あん　ちゅう　れつ
氏　　　　　　名　安　　忠　　烈

授　与　学　位　博士（工学）
学位授与年月日　平成２７年3月２５日
学位授与の根拠法規　学位規則第４条第１項
研究科，専攻の名称　東北大学大学院工学研究科（博士課程）機械システムデザイン工学専攻
学位論文題目　Synthesis of Carbon Nanotubes-Metal Composite Thin Films for Microsystem Applications（マイクロシステム応用のためのカーボンナノチューブ-メタルコンポジット薄膜の合成）
指　導　教　員　東北大学教授　小野　崇人
論文審査委員　主査　東北大学教授　小野　崇人　東北大学教授　堀切川　一男
東北大学教授　三浦　英生　東北大学教授　橋田　俊之

論文内容要旨

Carbon nanotechnology has gained significant attention, energized by discoveries such as fullerenes, followed by carbon nanotubes (CNTs) and also, the latest addition to the carbon family, graphene. CNT has generated huge activity in most areas of science and engineering due to its physicochemical properties and the combination of superlative thermal, mechanical, and electrical properties. These properties makes CNT ideal candidate as advanced filling materials in composites. Since the last decade, a number of investigations have been carried out using CNT as reinforcement nanomaterial in different materials, such as polymer, ceramic and metals. There has been an increase in the number of publications on CNTs-metal composite. These articles address various aspects, such as processing, modelling of mechanical properties, microstructure and the chemical interaction of CNTs with metals. CNTs-metal composites make use of CNT for microsystem applications that metal technology has not tried and achieved. Among the CNTs-metal composites processed using electrochemical deposition, the second most popular route of the synthesis of the CNTs-metal composite for microsystem applications, CNTs-Cu composite and CNTs-Ni composite are mainly developed because Cu and Ni are the most popular metal materials which can be obtained by electrochemical deposition. In this thesis, CNTs-metal composites with two typical kinds of CNT alignment, vertically aligned CNTs in CNTs-Cu composite and randomly dispersed CNTs in CNTs-Ni composite, are synthesized by new development methods for more effective microsystem applications. An overview of thesis content and organization is illustrated in Fig. 1. CNT and CNT composite are introduced in chapter 1 including the structure, property and growth mechanism of the CNT. Also the present research background of the CNT composite, especially about CNTs-metal composite with vertically aligned CNT and randomly dispersed CNT in the composite for microsystem application is described.

CNTs can be vertically grown on a substrate by chemical vapor deposition (CVD), but the formed CNT forest has intrinsic spaces between the CNTs. These spaces adversely reduce the benefit of the high thermal and electrical conductivities of the CNTs.

Furthermore, there is van der waals attraction between the CNT and the substrate, but the attraction force is not strong enough to endure contact pressure. Filling of Cu into the spaces between CNTs decreases the thermal interface resistance between the nanotubes for applications as a thermal interface in an electronic package of high-power device and thermoelectric device. However, the volume of the remained voids in the directly electroplated CNTs-Cu composite is not reported and discussed although the voids can be observed in the composite. The synthesis of CNTs-Cu composite with smaller volume of the remained voids is expected to improve the thermal interface property. In the work on the synthesis of CNTs-Cu composite thin film, a novel process for filling Cu into vertically grown CNT forest using combination of supercritical fluid deposition (SCFD) and electroplating has been originally developed. The objective of this research is filling the intrinsic voids between vertical CNTs with high density of Cu to decrease the thermal contact resistance of the CNTs-Cu composite.

