 5 days stayed in the bottle)

This means that it is difficult to distribute the material in other matrix. To overcome this problem we functionalized the CNTs to form CNT-COOH and CNT-$C_6H_4NH_2$. The CNT-COOH is easily formed by adding 1g CNT into 0.1 mol. HNO_3 and 0.3 mol. H_2SO_4 at 80^{o}C and ultrasonic vibration for 4 hours. The product was then filtered and dried at 80^{o}C for 24 hours. Infrared absorption measurement has confirmed the formation of C-COOH bonds at the defect locations of the CNT. A direct evidence of the fictionalization is the CNT-COOH is totally soluble in the water as shown in Fig. 2 (B1). On the same approach, the CNT-$C_6H_4NH_2$ was also easily formed by adding the CNTs materials in Diazo salt at 60-70^{o}C for 24 hours and then filtered and dried at 80^{o}C for 24 hours. Fig. 2 (B2) confirmed the CNT-$C_6H_4NH_2$ is totally soluble in water even for 5 days. The mechanism for the solubility is that the functionalized CNT was polarized in water and they charged the same sign and tend to repulsed each other in the solution. The fictionalization of the CNT is important to improve the dispersion of the CNTs in the master material.

2. Result of application of CNTs in thermal matching media

We have investigated the possibility of applying the CNTs material by adding the functionalized CNTs into commercial silver base thermal grease for PC. Fig. 3 show the thermal conductivity of the CNTs materials compared with other element. It is seen that the CNTs material has the highest value and is the ideal materials for the thermal matching media. We propose to utilize CNTs and diamond in the thermal management system for a personal computer as shown in Fig. 4.

Fig. 3. *Thermal conductivity of CNTs and other materials*

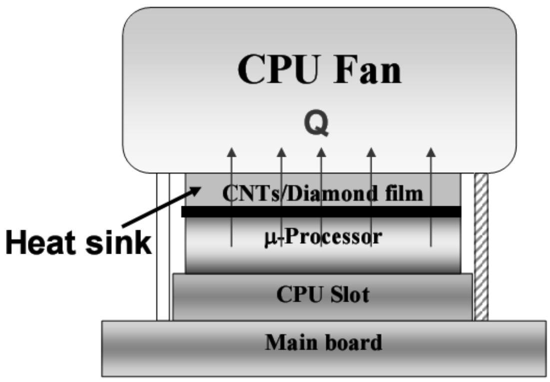

Fig. 4. *Schematics of the thermal dispersive system of the CPU using CNT and diamond*

Fig. 5. *Image of the commercial silver paste for PC (Star Company)*

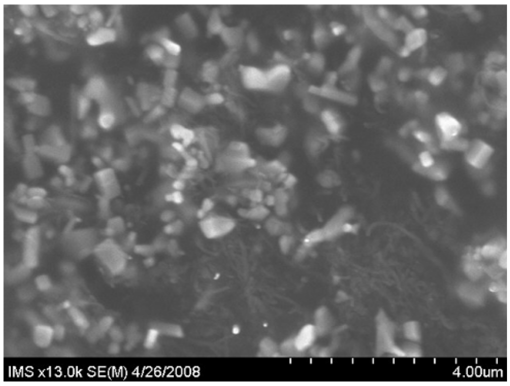

Fig. 6. *SEM image of 2% CNTs thermal compound*

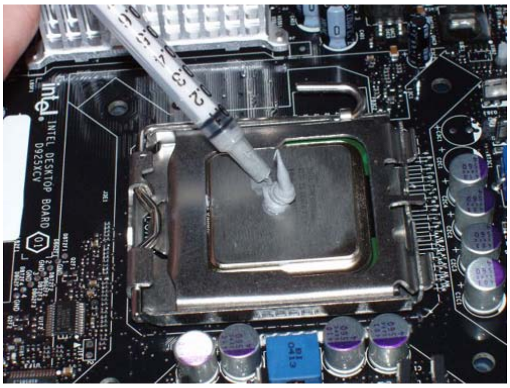

Fig. 7. *Image of pasting the CNTs thermal compound on the surface of the CPU*

A thin layer of the CNT/diamond thermal matching material will be placed in between the surface of the micro processor and the heat sink of the CPU. The computer will be operated and the thermal dissipation efficiency and thermal response is evaluated by directly measure the temperature of the μ-processor using a dedicate software and a temperature sensor built-in inside the μ-processor. Since the surface of the CPU and the heat-sink is not entirely flat, there are many tiny gaps between the two components that make a negative effect on the heat transfer. Material with high thermal conductivity is needed to fill these gaps and improve heat transfer between the CPU and the heat-sink as shown in Fig. 4. We chose a personal computer: Intel Pentium IV, 3.066 GHz, 512 MRAM, 80 GB Hard-disk and Window XP sp2 operating system.

