Field Emission Current Enhancement in CNTs by Laser Irradiation

Taewon Jeong[a*], SeGi Yu[a], Whikun Yi[a], Changsoo Lee[a], Jeonghee Lee[a*], Jungna Heo[a], Ji-Beom Yoo[b*], Wonseok Kim[c], Y. H. Lee[c], and J. M. Kim [a*]

Abstract

Field emission characteristics of carbon nanotubes(CNTs) on four kinds of metallic substrates have been investigated under the irradiation of a laser. The field emission measurement reveals that after laser irradiation the current was increased and new humps at the field emission current was found. The current enhancement was thought to have occurred due to the fact that the electrical contact between CNTs and metals was improved due to the irradiation of the laser.

Keywords : field emission, carbon nanotubes, laser irradiation

1. Introduction

Field emission(FE) from carbon nanotubes(CNTs) is of great importance, especially in the area of flat panel display device, such as field emission displays(FEDs) [1,2]. The electron emitters for a FED are required to be long-lived and stable, and to possess a low threshold voltage for the initiation of FE[3,4].

A number of researches on field emission from CNTs are restricted to the electron emission from vertically aligned CNTs, such as CNTs grown by chemical vapor deposition (CVD) [5] or CNTs prepared by screenprinting and subsequent rubbing[1]. Due to its high geometric aspect ratio, the extremely high field enhancement factor of CNTs leads to very low macroscopic turn-on filed. However, this strong electric field is screened by the high density of vertically aligned CNTs, which are grown by CVD, by summing up the electric field of an individual CNT. Moreover, if CNTs are too sparsely distributed, CNTs yield low current density even at the high electric field. Therefore, for the best performance of a FED, optimum density of CNTs is required.

Most of CNTs prepared by CNT-dispersed solution are parallel to the substrate, unlike CNTs prepared by CVD or screenprinting [6,7]. However, these parallel CNTs can be promising field emitters, since the density of CNTs can easily be controlled by varying the density of CNTs in the solution. Even though those CNTs turn on at higher electric field than vertically aligned CNTs, the electric field is still considered to be lower than the conventional metallic and diamond emitters. Recently, the solution-based CNT attachment was adopted in the fabrication of triode-type CNT field emitters[6]. Due to its simple fabrication process, this approach is considered to be one of the promising ways to construct triode-type CNT FED, since *in-situ* CNT growth in the triode holes is rather difficult to control and is still in the developing phase[8].

Electrical contact between CNTs and metals has

Manuscript received August 10, 2001; accepted for publication November 27, 2001.
This work was supported by the Korean Ministry of Science and Technology, under the National Creartive Research Initiative Program.
* Member, KIDS.
Corresponding Author : J. M. Kim
a. The National Creative Research Initiatives Center for Electron Emission Source, Samsung Advanced Institute of Technology, P. O. Box 111, Suwon 440-600, Korea.
b. Center for Nanotubes and Nanostructured Composite, Sungkyunkwan University, Suwon 440-746, Korea.
c. Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea.
E-mail : jongkim@sait.samsung.co.kr **Tel** : +31 280-8197
Fax : +31 280-9349

been an important issue, since poor contact between them leads to inferior field emission or I-V characteristics of CNTs[9,10,11]. Several attempts have been made to improve electrical contact of CNTs – electron bombardment on the contact area selectively by introducing defects in the CNTs[12], thermal annealing by forming metal carbide interface layers between CNTs and metal [13], or dipping CNTs into liquid Hg [14]. In this report we propose laser irradiation on the contact area as a new method of improving the electrical contact which has the advantage of controlling the area selectively and gradual improvement on the electrical contact[15]. Therefore, in this report the improvement of electrical contact by laser irradiation is investigated by measuring field emission of CNTs on the metallic substrate, where one of the simplest ways of solution-based CNT attachment, i.e., dispersing CNTs in the alcohol and subsequent drying up of the droplet of CNT-containing alcohol, is utilized.

2. Experiments

Multiwalled carbon nanotubes (MWCNTs) were grown on the silicon substrate with a Ni catalytic layer and a TiN adhesion layer by thermal CVD, where the growing temperature was 950 °C and the growing time was 25 min with C_2H_4 and H_2 gases[5]. The diameter and the length of those MWCNTs are measured to be 50 nm and 10 μm, respectively. MWCNTs were removed from the substrate by a sharp blade and were dispersed in the ethanol solution. Various metals – Al, Ni, Ag, and Au – were grown on the thermally grown SiO_2 substrate by sputtering, where the thickness of a metallic layer was maintained as 100 nm. As an adhesion layer, a 50-nm-thick titanium layer was grown on the substrate by sputtering before the growth of the metallic layer. The CNT-dispersed solution droplets were dropped on the metallic substrate and dried up. A scanning electron microscope (SEM) image of CNTs on the gold substrate is shown in Fig. 1, which reveals that most of the CNTs are lying on the substrate.

Field emission measurements were done by placing an indium-tin-oxide glass plate as an anode plate which can transmit the green laser light. A 140-μm-thick alumina spacer with a 2.55-mm-diameter circular hole was used, and FE currents were characterized at the cathode plate, i.e., the metallic substrate with CNTs, using a Keithley 6517 multimeter and a Keithley 2000 high voltage supplier. FE currents were measured from four samples described above before and after the 1 min irradiation of the laser light with the varying the laser power. During the measurement, the pressure in the vacuum chamber was maintained to be as low as 10^{-7} torr. The 532 nm laser light was used, which was corresponding to the second harmonics of a Q-switched pulsed Nd-Yag laser (Quantel, Brilliant IEC 825-1). The repetition rate of the laser was 10 Hz and the intensity of the light was varied from 0.13 to 7.4 mJ/pulse.

