Project Report

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Project Title: Understanding Size Effect in Cleavage Cracking in Thin Film Materials

I. Summary of Accomplishments

In order to understand and improve fracture resistance of thin films, a boron-doped polycrystalline silicon was investigated as a close analogue to all intrinsically brittle materials. The as-received material was in wafer form, with the thickness of 4 mm and the diameter of 200 mm. The resistivity was 0.55 Ω -cm. The grain size was in the range of 5-15 μ m. The silicon wafer was heated in a tube furnace at 450 °C for 0.5 h, followed by partial quenching in cold water, through which a large number of thermal cracks were produced. Under a XTL-VI stereo trinocular microscope, the cracks arrested by through-thickness grain boundaries were identified, and 15×15 mm rectangle pieces surrounding the crack tips were harvested and sliced into 200 μ m thick films by electrical discharge machining (EDM). In each group of pre-cracked films, the grains were of identical crystallographic orientations. The films were cleaned in a mixture of 4 parts of 98% sulfuric acid and 1 part of 30% hydrogen peroxide at 90 °C for 15 min, rinsed in deionized water, and slightly etched for 10 min. The etchant contained 7% of hydrofluoric acid, 75% of nitric acid, and 18% of acetic acid. After rinsing in ethanol, the films were dried in a vacuum furnace at 100 °C for 30 min, and then modified in a 20% toluene solution of chlorotrimethylsilane at 90 °C for 5 days, so that the pre-crack surfaces as well as the film surfaces were covered by a dense layer of hydrophobic silane groups. The surface treated films were mechanically polished to about 150 μ m thick, and finally thinned to 1-30 μ m through chemical etching in the hydrofluoric acid etchant. During etching, the sample was placed in a porous teflon container and the etchant was driven by an Omega FPU-500 peristaltic pump to flow across the sample surface at a constant rate of 30 ml/min. The etching rate was 3-5 μ m/min. Since the pre-crack surfaces were protected by the silane layer, the crack tips remained sharp and clear. Prior to the tensile test, the samples were thermal treated at 350°C in vacuum for 12 h and thoroughly cleaned in acetone and ethanol.

The thin film samples were then mounted on a microtesting machine, with both ends fixed on testing stages by a Loctite-411 glue. The testing machine was custom designed, capable of applying a tensile load at a rate of 10 μ m/sec, with the resolutions of load and displacement of 0.3 μ N and 20 nm, respectively. The fracture surfaces were observed in a

FEI XL30 environmental scanning electron microscope (SEM), as shown in Figs.1 and 2. Using the measured peak load, F_p , of grain boundary failure, the boundary toughness was calculated in the framework of linear elastic fracture mechanics [30]: $K_{gb} = (F_p / wt) \sqrt{\pi a} \cdot f$, where w and t are the width and the thickness of the thin film sample, respectively; a is the precrack length, and $f = 1.12 - 1.39(a/w) + 7.3(a/w)^2 - 13(a/w)^3 + 14(a/w)^4$ is the geometry factor. The results are shown in Fig.3.

Fig.1 Cleavage cracking across a through-thickness grain boundary in a thick-films sample. The arrow indicates the crack propagation direction.

Fig.2 Cleavage cracking across a through-thickness grain boundary in a thin-film sample. The arrow indicates the crack propagation direction.

When the film thickness is relatively large, e.g. when $t > 20 \mu\text{m}$, the cleavage front would break through the boundary at multiple locations simultaneously (Fig.1). At each BTP, the front first penetrates through the boundary quasi-stably, with the rest parts being arrested by the grain boundary. The characteristic distance between adjacent BTPs, D , is in the range of 5-10 μm . The PGBI are formed geometrically necessarily, since the fracture surfaces must shift from the cleavage plane of the grain behind the boundary ("B") to that of the grain ahead of the boundary ("A"). As the front penetration depth keeps increasing, eventually the PGBI would be separated apart by either shear fracture or shear yielding. The terrains in grain "A" are connected via secondary cracking, which leads to the formation of cleavage ridges. On the one hand, if the BTPs are far away from each other, the PGBI area would be large, demanding a large amount of work of separation. Before the local crack-tip stress can increase to the high level, new BTPs would be developed in between the existing ones, and thus D is lowered. On the other hand, if D is too small, while the area of PGBI can be minimized, the surface roughness in grain "A" associated with the formation of cleavage ridges increases. In these areas, the crack front advance is difficult; that is, some of the