The temperature of the CPU was measured by using a software Speed Fan 4.3.3 and the CPU was pushed to operate in full load mode by using the software Stress Prime 2004 ORTHOS. The CPU was also tested to work in over locking mode up to 3.8 GHz (125% speed compared to the original speed of the CPU: 3.06 GHz).

Multi-walled carbon nanotubes (MWCNTs) were produced by thermal CVD technique on iron mesh catalyst in a gas mixture of acetylene, hydrogen and nitrogen. The diameter and length of the grown MWCNTs used in this experiment was 20-80 nm, several tens µm, respectively. Typical SEM and TEM images of the grown MWCNTs are shown in Fig. 1. Functionalized MWCNTs was mixed with the commercial thermal compound mentioned above at different concentrations by mechanical method. The thermal matching media in a volume of 0.12 ml was carefully applied on an area of 3x3 cm^2 of the µ-processor as shown in Fig. 7. The thickness of the thermal matching media was approximately 130 um. The influence of the force between the heat sink and the processor can be avoided because we use the same volume of the thermal paste and use the same mechanical holding system of the CPU.

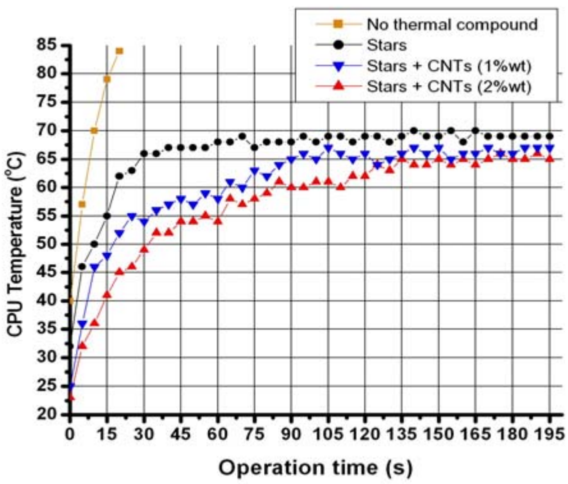

Fig. 8. *The temperature of the μ-processor as a function of working time in different configurations: no thermal paste (squared dots); commercial paste (circle dots); 1%CNT+comercial paste (downward triangle dots); and 2%CNT+comercial paste (upward triangle dots)*

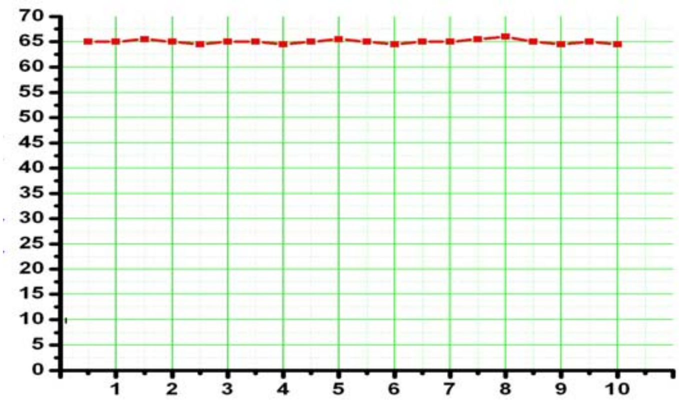

Fig. 9. *The temperature of the μ-processor using 2% CNT+ commercial paste working continuously for 10 days*