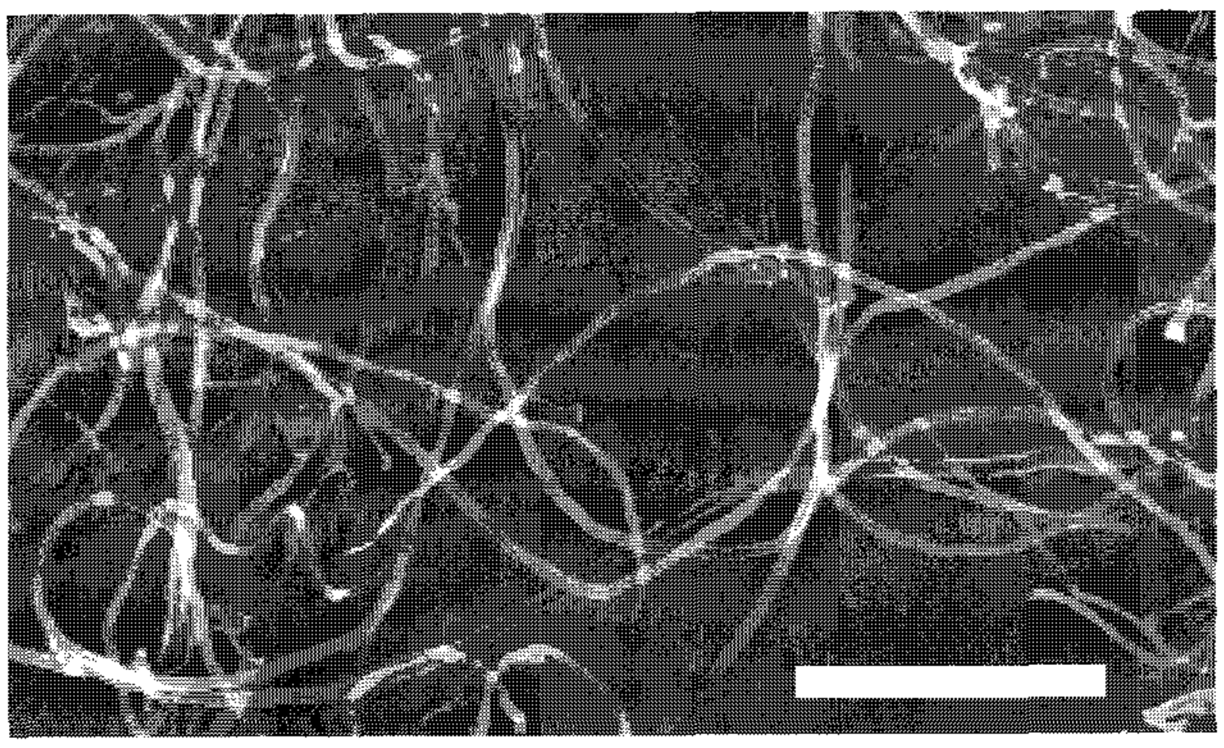
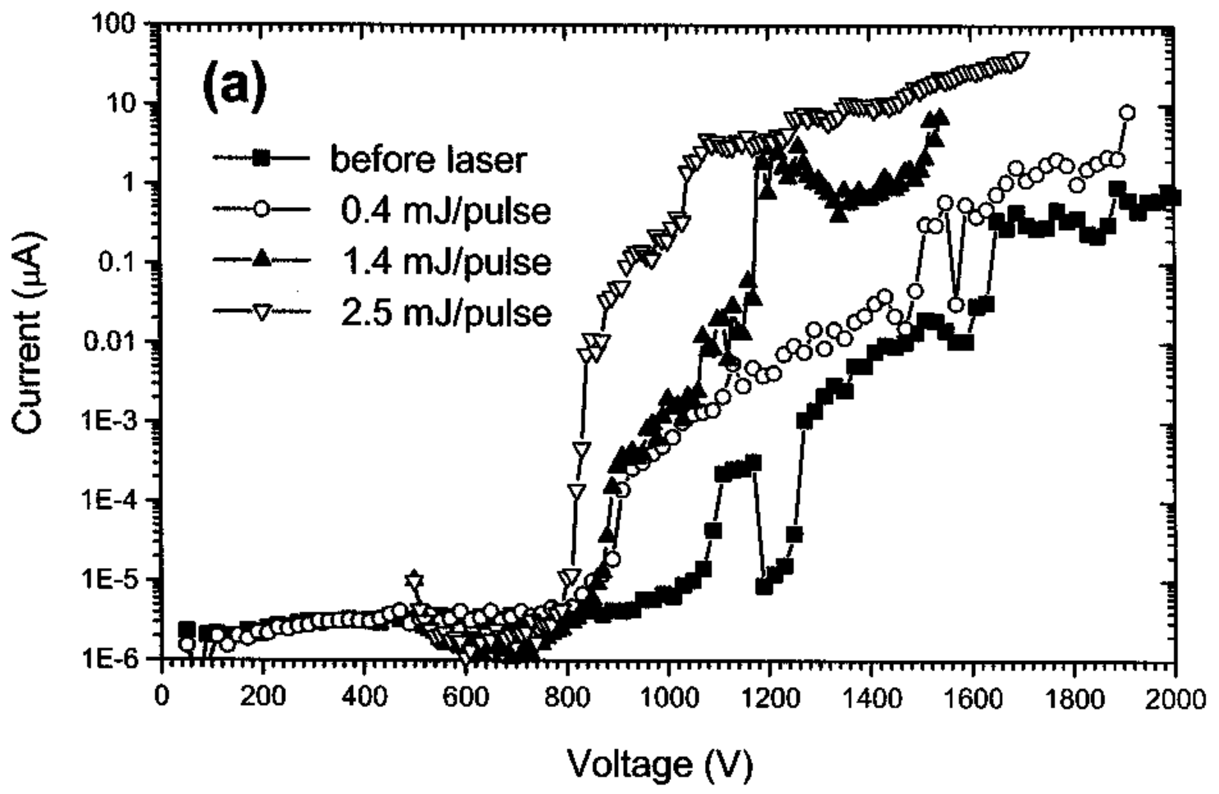


