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INFLUENCE OF FLUIDS ON THE ABRASION OF SILICON BY DIAMOND

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ABSTRACT

Silicon wafers ((100)-p-type) were abraded at room temperature in the presence of acetone, absolute ethanol and water by a pyramid diamond and the resulting groove depth was measured as a function of normal force on the diamond and the absorbed fluids, all other experimental conditions being held constant. The groove depth rates (depth of groove/s) are in the ratio of 1:2:3 for water, absolute ethanol and acetone, respectively, for a constant normal force. The groove depth rate is lower when the normal force is decreased. The abraded surfaces were examined by scanning electron microscopy. The silicon abraded in the presence of water was chipped as expected for a classical brittle material while the surfaces abraded in the other two fluids showed ductile ploughing as the main mechanism for silicon removal.

INTRODUCTION

Abrasive cutting and grinding is currently being used in the solar photovoltaic industry as one method to produce large area sheet silicon. Silicon ingots are sliced into wafers by: (1) inner diameter wafering, (2) multi-blade wafering using a slurry and (3) multi-wire wafering using a fixed abrasive. These methods rely on abrasive wear for cutting by the motion of diamond impregnated wires, abrasive wheels or silicon carbide slurries in water or an oil-based fluid carrier. Although abrasive cutting is used extensively, the basic mechanisms for abrasion, i.e., the interaction of the cutting tool and the silicon and the effects of the fluid in the process are still not well understood. An understanding of this process could lead to improvements in abrasive cutting technology and have a significant impact on the successful utilization of silicon for photovoltaics since this part of the processing represents $\sim 30\%$ of the cost of photovoltaic cell production [1].

It is well-known that besides lubrication and effects on the motion of the cutting tool, fluids can influence the surface mechanical properties of non-metals [2]. Fluid adsorption has been known to affect the surface hardness of non-metals. However, there is no general consensus as to the cause for the effect and no satisfactory model has yet been proposed [3]. The relation of fluid adsorption to the abrasive wear of semiconductors has not been investigated.

In this paper we present experimental results for the abrasion of a single crystal (100)-p-type silicon wafer by a pyramid diamond in three fluids. The experimental apparatus in essence is a simplification of the currently used silicon wafering methods discussed previously. It was of interest to evaluate the effects of abrasion rate on changing fluid environments, force on the abrading pyramid diamond and depth of damage and type of debris generated in the abrasion process. The abraded surfaces were studied by scanning electron microscopy (SEM). The results are interpreted in terms of fluid adsorption and its effects on surface mechanical properties of silicon.

EXPERIMENTAL PROCEDURES

Polished silicon (100)-p-type, three-inch diameter round wafers (sheet resistance 9-16 Ω -cm) were abraded at room temperature by a pyramid diamond while the fluid environment and load (F_n) on a pyramid-diamond were varied. A schematic of the experiment is shown in Fig. 1. The silicon was rotated past the stationary pyramid diamond at a speed of 0.56 rps. Sets of grooves were formed by varying the time of abrasion and F_n and only one fluid was used per wafer. The surface of each slice and the debris was examined by SEM and the depth of the groove vs. abrading time was determined. Polished cross sections of the wafer, which included the grooves, were etched for ~ 2 min. in a Sirtch etch to determine the depth of damage.

RESULTS

Representative SEM micrographs of the surfaces of the silicon wafers abraded in the presence of (a) water, (b) absolute ethanol and (c) acetone are shown in Fig. 2. The normal force, F_n , was 62 g and the abrading time was 1.8×10^3 s, all other variables being held constant. As can be seen, the groove surface appears brittle (a), ductile (b) and a mixture of the two (c). The depth of the groove vs. abrading time is shown in Fig. 3. As can be seen, the depth increases as a function of time and the rate is greater when absolute ethanol and acetone is used as compared with water. The rate of groove depth formation increases in the ratio of 1:2:3 for water, absolute ethanol and acetone, respectively, when F_n was 62 g. The rate decreased when F_n was lowered to 42 g.

A cross section of a wafer showing cracks emanating from the groove bottom is shown in Fig. 4. The cracks are sharp, extended for a significant distance into the wafer and are oriented along (110).

The debris expelled during the abrading process is shown in Fig. 5. The surface of the silicon in 5(a) has debris deposits some of which show sharp cleavage facets of the type observed in brittle fracture of ceramic materials. The debris shown in (b) also has these same features--sharp cleavage facets.