Fig.3 The measured grain boundary toughness, K_{gb} , as a function of the film thickness, t . (a) Group 1 samples, with the twist angle, θ , and the tilt angles, ϕ , being 4.3° and 5.6° , respectively. (b) Group 2 samples ($\theta = 11.1^\circ$, $\phi = 4.2^\circ$). (c) Group 3 samples ($\theta = 7.6^\circ$, $\phi = 12.4^\circ$). (d) Group 4 samples ($\theta = 9.1^\circ$, $\phi = 17.2^\circ$).

BTPs would be deactivated, which effectively causes the increase of D . As the two competing mechanisms are in balance, the optimum BTP distance is reached and the resistance of grain boundary to cleavage cracking is minimized.

The cleavage plane in silicon can be either $\{111\}$ or $\{110\}$. The fracture toughnesses of them are slightly different by 3-4%, within the tolerance of the testing system. Thus, it will not be taken into account in the following discussion. Because of the relatively large number of possible cleavage planes, the twist and tilt misorientation angles across a boundary in silicon are usually smaller than 15° . The twist angle, θ , is more important compared with the tilt angle, ϕ , and their effects can be collectively described by

$$G = (\sin \theta + \cos \theta) / \cos^2 \phi + C \cdot \sin \theta \cos \theta / \cos \phi \quad (1)$$

where G is the normalized fracture resistance and C is a material parameter. Under this condition, since the BTPs distribute along the boundary quasi-periodically, the grain boundary toughness is determined by the averaged effects of them. Consequently, K_{gb} is quite independent of the film thickness, t . In a thin film sample ($t < 15 \mu\text{m}$), the boundary width is insufficient for multiple BTPs. As shown in Fig.2, where only a single BTP can be formed. This process is also depicted in Fig.4. Initially, the crack tip is arrested by the grain boundary. As the crack-tip stress intensity rises, the cleavage front penetrates through the boundary at the point where the local stress intensity is relatively high and the local fracture resistance is relatively low. While there may be more than one suitable sites for the front penetration, only one of them can be active; otherwise the increase in required crack growth driving force to overcome the crack trapping effect would be larger than the effect of decrease in PGBI area. Hence, further variation in t would lead to the change in PGBI structure. In a thick film, the PGBI area is determined by D . For a given material and loading mode, it is quite insensitive to the crystallographic orientation and may be regarded as a material constant. In a thin film, the PGBI area is geometrically affected. As t decreases, the required fracture work to separate the grain boundary is lowered; and vice versa. Thus, the fracture resistance is size dependent, which is shown in Fig.3.

Altogether four groups of thin-film samples were investigated, with the film thicknesses varying in the range of 2 to $15 \mu\text{m}$. In each sample, along the grain boundary there is only one BTP. In the same group, all the samples are sliced from the same pre-cracked bicrystal. Thus, they are of the same crystallographic orientation. Clearly, K_{gb} increases with t . For instance, for group 1 samples, the fracture toughness of grain boundary increases by about 20% as t rises from $2.4 \mu\text{m}$ to $12.5 \mu\text{m}$. For group 2 samples, as the film thickness increases from $3-4 \mu\text{m}$ to about $10 \mu\text{m}$, the boundary toughness increases by nearly 30%. The data of group 4 samples show that as the film thickness is larger than $20 \mu\text{m}$, the grain boundary toughness is no longer size dependent, which converges to the behavior of thick films. According to literature data, the fracture toughness of crystallographic plane of single crystal silicon is about $0.9-1.1 \text{ Mpa}\cdot\text{m}^{1/2}$, nearly 40% smaller than the measured thick-film boundary toughness. Through Eq.(1), the value of C can be determined as 3.4, close to the

Fig.4 A schematic diagram of a cleavage crack propagating through a through-thickness grain boundary in a free-standing thin film.

experimental data of large bicrystals. Note that since the crystalline structures of the silicon sample is nearly perfect, at the small length scale of the current study, the size dependent caused by the weakest-link effect should be negligible. Even if the weakest-link effect were detectable, it should cause a decrease in K_{gb} as the film becomes thicker. As t rises, the increase in K_{gb} directly reflects the PGBI effect.