We measured directly the temperature of the μ-processor during the operation of the computer in 100% usage CPU mode. Figure 8 is the measured temperature of the μ-processor as a function of working time in 100% usage CPU mode in four cases: (i) no thermal matching media, (ii) utilizing commercial thermal compound and (iii) 1%CNT- and 2% CNT- thermal compound. It is clearly seen from Fig. 8 that without thermal matching media, the temperature of the μ-processor quickly reached 85^{o}C within 20 seconds and the computer was automatically shut down. This obviously confirmed the essential of the thermal matching media for the device. By using CNTs thermal compound 2% wt., the temperature increasing time and the maximum temperature of the μ-processor were 200 seconds and 65^{o}C, respectively. Whereas these values are 75 seconds and 70^{o}C for the commercial thermal compound. The measurement was repeated for many times and stable for long period of operation. Fig. 9 is the temperature of the μ-processor using 2% CNT+ commercial paste working continuously for 10 days using 2% CNT+ commercial paste. It is seen that the temperature of the CPU working in 100% usage CPU mode saturated at 65^{o}C. This confirmed the improvement of the thermal dissipation is absolutely attributed by the added CNTs component. Noted that 2% wt. CNTs was highest percentage in the paste that still keep the adhesive and sticking property of the media. The measurement was done in a room with temperature fix at 26^{o}C. The basic parameter on the thermal property of the commercial paste was not announced however the measurement results have confirmed the excellent thermal properties of the CNT materials.

The temperature increase of the μ-processor can be simply expressed by differential equation (1):

$$\frac{dT}{dt} = \frac{(P - J)}{C} \qquad (1)$$

Where T is temperature of the μ-processor, P is the radiate thermal power of the μ-processor, J is the rate of radiate heat flow and C is heat capacity of the system.

$$J = \frac{(T - T_0)}{R} \qquad (2)$$

Where R is heat resistance of thermal dispersive system, and T_0 is environmental temperature (T =26^{o}C). From equations (1) and (2), we have:

$$\frac{dT}{dt} = (P - \frac{T - T_0}{R})\frac{1}{C} \qquad (3)$$

$$\frac{dT}{dt} = \frac{PR + T_0 - T}{RC} \qquad (4)$$

$$\frac{dT}{PR + T_0 - T} = \frac{dt}{RC} \qquad (5)$$

Since the temperature of the μ-processor at the time t = 0 is slightly different from T_0 due to the running of the computer before starting to count the time so from equation (5) we have:

$$\int_{T_1}^{T} \frac{dT}{PR + T_0 - T} = \int_0^t \frac{dt}{RC} \qquad (6)$$

$$-\int_{T_1}^{T} \frac{d(PR + T_0 - T)}{PR + T_0 - T} = \frac{1}{RC}\int_0^t dt \qquad (7)$$

$$-\ln\left(PR + T_0 - T\right)\Big|_{T_1}^{T} = \frac{t}{RC} \qquad (8)$$

$$\ln\left(\frac{PR + T_0 - T}{PR + T_0 - T_1}\right) = -\frac{t}{RC} \qquad (9)$$

