Microfabrication of Carbon Nanotube Composite for Actuator Applications

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授　与　学　位	博士（工学）
学位授与年月日	平成２５年3月２７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	アクチュエータ応用のためのカーボンナノチューブ複合材料のマイクロ加工 (Microfabrication of Carbon Nanotube Composite for Actuator Applications)
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論文内容要旨

Recent technology advancement in micro/nano fabrication facilitates the fabrication of nanocomposite microstructures. In the last decade, extensive researches on CNT (carbon nanotube)-based nanocomposites have been performed increasingly. A variety of CNT-based nanocomposites have been successfully developed and investigated for many potential applications in microdevices ranging from microgripper structures, electrothermal microactuators and microresonant devices, structural materials for microactuators etc.

The CNT-based composites are a promising new class of structural materials for the mechanical components of MEMSs (Microelectromechanical Systems). They have potential applications for microactuators with low stiffness and high natural frequencies. Microactuators in the current generation of MEMSs are either monolithic structures or layered composites of laminated thin films, and the material of choice for low stiffness, high frequencies actuators should exhibit a combination of relatively low Young's modulus and high wave velocity. The CNTs used as reinforcement in the composites have two distinctive advantages, i.e. small size with low density, and exceptional mechanical properties. Thus, the CNT reinforced composites are a natural starting point in the development of nanocomposites for microactuators.

The pyrolysis carbon micro/nano structures, which are formed by pyrolyzing patterned organic polymer precursors, have been studied by various researches. Various microfabrication methods for pyrolysis of carbon micro/nano structures that utilize polymer precursors have been proposed by now. Some methods for the fabrication of freestanding carbon structures have been reported, and it has been demonstrated to fabricate high-aspect ratio carbon microstructures, suspended carbon microstructures, multi-level 3D carbon microstructures, various carbon nanostructures, and carbon micro-cantilevers. In these fabrication processes, polymers patterned by conventional photolithography, such as photolithography and EB (Electro Beam) lithography. Additionally, carbon micro/nano structures also have been fabricated by employing other methods such as soft lithography (using polyimethysiloxan molds, PDMS molds), nanoimprint, and anodic aluminum oxide nanoporous using as templates combined with pyrolysis or carbonization at high temperatures in inert gas atmosphere.

The physical and chemical properties of pyrolysis carbon structures make it a potential candidate for the preparation of mcirodevices, and such carbon structures have been investigated for applications in MEMSs, such as three-dimensional microbattery, glucose sensors, DNA detection, biosensors, and on-chip supercapacitors etc. Pyrolysis carbon is electrically conducting, also has a wide electrochemical stability window and low coefficient of thermal expansion, thermally stable in a non-oxidizing environment at temperatures higher than 3000 °C, high corrosion- and strong acid- resistance, inert over a wide range of electrical potentials.

From the view point of micromechanics, one critical issue in the MEMSs, including microactuators, XY microstage, micromirror, and optical scanners etc., is the difficulty in obtaining both large displacement/deflection and no plastic deformation with good stability. Si has been often used as an elastic material in MEMSs, due to its high Young's modulus, no plastic deformation and no mechanical hysteresis, but the brittleness and hard spring are its disadvantages in the large demands for soft spring structures with large displacement/deflection. For the solution in obtaining both of large displacement/deflection and small plastic deformation in the MEMSs, other candidates with expected lower Young's modulus than Si and smaller plastic deformation than polymer should replace Si as an elastic material for actuators, and CNT-carbon composite is one of the candidates.

The lower Young's modulus of carbon-based material compared to that of silicon can be an advantage in applications where the brittleness of silicon is a limiting factor (for example, silicon structures driven by actuators), and the smaller plastic deformation than that of polymer also can be an advantage in applications where the large mechanical hysteresis of polymer is a limiting factor. Thus, the fabrication, characterization, and investigation of applications of carbon micro/nano structures have garned much more attention recently. The investigation of the micromechanical properties of the microstructures is an important way for the design of the MEMSs with various micro units incorporated, also important for the applications of this functional carbon or CNT-carbon microstructures.

In this research, the CNT-carbon composite microstructures has been chosen as one of candidates as an elastic material in microactuators with expected micromechanical properties. The effective and successful fabrication process including Si micromolding and pyrolysis of patterned resist mixed with CNTs for CNT-carbon composite microstructures was first reported. Morphology, shrinkage, density change, weight loss and micromechanical properties including hardness and Young's modulus of this composite were investigated.