The size sensitivity of fracture toughness of group 1 samples is weaker than that of the other 3 groups, which may be attributed to that their crystallographic misorientation angles, especially the twist angle, are the smallest (Fig.3). When the twist angle is small, as film thickness varies, the change in PGBI area is less pronounced, and thus the associated variation in fracture work is less evident. Note that, even though the twist angles of groups 2, 3, and 4 are quite different, their K_{gb} - t relationships are somewhat similar, indicating that as the twist angle exceeds a critical range, the PGBI area is sufficiently large so that direct shear separation is difficult. The crack front first penetrates across the boundary and propagates forward in grain "A". The PGBI is left behind the advancing front, acting as tough reinforcements bridging the fracture flanks together. Consequently, the criteria of unstable crack growth in grain "A" is not directly dependent on θ . Because mixed-mode fracture is unfavorable, the critical range of twist angle should be relatively small.

The size effect discussed above is related to the break-through mode of cleavage crack across grain boundary, which must be taken into account in MEMS or NEMS design when the characteristic length scale is smaller than a few μm . It is envisioned that, with the same thickness, if the film contains multiple layers of grains, e.g. if the film deposition process is interrupted for a few times, along the thickness direction there would be a number of grains, and thus when a crack propagates its front has to be sectioned. Under this condition, the overall toughness may be increased. That is, resistance to cleavage cracking at triple grain boundary junctions tends to be higher. As the crystallographic orientations of the two grains ahead of the crack are different by only a few degrees, the cleavage front advance becomes quite jerky (Fig.5). The crack first enters the grain of weaker boundary toughness and then turns into the other grain from the lateral direction, somewhat similar with the kink motion along a screw dislocation. Consequently, the overall fracture resistance cannot be analyzed in the framework of line-average theory.

In addition, a few irregular cracking modes at grain boundaries were analyzed. For instance, it was noticed that other than the crystallographic orientation, the orientation of the grain boundary plane also plays a critical role. With respect to the initial crack surface, if the inclination angle is relatively small, the crack tends to penetrate across the boundary; if the angle is large, the crack may either bifurcate along the boundary or turn back on another

Fig.5 SEM microscopy of a cleavage crack turning around a triple junction. The crack propagates from the bottom to the top.

Fig.6 SEM microscopy of cleavage bifurcation at a grain boundary. The crack propagates from the top to the bottom.

crystallographic plane (Fig.6). The former is triggered by crack front transmission, and the latter may results in a higher critical crack growth driving force.

If the fracture surface is not planar, the river markings can significantly affect the cleavage front behaviors at grain boundaries. Three ridge-boundary interaction modes were identified. If the cleavage ridge was relatively deep, it could directly bypass a grain boundary. If it was relatively shallow, it would act as a stress concentrator promoting cleavage front transmission. It was also observed that due to the smoothing effect, the surface could become effectively less rough across a grain boundary.

When the orientations of two adjacent grains are correlated, the crack may bypass the boundary through a “tunneling” process. Similar behavior can also be achieved if the crack path curves in the grain-boundary-affected zone. Moreover, the separation of crack flanks can be aided by secondary cracking. These irregular modes of crack front behavior tend to lower the effective boundary toughness.

Other than grain boundaries, twin boundaries are also of a toughening effect. Depending on the orientation of cleavage plan and the twin system, the crack surface may either be planar or become jerky across the first boundary, while across the second boundary the cleavage ridges tend to re-combine back into a single plane. The crack behavior at the first twin boundary is considerably influenced by the twin width, indicating that the anisotropy of crack-tip stress field is essential.