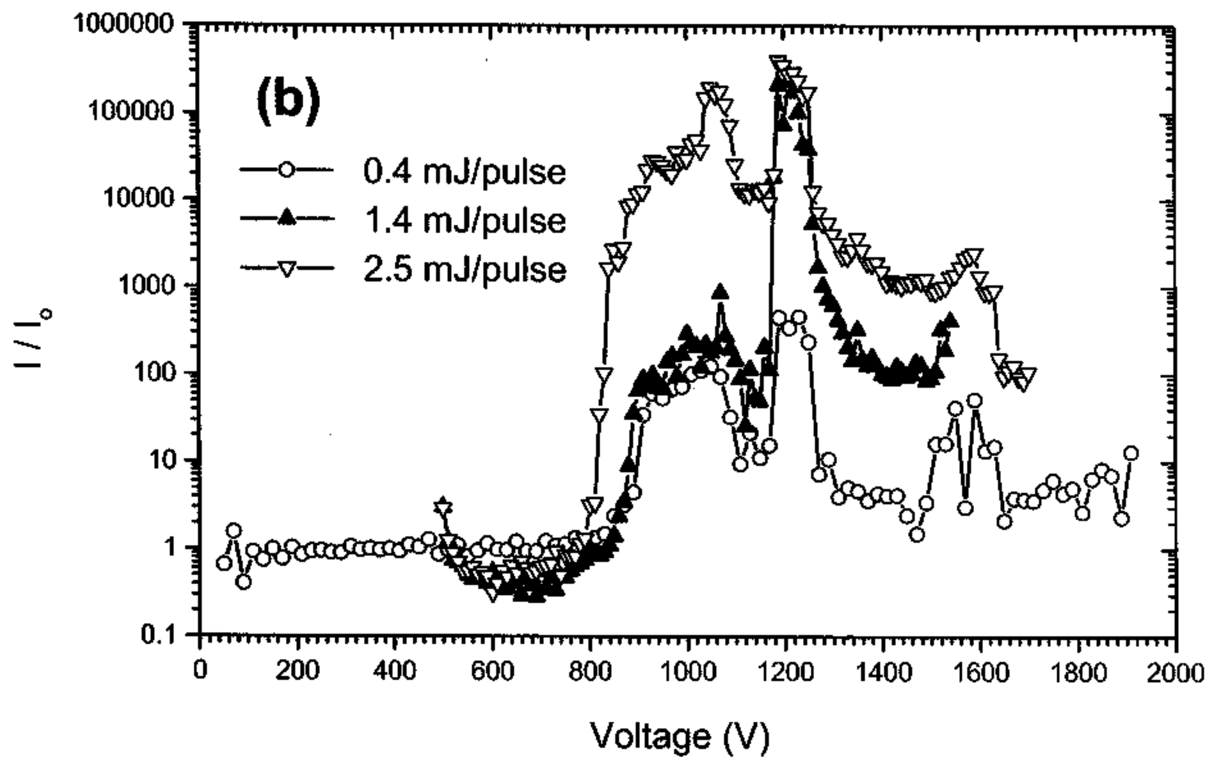
Fig. 1. SEM images of MWCNTs on the gold substrate. The white horizontal bar corresponds to 1 um.

3. Results and Discussion

Figs. 2 to 5 are the plots of FE currents of CNTs on the silver, gold, aluminum, and nickel substrates, respectively. The second part of each figure, i.e., Figs. 2(b)-5(b), is the relative current intensity which is defined by the ratio of the current intensity after to before the laser irradiation, i.e., I/I_o. From those figures, it is clear that the laser irradiation enhances the field emission current significantly regardless of metal substrates. After drying CNT-dispersed solution droplets, CNTs are not considered to have good electrical contact to the underlying metal surface, possibly due to presence of unwanted solvents between CNTs and metal layers. The CNTs on the silver substrate indicate that the initial contact was poor, i.e., the fluctuations in the initial current measurement before the laser irradiation (marked by solid squares in Fig. 2(a)) near 1200 and 1600 V, whereas the current measurements for other metal substrates before laser irradiation do not reveal any distinct current fluctuation. Thus, the fluctuations near the two voltages mentioned above in Fig. 2(b) may not reflect genuine current fluctuation, since the dip in Fig. 2(a) for I_o starting around 1160 V contributes to the current fluctuation in Fig. 2(b). Since such poor contact problem between CNTs and metallic electrodes has been serious obstacle for CNTs, numerous methods, such as thermal annealing[13] and electron beam irradiation, have been tried[12].



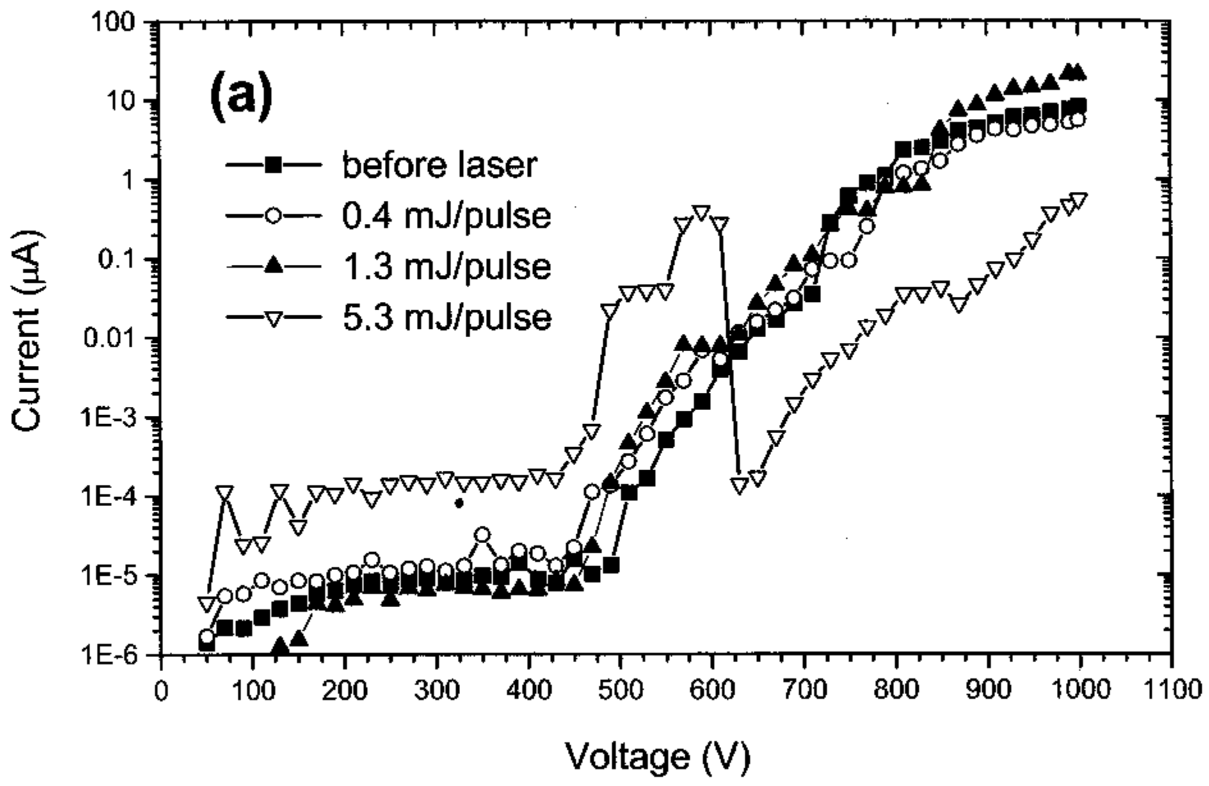
(a)



