



## Manufacturing & Prototyping

### Fluorine-Based DRIE of Fused Silica

**A suitable choice of process parameters enables etching of vertical side walls.**

*NASA's Jet Propulsion Laboratory, Pasadena, California*

A process of deep reactive-ion etching (DRIE) using a fluorine-based gas mixture enhanced by induction-coupled plasma (ICP) has been demonstrated to be effective in forming high-aspect-ratio three-dimensional patterns in fused silica. The patterns are defined in part by an etch mask in the form of a thick, high-quality aluminum film. The process was developed to satisfy a need to fabricate high-aspect-ratio fused-silica resonators for vibratory microscopes, and could be used to satisfy similar requirements for fabricating other fused-silica components.

The development of the process involved manipulation of some process parameters, including the selection of gases, the mixture ratios of the gases, the process pressure, and power of the radio-frequency signal used to excite the

ICP. It was found that polymeric materials that contained silicon and/or fluorine were formed on the side walls during etching and were subsequently etched away, resulting in anisotropic etching. It was also found that helium added to gas mixtures contributes to cooling of substrates and thereby helps in forming vertical side-wall patterns.

One version of the process was found to effect etching of vertical side walls in 100- $\mu\text{m}$ -deep fused silica at a rate of about 0.4  $\mu\text{m}/\text{min}$ . Some of the parameters of this version of the process were the following:

- ICP power 1.2 kW;
- Reactive-ion etching power 0.5 kW;
- Process pressure 6 mtorr ( $\approx 0.8$  Pa);
- Gas mixture of 1 part  $\text{C}_4\text{F}_8$  to 1.6 parts of  $\text{H}_2$ ; and
- Thickness of aluminum mask 5  $\mu\text{m}$ .

The rate of etching of the fused silica was found to be about 5 times the rate of etching of the aluminum.

*This work was done by Karl Yee, Kirill Shcheglov, Jian Li, and Daniel Choi of Caltech for NASA's Jet Propulsion Laboratory.*

*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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### Mechanical Alloying for Making Thermoelectric Compounds

**Constituents are ball-milled into a powder, which is then hot pressed.**

*NASA's Jet Propulsion Laboratory, Pasadena, California*

An economical room-temperature mechanical alloying process has been shown to be an effective means of making a homogeneous powder that can be hot-pressed to synthesize a thermoelectric material having reproducible chemical composition. The thermoelectric materials to which the technique has thus far been applied with success include rare-earth chalcogenides [ $\text{La}_{3-x}\text{Te}_4$  ( $0 < x < 0.33$ ) and  $\text{La}_{3-x}\text{Yb}_y\text{Te}_4$  ( $0 < x < 1, 0 < y < 1$ )] and Zintl compounds (including  $\text{Yb}_{14}\text{MnSb}_{11}$  and  $\text{Yb}_{14}\text{BiSb}_{11}$ ). The synthesis of a given material consists of the room-temperature thermomechanical-alloying process followed by a hot-pressing process. Relative to synthesis of nominally the same material by a traditional process that includes hot melting, this synthesis is simpler and yields a material having superior thermoelectric properties.

The room-temperature mechanical alloying process is, more specifically, a

ball-milling process. It begins inside an argon-filled glove box, wherein elemental constituents in amounts corresponding to their desired proportions in the thermoelectric material to be synthesized are loaded into a vial that contains milling balls. The vial and milling balls are made of a material compatible with the material to be synthesized. (For synthesizing  $\text{Yb}_{14}\text{MnSb}_{11}$ , one uses a vial and balls made of tungsten carbide; for synthesizing  $\text{La}_{3-x}\text{Te}_4$  or  $\text{La}_{3-x}\text{Yb}_y\text{Te}_4$ , one uses a vial and balls made of stainless steel.) Next, the filled vial is removed from the glove box and clamped onto a commercially available mixer/mill machine, which is used to shake the vial for as long as 40 hours to effect ball milling.

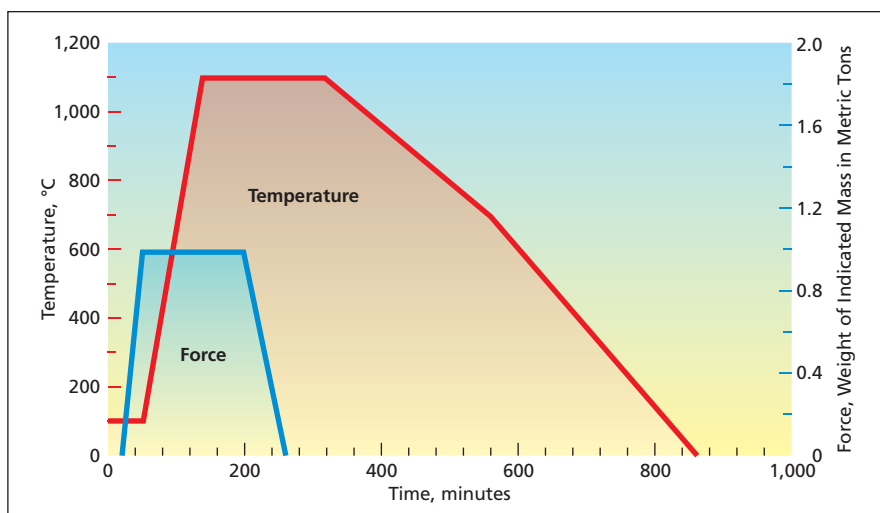
After ball milling, the vial is returned to the glove box, wherein the powder produced by the ball milling is loaded into a graphite die for hot pressing.

