Transactions of the Materials Research Society of Japan 29 [2] 477-480 (2004)

Cosmo-mimetic Helical/Spiral Materials and Their Potential Applications

S. Motojima, X. Chen, S. Yang, H. Iwanaga[1], Y. Hayashi[2], and C. Kuzuya[3], Y. Hishikawa[3]

Faculty of Eng., Gifu Univ., Gifu 501-1193, Japan, Fax: 058-293-5012, e-mail: motojima@apchem.gifu-u.ac.jp.

[1]Faculty of Eng., Nagasaki University, Nagasaki 852-8521, Japan, [2]Nagoya Inst. Technol., Nagoya 466-8555, Japan, [3]CMC Technol. Develop. Co. Ltd., Kakamigahara 509-0180, Japan.

As can be seen in the great maelstrom of the cosmos, the double helix of DNA, α-helix of proteins, screw dislocation in solids, three dimensional (3D) helical/spiral structure is the fundamental structure of all objects. Recently various novel materials with the 3D-helical spiral structure and coil diameters ranging from nm to μm orders, such as carbon microcoils/nanocoils, helical polyacetylene, helical ceramic fibers/tubes or helical organic polymers, etc. were prepared by the CVD, sol-gel, or template processes. These helical/spiral-structured materials are potential candidates for electromagnetic wave absorbers in the GHz regions, hydrogen absorbers, field emitters, tunable microdevices, microsensors, microactuators, chiral catalysts, capacitors, energy convertors, etc. The carbon microcoils/nanocoils (CMC) with a coil diameter of several micrometers to several hundred nanometers could be prepared with very high reproducibility by the catalytic pyrolysis of acetylene by controlling chemical reaction fields. In this study, the potential applications, as well as the preparation conditions, morphologies, and some properties of the CMC will be present.

Key words: carbon microcoils, electromagntic wave absorption, tactile sensors

1. INTRODUCTION

In the Cosmos and in nature, maelstrom, spiral, helical or coiling structures, such as a whirled air (typhoon), whirled seawater, vine plants, shellfish, proteins, DNA, etc. are commonly observed. The helical/spiral shapes are also commonly observed in artificial water screw, spiral staircases, retaining screw, bolt/nut, screw dislocation in solid, etc. Furthermore, electromagnetic waves, spirit or mind, economic cycle, etc. have also a helical/spiral motion pattern. That is, the 3D-helical/spiral structures are the fundamental structure of many natural objects, including science and human livings. Helical morphologies of DNA or proteins have essential and critical functional roles in living bodies. Recently, double helix-shaped DNA, single-helix-shaped proteins, or chiral carbon nanotubes are attracting extreme interests in nanotechnology and biotechnology. However, materials with 3D-helical/spiral structures with micrometer to nanometer order dimensions have not been commercially available.

In 1990, we first found that regular-coiled carbon fibers (carbon microcoils/nanocoils, CMC/CNC) could be obtained with high reproducibility by the catalytic pyrolysis of acetylene containing a small amount of sulfur impurities over transition metal catalysts [1], and then extensively examined the preparation conditions, morphology, growth mechanism, and some properties in detail [2-5]. We named "cosmomimetic carbon coil" for these carbon coils after "biomemetic" [6].

The helical/spiral materials are expected to have novel functionality and many potential applications such as tunable micro-devices/sensors, electromagnetic absorbers, energy changing materials, hydrogen absorbers, sensors, field emitters, chiral catalysts, activators of organisms, etc. Especially, the CMC is a promising candidate as a novel electromagnetic (EM) wave absorber, especially in the GHz range, because of its micro-coiling morphology and appropriate electrical conductivity [7-13]. That is, the micro-coiling morphology is the most effective and ideal one for the generation of inductive current by Faraday's Law of Electromagnetic Induction resulting in the effective absorption of EM waves. Actually, the carbon coils can absorbs EM wave in the GHz region without reflection. In addition to their various potential applications, the growth mechanism is very interested in scientific view point.

In this study, we prepared the CMC/CNC by the various activated chemical vapor deposition process, and examined the morphologies and some properties of the CMC/CNC, and discusses the potential applications.

2. EXPERIMENTAL

The CMC was prepared by the catalytic pyrolysis of acetylene at 700-800℃. Ni powder was generally used as a catalyst. As a heating element, electric heater (AC, DC) or gas burner was used. For the activation of chemical reactions and the growth of CMC/CNC, outer and/or inner energetic field, such as electromagnetic, magnetic, supersonic, or plasma field, were applied in the reaction atmosphere.