DISCUSSION

As seen in Fig. 3, the groove depth vs. abrading time is significantly influenced by the fluid in contact with the silicon surface. In addition, the following was also observed: (a) the depth also varied with F_n as expected and with mixtures of acetone and distilled water [4], (b) no significant differences could be detected in the debris shape when the fluid was changed, (c) the SEM micrographs clearly show that the mechanism for silicon removal changes when the fluid environment is changed; the surfaces abraded in the presence of acetone and ethanol have a similar morphology to abraded metals [5] and (d) there appears to be an incubation time in the wear rate. Considering that all experimental conditions remained constant except for changes in fluid and F_n , the above can be modeled as adsorption of the fluid on the silicon surface and the effect of adsorption on surface hardness.

Rabinowicz and co-workers [6] derived a relationship for abrasive wear by a rigid conical asperity carrying a load L and sliding through a distance S . The expression relating L to the material hardness p and geometry of the cone is

$$L = p \cdot \pi/4 \cdot W^2$$

where W is the diameter of contact of the cone. The groove area A_g , which is the projected area of the penetrating cone in the vertical plane, is given by

$$A_g = \frac{1}{4} \cdot W^2 \cdot \tan\theta = \frac{L \tan\theta}{\pi p}$$

where θ is the slope angle of the cone measured from the plane of the surface. Thus when the cone moves through a distance S , it will sweep out a volume V given by

$$V = \frac{L \cdot S \cdot \tan\theta}{\pi p}$$

Substituting $S = t(\omega r)$, $V = 2\pi r A_g$, $\omega = 0.56$ rps, $\theta = 62^\circ$ and $L = 62g$, where t is the abrading time and r the radius of the abraded groove, the hardness can be expressed as

$$p = (6.1/A_g) \left(\frac{kg}{mm^2} \right)$$

The hardness p is therefore related to the groove geometry and the slope of the groove depth vs. time with all other experimental conditions being held constant. Since the fluid environment influenced A_g , then consequently the surface hardness is also affected. Using the above equation we find that the fluid adsorption changed the surface hardness of the silicon in the ratio of 1:0.5:0.3 for water, ethanol and acetone, respectively.

The effect of fluid adsorption on hardness of silicon have previously been reported by Ablova [7] who observed a surface softening by adsorption

of water. Westbrook and Gilman [8] also found a softening (up to 60%) in silicon when indentations were carried out in the presence of a small potential between an indenter and the silicon surface. Some recent results of Yost and Williams [9] showed a minimum in hardness for n- and p-type silicon with concentration NaCl and $\text{Na}_4\text{P}_2\text{O}_7$ for a maximum in the negative zeta potential which was interpreted to mean that the hardness change with zeta potential is related to the surface charge and the influence on the charge carrier concentration at the surface. The surface charges were thought to interact with charged kinks at dislocations. Recently Cuthrell [10] has expanded on the adsorption model by relating the drilling rate of glass to the dielectric constant of the fluid in contact with the surface. The dissociation of the fluid into singly and multiply charged ions (as evidenced by the dielectric constant) was found to correlate with drilling rate. Applying these ideas to the abrasive wear of silicon in our case, the slope of the groove depth which varies as 1:2:3 for water, ethanol and acetone, respectively, compares with the dielectric constants which vary in the ratio of 1:1.2:3.8 for these same fluids. Although the correlation does not appear good, the variation is in the right direction and additional experiments are under way to test this hypothesis.

Cracks at the bottoms of the grooves were evident and the length of the cracks were also related to the type of fluid in contact with the surface. Although it was expected that the number and length of subsurface cracks should be smaller for the ductile mode wear groove, this was not found to be the case. Similar results of subsurface cracking was observed in MgO and explained by dislocation interactions resulting from a redistribution of resolved shear stresses during sliding. It was speculated that the internal cracks do not have a direct influence on the increase of wear [11] in that case but a correlation does exist in our results of abrasion of silicon.

SUMMARY

The results of this study may be summarized as follows:

- (1) Fluid environments in contact with (100)-p-type silicon affect the wear rate. The rate varies proportionately as 1:2:3 for water, ethanol and acetone, respectively, for a conical diamond abrading silicon at room temperature.
- (2) The deformation mode changes from brittle to ductile when the fluid is changed.
- (3) The abraded debris is not noticeably different when the fluid environment is changed.
- (4) Subsurface cracks are present at the bottoms of the abraded grooves. Their length is also affected by the fluid environment.
- (5) The surface hardness of silicon is influenced by fluid adsorption and there appears to be a correlation of the groove depth with the dielectric constant of the fluid.