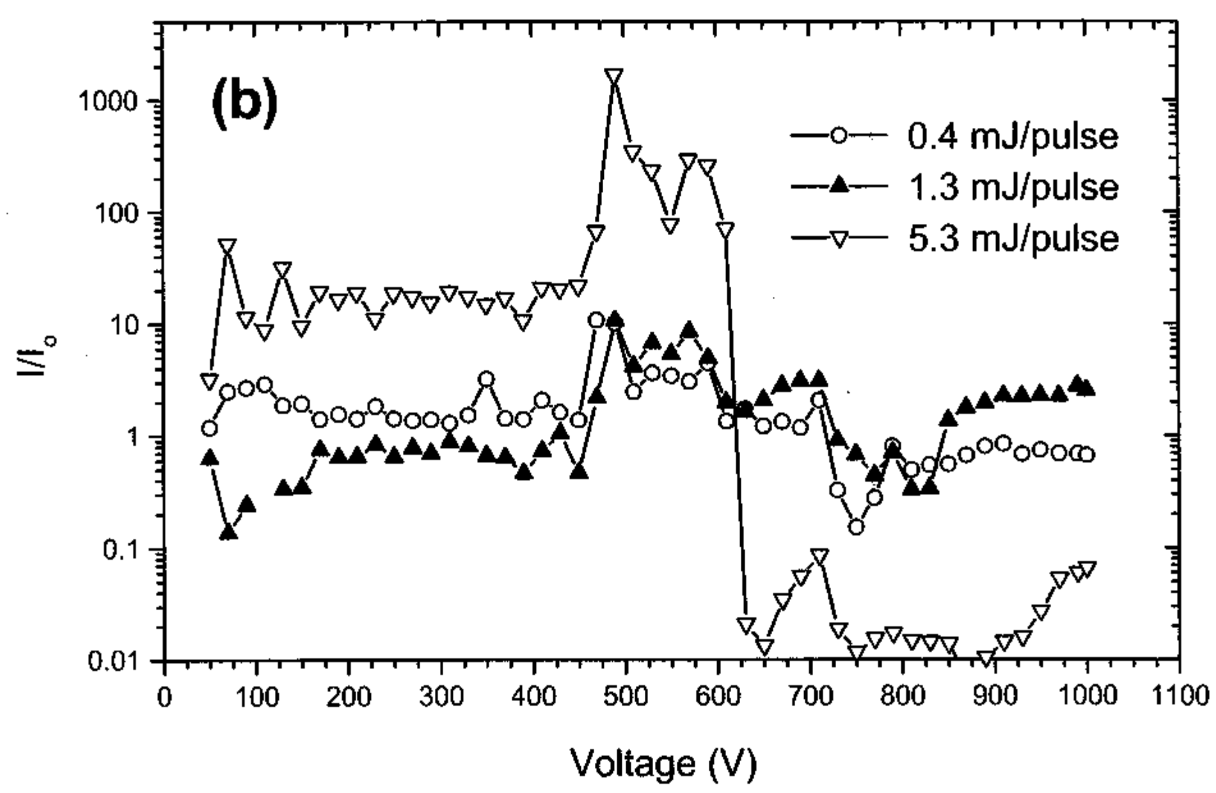
(b)

Fig. 2. (a) I-V characteristics and (b) relative current intensities of CNTs after laser irradiation, which are divided by the current intensity before the laser irradiation, on the silver substrate.

The overall amount of current enhancement after laser irradiation is quite satisfactory considering the fact that most of CNTs are lying on the substrate (See Fig. 1). For the case of CNTs on the gold substrate, except for the large fluctuation in the current at the laser power of 5.3 mJ/pulse, there is no distinctive increase observed in the field emission current. This may be caused by the fact that gold is very inactive metal that does not make chemical bondings with other elements and the work function of the gold is higher than that of CNTs. Thus, gold exhibits different laser-induced current behavior in Fig. 6 with respect to the other metals. All three metals except gold exhibit an overall large current enhancement by irradiation of a laser with the current saturation for high laser power (See Figs. 2-6). That is, the current enhancement reaches the maxima around the laser power of 1.5 ~ 2.0 mJ/pulse, after which the current is decreased to the lower power. This may be caused by the fact that too intense laser light heats up the sample leading to damage to CNTs, themselves, or to the contact points between CNTs and the metal layer.