3. RESULTS AND DISCUSSION

It was found that the coil yield was generally increased by the application of these outer or inner energetic fields, except for the application of plasma field as shown in Table 1. The

Table 1. Activated CVD process for the preparation of carbon coils.

CVD method	Excitation Device	Yield	Morphology
Thermal CVD	Electric Heater, Gas Heater, IR Heater, etc.	Base	Double Helix Carbon Microcoils
Electromagnetic Wave CVD	AC/DC Outer Electric Heater + AC/DC Bias or AC/DC Inner Electrode	Increase	Double Helix Carbon Microcoils
Ultrasonic Wave CVD	Electric Heater + Ultrasonic Wave Oscillator	Increase	Double Helix Carbon Microcoils
Magnetic Wave CVD	Electric Heater + Permanent Magnet	Increase	Single Helix Carbon Nanocoils
Plasma CVD	Electric Heater + Plasma Activated Gas	Decrease	Single Helix Carbon Microcoils

CMC obtained using gas burners have circular or elliptical fiber cross-section (circular fiber CMC). On the other hand, the CMC obtained using electric heater has a rectangular or flat fiber cross-section (flat fiber CMC). Fig. 1 shows the representative flat fiber CMC obtained by conventional thermal CVD process using AC heater. It can be seen that the CMC have flat fiber cross-sections and with a constant coil diameter of 5-10 μm and a constant coil pitch. The CMC with flat fiber cross-section may be caused by the effect of electromagnetic field emitted from the outer AC heater. It was reported that the thin quasi-liquid or liquid crystal-like Ni-C-O-S phase was

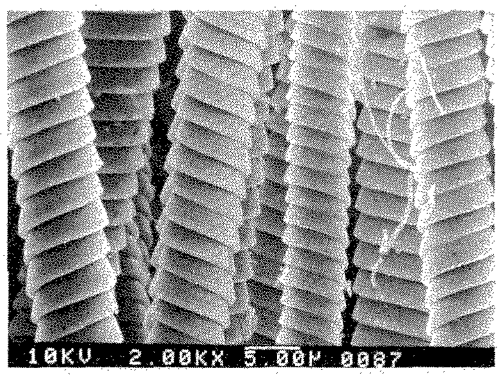

Fig. 1. Representative regular carbon microcoils with constant coil diameter and coil pitches along the coil.

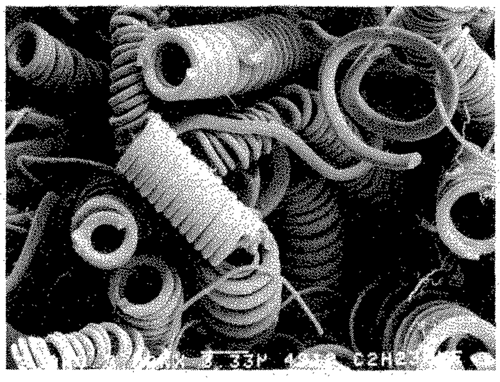

Fig. 2. Shortly ruptured carbon microcoils.

observed on the surface of a catalyst grain present on the coil tip [14]. The electromagnetic properties of this quadruple phase are not known. However, the Ni-C-O-S thin layer may be deformed and elongated to the direction of EM force if the layer is paramagnetic or elongated to the vertical direction of EM force if the layer is diamagnetic. Accordingly, the flat fiber CMC is obtained using AC heater because that the shape of fiber cross-section is mainly determined by the shape of the catalyst grain. Fig. 2 shows the CMC observed in the bottom part of the long CMC after a 2-h reaction time. These CMC were formed at an initial growth stage of the reaction times and are circular fiber CMC. That is, the CMC formed at an initial growth stage is circular fiber CMC following to flat fiber CMC with increasing reaction time. These results indicate that the catalyst form is bulky at an initial stage following changing to the elongated form by the effect of EM field.

