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The surface energy of Si, GaAs, and GaP

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The surface energy of various planes in Si, GaAs, and GaP was measured by the use of a modified spark discharge method, previously used successfully in metals. Surface energy values were determined for the following cleavage planes in these crystals: Si $\{111\} \sim 1.14$ J/m^2, Si $\{110\} \sim 1.9$ J/m^2, GaAs $\{110\} \sim 0.86$ J/m^2, and GaP $\{110\} \sim 1.9$ J/m^2. The Si surface energy value was compared with previous experimental measurements. The Si $\{110\}$, GaAs $\{110\}$, and GaP $\{110\}$ values were compared only to theoretical estimations, since as far as it is known, the surface energy of these planes have never been measured experimentally. Berg-Barrett x-ray topography and chemical etch pit analysis verified that plastic relaxation did not occur under the test conditions used. The cleavage surface energies determined in this work were in good agreement with previous theoretical estimations. Experimental observations confirmed a lack of plastic energy dissipation and a stability of cleavage propagation which indicated that the measured surface energies were close to the intrinsic values.

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I. INTRODUCTION

In principle the use of the modified Griffith[1] approach enables the effective surface energy γ_c of a crystal to be determined by measuring the normal force required to separate the crystal along a given $(hk\,l)$ plane. In order to relate the effective surface energy measured by this method to the intrinsic surface energy γ_s, that is, the energy associated with a free surface, all energy dissipation factors unrelated to the breaking of interplanar bonds must be taken into account.

The usual technique for measuring γ_c on Si crystals have used the double cantilever beam (DCB) test developed by Gilman.[2] In this method, a steel wedge is driven into the side of a compressively loaded specimen in order to introduce a precursor crack. The compressive stress field is necessary to stop the initial crack from running thorough the entire cross section of the specimen. However, difficulties arise in employing the DCB test to the case of brittle solids as reviewed by Evans.[3] The main problems associated with this DCB method include complex bending moment corrections, ill-defined precursor crack conditions, and deviations from the cleavage plane during crack propagation.

Values reported for γ_c, measured by the DCB method for the $\{111\}$ planes in Si, have reported a wide variation ranging from 1.23–2.50 J/m^2. As far as it is known to the present authors, experimentally determined values of γ_c for $\{110\}$ planes in GaAs and GaP do not appear to exist in the literature.

An alternative method for measuring γ_c, previously untried in brittle solids, is reported in the present investigation following the work of Hull, Beardmore, and Valentine[4] (HBV). This technique used an explosive electrical spark discharge to introduce into the appropriate cleavage system of the crystal a precursor crack of controlled dimensions and morphology. The crack is then expanded by the application of a tensile force acting perpendicular to the cleavage plane (this is commonly referred to as a mode I failure in fracture mechanics terminology). This method achieves nearly ideal conditions necessary for applying the modified Griffith criteria for determining γ_c for a particular $(hk\,l)$.

The application of the HBV technique was used to measure the γ_c of the $\{111\}$ and $\{110\}$ planes in Si and the $\{110\}$ planes in GaAs and GaP. Subsidiary observations of the dislocation structures by chemical etch pit and Berg-Barrett x-ray topography were used to assess the possible role of plastic relaxation, if any, in influencing the magnitude of γ_c. These results are discussed in the context of previous theoretical work on the intrinsic energies of these crystals.

II. EXPERIMENTAL PROCEDURE

The single-crystal test specimens used in this study were supplied by Philips Laboratories of the North American Philips Corporation. The Si single crystals were n-type, P-doped with a nominal initial dislocation density, < 200 cm^{-2}, and a resistivity of 0.14 Ω cm. GaAs crystals were n-type, Si-doped, and had an as-grown dislocation density below 1000 cm^{-2}. The GaP specimens were from undoped crystals with a dislocation density in the 10^5 cm^{-2} range. Test samples were cut from 0.2-cm-thick, as received, slabs which had been polished to standards typical of device grade surface preparations. Specimens $1.5 \times 0.5 \times 0.2$-cm thick were fabricated from these slabs using a low speed diamond saw in combination with mechanical and chemical polishing to remove the associated cutting damage following the techniques reported in the literature for Si[5], GaAs[6], and GaP.[7]

A relatively simple spark discharge device was constructed to enhance the spark cracking behavior of these materials.[8] This apparatus consisted of a bank of charged capacitors in which one terminal was connected to a sharpened tungsten electrode and the other terminal wired to the test specimen. The spark discharge produces localized deformation and cracking on the surface of the specimen. Various discharge parameters, such as input spark energy, dielectric media, specimen temperature and specimen orientation can be easily varied to provide for the optimum spark cracking conditions in these materials.