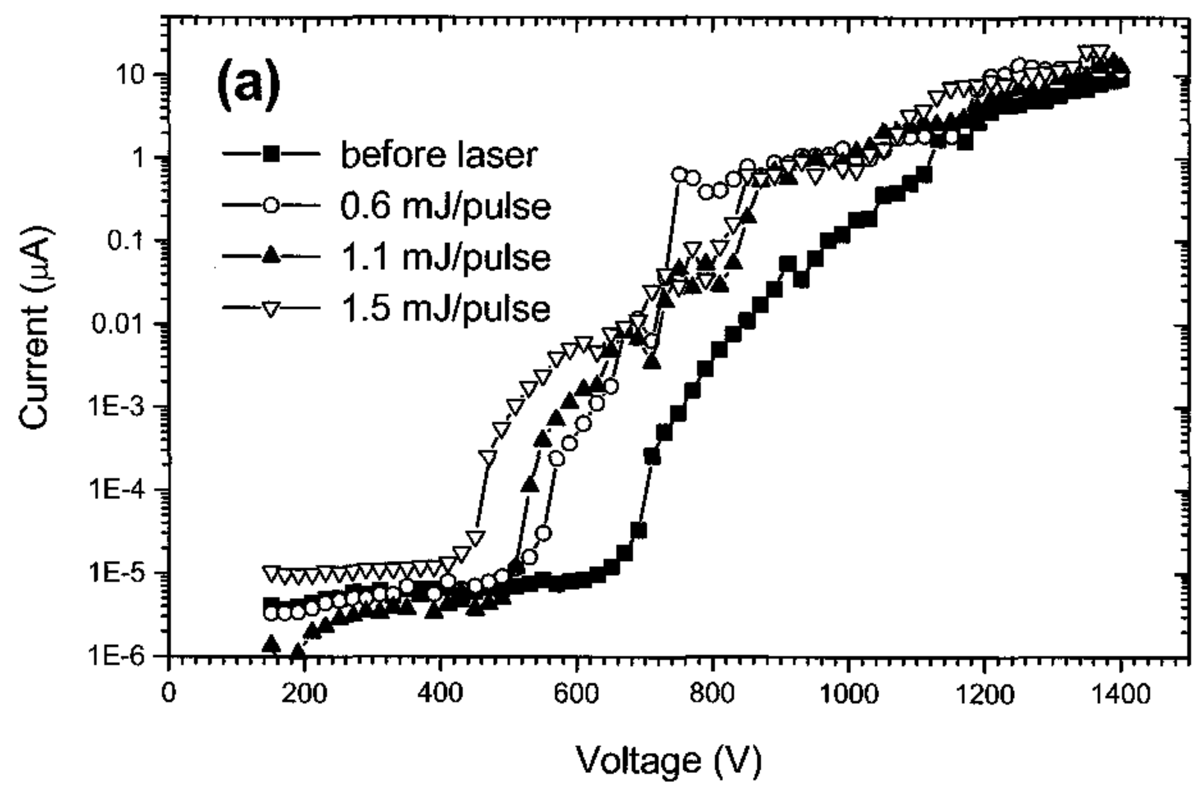
(a)



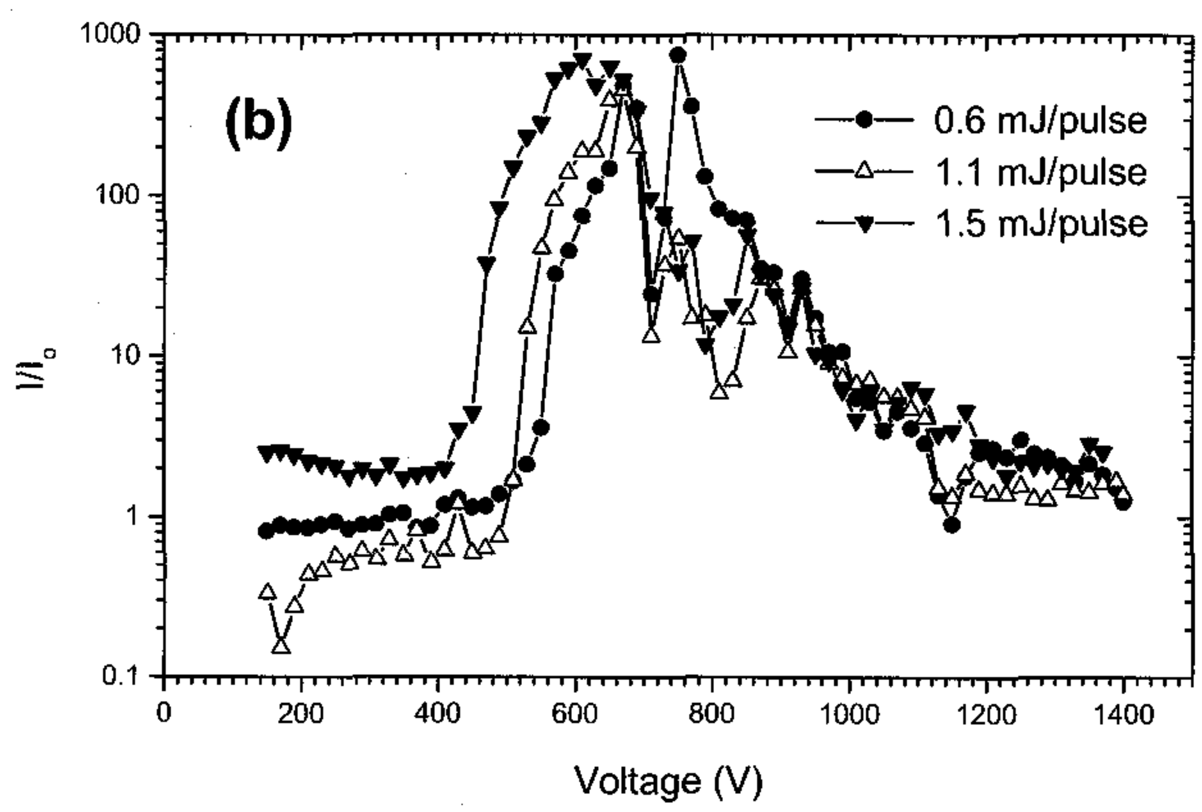
(b)

Fig. 3. (a) I-V characteristics and (b) relative current intensities of CNTs after laser irradiation, which are divided by the current intensity before the laser irradiation, on the gold substrate.