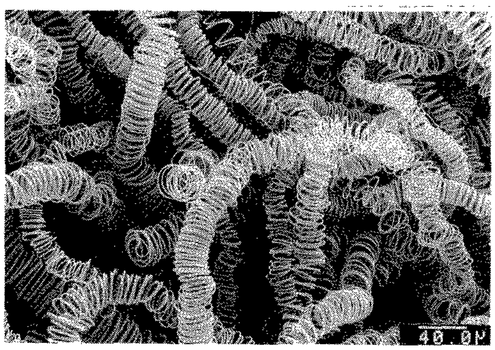

Fig. 3. Irregularly coiled carbon microcoils with large coil diameters.

The CMC with various morphologies were obtained mixing with regular CMC as shown in Figs. 1-2. Fig. 3 shows the CMC with large coil diameter of 20-40 μm with small fiber diameter and irregular coil pitch. It was found that these CMC have very high elasticity and could be extended up to 5-15 times original coil length and contracted to the original coil length after releasing the stress. Fig. 4 shows the twined CMC of different coil length. Fig. 5 shows the single coils with flares in an inner side of the coils. Sometimes, apparently periodic-bended or sine curved fibers were observed. However, it could be seen that these fibers were also a CMC with large coil pitch as shown in Fig. 6. In this figure, a striation was observed along the fiber axis, suggesting that this single coil is a twin coil composed of a fiber A and B. Fig. 7 shows the concentric-coiled flat fibers.

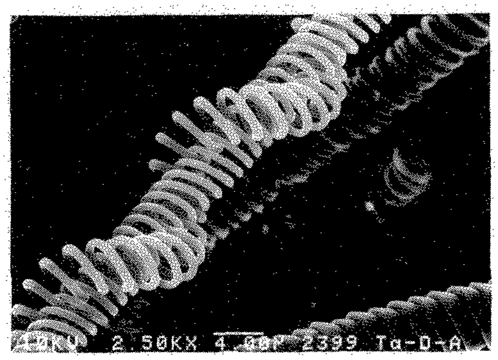

Fig. 4. The twined carbon microcoil with different coil length

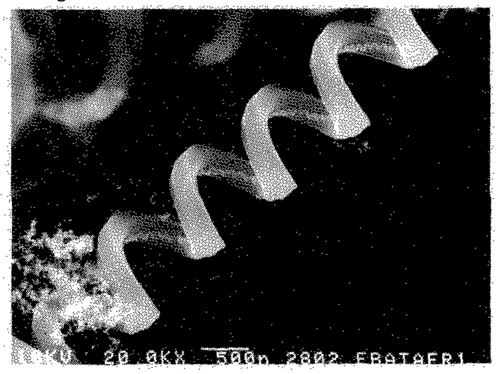

Fig. 5. Single coil with flares in the inner side of thecoil.

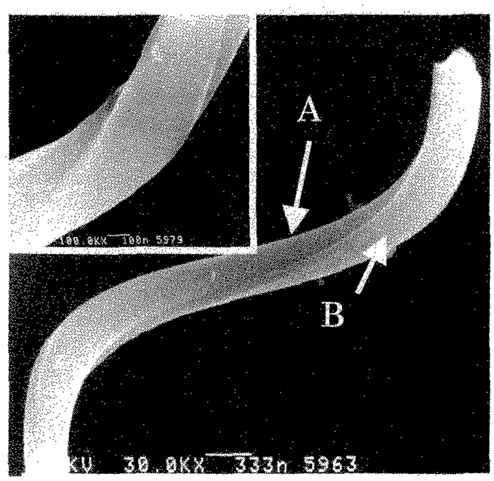

Fig. 6. The arbon coil with a very large coil pitch.

The well-formed diamond-like catalyst grain was usually observed on the tip of the coils. Sometimes, irregular-formed catalyst grain, such as shown in Fig. 8, were observed. Small fine catalyst grains can be seen on the surface of a catalyst grain (arrow in Fig. 8a). In Fig. 8b, a large amount of secondary grown thin carbon nanofibers is observed on the coil tip. These phenomena may be caused by that the catalyst grain was finely ruptured by steep decreasing temperature at the reaction stopping.

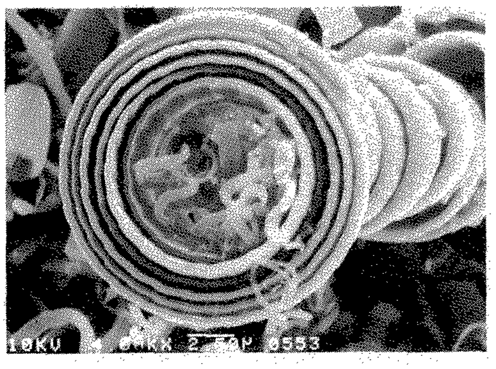

Fig. 7. Conically coiled ribbon-like-fiber.

