Materials & Coatings

Use of Functionalized Carbon Nanotubes for Covalent Attachment of Nanotubes to Silicon

This method enables the introduction of carbon nanotubes onto all types of silicon-based devices and silicon surfaces.

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The purpose of the invention is to covalently attach functionalized carbon nanotubes to silicon. This step allows for the introduction of carbon nanotubes onto all manner of silicon surfaces, and thereby introduction of carbon nanotubes covalently into silicon-based devices, onto silicon particles, and onto silicon surfaces.

Single-walled carbon nanotubes (SWNTs) dispersed as individuals in surfactant were functionalized. The nanotube was first treated with 4-t-butylbenzenediazonium tetrafluoroborate to give increased solubility to the carbon nanotube; the second group attached to the sidewall of the nanotube has a silyl-protected terminal alkyne that is de-protected *in situ*. This gives a soluble carbon nanotube that has functional groups appended to the sidewall that can be attached covalently to silicon. This reaction was monitored by UV/vis/NJR to assure direct covalent functionalization.

Once the reaction to form the appropriately functionalized carbon nanotube was complete, the nanotube solution was passed through a plug of glass wool to

remove particulates. This filtered solution was then flocced by diluting with acetone, and filtered through a Teflon membrane. The collected solid was dispersed in dimethylformamide (DMF) with sonication and filtered once again through a Teflon membrane. The functionalized material was then dispersed in dry DMF and assembled onto silicon by hydrosilation. The assembly was conducted by treating the nanotube solution with a catalytic amount of triphenylcarbonium tetrafluoroborate and submersing a hydrogen-passivated silicon sample in the solution. The assembly mixture was agitated with warming for 12 hours. After that time, the silicon sample was rinsed with organic solvent and dried with a stream of nitrogen. The assembly was characterized by AFM (atomic force microscopy).

The most immediate and obvious use of this procedure is the covalent attachment of carbon nanotubes onto silicon. This method allows for the attachment of individual (not bundles) carbon nanotubes. With this methodology, the highest temperature required to regen-

erate the pristine carbon nanotube is 450 °C.

Although other methods exist to introduce carbon nanotubes into silicon-based devices, this methodology is selective for silicon and allows for the generation of working devices at a much lower temperature.

This work was done by James M. Tour, Christopher A. Dyke, Francisco Maya, Michael P. Stewart, Bo Chen, and Austen K. Flatt of Rice University for Johnson Space Center. Further information is contained in a TSP (see page 1).

In accordance with Public Law 96-517, the contractor has elected to retain title to this invention. Inquiries concerning rights for its commercial use should be addressed to:

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Flexible Plug Repair for Shuttle Wing Leading Edge

Thin, flexible plugs conform to surfaces.

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In response to the Columbia Accident Investigation Board report, a plug repair kit has been developed to enable astronauts to repair the space shuttle's wing leading edge (WLE) during orbit. The plug repair kit consists of several 17.78-cm-diameter carbon/silicon carbide (C/SiC) cover plates of various curvatures that can be attached to the refractory carbon-carbon WLE panels using a TZM refractory metal attach mechanism. The attach mechanism is inserted

through the damage in the WLE panel and, as it is tightened, the cover plate flexes to conform to the curvature of the WLE panel within 0.050 mm. An astronaut installs the repair during an extravehicular activity (EVA). After installing the plug repair, edge gaps are checked and the perimeter of the repair is sealed using a proprietary material, developed to fill cracks and small holes in the WLE.

In developing the plug repair concept, several issues had to be addressed

including material, design, performance, and operability. An oxyacetylene torch was calibrated to heat a specimen to WLE entry temperatures and was used to screen candidate repair materials. Promising materials were then tested in the Johnson Space Center arc-jet test facility to determine their resistance to oxidation in a hypersonic environment. C/SiC was selected as the cover plate material because of its superior strength and resistance to oxida-

tion. In order to raise its operational temperature limit, a proprietary oxidation barrier coating was developed. TZM was selected as the attach mechanism material because of its manufacturability and structural performance as well as its ability to withstand the plasma environment when coated with the oxidation barrier coating.

Prior art involved square, inflexible plugs that were too small to provide complete WLE coverage and would also create protuberances into the hypersonic flow that would overheat during operation. This innovation is an evolution of the prior art in that the current

plug is a thin, flexible double-curved shell with rounded edges, which facilitates a deformed shape that conforms to the WLE geometry with minimal disturbance of the flow.

