

L. V. Gregor
P. Balk
F. J. Campagna

Vapor-Phase Polishing of Silicon with H_2 -HBr Gas Mixtures

The production of smooth, flat, and clean surfaces on semiconductors, such as silicon and germanium, for the fabrication of planar devices is generally achieved by a combination of mechanical and chemical polishing procedures. With suitable equipment and fine polishing grit a skilled operator can mechanically polish a silicon single-crystal disk to optical flatness. Such treatment leaves a mechanically-damaged surface layer on the polished sample that is removed by a chemical etching procedure which removes more silicon while retaining the smooth, flat surface.

An extensive body of knowledge, much of it empirical, has been developed concerning various methods of polishing and etching.^{1,2} Recently, there has been considerable interest in anhydrous chemical polishing of silicon by means of a high-temperature gas-solid reaction. Indeed, the use of mixtures of HCl and H_2 at elevated temperatures to polish silicon surfaces prior to epitaxial deposition of silicon is widely practiced. Further, it has been the subject of experimental studies,³ and of a theoretical investigation of the equilibrium behavior and product distribution in the Si-H-Cl system as a function of concentration ratios and temperatures.⁴ The reverse of this process, namely, the reaction of $SiCl_4$ or $SiHCl_3$ with hydrogen, to form silicon, is well known and represents a practical method for obtaining epitaxial layers.⁵⁻⁸

Investigation of the etching behavior of other hydrogen halides has been less extensive. For HBr, little has been reported beyond the fact that it reacts with silicon at elevated temperatures,⁹ and that it acts as a nonpreferential etching gas for {111} silicon crystal surfaces.^{10,11} Recently, also, H_2 -HI mixtures have been shown to be capable of polishing silicon surfaces.¹² It is of interest to explore the feasibility of using the H_2 -HBr system for the same purpose on a routine basis. Specifically, the present paper gives the results of an investigation of the vapor-phase polishing of single crystal silicon surfaces by H_2 -HBr mixtures. The rate of removal of silicon was determined as a function of gas concentration and silicon surface

temperature, and the effect of crystal orientation and resistivity investigated. An experimental comparison of this system with some features of the H_2 -HCl method has shown that H_2 -HBr mixtures gave smooth surfaces more readily than H_2 -HCl.

Experimental technique

• Apparatus

The gas-phase polishing system was conventional in design and employed rf induction heating so that the operating temperature could be rapidly changed. This capability is particularly attractive if further processing, like oxidation, will be carried out in the same apparatus. The maximum rated output of the rf generator was 5 kW.

To avoid contamination of the gas phase and to allow subsequent oxidation *in situ*, it was imperative to separate the graphite susceptor completely from the reaction area. This was realized in two basic susceptor designs. The *ramp susceptor* (Fig. 1a) consists of a block of high-density graphite with a sloping ramp, encased in a fused silica envelope attached to the cap of the reactor. For this approach the silicon specimen was placed directly on the ramp. The *cylindrical susceptor* (Fig. 1b) is an annular shell of graphite which slips over the reactor tube and is enclosed by an outer silica tube. Here the samples were supported on a sloped quartz ramp or, if polishing on both sides was required, were held vertically in a slotted quartz plate or suspended from quartz hooks. While hot, both susceptors are surrounded with argon to prevent combustion. Both types eliminate any contact between the graphite surface and the reactor gases or the silicon sample. The rate studies to be described were performed with the cylindrical susceptor. In this case the sample temperature was measured through a slot in the susceptor using a calibrated Pyro micro-optical pyrometer. The apparent surface temperature, as obtained from the pyrometer reading, was estimated to be within $\pm 10^\circ C$ of the actual specimen temperature.