The initial layout of CNTs on the metal surface becomes unstable from the viewpoint of electrical contact, which can be found by the fact that the initial field emission measurement strongly reflects this CNT layout. Therefore, for the silver case it was found that the field emission current (I_o) before the laser irradiation was very small, which resulted in huge relative current (I/I_o) increase after laser irradiation. The comparison of relative current enhancement in Fig. 6 among other metal substrates should be cautious, as it may distort the field emission characteristics by the involvement of unstable initial current measuring. What we can understand from Fig. 6 is the tendency of current enhancement with variation of the laser power, rather than the comparison of field emission currents among metal substrates.



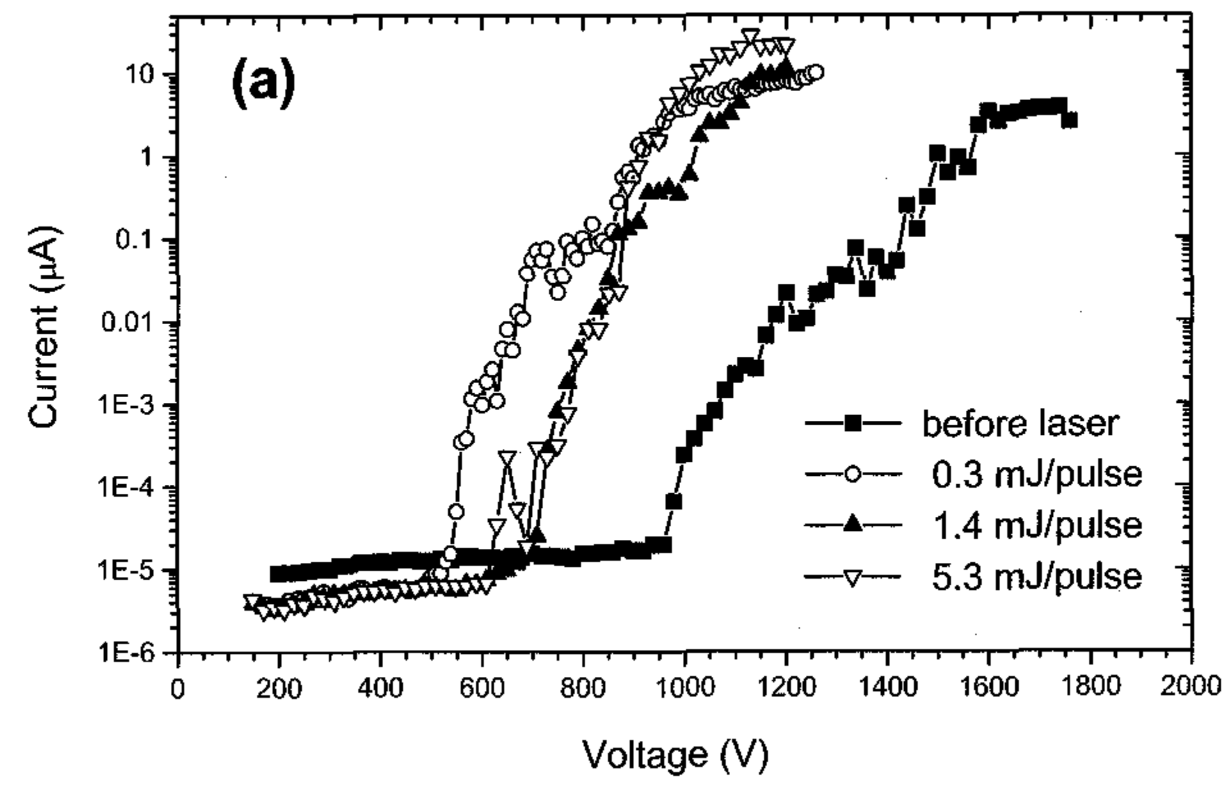
(a)



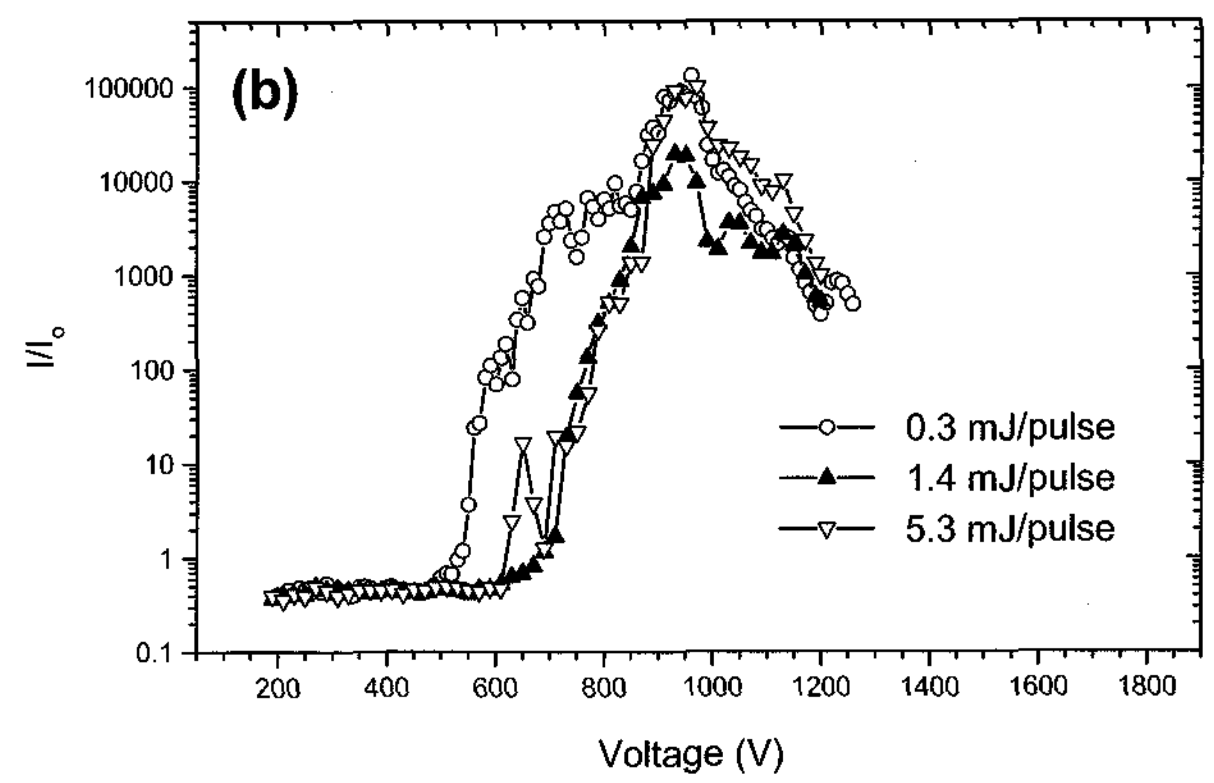
(b)