To better understand the experimental results, a number of theoretical and computational analyses have been performed on the fracture toughness of grain boundaries of various properties. If the boundary is sufficiently tough such that it would not yield even after the cracking trapping effect is fully overcome, the boundary fracture resistance can be estimated as

$$\frac{G_{\text{tot}}}{G_{\text{sc}}} = \left\{ \frac{w}{t} + \left[2.4 - 0.3 \frac{t}{w} \right]^2 \cdot \left(1 - \frac{w}{t} \right) \right\} \frac{1}{\cos \theta \cdot \cos \varphi} + \beta \frac{\tan \theta}{4} \frac{t}{w} \left[1 - \left(\frac{w}{t} \right)^2 \right] \quad (2)$$

where G_{tot} is the boundary resistance; G_{sc} is the resistance of a single crystal; t is the film thickness; θ and φ are the twist and tilt misorientation angles, respectively; and w and β are material constants. Equation (2) gives the upper estimate. If the grain boundary is relatively weak so that it is separated simultaneously as the cleavage front bypasses it, its fracture resistance can be assessed in the framework of R-curve analysis, which provides the lower estimate. The experimental data scatter nicely in between these two limits, suggesting that the grain boundaries under investigation are separated apart through a mixed mode.

Fig.7 (a) Microscopy of a cleavage ridge at a grain boundary. The crack propagates from the left to the right. (b) Microscopy of the smoothing process of a fracture surface. The crack propagates from the left to the right. (c) A schematic diagram of the penetration process of a sectioned cleavage front at a grain boundary.

When the crack surfaces are not perfectly flat, i.e. as there are river markings, three interaction modes of cleavage ridges with grain boundaries are identified (Fig.7). When the cleavage ridges in the grain behind the boundary are relatively deep and far apart from each

other, the front segments between them transmit across the boundary quite independently. If the river markings are small and close to each other, they can trigger cleavage facet nucleation in the next grain. While the numbers of river markings are about the same, the ridge depth in the two grains can be quite different. Due to the promotion effect of sharp corners, the barrier effect of grain boundary can be reduced. Finally, if secondary separation can take place along the boundary direction, the river markings in the first grain can be smoothened.

While the behaviors of majority of grain boundaries in silicon thin films are dominated by the regular mode, in which the boundary is sheared apart after the cleavage front penetrates at break-through points, secondary cracking can take place under a certain conditions. If the orientations of the two grains across a boundary are correlated, the cleavage crack can directly enter the grain ahead of the boundary through a “tunneling” effect (Fig.8). If the incident angle is relatively small, in the grain-boundary-affected zone the crack path can deviate and converge to the boundary plane, after which the crack can bypass the boundary without boundary separation (Fig.9). Even when the crack penetration has taken place, if the break-through-point distance is relatively large, secondary cracking can occur in the grain ahead of the boundary so that the separated boundary area is reduced. In these irregular crack front transmission modes, the effective boundary toughness is lowered, as shown in Fig.10.

In addition to grain boundaries, the interaction between cleavage crack and twin boundaries is also investigated, by using samples etched in a circulating system (Fig.11). When a crack encounters a twin boundary, there are three main front transmission modes. When the twist misorientation of cleavage planes across the first twin boundary is relatively small, the fracture surface tends to transmit smoothly into the twin (Fig.12). If the twist angle is relatively large, planar transmission mode dominates (Fig.13). As the twist misorientation further increases, the crack plane can break down into a number of terrains, as shown in Fig.14. After the crack front bypasses the second twin boundary, the fracture surface tends to be planar. In addition to the orientation of crack plane and the twin system, the crack front transmission can also

Fig.8 (a) SEM fractography and (b) schematic diagram of secondary cracking in grain-boundary-affected zone. In the SEM image the crack propagates from the top to the bottom. The arrow indicates the grain

Fig.9 (a) SEM fractography and (b) schematic diagram of curving of cleavage path in grain-boundary-affected zone. The crack propagates from the right to the left. The arrow indicates the grain boundary.

Fig.10 SEM fractography of cracking on multiple cleavage planes in the grain ahead of the boundary. The crack propagates from the left to the right. The arrows indicate the secondary cleavage planes.

be associated with the effects of the orientation of film surface, the film thickness, as well as the twin width. In all the cases, the fracture resistances offered by twin boundaries are considerably higher than that of single crystals, suggesting that twins can act as obstacles to cleavage crack propagation.