$$\frac{PR + T_0 - T}{PR + T_0 - T_1} = e^{-\frac{t}{RC}} \qquad (10)$$

$$PR + T_0 - T = (PR + T_0 - T_1)e^{-\frac{t}{RC}} \quad (11)$$

$$T = (PR + T_0) - (PR + T_0 - T_1)e^{-\frac{t}{RC}} \quad (12)$$

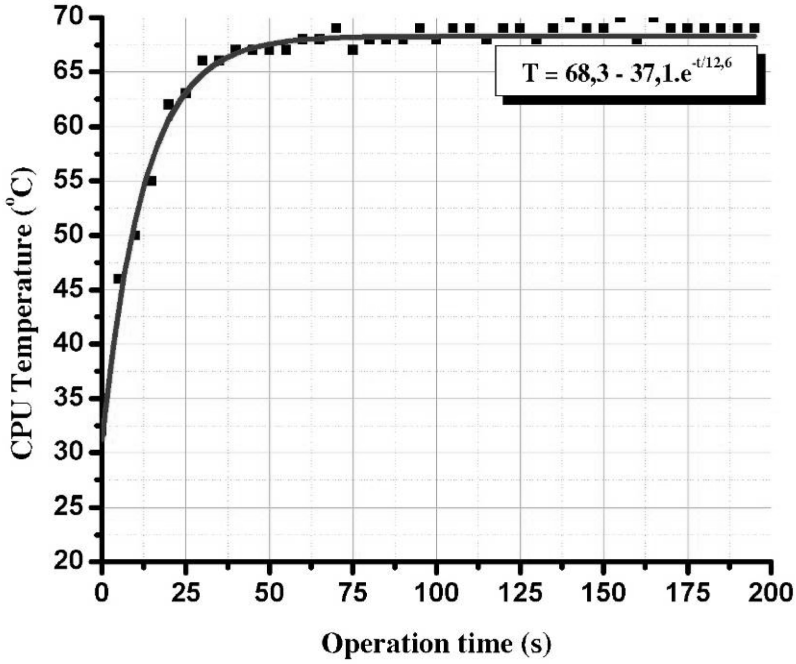

Fig. 10. *The graph of fitting exponential function of μ-processor temperature when using commercial thermal compound*

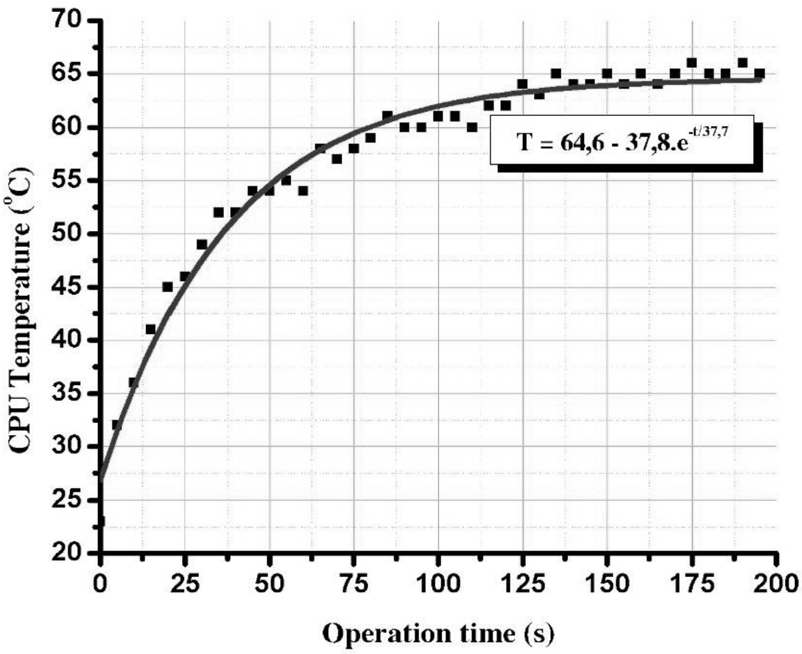

Fig. 11. *Graph of fitting exponential function of μ-processor temperature when using CNTs thermal compound*

Thus, temperature T of the μ-processor increases as an exponential function of working time t:

$$T = a - be^{-\frac{t}{c}} \tag{13}$$

Where:

$$a = PR + T_0; b = PR + T_0 - T_1; c = RC \tag{14}$$

Figures 10 and 11 showed the measured and fitting results according to equation 13 of the µ-processor's temperature as a function of working time for the commercial and CNTs-thermal compounds, respectively. The fitting results showed a function $T = 68.3 - 37.1e^{-\frac{t}{12.6}}$ (^{o}C) for commercial compound and $T = 64.6 - 37.8e^{-\frac{t}{37.7}}$ (^{o}C) for CNTs-thermal compound. The fitting curves excellently matched with the measured values. Noted that the values of P (radiate thermal power of the µ-processor) and T_0 do not depends on the nature of thermal dissipation media. The value of T_1, R and C depend on the type of thermal matching media. For the case of using commercial thermal compound matching media, we have:

$$PR_1 + T_0 = 68.3 \tag{15}$$

$$PR_1 + T_0 - T_1 = 37.1 \tag{16}$$

$$R_1C_1 = 12.6 \tag{17}$$

For the case of using CNT thermal compound matching media, we have:

$$PR_2 + T_0 = 64.4 \tag{18}$$

$$PR_2 + T_0 - T_2 = 37.8 \tag{19}$$

$$R_2C_2 = 37.7 \tag{20}$$

From equations (15)-(20) and T_0=26^{o}C, we received: T_1=31.2^{o}C; T_2=26.8^{o}C; PR_1=42.3; R_1C_1=12.6; PR_2=38.6; R_2C_2=37.7; R_1/R_2=42.3/38/6=1.0958 and C_1/C_2= (R_1/R_2).(12.6/37.7=0.305 or C_2=3.279C_1. These analysis values confirmed that the heat capacity of the system with CNTs thermal compound (C_2) was more than three times larger than that with the commercial thermal compound (C_1).

