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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）	
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要約

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.

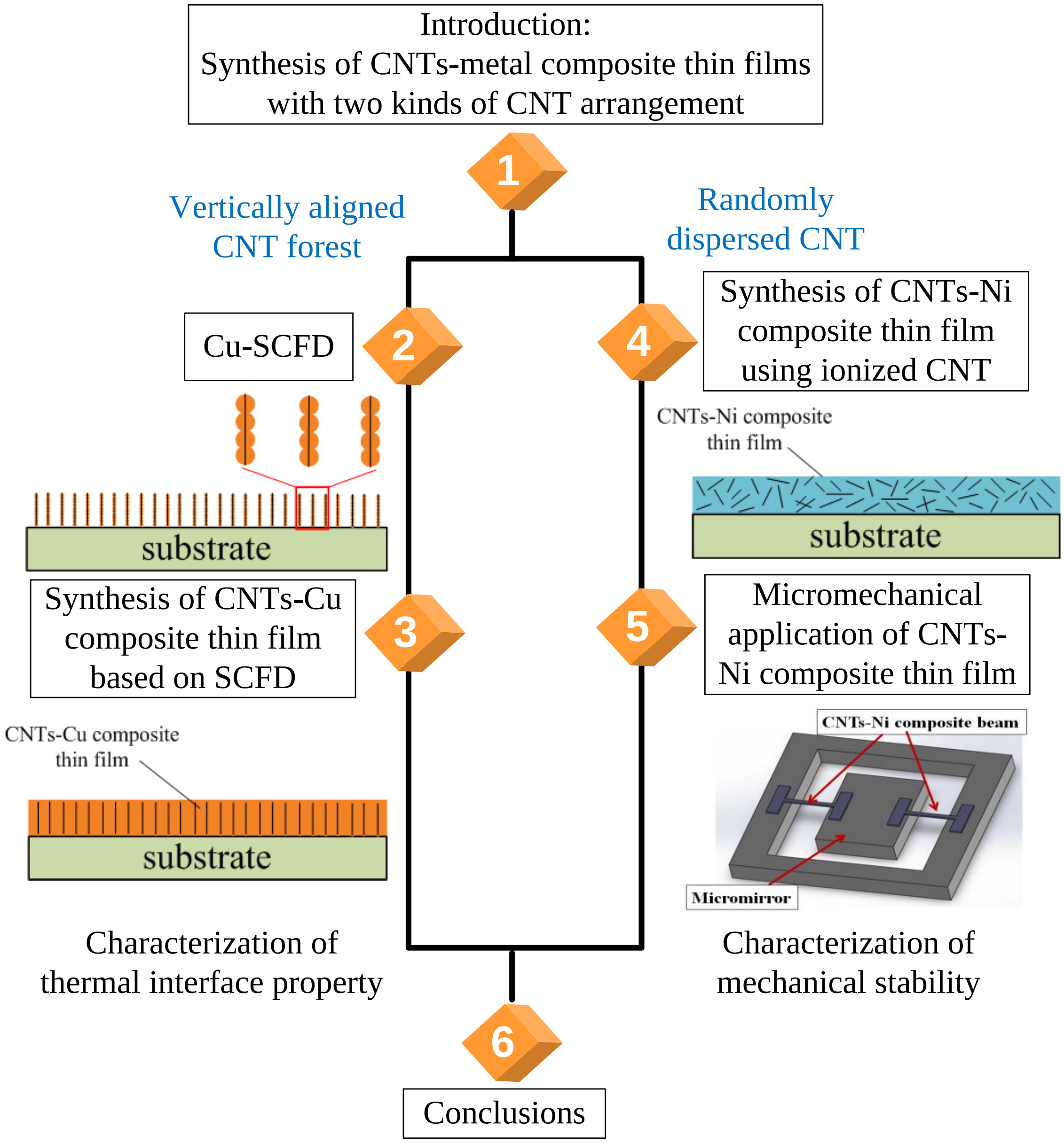

Figure 1: An overview of thesis content and organization.

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.