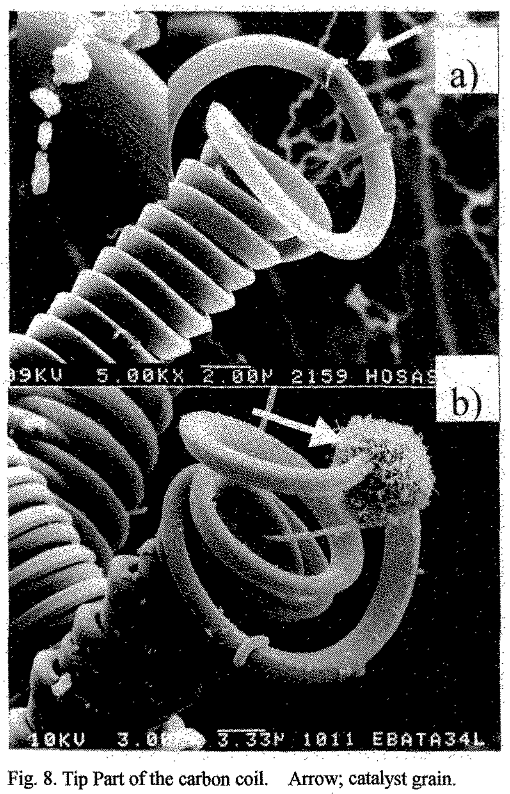

Fig. 8. Tip Part of the carbon coil. Arrow; catalyst grain.

Using fine metal particles as the catalyst, carbon nanocoils (CNC) with the coil diameter of nm orders could be obtained at relatively lower reaction temperature of 700-750℃. Fig. 9 shows the CNC obtained using a Ni-Fe mixed fine catalyst at 700℃, in which the CNC was co-deposited with the CMC. The CNC could selectively obtained by controlling the reaction conditions. The CNC were generally a single-helix coil with twisted form as shown in Fig. 9b and the coil diameter was 50-500nm. Fig. 10 shows an interesting carbon nanocoils, in which a carbon fibers with dumbbell-type cross-section was twisted to from a single-helix CNC with a coil diameter of 300 nm. Using Pt/Pd thin films sputter-coated on a silica substrate was used as the catalyst, a large amount of single-helix CNC were obtained. The coiling direction (coiling-chirality) of the CNC was usually the same though a piece of coil. However, using the Pt/Pd catalyst, the CNC with changing coiling-chirality were frequently observed as shown in Fig. 11. The similar phenomena of changing coiling-chirality was observed by S. Yang et al. [15]. However, the reasons of changing coiling-chirality are not known yet.

It was found that various ceramic microcoils/microtubes could be easily obtained by vapor phase metallizing, vapor

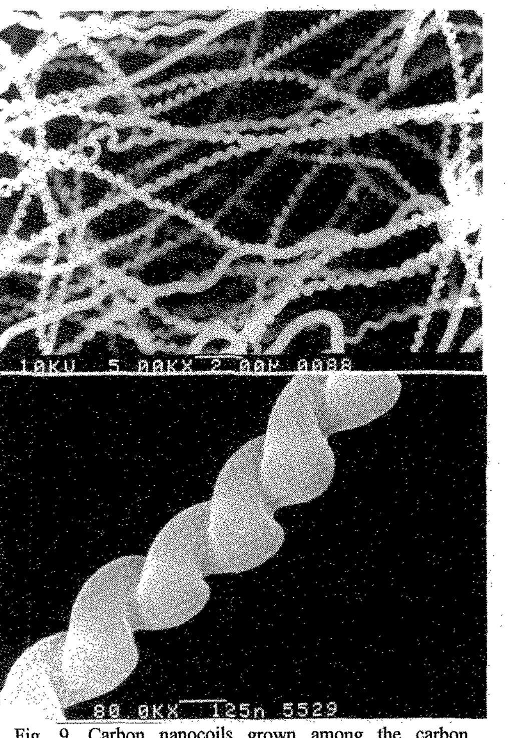

Fig. 9. Carbon nanocoils grown among the carbon

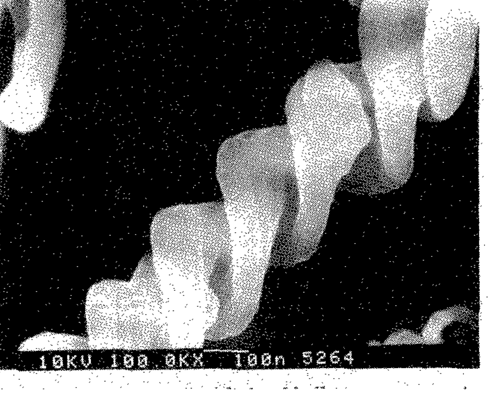

Fig. 10. A carbon nanocoil with dumbbell-type cross-section.