The fabrication process of hybrid microstructures consisted of CNT-carbon composite microstructures and Si are successfully fabricated by Si micromolding and pyrolysis of a resist (SU-8 50) mixed with 1 wt. % CNTs. In the fabrication process, the SU-8 mixed with CNTs was filled into the Si micromolds that fabricated by deep ICP-RIE (Inductively Coupled Plasma Reactive Ion Etching), then the patterned CNT/SU-8 was converted to CNT-carbon microstructures at temperature of ~600 °C under inert atmosphere. Then, the Si substrate was patterned by deep ICP-RIE to release the composite microstructures. The CNT-carbon composite microstructures with dimensions from 10 micrometers to several hundred micrometers can be fabricated by pyrolysis process from the patterned CNT/SU-8 composite. The lateral shrinkage can be negligible in the fabrication process. The weight loss of composite microstructures after 400 °C and 600 °C pyrolysis process are 39% and 40%, respectively. The vertical shrinkage of thin films after 400 °C and 600 °C pyrolysis process are 56%, and 65% relative to the initial pre-baked films, respectively. The resulting composite microstructures including cantilevers, crossbar rings, both-side bridged microstructures etc., with a maximum high aspect ratio of ~34 can be successfully fabricated by this novel fabrication method, that could be an advantage for microactuators with high displacement and high sensitivity etc. From the SEM images from the pulled-out nanotubes in the crack section and fracture section of the fabricated composite microstructures, we can estimate the average diameter of the nanotubes of 94 ± 41 nm, that is larger than that of original nanotubes. This research provides a simple approach that is compatible with microfabrication technology and is capable of fabricating composite microstructures with reproducible shape and dimensions, at desired locations.

For the purpose of investigation of the micromechanical properties of this CNT-carbon nanocomposite, the nanoindentation test was utilized to measure the hardness of the obtained composite films, and applied load-indentation depth (W-d) curves with loading and unloading stages were obtained in these measurements. The hardness represents the resistance to local plastic deformation of materials, which is equivalent to the average work done by the indenter. The viscosity and hardness can be increased by adding 1 wt. % CNTs to the carbon microstructures. The density and hardness of the composite can be increased as pyrolysis temperatures increased from 400 °C to 600 °C. The hardness can be increased ~10.8% and ~45.3%, after 400 °C and 600 °C pyrolysis process, respectively. The SU-8 film and CNT/SU-8 film have negligible elastic recovery after unloading the indenter. After 400 °C or 600 °C pyrolysis process, both of the carbon film and CNT-carbon film have large elastic recovery and small plastic deformation after unloading the force. They can be considered as plastic/elastic material.

The Young's modulus of the composite cantilevers calculated from their resonant frequencies by laser Doppler vibrometer, was 6.73 ± 3.23 GPa, that were below the expected value. These low Young's modulus should results from the voids in the composite microstructures. The stress-strain behavior of the carbon and CNT-carbon composite both-side bridged microstructures measured by micro tensile test system shown that both of them have low fracture strength, as ~13 MPa of carbon, and 40 MPa of CNT-carbon. The low fracture strength can be due to the cracks in the microstructures.

The microstage is a micropositioning device, capable of precise motion in moving and positioning an object, with a relatively high degree of accuracy, therefore, it has various applications in MEMSs, such as scanned probe devices, optical pickup heads, sensor positioning and micro tools. The positioning of microstage is a critical issue for the successful miniaturization of mechanical systems such as high density data storage system and nanolithography. Such microsystems generally require the well-controlled stages with larger strokes, higher resonant frequency and lower driving voltages in actuation. In this research, a Si-PZT ($PbZrTiO_3$) hybrid XY-microstage with "CNT-carbon composite" hinges is designed and fabricated, the design criteria for the microstage system was chosen on the basis of its application for high density data storage systems. The Si is used as a base material and the stacked PZT ($PbZrTiO_3$) actuators were used to drive the stage. The design of the proposed XY-microstage driven by stacked PZT actuators with Moonie amplification structures arranged so that the movement in both the X and Y directions are controlled by actuators. This microstage is made of a Si substrate with a size of $20 \times 20 \times 0.4$ mm^3. The CNT-carbon composite is partially used for the flexible hinge parts in the Si-PZT hybrid XY-microstage since the CNT-carbon composite has a low elastic constant and small mechanical hysteresis. The Young's modulus and hardness of the composite can be smaller than that of Si; therefore, the moving parts in the microstage can be more flexible.