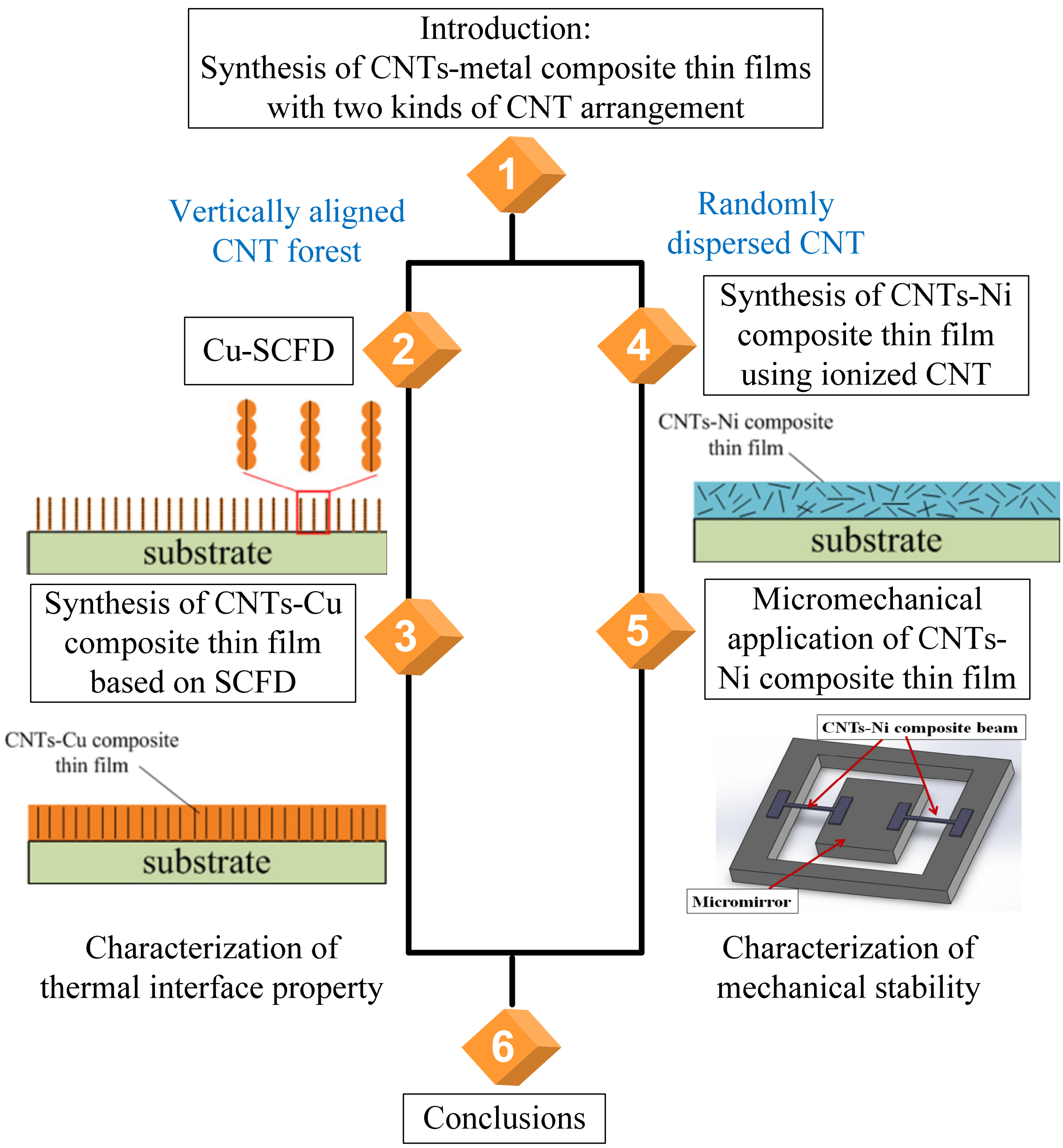

Figure 1: An overview of thesis content and organization.

Deposition principle of SCFD and a detailed experimental procedure about Cu-SCFD is described in chapter 2. Design consideration of SCFD system and SCFD reactor are described since the SCFD need to be operated at high pressure and high temperature condition. Some experimental results, such as Cu-SCFD on Si substrate and in Si trench structure, also on a CNT forest are demonstrated.

In chapter 3, the synthesis process, results and characterization of the CNTs-Cu composite thin film are described. The detailed synthesis process based on SCFD is described and the synthesis results are shown to confirm the effectiveness of the SCFD. Then, thermal interface property of the synthesized CNTs-Cu composite thin film is evaluated by measurement of thermal contact resistance. The density of the synthesized CNTs-Cu composite was 8.2 ± 0.3 g/cm^3, and the ratio of remained voids volume to the total volume was 3~6 %. The ratio of remained voids volume without SCFD process was 18~19 %. The Cu-SCFD layer on CNTs surface functions as a seed effectively for electroplating process. The CNTs-Cu composite shows clearly lower thermal resistance compared to the composite without SCFD process. Lower resistance is obtained by increasing process time. The CNT brush combined with the composite shows lower thermal resistance in comparison with the composite at high contact pressure.