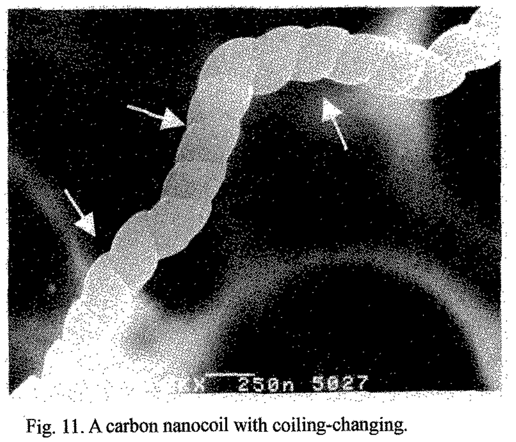

Fig. 11. A carbon nanocoil with coiling-changing.

phase nitrizing, siliconizing, boronizing after the metallizing, or by sol-gel coatings on the surface of the CMC as the template. The coiling morphologies of the CMC could perfectly be reserved even after the modification process of the CMC. Fig. 12 shows the modification processes of the CMC to obtain various ceramic microcoils/microtubes. The electrical resistivity of the bulk CMC increased by the metallizing, carbonizing, or nitrizing, and attained 0.01-0.001Ωcm depending on the bulk density.

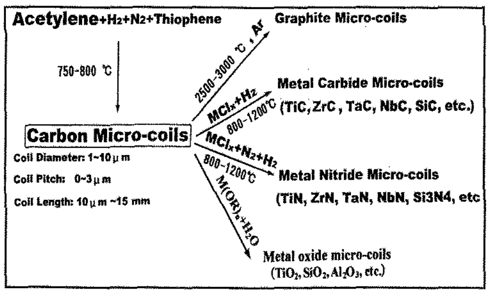

Fig. 12. Modification process of carbon coils.

Table 2 shows the representative physical properties of the as-grown CMC. It was observed that 1-1.4 wt % hydrogen was contained in the as-grown CMC. The as-grown CMC was almost amorphous structure with the density of 1.81-1.88 g/cm^3 and specific surface area of 100-140 m^2/g. These values were affected by the reaction conditions, especially by the application of external energetic field.

Y. Kato et al. [16] reported that the CMC could induce an electromotive force by the application of alternative or static magnetic field, suggesting that the CMC could absorb the electromagnetic (EM) waves. The as-grown CMC was embedded into matrix of a polyurethane, polymetylmethacrylate (PMMA) or polysilicone resin. It was observed that the CMC could effectively absorb the EM waves, especially of GHz regions, by the Faraday's Law of Electromagnetic Induction. For example, CMC(1-2wt%)/PMMA beads could absorb by > –20dB(>99%) of the EM waves of 60-100GHz. Accordingly, the CMC is the potential candidate as the novel EM waves absorbers in the GHz regions. The CMC have super-elasticity and also the electrical resistivity was increased by the extension. Accordingly, outer stresses applied to the CMC composite, by which the extension and/or contraction motion of the CMC is induced, may be detected by the change of the electrical resistivity. We prepared the novel tactile sensors made of

Table 2 Properties of carbon microcoils/nanocoils

1) **Chemical composition (wt%)** : C=97.5-98.2, H=1-1.4, S=0.03-0.09.
2) **Crystal structure**: As-grown CMC is amorphous with fine carbon grains (-50nm) to the central part of carbon fiber without a pore in the fiber axis. The amorphous as-grown CMC graphities gradually with increasing heat-treatment temperature, and form the graphite layers with herring-bone structure at 2500-3000℃in CO+CO_2.
3) **Density**: 1.81-1.88 g/cm^3
4) **Specific surface area**: 100-140m^2/g
5) **Average pore size**: 4nm
6) **Bulk (powder) electrical conductivity**: 10-0.1 Ωcm
7) **Heat conductivity**: 0.045-0.056 W/m/K

