

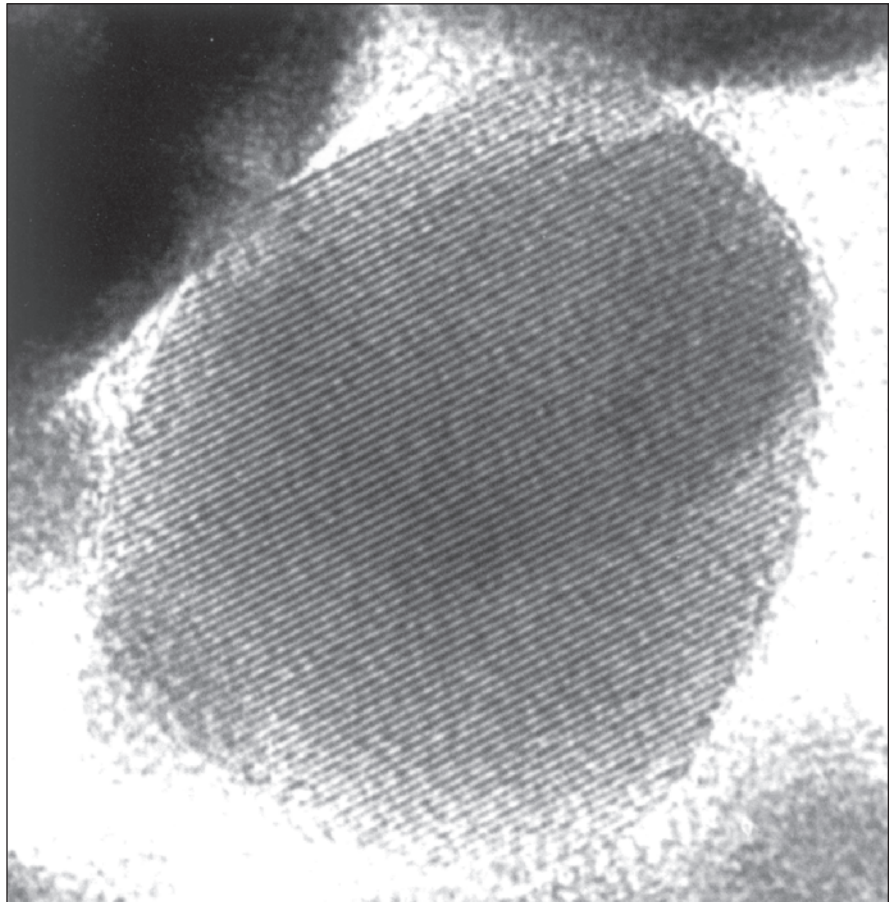
Process for Making Single-Domain Magnetite Crystals

Crystals can be chemically pure and free of defects.

Lyndon B. Johnson Space Center, Houston, Texas

A process for making chemically pure, single-domain magnetite crystals substantially free of structural defects has been invented as a byproduct of research into the origin of globules in a meteorite found in Antarctica and believed to have originated on Mars. The globules in the meteorite comprise layers of mixed (Mg, Fe, and Ca) carbonates, magnetite, and iron sulfides. Since the discovery of the meteorite was announced in August 1996, scientists have debated whether the globules are of biological origin or were formed from inorganic materials by processes that could have taken place on Mars. While the research that led to the present invention has not provided a definitive conclusion concerning the origin of the globules, it has shown that globules of a different but related chemically layered structure can be grown from inorganic ingredients in a multistep precipitation process. As described in more detail below, the present invention comprises the multistep precipitation process plus a subsequent heat treatment.

The multistep precipitation process was demonstrated in a laboratory experiment on the growth of submicron ankerite crystals, overgrown by submicron siderite and pyrite crystals, overgrown by submicron magnesite crystals, overgrown by submicron siderite and pyrite. In each step, chloride salts of appropriate cations (Ca, Fe, and Mg) were dissolved in deoxygenated, CO₂-saturated water. NaHCO₃ was added as a pH buffer while CO₂ was passed continuously through the solution. A 15-mL aliquot of the resulting solution was transferred into each of several 20 mL, poly(tetrafluoroethylene)-lined hydrothermal pressure vessels. The vessels were closed in a CO₂ atmosphere, then transferred into an oven at a temperature of 150 °C. After a predetermined time, the hydrothermal vessels were removed from the oven and quenched in a freezer. Supernatant solutions were decanted, and carbonate precipitates were washed free of soluble salts by repeated decantations with deionized water.



This **Transmission Electron Micrograph** shows a defect-free magnetite crystal with a (111) orientation, produced by thermal decomposition of siderite. The lattice fringes are spaced at 4.8 Å.

The procedure as described thus far was repeated for each subsequent step, except that a chemically different solution was added to the washed carbonate precipitates left in the hydrothermal vessels from the previous steps. Sulfur was included in the second and fourth steps to form Fe sulfides in addition to siderite. Hence, each globule comprised an ankeritic core (formed in step 1) followed by concentric zones of siderite + pyrite (formed in step 2), magnesite (formed in step 3), and siderite + pyrite (formed in step 4).

The carbonate + pyrite globules thus synthesized were heated to, then cooled from, 470 °C in a differential scanning calorimeter at the rate of 20 °C/min in a stream of CO₂ at a pressure of 13.3 kPa.

