

**NBSIR 76-1019**

# **Notes on the Preparation of Silicon Density Artifacts**

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**Mechanics Division**  
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# Notes on the Preparation of Silicon Density Artifacts

R. M. Schoonover

## 1.0 Introduction

Now that single crystal silicon is in use as a working standard of density, we at NBS are being asked by potential users just how a crystal should be prepared for this application. There is a vast technical knowledge available in the semiconductor manufacturing industry regarding silicon fabrication techniques. These are largely inapplicable for density artifact manufacture due to differences in applications. These notes are an attempt to compile the basic information required for the successful fabrication of a density artifact working standard.

Many of the techniques described here are standard optical polishing and grinding techniques. Considerable effort is expended to decrease the possibility of chipping the artifacts. However, this occurrence is not disastrous because density information is the primary characteristic of this type of artifact. Therefore, chipping of the artifact changes its mass and volume but not its density since it is a homogeneous object. A simple mass value assignment restores both mass and volume information to the artifact.

## 1.1 Desirable Characteristics of Artifact

The restraints placed on the artifact density standard can be delineated into two basic considerations: (1) stability and (2) transfer of the density unit, that is to make use of the density knowledge embodied in the artifact. The thrust here is directed toward practical things and we discuss what should be avoided to maintain stability and to optimize transfer of the unit. We accept the theoretical long term stability of single crystal silicon.

## 1.2 Density

Transfer of the density unit from a silicon working standard to any other suitable object is best accomplished with the hydrostatic weighing technique [1]\*. The loss in weight due to the buoyant force of the liquid is maximized for silicon due to its relatively low density. Ideally, the force exerted by the crystal mass should be near the load capacity of the balance used to measure buoyant loss, thereby minimizing the effects of balance imprecision.

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\* The numbers in brackets refer to similarly numbered references at the end of this paper.

### 1.3 Homogeneity

There are subtle connotations relating to the homogeneity of the silicon artifact. We are interested here in density but need to know the artifact volume in order to transfer the knowledge contained therein. If the crystal is not homogeneous in structure, all density knowledge would be lost whenever its mass and volume were changed such as when accidentally chipped. However, when a homogeneous sample is chipped, we need only to redetermine its mass to assign a new volume based on previous density information.

Since two or more standards are desirable for redundancy in the transfer density, a simple test for homogeneity is to determine the density of two or more crystal artifacts fabricated from the same boule. If the measured differences do not exceed a few parts per million in density (a normal range) then the crystals are probably acceptable for use as artifact standards. X-ray diffraction techniques provide another method for detecting defects in the crystal lattice.

## 2.0 Special Requirements

### 2.1 Geometry

Most metrology laboratories follow the custom of minimizing surface area to mass ratio as a desirable practice in mass measurement. Without proof, this procedure is recommended for silicon crystals and large surface area to mass ratios should be avoided. A far more practical reason for minimizing this ratio is evident during the hydrostatic weighing process when the surrounding medium is one to two thousand times more dense than the air during a mass determination. Large surface areas can couple the balance beam most effectively to turbulence in the hydrostatic fluid. When turbulence is present in the liquid, momentum is imported to the beam via the large surface area of the artifact on the balance pan. Damage to the balance beam may result.

Ideally, a sphere has the best surface area to mass ratio, but a good compromise is the right circular cylinder whose height is equal to its diameter. One should choose a silicon boule diameter that approximates this condition if possible.

### 2.2 Freedom from Cracks

The one defect that can manifest itself in the most insidious manner is an undetected crack within the crystal structure. Ideally, one would like to perform cutting and grinding

operations in a way that minimizes the production of cracks. Preventive techniques are discussed in a different section of this paper. However, in the initial stages of fabrication, cracks may become apparent to the eye, but in any case should be looked for in detail during all phases of manufacture of the artifact.

Cracks generally are not visible until some initial etching has removed cutting and grinding work damage and the surfaces begin to appear polished. A low power (10X) microscope may be helpful in looking for cracks. The most likely places to look for cracks are near edges and wherever grinding has been done. If a crystal has been centerless ground as many boules are, there is a lot of surface area where cracks may be hidden. Cracks should be cut away as early as possible in the mass adjustment process if a particular finished mass value is desired.

The finished artifact must be free of cracks or it will be unreliable as a density standard. The effect usually manifests itself by producing large dispersions in the density values assigned by repeated measurement.

### 2.3 Beveled Edges

The finished geometry of the silicon artifact should be free of sharp edges. There are two very important reasons for this requirement. They are (1) less chance of chipping and (2) less risk of a crack occurring if dropped. The reasons cracks must be eliminated are obvious and have already been discussed. Chipping, on the other hand, changes the crystal mass. The volume assignment for a given crystal is directly proportional to mass and is necessary to the hydrostatic volume ratio comparison used to assign density values to other objects.