Fig.11 Schematic of the etching system.

Fig.12 A SEM image of smooth transmission of cleavage surface across a twin boundary. The crack propagates from the top to the bottom.

Fig.13 (a) A SEM image and (b) a schematic diagram of planar transmission of cleavage surface across a twin boundary. The crack propagates from the right to the left.

Fig.14 (a) A SEM image and (b) a schematic diagram of sectioned transmission at the first twin boundary and recombination of cleavage facets at the second boundary. The crack propagates from the right to the left.

The fracture resistance of individual high-angle grain boundaries and a field of randomly oriented grain boundaries is modeled through energy equilibrium analysis and/or R-curve type analysis. The numerical results support the experimental observations shown above. The details of the models are published in [14-18] in the following section.

By analyzing the resistance offered to cleavage crack front propagation by side grain-boundary sections, it is found that the toughening effect associated with the irregular boundary failure mode is significant. In such a failure mode, the crack front does not penetrate through the entire grain boundary uniformly. Rather, it first bypasses the boundary in the central part, leaving the side boundary sections behind as bridging components. The side boundary sections are separated apart through plastic shearing, after both sides of them have been exposed to the cleavage fracture surface. The nonuniform crack front behavior causes a significant crack trapping effect, which, in addition to the fracture work of grain boundary separation, can increase the overall fracture resistance by an order of magnitude. A closed-form equation is obtained to capture the toughening effect:

$$\hat{K} = \sum_{i=0}^3 \lambda_i \left(\frac{w_s}{d_g} \right)^i \quad (3)$$

where $\lambda_i = \{1, 18.6, -17.1, 162.9\}$ ($i = 0, 1, 2, 3$) are coefficients obtained through data fitting. Promotion of the nonuniform grain-boundary failure mode may be achieved by controlling the external loading, the texture, and/or the grain shape/size distribution.

Fig.15 Schematics of nonuniform cracking across a high-angle grain boundary: (a) the three-dimensional view; and (b) the side view, where the R-curve behavior is shown.

Fig.16 The grain boundary toughness (K_{gb}) and the critical width of break-through window (W_{bt0}) as functions of the grain boundary ductility (ε_0).

Fig.17 The boundary toughness as a function of the crystallographic misorientation.

A R-curve type analysis suggests that the critical condition of the transition from stable break-through window expansion to unstable crack advance is determined not only by the magnitude of crack growth driving force, but also by its increasing rate (Fig.15). The persistent grain boundary outside the break-through window causes a significant crack trapping effect, which can result in a large increase in grain boundary toughness by 5-6 times (Fig.16), compared with the local fracture toughness inside the break-through window. The overall fracture resistance offered by a high-angle grain boundary is quite insensitive to the elastic properties and the grain size (Fig.17). The dominant factors are the grain boundary ductility as well as the crystallographic misorientation, particularly the twist misorientation.

II. List of Publications

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11. Chen, J.; Qiao, Y. Bifurcation and deviation of cleavage paths at through-thickness grain boundaries. *Met. Mater. Trans.* **39A**, 2040-2044 (2008)
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15. Lu, W.; Chen, J.; Kong, X.; Chakravarthula, Qiao, Y. Nonuniform cleavage cracking across persistent grain boundary. *Mech. Mater.* **43**, 567-573 (2011).
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18. Lu, W.; Chakravarthula, S. S.; Chen, J.; Qiao, Y. Propagation of a cleavage crack front across a field of persistent grain boundaries. *Int. J. Solids Struct.* **49**, 584-589 (2012).

III. List of People Working on the Project

Yu Qiao, Professor, PI
 Alice Han, Postdoctoral Scholar (development of experimental techniques)
 Jin Chen, Graduate Student (microtensile experiment)
 Xinguo Kong, Graduate Student (theoretical analysis)
 Weiyi Lu, Graduate Student (materials preparation)
 Falgun B. Surani, Graduate Student (data analysis)
 Srinivas S. Chakravarthula, Graduate Student (data analysis)