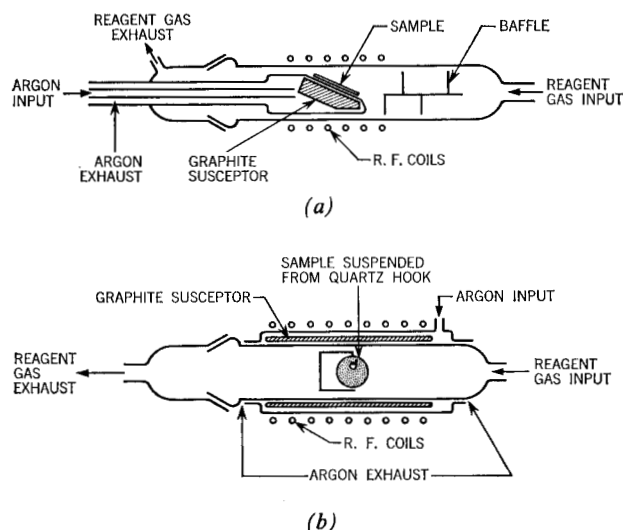


Figure 1 Schematic diagrams of reactors for vapor polishing. The main polishing tube has an I.D. of 50 mm.: (a) With graphite ramp susceptor; (b) with cylindrical graphite susceptor (length of susceptor: 170 mm).

The desired conditions of gas flow and composition were obtained using a needle valve inlet and a floating-ball Brooks flow meter for each gas. Incorporated into the system were a Zeolite trap immersed in liquid nitrogen, for hydrogen purification, and two conventional spiral traps chilled with dry ice and acetone for the removal of water vapor and other condensable gases from the H_2 -HX gas mixtures. (Here and elsewhere "HX" refers to hydrogen halides.)

Materials

Hydrogen was obtained from the laboratory supply at a nominal purity of 99.94%. HBr was supplied by a commercial source at a nominal purity of 99.8%. HCl was purchased from two suppliers as "99%" and "electronic grade" respectively. Mass spectrometric analysis (Table 1) showed that all hydrogen halides contained considerable quantities of other substances, particularly air. For this reason new cylinders of HCl or HBr were bled for a period of time to remove the impurities before attempting to use their contents.

Silicon wafers were cut from $\langle 111 \rangle$ grown single-crystal ingots of zone-refined silicon obtained from Dow-Corning Corporation, or from dislocation-free material prepared at this laboratory. Wafer diameters ranged from 12 to 30 mm; wafer thicknesses, from 0.25 to 1 mm. The wafers were cut with a diamond saw and then mechanically lapped with 12.5 μ alumina grit. Next, they were cleaned in an ultrasonic bath with organic solvents and water.

Table 1 Data from mass-spectrometrical analysis of samples of the HCl and HBr gases used in this investigation.*

Initial Impurities, Mol %		Subsequent Impurities, Mol %
HCl (Supplier A)		
C_2H_2	0.1-0.2	0.1-0.2
O_2	1.5	0.07
N_2	7.5	0.35
CO_2	0.07	0.03
HCl (Supplier B)		
C_2H_2	0.004	0.005
O_2	2	1.4
N_2	7	6.8
CO_2	0.03	0.008
A	0.28	0.13
HBr (Supplier B)		
A	27	0.064
O_2	0.12	0.036
N_2	12.5	0.14
HCl	5.0	0.82

* The "initial impurities" were measured in the full cylinders, "subsequent impurities" were measured after bleeding off approximately 10% of the contents.

For the rate measurements the samples were subsequently chemically polished in a rotating beaker using a mixture of 1 part HF (48%), 2 parts glacial acetic acid, and 3 parts HNO_3 (70%) by volume.

Procedure

After the pretreatment described above, wafers were inserted into the susceptor. A hydrogen flow of 6 liters/min at 1 atm and 23°C was established (linear velocity, 300 cm/min), and the temperature was raised to the desired value and allowed to stabilize for 1 minute. Next, the polishing reaction was started by admitting HBr (or HCl) to the gas stream. To terminate the operation, the flow of HBr (or HCl) was cut off, the system flushed with hydrogen for 2 minutes, and then allowed to cool in flowing hydrogen. When the system approached room temperature, it was flushed with argon to remove hydrogen. For the rate measurements reported in the following section, the weight loss of the samples was determined with an analytical balance. This amount of material was assumed to be removed from one side in an equiplanar slab of uniform thickness, since the ramp-type support used in these experiments leaves one surface unexposed. The above assumption introduces a small error (less than 5%) in the rate data in that the samples become very lightly polished along the edges of the unexposed surface. Moreover, the rate of attack on the exposed surface is somewhat greater near the edges than in the central region, Fig. 2. The etch rates were reproducible from sample to sample within $\pm 5\%$.