III. Conclusion

According to the project, we have fulfilled the work successfully. The CNTs materials has been successfully functionalized and effectively applied in the thermal matching media for micro processor of a personal computer. The work has confirmed the following:

- The CNTs materials were successfully functionalized to form CNT-COOH and CNT-$C_6H_4NH_2$. The functionalized CNTs can be well dispersed in the solution that is important to apply the CNT in composite materials.
- The functionalized CNTs material can be added to a commercially available thermal paste up to 2% and still keeping the sticking properties of the paste.
- The 2% CNT-thermal paste can reduce the temperature of the micro processor down to 65^{o}C, prolong the thermal increasing time and work without any deduction of the system for more than 10 days in full load 100% *100%* usage CPU mode.
- The 2% CNT-thermal paste can lead the CPU work in over locking mode up to 125% the default speed of the CPU without over the safety temperature.
- A draft model and calculations for the thermal response were proposed and carried out. The calculations were well suited with the experiment data.
- The results related to the project was published and presented at 01 Invited talk and 01 presentation at the International Conference the APCTP-ASEAN Workshop on Advanced Materials Science and Nanotechnology, September 15-20, 2008, NhaTrang-Vietnam, 01 book chapter published in "Nanotechnology R&D and Business Trends in the Asia Pacific Rim", World Scientific Publisher, Singapore, 2009, and a manuscript submitted to the Journal of Diamond and Related Materials Journal.

IV. Petition

Within 1 year working of the project, we have found that the CNTs can be realized not only for PC but also can be used for other high power electronic systems and many other civil applications if the prize of the CNTs materials be decreased. It is perfect for us if the AOARD could consider supporting for another 1 or 2 year (2009-2010) to continue the works that focus to the following points:

- Apply the CNT materials (both multiwall and singlewall CNTs) in the best quality silver paste with well defined thermal dissipation parameter and to clarify the thermal dissipation parameter of the CNT based paste.
- Apply the CNTs in solid film (100% CNT without the silver paste matrix) to the PC system
- Apply the CNTs in high power laser system and to *on-time* monitor the improvement in the lasing and corresponding electronic characteristics
- Apply the CNTs in high power LED and realize such high power-well thermal dissipation LEDs in the lighting lamp

IV. List of publication related to the work

1. Bui Hung Thang, Phan Ngoc Hong, Phan Hong Khoi, Phan Ngoc Minh, "*APPLICATION OF MULTI-WALLED CARBON NANOTUBES FOR THERMAL DISSIPATION IN A MICRO-PROCESSOR*", APCTP–ASEAN Workshop on Advanced Materials Science and Nanotechnology (AMSN2008) - Nha Trang, Vietnam – September 15-21, 2008, pp. 506-511

2. Phan Ngoc Minh, Phan Hong Khoi, "*CARBON NANOTUBE: A NOVEL MATERIALS FOR APPLICATIONS*", APCTP–ASEAN Workshop on Advanced Materials Science and Nanotechnology (AMSN2008) - Nha Trang, Vietnam – September 15-21, 2008, pp. 27-36

3. Phan Hong Khoi, Phan Ngoc Minh, *Infrastructure research and development of nanotechnology in Vietnam*, a book chapter in "*Nanotechnology R&D and Business Trends in the Asia Pacific Rim*", World Scientific Publisher, Singapore, 2009, pp. 306-345

4. Phan Ngoc Minh, Bui Hung Thang, Phan Ngoc Hong, Phan Hong Khoi, "*RESULTS ON THERMAL DISSIAPATION IN MICRO-PROCESSOR USING CARBON NANOTUBES*", Manuscript submitted to the Journal of Diamond and Related Materials.