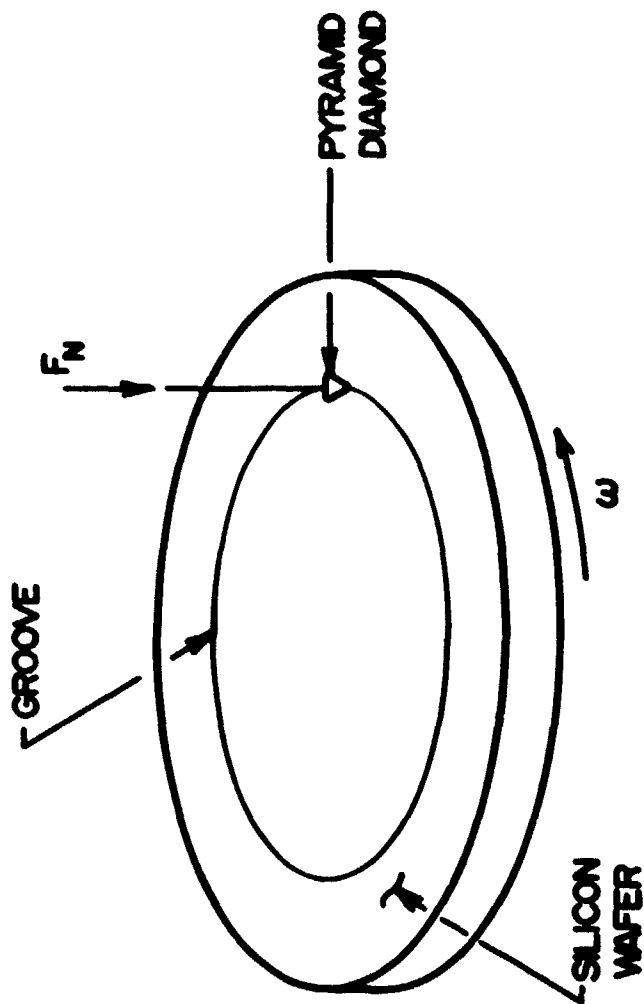


Fig. 1. A schematic representation of the experiment for abrading silicon by diamond. Grooves are produced on the silicon wafer and the groove depth is measured as a function of time, fluid environment and normal force on the diamond. The surface of the silicon is examined by scanning electron microscopy (SEM) for mode of silicon removal.

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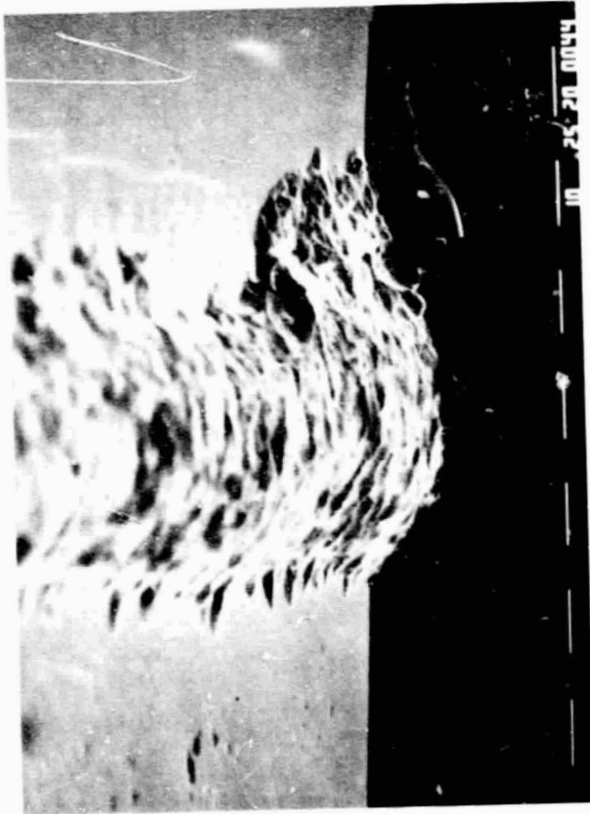


Fig. 2. Scanning electron micrographs of silicon abraded at room temperature by a pyramid diamond in the presence of H₂O (upper left), absolute ethanol (upper right) and acetone (lower left). The normal force on the diamond was 52 g and the abrasion time was 30 min, all other conditions being held constant. The mechanism changes from brittle (upper left) to ductile (upper right) to a mixture of the two (lower left).



