

Low-Power RIE of SiO₂ in CHF₃ To Obtain Steep Sidewalls

Process parameters are chosen carefully to minimize deleterious effects.

A reactive-ion etching (RIE) process has been developed to enable the formation of holes with steep sidewalls in a layer of silicon dioxide that covers a silicon substrate. The holes in question are through the thickness of the SiO₂ and are used to define silicon substrate areas to be etched or to be built upon through epitaxial deposition of silicon. The sidewalls of these holes are required to be vertical in order to ensure that the sidewalls of the holes to be etched in the substrate or the sidewalls of the epitaxial deposits, respectively, also turn out to be vertical.

The pattern of holes in the SiO₂ mask is established by use of a photoresist mask on top of the SiO₂. The holes in the photoresist mask must also have vertical sidewalls. Prior techniques for etching the SiO₂ areas exposed through the holes in the photoresist mask include wet chemical etching by use of HF and dry chemical etching by use of a gas mixture that gives rise to HF vapor during the etching process. The disadvantage of wet chemical etching is that it does not yield well con-

trolled, vertical sidewalls. The disadvantage of dry chemical etching as described above is that the SiO₂ is etched so quickly that one cannot ensure verticality of the sidewalls; in addition, the etching process causes the deposition of a carbonaceous polymeric residue that is thick enough to make it impossible to etch uniformly through the total thickness of the SiO₂.

The essence of present RIE process is anisotropic etching of SiO₂ in CHF₃ with power kept low enough so as not to alter the shapes of the photoresist sidewalls and thereby to keep the SiO₂ sidewalls close to vertical. Unlike the mixtures of gases used previously, CHF₃ does not give rise to HF during this process. The recipe for this process is the following:

First Etch — CHF₃ flowing at a rate between 10 and 15 standard cubic centimeters per minute; power between 30 and 50 W; and pressure between 0 and 20 mtorr (between 0 and 2.7 Pa). The etch rate lies between 6 and 9 nm/s.

Second Etch — Same parameters as those of the first etch. The etching time should be

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Pasadena, California

the time needed to complete the etch at the etch rate calculated from the result of the first etch.

By proceeding according to this recipe, one can minimize the buildup of the polymer and prevent both over-etching and undercutting. The angles between silicon substrates and sidewalls produced by this process range from 70° to 90°.

This work was done by Tasha Turner and Chi Wu of Caltech for NASA's Jet Propulsion Laboratory. 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 Intellectual Property group

JPL

Mail Stop 202-233

4800 Oak Grove Drive

Pasadena, CA 91109

(818) 354-2240

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Annealing Would Improve β"—Alumina Solid Electrolyte

The objective is to prevent a sudden reduction of ionic conductivity.

A pre-operational annealing process is under investigation as a potential means of preventing a sudden reduction of ionic conductivity in a β"—alumina solid electrolyte (BASE) during use. On the basis of tests described below, the sudden reduction of ionic conductivity, followed by a slow recovery, has been found to occur during testing of the solid electrolyte and electrode components of an alkali metal thermal-to-electric converter (AMTEC) cell. This conductivity reduction may be observed quite infrequently; at lower operating temperatures, T < 1,073 K, it is not usually observed at all, while at T = 1,123–1,173 K, hundreds of hours may pass before conductivity reduction occurs. Only on tests running at higher operating temperatures for thousands of hours is this phenomenon regularly exhibited. The reduction of ionic conductivity would degrade the performance of an AMTEC cell. A pre-operational annealing process would help to sustain performance.

The tests involved, among others, maintaining BASE at a temperature between 1,050 and 1,170 K in the presence of low-pressure sodium vapor — an environment similar to that in a sodium AMTEC cell. It was observed that after a few tens to hundreds of hours in this environment, the ionic conductivity of BASE can fall suddenly to a lower value, and thereafter recover during several tens of hours. The decrease in ionic conductivity has been attributed to the formation of nanometer-thickness cracks, which would be high-resistance paths with respect to conduction of ions. The recovery of ionic conductivity has been attributed to closing of the cracks through sintering of β"—alumina grains.

The approach to annealing is based on the following line of reasoning: Some NaAlO₂ is incorporated into BASE during manufacture to facilitate sintering the ceramic to near 100-percent density. It is hypothesized that the cracks are initiated by the formation of voids, which, in turn,

NASA's Jet Propulsion Laboratory,
Pasadena, California

form as a result of (1) a reaction in which NaAlO₂ is converted to Na₂O and either β— or β"—alumina and (2) some or all of the Na₂O escapes by vaporizing. If this hypothesis is correct, then it should be possible to perform a pre-operational anneal to (1) force the conversion of NaAlO₂ and the formation of voids and (2) sinter the BASE to close the voids. Sintering should strengthen the material and thereby help to prevent the formation of voids and microscopic cracks during operation. In addition, if the loss of NaAlO₂ during operation contributes to the loss of subsequently recoverable ionic conductivity, then the removal of NaAlO₂ in the pre-operational sintering process should help to stabilize the high-temperature ionic conductivity of BASE.

In an experiment, samples of β"—alumina ceramic containing ≈1 weight percent of NaAlO₂ were packed in a mixture of lithia-stabilized β"—alumina powder and sodium β—alumina powder in a loosely capped crucible, and annealed at a tem-

perature of 1,400 °C (1,673 K) in a vacuum for various times up to 100 hours. (The powder mixture was used to establish fixed low sodium Na₂O activity characteristic of the β/β' phase boundary. The Na₂O activity of this mixture is much lower than that above NaAlO₂ and facilitates the loss of Na₂O from the NaAlO₂ in the ceramic as well as sintering to close voids at grain boundaries.)

The β'—alumina samples were found to have lost an average of between 0.4 to 0.5 percent of mass during the 100-hour anneal; this amount of loss is consistent with the conversion of most of the NaAlO₂ to β— or β'—alumina. (Complete conver-

sion would entail a mass loss of 0.5 percent.) Qualitative tests showed the mechanical characteristics of the samples to have been improved by the anneal.

At this time, high-temperature tests of limited duration have indicated the superiority of the treated BASE, but reproducible tests over thousands of hours are necessary to confirm that microcracking has been eliminated. The ionic conductivity of the treated BASE is also measured to be higher than untreated BASE at 1,073 K in low-pressure sodium vapor. Microcracking resulting in loss of conductivity was not observed with treated BASE in one high-temperature experiment, but this result

must be duplicated over very long testing times to be sure of the effect. Shorter annealing times (10 to 20 hours) were found to result in significantly less loss of mass; it may be necessary for the packed powder mixture to evolve some Na₂O before the Na₂O can leave the ceramic.

*This work was done by Roger Williams, Margie Homer, Margaret Ryan, Roger Cortez, Virgil Shields, and Adam Kisor of Caltech for **NASA's Jet Propulsion Laboratory**. Further information is contained in a TSP [see page 1].*
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