Fig. 4. (a) I-V characteristics and (b) relative current intensities of CNTs after laser irradiation, which are divided by the current intensity before the laser irradiation, on the aluminum substrate.

The interesting part in this experiment is the existence of current humps around 500 ~ 1000 V depending on the metal substrate. This feature is enlarged in the second part of Figs. 2-5, where the current intensities after laser irradiation are normalized by the values before the laser irradiation. This may be due to the resonance of field emission at the absorbates or surface state of the CNT tips which was suggested by



(a)



(b)

Fig. 5. (a) I-V characteristics and (b) relative current intensities of CNTs after laser irradiation, which are divided by the current intensity before the laser irradiation, on the nikel substrate.

E. Miranda, *et al.* [16]. Due to the heat transfer from laser, it is believed that metals around the CNTs slightly melt leading to formation of metallic coating on CNTs. It is not clear that the metal atoms on CNTs are of physisorption or chemisorption. Nonetheless, it is considered that metal carbide, i.e., chemical bonding between them, like CNTs and Ti atoms [13] is not plausible, since domain for metal carbide formation for Al, Au, Ag, and Ni in the phase diagram of temperature—carbon-weight-percent is very limited. These absorbated metal atoms surrounding CNTs are considered to play a dominant role in the enhancement of field emission. Thus, after laser irradiation, the electron path for field emission is changed to CNT-metal-vacuum from CNT-vacuum. Since the work function of gold is greater than that for CNTs[17], electron emission through gold atoms has little advantage over emission directly from CNTs resulting in rather reduction in the emission current. Since the work function of Al, Ag, and Ni are generally smaller than that of a CNT [17], all three cases have benefits from new emission paths which are created by laser irradiation. However, the low melting temperature of aluminum (933.5 K) may contributre to poor current enhancement for high laser power due to possible that evaporation of aluminum atoms. It is also possible that defects formed in CNTs by laser irradiation contribute to the enhancement of emission current like electron beam irradiation[12].

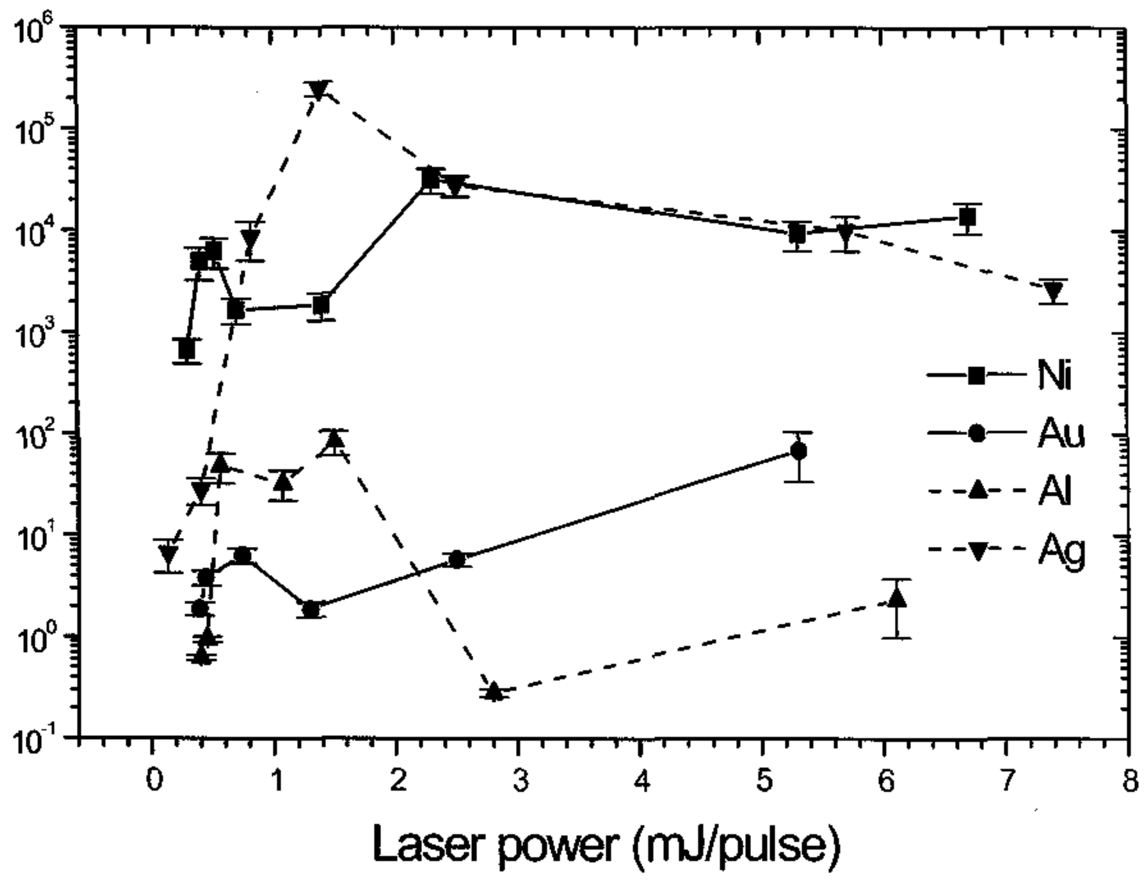


Fig. 6. The average values of relative current intensities as a function of the laser power. The vertical bars indicate the standard error.