CMC(1-2 wt%)/polysilicone resin composite. The changes of electrical resistivity, capacitance and inductance of the composite (sensors) under applying stresses were measured by two electrodes. It was found that different stresses, pressing by fingers, sticking by a needle, picking by tweezers, etc, could be detected by different wave-forms. Furthermore, temperature from fingers, electromagnetic wave emitted from a mobile phone, etc. could be also detected as different wave-forms. That is, the CMC/polysilicone composite sensors have potential applications to tactile sensors of endoscope, catheter, detection sensors of human barried in debris by earthquacke, manipulation sheet, etc., or as artificial skin of humanoid robot, etc. Table 3 summarizes the potential applications of the CMC.

Table 3 Potential applications of carbon coils.

1	**Electromagnetic Absorbers**	**(1) Beads** **(2) Forms** **(3) Ceramic Beads** **(4) Super-thin EM Absorbers for Aerospace**
2	**Tactile Intelligent Sensors**	**(1) Humanoid Robot Sensors** **(2) Medical Robot Sensors** **(3) Aerospace Sensors**
3	**Micro-Antenna**	**(1) Micro-Antenna for Aerospace** **(2) Array Antenna with High Gain·High Functionalities**
4	**Cosmetics**	**(1) Activation of Metabolism,** **(2) Promotion of the Formation of Collagen in Skin Cell**
5	**Etc.**	**(1) Composites with Super-Elasticity** **(2) Tunable Heating Materials** **(3) Fibers and Papers Containing CMC**

4. CONCLUSIONS

The carbon microcoils/nanocoils were obtained by various activated CVD process, and the morphologies and some properties were examined. It was found that the CMC have high electromagnetic absorption properties and high sensing properties for different stress or subtle energies, and have potential applications as electromagnetic wave absorbers, tactile sensors, etc.

References

[1] S. Motojima, M. Kawaguchi, K. Nozaki, and H. Iwanaga, Appl. Phys. Lett., 56, 321-323 (1990).

[2] S. Motojima, I. Hasegawa, S. Kagiya, M. Momiyama, M. Kawaguchi, and H. Iwanaga, Appl. Phys. Lett., 62, 2322-2323 (1993).

[3] X. Chen and S. Motojima. J. Mater. Sci., 34, 5519-5524 (1999).

[4] S. Motojima, X. Chen, W.-In Hwang, T. Kuzuya, K. Kohda, and Y. Hishikawa, Electrochem. Soc. Proc., 2000-13, 379-384 (2000).

[5] X. Chen, W.-In Hwang, and S. Motojima., Mater. Technol., 18, 229-237 (2000).

[6] S. Motojima and X. Chen, J. Appl. Phys., 85, 3919-3921 (1999).

[7] S. Motojima and H. Iwanaga, Tanso, 174, 215-224 (1996).

[8] S. Motojima, H. Iwanaga, and V.K. Varadan, Hyomen, 36, 140-148 (1998).

[9] W.-In Hwang, X. Chen, C. Kuzuya, K. Kawabe, and S. Motojima, Carbon, 38, 565-568 (2000).

[10] W.-In Hwang, K. Kawabe, and S. Motojima, Mater. Sci. Eng., B86, 1-6 (2001).

[11] Y. Hishikawa, C. Kuzuya, S. Hirako, W.-In Hwang, and S. Motojima, Trans. Mater. Res. Soc. Jpn., 27, 39-42 (2002).

[12] C. Kuzuya, S. Motojima, M. Kohda, and Y. Hishikawa, Mater. Technol., 20, 3-9 (2002).

[13] C. Kuzuya, M. Kohda, Y. Hishikawa, and S. Motojima, Carbon, 40, 1991-2001 (2002).

[14] X. Chen, S. Yang and S. Motojima, Mater. Lett., 57, 48-54 (2002).

[15] S. Yang, X. Chen, and S. Motojima, Appl. Phys. Lett., 81, 3567-3569 (2002).

[16] K. Kato, N. Adachi, T. Okud, T. Yoshid, S. Motojima, and T. Tsuda, Jpn. J. Appl. Phys., 42, 5035-5037(2003).

(Received October 11, 2003, Accepted December 15, 2003)