Fig. 3 The depth of the groove ($\text{mm} \times 10^{-3}$) in silicon formed by a pyramid diamond at room temperature vs. abrasion time (s). The fluid environment was varied. The normal force was $F_n = 62 \text{ g}$.

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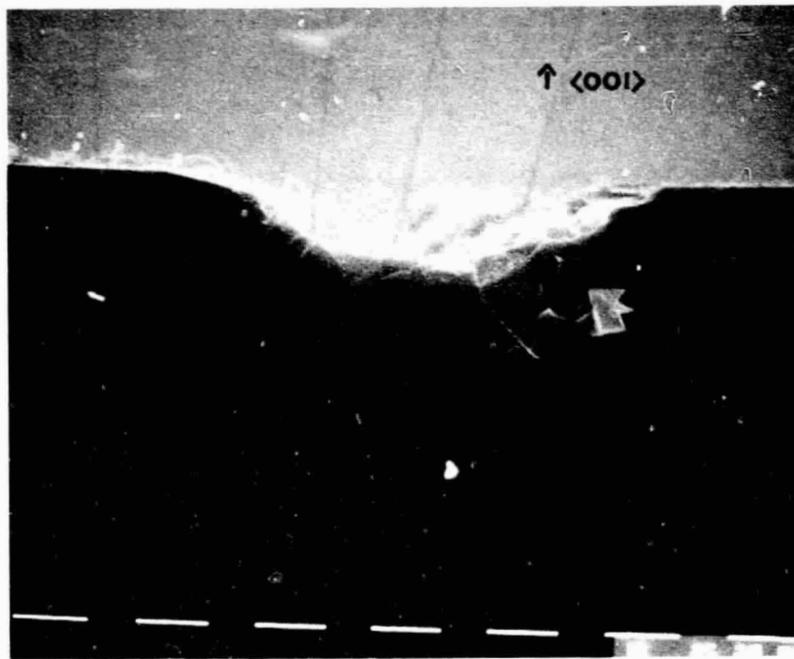
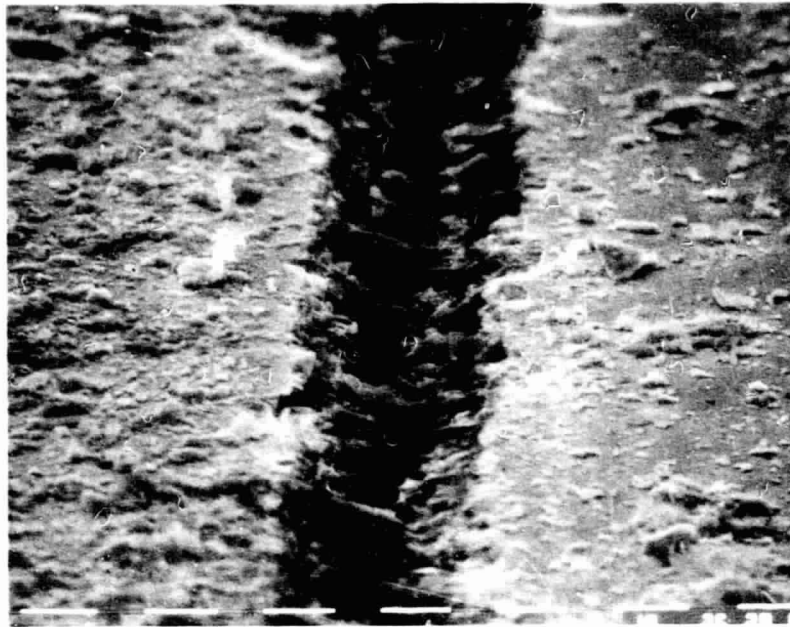
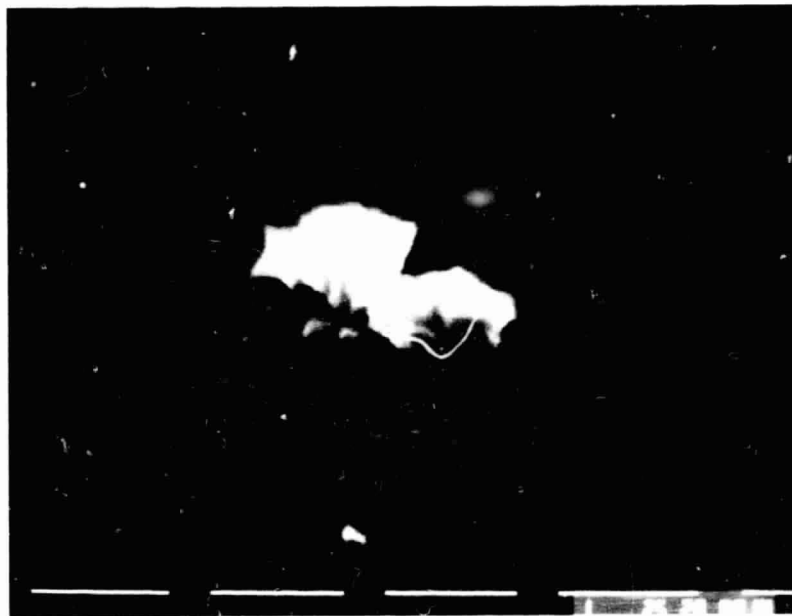