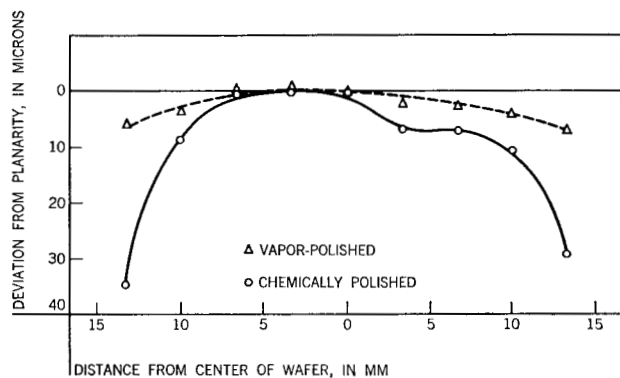


Figure 2 Deviation from planarity of surfaces of HBr-polished and chemically polished silicon wafers. The surface before polishing was flat within accuracy of measurement.

Results and discussion

• Rate of removal of silicon

In rate measurements of the type described above, it is necessary to determine whether the rate of removal is constant during the time of exposure to the etching gas. This was found to be the case within experimental accuracy. Furthermore, the absence of an induction period was established. No detectable weight loss could be observed upon exposure to hydrogen under the conditions of the experiment. The rate of removal of silicon is given in Fig. 3 as a function of HBr concentration at 1260°C. To allow comparison, Fig. 3 also shows the rates for HCl at 1280°C, under otherwise similar conditions. The temperature dependence of the etching rate for a 3% HBr mixture is shown in Fig. 4, where the rate is plotted logarithmically against the reciprocal of the temperature. The data points can be approximated by a line of constant slope over the temperature range investigated. Also depicted in this graph are the rates for the HCl process, obtained under identical conditions. It is interesting to note that, whereas the rate and its temperature dependence above 1240°C appear to be comparable to those for the HBr process, the rate falls off rapidly below this temperature. However, no speculation will be offered at this time regarding the nature of the rate limiting steps involved in these processes.

Also explored was a possible dependence of the etching rate on the bulk type and doping level, using *p*-type samples with resistivities between 0.06 and 1000 ohm-cm, and *n*-type samples with resistivities between 0.1 and 100 ohm-cm. A dependence of this kind was not found.

• Surface perfection

As mentioned before, silicon removal rates are somewhat greater near the edges of the samples than in the center; however, the deviation from planarity of an HBr-polished

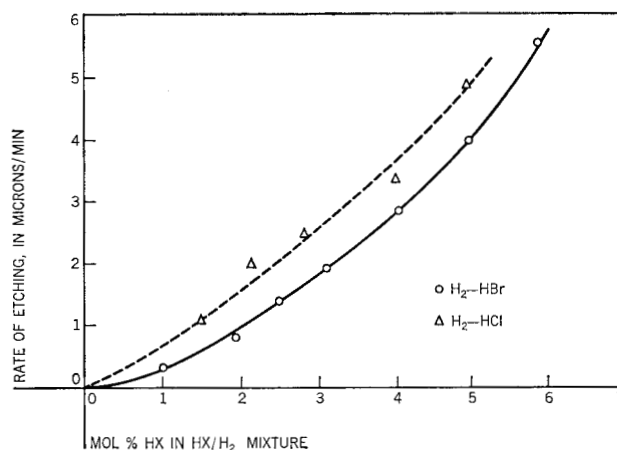


Figure 3 Rate of polishing versus gas composition for HBr at 1260°C and HCl at 1280°C.

surface is small compared to that obtained by chemical etching in a rotating beaker, as may be seen in Fig. 2. In both cases the same thickness of silicon (50 microns) was removed.

A significant finding from this investigation was that with HBr it is easy to produce a highly polished surface directly from a mechanically lapped wafer. This ability not only simplifies the processing of samples (by eliminating the need for mechanical or chemical polishing steps), but also gives a more uniform surface profile than would be obtained with the latter step included. Such uniform surfaces were reproducibly obtained at 1260°C,

Figure 4 Temperature dependence of polishing rate for HBr (3%) and HCl (3%).