4. Conclusion

Electrical contact properties between CNTs and four kinds of metals have been investigated under the irradiation of a laser by measuring field emission currents. It was found that the initial layout of CNTs on the metal was unstable from the viewpoint of electrical contact, which was confirmed by the fact that the initial field emission strongly reflected this CNT layout. The field emission measurement of CNTs on the metal substrate reveals that the current was increased after the irradiation of a laser. Furthermore, the humps at the field emission current measured after the laser irradiation may have been caused by resonant tunneling from the absorbate or surface states of CNTs. The field emission current enhancement resulted from the improvement of the electrical contact between CNTs and metals that was made by the irradiation of the laser, mainly by laser-induced thermal annealing.

References

[1] N. S. Lee, D. S. Chung, I. T. Han, J. H. Kang, Y. S. Choi, H. Y. Kim, S. H. Park, Y. W. Jin, W. K. Yi, M. J. Yun, J. E. Jung, C. J. Lee, J. H. You, S. H. Jo, C. G. Lee, and J. M. Kim, "Application of carbon nanotubes to field emission displays," Diam. Relat. Mater., vol, 10, pp. 265-270, 2001.

[2] S. Yu, S. Jin, W. Yi, J. H. Kang, T. Jeong, Y. S. Choi, J. Lee, J. Heo, N. S. Lee, J. B. Yoo, and J. M. Kim, "Undergate-type triode carbon nanotube field emission display with a microchannel plate," Jap. J. Appl. Phys. vol. 40, pp. 6088-6091, 2001.

[3] K. A. Dean and B. R. Chalamala, "The environmental stability of field emission from single-walled carbon nanotubes," Appl. Phys. Lett. vol. 75, pp. 3017-3019,1999.

[4] Y. Saito, K. hamaguchi, S. Uemura, K. Uchida, Y. Tasaka, M. Yumura, A. Kasuya, and N. Nishina, "Field emission from multi-walled carbon nanotubes and its application to electron tubes," Appl. Phys. A: Mater. Sci. Processing, vol. 67, pp. 95-100, 1998.

[5] Cheol Jin Lee, Dae Woon Kim, Tae Jae Lee, Young Chul Choi, Young Soo Park, Won Seok Kim, Young Hee Lee, Won Bong Choi, Nae Sung Lee, Jong Min Kim, Yong Gak Choi, and Soo Chang Yu, "Synthesis of uniformly distributed carbon nanotubes on a large area of Si substrates by thermal chemical vapor deposition," Appl. Phys. Lett., vol. 75, pp. 1721-1723, 1999.

[6] J. H. Lee, J. N. Heo, W. Yi, T. W. Jeong, SeGi Yu, Changsoo Lee, Wonseok Kim, J. B. Yoo, and J. M. Kim, "Field emission characteristics of self-assembled carbon nanotubes on the gold surface," submitted to J. Vac. Sci. Technol.

[7] M. Burghard, G. Duesberg, G. Philipp, J. Muster, and S. Roth, "Controlled adsorption of carbon nanotubes on chemically modified electrode arrays," Adv. Mat., vol. 10, pp. 584-588, 1998.

[8] Yun-Hi Lee, Yoon-Taek Jang, Dong-Ho Kim, Jin-Ho Ahn, and Byeong-kwon Ju, "Realization of gated field emitters for electrophotonic applications using carbon nanotube line emitters directly grown into submicrometer holes," Adv. Mat., vol. 13, pp. 479-482, 2001.

[9] J. Tersoff, "Contact resistance of carbon nanotubes," Appl. Phys. Lett. vol. 74, pp. 2122-2124, 1999.

[10] P. J. de Pablo, E. Graugnard, B. Walsh, R. P. Andres, S. Datta, R. Reifenberger, "A simple, reliable technique for making electrical contact to multiwalled carbon nanotubes," Appl. Phys. Lett. vol. 74, pp. 323-325, 1999.

[11] Jeong-O. Lee, Hwangyou Oh, Jae-Ryoung Kim, Kicheon Kang, Ju-Jin Kim, Jinhee Kim, and Kyung Hwa Yoo, "Nonlinear transport properties in multiwall carbon nanotube heterojunc-tions," Appl. Phys. Lett. vol. 79, pp.

1351-1353, 2001. (in press).

[12] A. Bachtold, M. Henny, C. Terrier, C. Strunk, C. Schoenenberger, J.-P. Salvetat, J.-M. Bonard, and L. Forro, "Contacting carbon nanotubes selectively with low-ohmic contacts for four-probe electric measurements," Appl. Phys. Lett., vol. 73, pp. 274-276, 1998.

[13] Y. Zhang, T. Ichihashi, E. Landree, F. Nihey, S. Iijima, "Heterostructures of single-walled carbon nanotubes and carbide nanorods," Science vol. 285, pp. 1719-1722, 1999.

[14] S. Frank, P. Poncharal, Z. L. Wang, W. A. de Heer, "Carbon nanotube quantum resistors," Science vol. 280, pp. 1744-1746, 1998.

[15] Whikun Yi, Taewon Jeong, Jungna Heo, Jeonghee Lee, SeGi Yu, Changsoo Lee, Gyeong Soo Park, Wonseok Kim, Younghee Lee, Jibeom Yoo, and J. M. Kim, "Field Emission Characteristics of Multiwalled Carbon Nanotubes upon Irradiation of laser Lights," submitted to J. Appl. Phys.

[16] E. Miranda, A. Faigon, and F. Campabadal, "Analysis of experimental current oscillations in MOS structures using a semi-empirical tunneling model," Solid State Electronics, vol. 41, pp. 67-73, 1997.

[17] Handbook of Physics Quantities, edited by I. Grigriev and E. Meilikhov (CRC Press, Boca Raton, 1997), Chap. 25.