Fig. 4 SEM micrograph of a cross section of a silicon wafer with cracks emanating from the groove bottom. Conditions were: $F_n = 62$ g, distilled water and 600 s abrading time.

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(a)



(b)

Fig. 5 SEM micrographs showing debris expelled during the abrading process conditions were: 75% acetone, 25% distilled H₂O, abraded for 30 min. with $F_n = 42$ g (a) and isolated debris generated under 100% acetone (b).

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DISCUSSION:

FRIZELL: How could you maintain, with normal ambient relative humidity, the identity of your acetone or your ethanol, both of which are terribly hygroscopic?

DANYLUK: That is a very good point. We have been very careful to do our experiment with fresh acetone and fresh ethanol. We open a fresh bottle, we put the fresh fluid on the silicon surface when we do the abrasion and within half an hour there is a possibility of H₂O absorption. I don't know how much that would be, though.

GALLAGHER: Do you think the fact that in one case you used a noncompressible fluid, water, and the rest of the time you use something that is compressible, could have made a difference in the actual force that you were seeing?

DANYLUK: We have tried to keep all of our experimental variables constant. That means that we don't vary a normal force at all. We essentially keep our pyramid diamond loaded, we just simply remove our slice and insert the next slice. The only changes that we have made in the results that I have been reporting are changes in fluid environment.

GALLAGHER: I guess my question should have been, how did you apply that force? Was it a dead weight?

DANYLUK: It is a dead-weight force, yes.

DYER: Since the abrasion process is mainly mechanical all of the time, I think we ought to keep in mind that this is a mechanical thing and were looking at the possibility of an environment influencing whatever the mechanical affect is. You have a stress field under a point source like that point load. You can even get a picture of that stress field or an idea of the picture of it from books on photoelasticity. It is very complicated, but the general shape of the stress field far away from the point is fairly well known, according to the principle of St. Venant.

Did you measure the friction difference between the water and the acetone and the alcohol? If there is a frictional difference, then that tangential force, if it is substantial, can have two different effects. First, it actually changes the magnitude of the entire stress field. You showed a large effect of going from 42 grams to 62 grams, so that if you had to push on it a little more hard with one tangentially than you did with the other, then you would essentially be increasing the basic size of the stress field. In addition to that, you would be increasing the tilt forward of that field. As you know from looking at the pictures in Frocht or some photoelasticity book, the sum of the two forces, the tangential and the vertical, if you take that vector, then the center of symmetry of that stress field is exactly along that axis. So you essentially tilt the stress field forward and change the things that stress fields do, either cracking or abrasion.

DANYLUK: Our rotation speed was 0.56 rps. So we are essentially at a very slow speed of rotation in the silicon. I think what you are referring to is basically more of a dynamic effect of a changing stress field. I don't think that we are in that regime with our experiment.

WOLF: After seeing the pictures of your grooves, and hearing of your experimental setup, I am wondering how much the bounce of the diamond could have been and how the different fluids could have provided different lubricating quality so as to alter the amount of bounce you might get as you pull the stylus along the groove.

DANYLUK: Well, we haven't measured the bounce, but we are at 60 grams. Our diamond is instrumented to record an acoustic signal. You can obviously hear a difference between the water and the acetone and the ethylene. There is probably some bounce occurring. When we looked at the ethanol grooves, there were some gouges at the bottoms of the grooves that lead us to believe that there may be some bounce occurring. I don't think that is a predominant effect in these experiments.

FRIZELL: Could it be that your lubricants evaporated more rapidly with the ethanol and the acetone than with the water?

DANYLUK: The surface is totally immersed in the fluid.

FRIZELL: Except that at the point of the diamond you got to those temperatures where you are evaporating more acetone than water.