論 文 の 内 容 の 要 旨

論文題目　Thermal properties of PDMS composite containing aligned CNTs
（配向CNT-PDMS複合材料の熱物性）

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The generation of micro/nanotechnology has required "*cooling*" as one of the major challenges. In the field of micro and nano electronics, those devices undoubtedly produce heat, which need to be minimized with efficient cooling to prevent the failure of performance. For decade, electronic devices such as integrated chips tend to reduce size and increase the speed and performance, which drive the thermal management more important due to the necessity for the sufficient cooling system. So far, cooling by air convection for electronics is the most widely used method, but this method has a serious limitation which is unable to increase degree of heat flux.

Thermal interface materials (TIMs) are one of the main bottlenecks for efficient heat transfer from integrated chips to heat sinks and ambient environment by filling micro-gap-interface between two contacting materials to improve thermal conduction instead of air gap: thermal grease, thermal gel, phase change materials, thermal conductive adhesive, thermal tapes ad pads. Among carbon allotropes-based TIMs, *carbon nanotubes* (CNTs) with high thermal conductivity and high aspect ratio is one of the most expected candidates acting as fillers since they enables to extend the study down to a further smaller scale than before.

Over the past few decades, CNTs have been studied to be used in various fields due to outstanding electrical, mechanical, and thermal properties since the discovery. The electric current density of metallic CNTs is found to be 4×10^9 A/cm^2 in theoretical study, about 1000 times than that of metals such as copper. In addition, the structure of sp^2 chemical bonding – stronger than that of sp^3 found in diamond – gives CNTs have exceptionally high mechanical property, up to 1.2 TPa for Young's modulus and 50 – 200 GPa for the tensile strength. Since it is difficult to measure directly thermal properties of an individual CNT due to the technical difficulties in nanoscale, thermal properties of CNTs have been investigated by theoretical simulation and calculation. Thermal conductivity of CNTs has been measured up to ~ 6000 W/mK surpassing that of diamond, even though the results of measured thermal conductivities are largely scattered.

CNTs contained in polymer enable to enhance thermal property of the polymer composite. Various factors have an impact on degree of improvement for the thermal property such as fabrication method, orientation, density, and types of CNTs. The fabrication methods are categorized into three types such as solution mixing, melt blending, in situ polymerization, and latex technology which have each advantages and limitations. In addition, the orientation of CNTs in polymer matrix is a critical factor due to their anisotropic structure, which leads to determine the thermal property of the composite. Enhanced thermal property of the composite is dependent on weight/volume percent of CNTs, however, their excess inclusion lead to debilitate thermal property rather than to improve. Either SWNT or MWNT should be chosen for a proper purpose of the composite with consideration of their difference for thermal behavior.

Electronic devices with the necessary to reduce size and increase the speed and performance have led cooling to be more important. This thesis work is motivated by potential applications that polymer composite containing CNTs as fillers is expected to be used for thermal interface material. Prior to study for the thermal performance of the composite, thermal behavior of CNT forest without polymer are investigated with several potential factors such as volume fraction, types of CNTs, and temperature. In addition, thermal conductivity of an individual CNT also is estimated with additional information. Then, thermal properties of polymer composite containing CNT forest are evaluated to be used for potential thermal applications. Moreover, this thesis work also focus on the development for a new fabrication method for polymer composites with CNT forests available applying for the size of tens of μm to enhance thermal transfer. Through a series of above studies, this PhD thesis aims to provide engineering knowledge to understand thermal behavior of both CNTs and polymer composite containing CNT forests, which can help to describe improved various applications by using the composites in the field of micro and nanotechnology.

The contact-free laser flash analysis (LFA) technique proposed by Parker *et al* measured thermal diffusivity of vertically aligned CNT (VACNT) forests with various volume fractions. As-grown VACNT forests have the volume fraction at most up to ~ 5 %, which represents the degree of the number of CNTs occupying the forest. Wardle *et al* introduced the mechanical densification to control the volume fraction of CNT forests. In this study, 4.15 % volume fraction of millimeter-long as-grown SWNT forest was squeezed up to 25.2 %. Measured thermal diffusivity for each volume fraction of SWNT forests should have been identical even though they are in different volume fraction, since it is intrinsic thermal property of a material representing the rapidity of the heat propagation thorough it. Hence, the result is unnatural that the increase of volume fraction resulted in high thermal diffusivity of SWNT forests. This potentially occurred because the suspending SWNTs in the forest, not directly involved in the thermal propagation from front to rear surfaces during the measurement of LFA, became to contribute for thermal transfer rather than to disturb, which causes to have higher thermal diffusivity. Indirectly, thermal conductivity of SWNT forest can be derived with additional information such as the specific heat and density. In addition, obtained thermal diffusivity and conductivity for MWNT forest were compared to those of SWNT forests. The comparison indicated that the CNT forest when composed of MWNTs has higher thermal properties than SWNTs. Marconnet *et al* reported the role of inner-walls MWNTs for thermal transfer that conducts phonons efficiently with less interacting to surrounding materials than outer shell. In fact, the increase of thermal diffusivity potentially results from the effect of suspending CNTs so that it can increase more than this measurement. The result can be explained by considering the intrinsic structural difference between SWNTs and MWNTs.

PDMS composite with VACNT forest were fabricated that the phenomenon of PDMS wetting CNTs is apparently close to the in-situ polymerization except the functionalized surface that CNTs are incorporated into liquefied polymer matrix in which cross-linking agent was added, resulting from capillary motion. The slow infusion of PDMS from the side direction potentially leads to prevent the composites from void-trap. Since the thickness of the CNT forests are relatively long up to 1 mm, it is possible to fully wet the CNT forests, up to the tip, by controlling quantities of PDMS. Remained voids trapped in the composites are removed by giving enough time to polymerize in a vacuum desiccator. Since the infiltration of polymer matrix into CNT forest is one of the main factors to determine the quality of the composite when using the technique to pour polymer on to CNT forest, scanning electron microscopy characterized the degree of PDMS infiltration in CNT forest. On the other hand, thermal diffusivity of the composites was enhanced by the various volume fractions of VACNT forests up to 7.86 mm^2/s with 20.3 % of SWNTs, and 6.65 mm^2/s with 12.2 % for MWNTs. Derived thermal conductivity of each SWNT and MWNT forest was discussed by comparing to the theoretical prediction model of the composite for aligned continuous CNTs proposed by Nan *et al*.

A facile fabrication method, called *side-intrusion method* was proposed to use for applying to tens of μm long VACNT forests, which is practical size-scale in TIMs for such integrated chips. The method enables to make the polymer composite uniform and well-aligned, but requires no treatment. The composites fabricated from the side-intrusion method are characterized the degree of PDMS infiltration into CNT forest, and vertical alignment of CNTs in PDMS composite by Raman spectroscopy. As a result, it was confirmed that PDMS uniformly infiltrated into the VACNT forest by capillarity even without deteriorating the aligned morphology.

The obtained result in this thesis work possibly provides engineering knowledge to understand thermal behavior of both CNTs and polymer composite containing CNT forests, which potentially help to imagine various applications with improved thermal property by using the composites in the field of micro and nanotechnology.