Another consideration that makes a stable crystal mass desirable is one of man hours of labor. The effort required to prove that crystal mass has not changed with use is considerably less than to prove that it really has and to assign a new value to it.

## 3.0 Method of Fabrication

### 3.1 General

If a crystal is to be cut and etched to a particular mass value, the starting mass must be higher than the finished value. The best procedure is to cut the crystal oversize, grind bevels or radii on sharp edges, provide for identification and etch away work damage. At this point, one can judge whether or not further cutting or grinding is required. If so, the resulting work damage can be confined to one end of a cylinder or one side of a rectangular structure.

Most of the cutting and grinding procedures are standard techniques encountered in the optical grinding and polishing operations. The hand grinding and etching necessary to obtain a particular mass value can be performed by the laboratory worker himself as the required skill is quickly developed.

### 3.2 Sawing

Sawing is best done by a diamond saw with the specimen bonded to a support block. Slow, safe feed rates should be used to avoid breaking the crystal. Free hand sawing on a cutoff wheel is possible for small boule diameters but not recommended. Allow about 10% more mass, for samples of 200g or less, than is required to compensate for etching and unforeseen problems. One can expect to remove about .005" [2] of depth from a ground surface before encountering virgin material.

### 3.3 Grinding

In the author's opinion, most cracks originate in the grinding process, therefore heavy grinding on machines is to be avoided if possible. When a crystal boule can be purchased without surface grinding having been done, the potential user can then proceed with his special interest in mind.

Hand grinding of flat surfaces on a stationary plate or a slow turning grinding lap is the best procedure for removing mass and should be performed after the edges have been beveled. This helps to prevent chipping and cracking during the grinding operation. Ordinary window glass will suffice as a lapping plate using water and an abrasive as one would on a lap. For gross removal, a very course grit abrasive such as a synthetic aluminum oxide of 50-80  $\mu\text{m}$  size is used. To finish, a finer size, such as 20  $\mu\text{m}$  is used before etching.

### 3.4 Beveling Edges

In place of sharp edges, a beveled edge or radius is preferred. There are two satisfactory methods for removing sharp edges that will not cause cracks, and a third that involves some risk. A skilled operator can grind free hand against the side of a cutoff wheel made of molded rubber in which abrasives are imbedded. The disc is slightly flexible and contact pressure can be kept low. Another method is to turn a cylindrical specimen on a lathe and use a small piece of wood coated with abrasive to grind a curvature on the edges.

The cutoff wheel leaves a rough surface that requires a considerable amount of etching to achieve a satisfactory polish but is very adaptable to most shapes. The lathe method is restricted to cylinders and is the slower method, but has less work damage if the proper grit sizes are used.



A third method for grinding edges on a cylinder employs a contoured lens grinding lap that in essence is a spinning cone. The cylindrical crystal artifact is held so that only the edge contacts the cone walls where the grinding takes place. Initially, care must be taken with this method to avoid chipping the sharp edges.

### 3.5 Lapping

Lapping highly polished surfaces on crystal artifacts is not necessary, since the crystal will still require an acid etch to remove all work damage. There is a lapping process that uses acid to remove work damage generated by the lapping process itself, producing an optical quality surface. However, optical quality surfaces on the crystal artifact are unnecessary.

### 3.6 Etchants

The metrologist is probably aware of all of the aforementioned techniques used to shape a silicon crystal and to adjust the mass. The methods are standard techniques used on a variety of glasses. The acid etch may not be a familiar procedure and the metrologist will probably do this himself. Extreme care should be given to personal protection from the acid solutions as their action is instant in the destruction of tissue. This is especially true of hydrofluoric acid. Other than these precautions, the techniques are simple.

There are various etchant solutions used in the semiconductor industry. Described here are three solutions with which the author has had experience. They can be characterized as having slow, moderate and fast etching rates. The formulations by volume for these etchant solutions are as follows:

<u>Etch</u>	<u>Ratio</u>	<u>Chemical</u>	<u>Strength</u>	<u>Grade</u>
Fast	1 Part	Hydrofluoric Acid (HF)	48%	Reagent ACS
	1 Part	Nitric Acid (HNO <sub>3</sub> )	70%	Reagent ACS
	1 Part	Acetic Acid (CH <sub>3</sub> OOH)	Glacial	Reagent ACS
Moderate	5 Parts	HNO <sub>3</sub>	SAME AS ABOVE	
	3 Parts	HF	"	"
	4.5 Parts	CH <sub>3</sub> OOH	"	"
Slow	1 Part	HF	"	"
	20 Parts	HNO <sub>3</sub>	"	"

To prepare these acid solutions and to use them as well, a few precautions should be observed. From a safety standpoint, an exhaust hood with a source of water is mandatory. Eye protection and gloves should also be used. The axiom of not pouring water into acid should be observed when handling acids. All beakers, bottles, etc. should be cleaned and dried before use to prevent contamination of the etchant solution. The etchants can be stored in polyethylene bottles with no harmful effects and with safer handling. Since hydrofluoric acid etches glass, this precludes the use of glassware as a storage container. The best policy is to use all polyethylene beakers and bottles in these procedures.