The Young's modulus and bending strength of multi-walled CNTs (MWCNTs) have been reported to be approximately 1 TPa, as much as 14 GPa, respectively. Therefore, researches for practical applications of CNTs, especially CNT composites, have been actively pursued. The objective of addition of CNTs in the composite is to increase the tensile strength, and to increase the elastic modulus of the composite. Both of these effects are due to the fact that the CNTs have a higher stiffness and strength compared to the metal matrix. As a type of CNTs-metal composites, a CNTs-Ni composite can substantially improve Young's modulus, hardness, tensile strength and fracture strength in comparison with a Ni film due to the hardness improvement by CNTs and the good interfacial bonding between the CNTs and the Ni matrix. However, CNT content in the CNTs-Ni composite is not mentioned in these studies, thus it is difficult to compare the improvement effect in mechanical properties statistically. Moreover, synthesis method for reinforcement of higher weight percentage CNT in the CNTs-Ni composite have not been attempted and accomplished, and practical application of the composite have not been reported because these studies are constrained within a stage of material development.

On the other hand, resonant scanning micromirrors based on microfabrication technologies have been conceptualized for a wide range of image display applications. It requires high resonant frequency, wide scanning range and mechanical stability during operation, which highly depends on the mechanical elements of the micromirror. Therefore, the CNTs-Ni composite can be one of candidates for some applications of the scanning micromirror in which the micromechanical elements of the micromirror are difficult to satisfy critical mechanical requirements.

In the work on CNTs-Ni composite thin film with randomly dispersed CNTs, a new electroplating method of a CNTs-Ni composite thin film with a high content of CNTs are presented and the mechanical property of the composite are evaluated. The fabrication and characterization of a micromirror with the CNTs-Ni composite beams are presented and the shear modulus of the composite beams compared with the pure Ni is evaluated. To confirm the ability of the composite beams, mechanical stability of the micromirror is evaluated in terms of the resonant frequency stability, and scanning angle of the micromirror is demonstrated. The objective of this research is to synthesize the CNTs-Ni composite thin film with higher content of randomly dispersed CNTs in the composite, improve the mechanical property compared with the pure Ni film, and characterize the mechanical stability of the fabricated micromirror with the CNTs-Ni composite beams for micromechanical application of the composite.

In chapter 4, a new dispersion electroplating of a CNTs-Ni composite thin film with positively charged CNTs is described. CNTs are pretreated through a procedure of CNT purification and surface ionization with positive charges, and introduced into a Ni electroplating solution. The content of CNT in the electroplated composite by pulse-reverse control deposition was 2.2 ± 0.4 wt%, and the volume of voids in the composite is 2 ~ 5.6 %. The ultramicroindentation hardness of the CNTs-Ni composite thin film is measured using the mechanical property tester for characterization of the composite. The measured ultramicroindentation hardness of the composite is 18.6 ± 2.0 GPa, it was enhanced from 13.8 ± 1.8 GPa of the hardness of the Ni film by the addition of the CNTs. Based on the mechanical strength of the CNTs-Ni composite by the addition of the CNT, the composite would be applicable to micromechanical elements for MEMS and microdevices.

In chapter 5, a Si micromirror with the CNTs-Ni composite beams is designed and fabricated. According to measurement result of resonant frequency of the micromirror, it is found that the experimental shear modulus of the composite beam is comparable with the theoretical value of the composite beam and the addition of CNTs in the composite effectively improve the shear modulus compared with the pure Ni. The resonant frequency of the fabricated micromirror at the fundamental vibration mode is kept at a stable value with the maximum variation of 2.7 Hz, 0.25% to the stable resonant frequency during the long term stability test. The variation rate is smaller than that of 0.66 % of a micromirror with electroplated Ni beams. A scanning angle of the micromirror with the composite beams was kept at a stable condition of 20^{o} during the stability test. The variation of the scanning angle with the CNTs-Ni composite beams was approximately 4^{o}. It is obviously smaller than that of the scanning angle with the Ni beams, approximately 13^{o}, during the much longer measurement time. The optimal design of the Si micromirror and the CNTs-Ni composite should be considered for appropriate applications.