- In the case of  $\text{Yb}_{14}\text{MnSb}_{11}$ , it is neces-

sary to sandwich the powder between two graphite foil layers at each end. In ascending order, the resulting assembly inside the die consists of one or more spacer(s), two graphite foil layers, the powder, two more graphite foil layers, and a plunger that presses down on the aforementioned components.

- In the case of  $\text{La}_{3-x}\text{Te}_4$  or  $\text{La}_{3-x}\text{Yb}_y\text{Te}_4$ , the plunger is made of graphite, the inside of the die is lined with graphite foil, and the powder touches the top and bottom spacers, which are coated with boron nitride to prevent adhesion.

The die and its contents are then placed in a hot press, wherein the powder is subjected to a temperature-vs.-time and a pressure- (or force)-vs.-time profile, specified for the material to be synthesized (for example, see figure), to consolidate the powder into a solid mass of requisite density. After this hot pressing, the mass is removed from the die. In the case of  $\text{La}_{3-x}\text{Te}_4$  or  $\text{La}_{3-x}\text{Yb}_y\text{Te}_4$ , the



These **Temperature and Force Schedules** are followed in hot pressing of  $\text{La}_{3-x}\text{Te}_4$  or  $\text{La}_{3-x}\text{Yb}_x\text{Te}_4$  powder to consolidate it into a solid mass having superior thermoelectric properties. The force indicated here is calculated to yield a specified pressure when exerted over an area slightly more than 12 mm in diameter.

mass is sanded to remove graphite foil and boron nitride from its surface.

This work was done by Chen-Kuo Huang, Jean-Pierre Fleurial, G. Jeffrey Snyder, Richard Blair, and Andrew May of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

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## Process for High-Rate Fabrication of Alumina Nanotemplates

Approximately regular hexagonal arrays of holes are formed in an anodizing process.

NASA's Jet Propulsion Laboratory, Pasadena, California

An anodizing process, at an early stage of development at the time of reporting the information for this article, has shown promise as a means of fabricating alumina nanotemplates integrated with silicon wafers. Alumina nanotemplates are basically layers of alumina, typically several microns thick, in which are formed approximately regular hexagonal arrays of holes having typical diameters of the order of 10 to 100 nm. Interest in alumina nanotemplates has grown in recent years because they have been found to be useful as templates in the fabrication of nanoscale magnetic, electronic, optoelectronic, and other devices. The present anodizing process is attractive for the fabrication of alumina nanotemplates integrated with silicon wafers in two respects: (1) the process involves self-ordering of the holes; that is, the holes as formed by the process are spontaneously arranged in approximately regular hexagonal arrays; and (2) the rates of growth (that is, elongation) of the holes are high enough to make the process compatible with other processes used in the mass production of integrated circuits.

In preparation for fabrication of alumina nanotemplates in this process, one first uses electron-beam evaporation to deposit thin films of titanium, followed by thin films of aluminum, on silicon

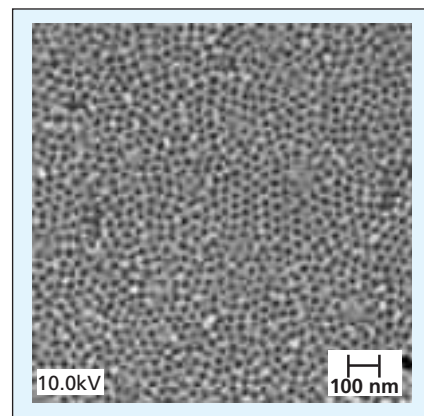
wafers. Then the alumina nanotemplates are formed by anodizing the aluminum layers, as described below.

In experiments in which the process was partially developed, the titanium films were 200 Å thick and the aluminum films were 5 µm thick. The aluminum films were oxidized to alumina, and the arrays of holes were formed by anodizing the aluminum in aqueous solutions of sulfuric and/or oxalic acid at room temperature (see figure). The diameters, spacings, and rates of growth of the holes were found to depend, variously, on the composition of the anodizing solution, the applied current, or the applied potential, as follows:

- In galvanostatically controlled anodizing, regardless of the chemical composition of the solution, relatively high current densities (50 to 100 mA/cm<sup>2</sup>) resulted in arrays of holes that were more nearly regular than were those formed at lower current densities.
- The rates of elongation of the holes were found to depend linearly on the applied current density: the observed factor of proportionality was 1.2 (µm/h)/(mA/cm<sup>2</sup>).
- For a given fixed current density and room temperature, the hole diameters were found to depend mainly on the chemical compositions of the anodizing

solutions. The holes produced in sulfuric acid solutions were smaller than those produced in oxalic acid solutions.

- The arrays of holes produced in sulfuric acid were more ordered than were those produced in oxalic acid.
- The breakdown voltage was found to decrease logarithmically with increasing concentration of sulfuric acid.
- The breakdown voltage was also found to decrease with temperature and to be accompanied by a decrease in hole diameter.
- The hole diameter was found to vary linearly with applied potential, with a



This **Alumina Nanotemplate** was made by room-temperature anodizing in an aqueous solution of 40 volume percent sulfuric acid at a current density of 50 mA/cm<sup>2</sup>. The hole diameter is 17 nm and the porosity is 16 percent.