The repair plug is designed to capitalize on flexibility and curved shape in order to minimize the number of cover plates required. The current design reduced the number of unique plug shapes required to cover critical WLE regions from over 1,300 to less than 20. Non-linear finite element analysis, including contacting surfaces, was used to model the plug during installation and operation. Computa-

tional fluid dynamics and thermal analysis were used to predict plug temperatures during entry.

Three Dimensionally Interlinked, Dense, Solid Form of Single-Walled CNT Ropes
The nanotube block has high mechanical strength and resistance to indentation.

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A 3D networked, dense form of single-walled carbon nanotubes (SWNT) has been made through isotropic shrinking of a gel-like SWNT-water paste by very slow evaporation. Approximately 35 g of Raw HiPco nanotubes were cleaned by the method of soft baking (250 °C for 15 hours in air saturated with water vapor) in a glass beaker followed by leaching with concentrated hydrochloric acid. Typically, one liter of concentrated hydrochloric acid was added to the soft-baked voluminous mass in the same large beaker, and allowed to digest at room temperature with stirring overnight. The acid-digested SWNT slurry was filtered through a large porcelain Buchner funnel under atmospheric pressure.

The slurry was continuously flushed, while still in the funnel, with a very slow but steady stream of deionized water employing a peristaltic pump. This process, referred to as "washing," continued until the filtrate water dripping from the Buchner funnel was clear, colorless, and neutral to a pH paper. This took about 15 liters of water to flow through the slurry over a day. At this point, the water pump was stopped and the SWNT-water slurry was allowed to drain the excess water for about 10 hours. The resulting thick paste of SWNT-neutral water was transferred to a beaker. The beaker was covered with aluminum foil with few holes and allowed to dry very slowly in a hood at room temperature. In about eight weeks, the sam-

ple gradually dried isotropically to a cylindrical dense mass referred to as a carbon nanotube block (CNB).

There was no carbonaceous matter sticking to any of the glass surface where the SWNT-water paste made contact. The approximate dimensions of the cylindrical SWNT block that weighed 28 g were 1.5 in. ($\approx$3.8 cm) in diameter and 1.25 in. ($\approx$3.2 cm) in height. The bottom portion of the cylinder that was in contact with the beaker surface was slightly wider, indicating some resistance to shrinking. The cylindrical mass also consisted of several pores. The cylindrical mass was very tough and could not be broken with a small hammer using considerable force. The mass of the solid could be polished over a fine grain emery paper or even a smooth, stainless steel surface indicative of alignment at finer levels.

When attempting to cut with a sharp knife edge, the mass showed extreme resistance to the back-and-forth movement of the blade and indentation. Small portions were cut out of the solid block using a hacksaw and experimented. A small piece of the block was placed in water. It floated initially for a few minutes, but sank subsequently, indicative of a density >1 g/cm^3.

Two small portions (total volume approximately 1 cm^3) were placed in a small, conical flask, and 25 ml of 100-percent H$_2$SO$_4$ was added to that and closed with a ground-glass stopper. The

small pieces floated in 100-percent H$_2$SO$_4$. The SWNT block gradually swelled in volume and occupied the whole of the liquid volume ($\approx$25cm^3) in two days. The SWNT/100-percent H$_2$SO$_4$ paste was very rigid and did not show fluidity. Scanning electron microscopy of the block showed evidence for the block to be constituted by packing of densely placed SWNT ropes. The polished surface showed evidence of a very high degree of smoothness up to 200 nm. The novelty and significance of this solid is the clear presence of a three dimensionally connected dense network of SWNT (with high mechanical strength) in a bulk form.

One immediate problem this new form of SWNT solves is handling. The dense form of SWNT is much easier to handle than the pristine forms of SWNT that could easily form potentially hazardous aerogels. The other bulk form of SWNT, known as buckypaper, needs ample time, equipment, and manpower to process; lacks mechanical strength; mostly retains the surfactants used in the process as organic impurities; and poses problems in redispersion to single-tube levels. The CNB, on the other hand, is made in a single step from the water-SWNT gel-like paste without recourse to any surfactant, possesses extreme mechanical strength, and can be redissolved in strong acids.