This heat treatment converted the siderite + pyrite to magnetite + pyrrhotite. The magnetite crystals are believed to have formed from the thermal decomposition of the siderite crystals in the reaction $3\text{FeCO}_3 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$. The magnetite crystals were found to have a variety of shapes, to have linear dimensions of predominantly 10 to 100 nm (in the superparamagnetic-to-single-domain size range), to be chemically pure, and to be free of structural defects (see figure).

Magnetite powders are essential ingredients of magnetic recording tapes. Powders made from single-domain magnetite crystals may enable the production of magnetic tapes capable of storing data at densities greater than

are now possible, provided that the process can be refined so that the magnetite globules are mostly elongated along their (111) crystallographic axes. At the time of reporting the information for this article, scanning-electron-microscopy and electron-diffraction experiments to determine length-to-width

ratios and crystallographic orientations were under way.

This work was done by D. C. Golden of Hernandez Engineering; Douglas W. Ming, Richard V. Morris, Gary E. Lofgren, and Gordon A. McKay of Johnson Space Center; and Craig S. Schwandt, Howard V. Lauer, Jr., and Richard A. Socki of Lockheed Martin.

This invention is owned by NASA, and a patent application has been filed. Inquiries concerning nonexclusive or exclusive license for its commercial development should be addressed to the Patent Counsel, Johnson Space Center, (281) 483-0837. Refer to MSC-23326.

A New Process for Fabricating Random Silicon Nanotips

This process is relatively simple and inexpensive.

NASA's Jet Propulsion Laboratory, Pasadena, California

An improved process for the fabrication of random arrays of silicon nanotips has been demonstrated to be feasible. Relative to other such processes, this process offers advantages of low cost and simplicity. Moreover, this process can readily be combined with other processes used to fabricate integrated circuits and other monolithic silicon structures.

Arrays of silicon nanotips are subjects of research and development efforts directed toward utilizing them as field emitters in flat-panel displays, vacuum microelectronics, and microwave devices. Other silicon-nanotip-fabrication processes developed thus far predominantly include lithography, etching, and/or elaborate deposition steps followed by oxide sharpening steps and are both process intensive as well as expensive. In addition to being cheaper and simpler, the present process can efficiently produce silicon nanotips that range in height from a few microns to several tens of microns and are distributed over large areas.

The process mentioned here can be summarized as consisting of (1) the growth of micro-etch masks on a silicon substrate, followed by (2) etching away of the masks, along with some of the substrate, to make an array of sharp tips. In the first step of the process, a cleaned silicon substrate is subjected to reactive ion etching (RIE) in a certain mixture of oxygen and carbon tetrafluoride under radio-frequency excitation. This process step results in the growth of fluorine based compounds in the form of stumps randomly distributed

on the substrate. These stumps are known in the art as "polymer RIE grass." The dimensions of these stumps are of the order of hundreds of nanometers, the exact values depending on process time and gas composition. The areal density of the stumps decreases with increasing process time as they grow and merge with neighboring stumps. These stumps constitute the micro-etch masks for the next step of the process.

In the second step of the process, the substrate covered with the micro-etch masks is subjected to deep reactive ion etching (DRIE) process, which consists of cycles of reactive ion etching alternating with passivation (the Bosch process). The gas used in the etching substeps is sulfur hexafluoride (SF_6); the gas used in the passivation substeps is octafluorocyclobutane (C_4F_8). The portions of the substrate directly under the RIE grass stumps are etched more slowly than are the portions between the stumps. Hence, what remains at the end of the process, after the stumps and parts of the substrate have been etched away,

are silicon spikes where the stumps were (see figure).

In a variation of the process, one starts with a silicon or silicon-on-insulator substrate with the intent to etch through the full thickness of the substrate. That is to say, one chooses the thickness so that the DRIE step releases individual nanotips. Such individual silicon nanotips may have utility as microscopic probes in biomedical applications.

This work was done by Harish Manohara of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

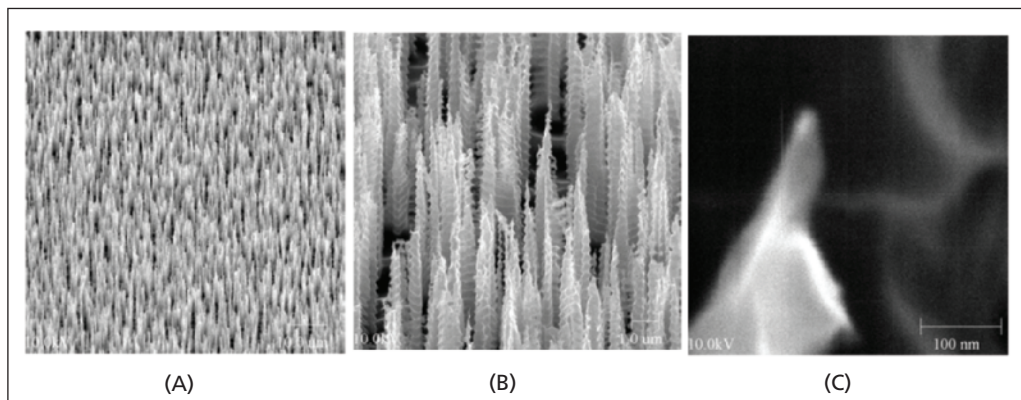
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An Array of Silicon Nanotips, shown here at three different magnifications, was fabricated as described in the text. The heights of these nanotips range from about 5 to about 6 μm . The average diameter of the sharp tip portions is about 20 nm. The scalloping of the sides is an artifact of the DRIE process.