Finally, the conclusions of this thesis are described in chapter 6. There is a lot of scope for potential applications of CNTs-metal composite thin film and further study in this field such as heat sinks for thermal management, microbeams, microgears using the desired thermal, mechanical and electrical properties of CNTs-metal composites. The studies about synthesis of the CNTs-Cu and CNTs-Ni composites in this thesis would lead to appropriate applications for MEMS, sensors, electronic packaging, and so on.

論文審査結果の要旨

カーボンナノチューブは，ユニークな熱的，機械的な特性を持ち，カーボンナノチューブを補強材として含めた複合材料は，優れた特性を示すものと期待されている。一方，マイクロ熱デバイスにおける熱伝達効率やマイクロシステムの機械部材の強度が問題となっており，カーボンナノチューブ複合材料のマイクロシステムへの応用により優れた熱伝導特性，あるいは優れた機械特性を示す材料の実現が期待される。本論文では，マイクロシステムへの応用が適用可能な，カーボンナノチューブと金属の複合体からなる薄膜の合成方法を開発し，その薄膜材料の機械的，熱的測定を評価している。本論文は，これらの研究成果をまとめたものであり，全編 6 章からなる。

第 1 章は緒言であり，本研究の背景や目的について述べている。

第 2 章では，超臨界成膜装置の開発と Cu の堆積について述べている。超臨界二酸化炭素に金属錯体を混入し，熱分解により良質の金属を堆積させることができ，超臨界流体が小さな隙間を通りやすい性質を利用して，均一な膜厚が得られることを示している。これは，カーボンナノチューブとの複合薄膜を形成するために重要な成果である。

第 3 章では，超臨界成膜装置を利用した高配向カーボンナノチューブ - Cu 複合薄膜の形成とその熱的な性質について述べている。化学気相合成法を用いて形成した垂直配向のカーボンナノチューブを，超臨界成膜と Cu の電界メッキの複合プロセスを利用して埋め込むことに成功している。また，表面に機械的に柔軟なカーボンナノチューブを露出させ，他の材料との熱接触を容易にすることで，低い界面熱抵抗が得られることを実証している。これは，熱伝導を利用するマイクロデバイスへの応用における界面材料としての利用が期待でき，重要な成果である。

第 4 章では，電界メッキを利用した無配向カーボンナノチューブ - Ni 複合薄膜の合成とその機械特性評価について述べている。この合成法では，カーボンナノチューブを分散したメッキ浴中でカーボンナノチューブの表面を正に帯電させるために表面修飾材を添加することを特徴としている。表面が正に帯電したカーボンナノチューブは，電界メッキによる膜の形成中に負極側に引き寄せられて複合薄膜が形成され，約 2.2 重量%の高密度複合膜の形成に成功している。製膜した複合薄膜は，超ミクロ押込試験の結果から，純 Ni 薄膜に比べて大きな硬さを示しており，良好な分散がなされていることが示されている。これらの結果は，カーボンナノチューブ金属複合材料を形成するための新しい技術として重要な成果である。

第 5 章では，カーボンナノチューブ Ni 複合材料をマイクロミラーの機械部材への適用について実証している。開発した複合電界メッキ技術を微細加工技術に適用し，マイクロミラーの作製に成功している。マイクロミラーを支持するねじれ梁を複合電界メッキにより作製している。また，マイクロミラーを大きな角度で振動させたときの共振周波数の安定性を評価し，純 Ni のねじれ梁からなるマイクロミラーと比較して良好な特性を持つことを示している。これらの成果は，開発したカーボンナノチューブ複合電界メッキがマイクロシステムに応用できることを示した重要な成果である。

第 6 章は結論である。

以上要するに本論文は，マイクロシステムへの応用の目的で，高配向，あいるは無配向のカーボンナノチューブを金属で埋め込んだカーボンナノチューブ金属複合薄膜技術を開発して重要な成果を得たものであり，機械システムデザイン工学および微小機械構成学の発展に寄与することが少なくない。

よって，本論文は博士(工学)の学位論文として合格と認める。