In the fabrication process of the microstage, the CNT-carbon hinge parts are formed by the process including Si micromolding and pyrolysis. Then, two stacked PZT actuators are assembled into the XY-microstage. The fabrication starts from patterning of the Si micromolds by photolithography and deep ICP-RIE. A resist SU-8 50 mixed with 1 wt. % of CNTs was used as a filling material and was filled into the Si micromolds by backside pumping, squeezing, and remained CNT/SU-8 on the substrate was removed by O_2 plasma. Then, the CNT/SU-8 was converted to CNT-carbon hinge structures by pyrolysis process under N_2 atmosphere. After the pyrolysis process, the microstage structure is formed by photolithography and deep ICP-RIE again. The piezoelectric actuator was fabricated in a stacked arrangement in order to produce a large stroke using a small voltage. The PZT stacked actuators with a size of $8 \times 0.5 \times 0.4$ mm^3 was fabricated from a PZT plate by process including electroplating and photolithography. The stacked PZT actuator is comprised of alternating PZT layers and nickel electrodes. Finally, the stacked piezoelectric actuators are assembled in the Moonie amplification structure in the microstage. This fabrication method including Si micromolding and pyrolysis offers an example that is effective and important for the investigation of applications of this composite utilized as microactuators in MEMSs.

Now the known physical properties of the CNT-carbon composite microstructures fabricated by our process are: lower Young's modulus and hardness than Si, chemically stable, ability to obtain high aspect ratio structures, fabrication method is compatible with microfabrication technology, controllable hardness and plastic deformation by adding CNTs with different pyrolysis treatment. Therefore, this CNT-carbon composite can be considered as a suitable candidate for a elastic material with potential applications in the microactuators, and for the solution in obtaining both large displacement/deflection and small plastic deformation in the MEMSs.

論文審査結果の要旨

マイクロアクチュエータは，様々な精密機械やマイクロシステムの基本要素として用いられている。一方，マイクロXYステージやマイクロミラーなど，小型化したシリコンのマイクロ要素においては，大きな変位や振れ角を発生させるために要素部材に圧電アクチュエータなどで大きな負荷がかかり，シリコンが脆性破壊することが問題になっている。一方，ポリマーを使ったマイクロシステムにおいては，柔らかなばね構造が容易に形成できるため，大きな変位が得やすいが，機械的なヒステリシスが発生するのが問題である。本論文では，多層カーボンナノチューブとポリマーの複合材料を加熱分解して形成したマイクロ構造の作製技術について述べている。開発したマイクロ構造部材は，シリコンよりも柔らかく，ポリマーよりも機械的なヒステリシスが少ないため，アクチュエータのばね構造材料として優れていることが示されている。また，マイクロＸＹステージにこの材料を組み込むプロセス技術を開発している。本論文はこれらの研究結果をまとめたもので，全編7章からなる。

第1章は序論であり，本研究の背景や目的について述べている。

第2章では，カーボンナノチューブ複合材料と熱分解カーボンについて述べている。種々のカーボンナノチューブ複合材料の形成方法，および焼結カーボンの形成方法，およびその問題点や応用について議論している。これらは，複合材料のマイクロ構造を形成するための重要な知見である。

第3章では，マイクロシステムで用いられる材料の評価方法について論じている。マイクロ構造の硬さ，ヤング率，およびひずみ特性などについての測定方法を比較，検討している。これは，複合材料の評価方法として有益な知見である。

第4章では，カーボンナノチューブ - カーボン複合材料のマイクロ加工技術について述べている。反応性イオンエッチングで作製したシリコンのモールドにカーボンナノチューブを均一に分散したポリマーを流し込み，焼結させてカーボンナノチューブ - カーボン複合材料からなるマイクロ構造を形成している。マイクロ構造の最大のアスペクト比は34程度であり，アクチュエーター―としての応用が期待できるマイクロ構造である。また，破断面の構造観察から，カーボンナノチューブと焼結カーボンの界面はすべりにくく，カーボンナノチューブが補強材としての性質を保持している。これらは，新しく開発したカーボンナノチューブ - カーボンの複合材料のマイクロ構造を作製する新しいプロセス技術を開発したものであり，重要な成果である。

第5章では，カーボンナノチューブ - カーボン複合材料からなるマイクロ構造の機械特性について述べている。単にポリマーを焼結して得られたカーボン構造に比べ，カーボンナノチューブを入れることにより，機械的なヒステリシスを小さくできることが示されている。また，そのヤング率はシリコンよりも小さく，よりフレキシブルなマイクロ機械構造を作製できることが示唆されている。これらの結果は，開発した複合材料のマイクロ構造は，マイクロシステムに応用できることを示す重要な成果である。

第6章では，開発したマイクロ複合材料のプロセス技術のマイクロＸＹステージへの応用について述べている。これは，重要な成果である。

第7章は結論である。

以上要する本論文は，カーボンナノチューブ - カーボン複合材料からなるマイクロ構造の作製に関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細加工学の発展に寄与するところが少なくない。

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。