### 3.7 Etching

Choosing which etchant to use depends on several factors. The fast etch solution will get very hot during the initial etch when work damage is being removed and tends to propagate cracks, scratches, etc. The moderate solution tends to increase over all time required but tends to leave a smoother finish and gives better control over the mass adjustment. The slow etchant solution is most useful where the final mass value is to be controlled in the 100 microgram region.

A good compromise is to use the moderate etchant to remove all work damage. At this point, visually inspect the crystal for cracks, deep scratches, and pits. Once the surface is acceptable, i.e., no cracks, scratches, or pits are evident, the etch rate can be increased using the fast etch. Then the moderate solution is used when the final mass value is close at hand. If further surface improvement is desired, continued moderate etching would be the method of choice.

Etching rates (grams/minute) vary with crystal surface area and are not reliable until work damage is removed. Then a stop watch and direct reading balance can be used to keep track of the rate of mass removal. The etch period must be uniform and a fresh solution used each time. For the fast etch, a period of 1½ minutes is about the maximum time unless a very large volume of etchant is used. The weaker etch solutions require somewhat longer periods of exposure.

The volume of etchant need only be two or three times the crystal volume but must completely cover the crystal. Smaller volumes of etchant like these will generate higher temperatures and accelerate the etch rate; larger volumes will have an opposite effect.

Before etching, the crystal and all utensils that will be in contact with the acid should be chemically cleaned. Initial

cleaning can be soap and water, followed, after drying, with one rinse in trichloroethylene and two in methanol. An alternate cleaning after soap and water is one rinse in benzene, one in acetone and two in methanol. After etching has begun, simply drying all utensils is sufficient unless contaminated. However, the crystal should be chemically cleaned each time to avoid oxide stains.

There are several ways to halt the etching process. The most reliable is to expeditiously remove the crystal and plunge (quench) it directly into a beaker of distilled water. Then follow with a tap water dilution until the acid is gone. A second method is to dilute the etchant with nitric acid, then distilled water, followed by tap water. All of these steps occur with the crystal in place. An abbreviated version is to omit the nitric acid dilution and begin with distilled water. These last two techniques can be dangerous since water is poured into acid and are not the recommended techniques. A problem with oxide formation on larger crystals occurs with the second method. The first method allows reuse of the etchant after short periods of etching several times, a convenient feature in adjusting to a particular mass.

### 3.8 Removing Cracks and Pits

Cracks are best removed by localized grinding with the cutting edge of a pliable cutoff wheel turning at its normal cutting speed. Of course, the work damage must be etched away afterwards so a visual re-examination can be performed. The cutoff wheel leaves a rough finish and requires heavier than normal etching to achieve a highly polished surface. Once the crack appears to have been removed, further surveillance of the site should be maintained during future etches. This will ensure that further localized grinding, if required, will begin while there is still an excess of crystal mass.

Pits (holes) are most likely to appear on the outer skin of the boule where grinding has been done and are not harmful in themselves. However, pits sometimes develop in cracks where the etch rate is likely to be accelerated. The finished product need not be free of pits but they should be removed when they may conceal a crack. Under the microscope, harmless pits appear as highly polished craters of uniform color. Beware of those with color change (silver to white in appearance) and those which take on the shape of a line. If a pit is particularly deep and sharp, it is likely to be a place to trap gas upon immersion in liquid. Although techniques are used to remove such gas, there is more assurance if the pit is removed in the same manner as a crack.

### 3.9 Identification

Avoid vibrating engraving tools as they can damage the crystal so deeply as to render it worthless. The safest techniques are to select a symbol that can be shaped from a gold wire about 0.5 to 1 mm in diameter and lay it on the crystal during the initial etch. The etch rate is accelerated at the point of contact thereby propagating a faint outline of the symbol. Waxing the specimen and removing wax in the shape of a symbol is another technique for etching symbols onto a crystal or the symbol can be sandblasted on the surface before etching. With extreme care, a diamond awl can be used to engrave the symbol using a very light scratch pressure.

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