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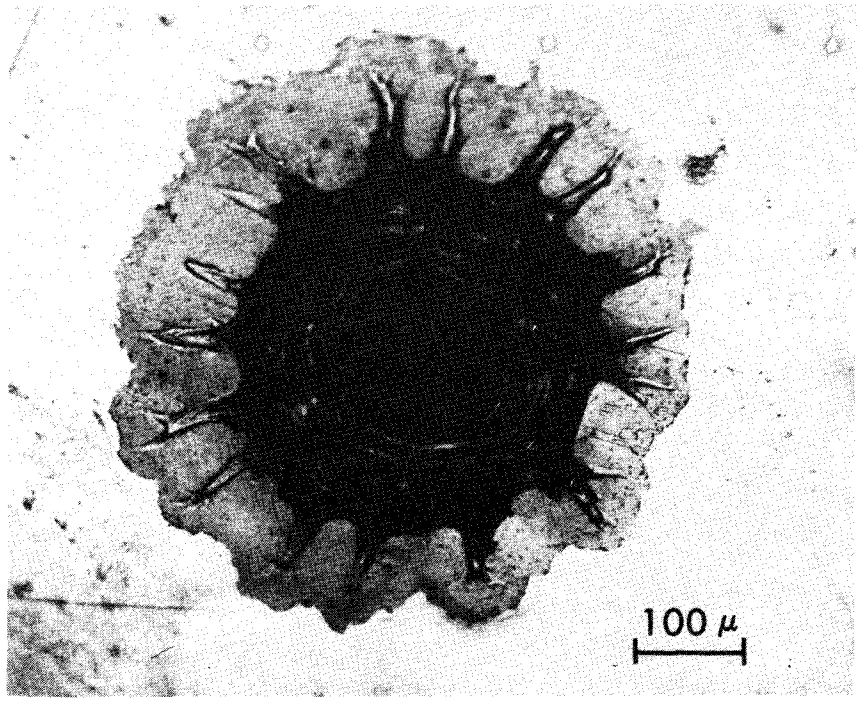
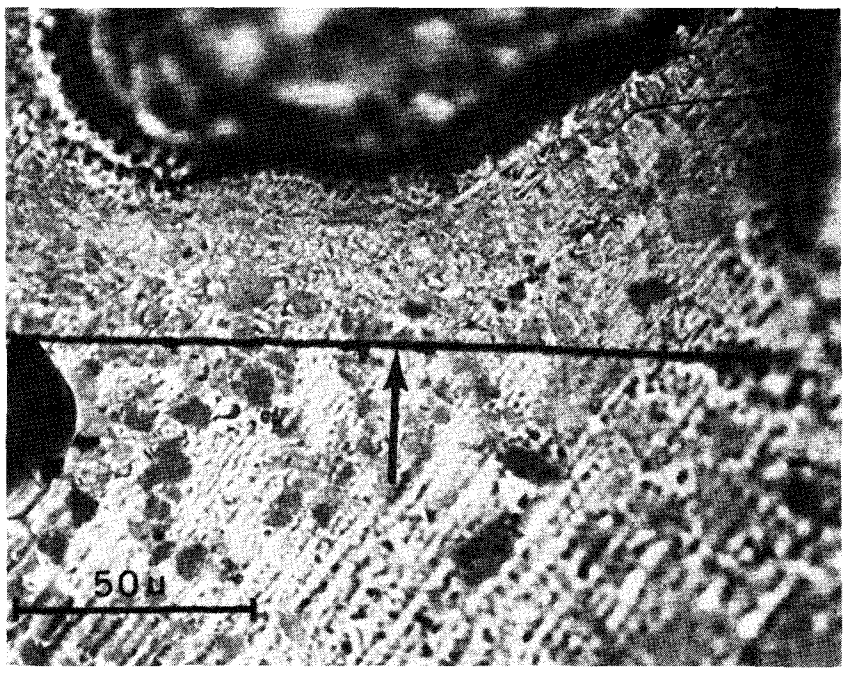
In Si, the procedure had to be slightly modified due to its relatively high bulk resistivity. The collection of the spark discharge onto the cathodic Si specimen required a film of Ag which was vapor deposited onto the surface of the specimen to a thickness of ~ 1000 Å. This film increased the conductivity enough to allow a spark discharge to occur. However, in both GaAs and GaP, the bulk resistivity was low enough for a discharge to occur without the need of any surface conducting film. No evidence could be found of the Ag film absorbing into the spark induced crater or into the precursor crack area as determined by microprobe analysis. The Ag film appeared to be "blasted away" by the action of the spark discharge. An example of such a crater is shown in Fig. 1.

After precracking, the test specimens were mounted into a self-aligning ball joint tensile grips using a cyanoacrylate adhesive. The specimens were mechanically tested on a "Table Model Instron" testing machine at a crosshead rate of 0.127 cm/min at 293 °K. Specimens were pulled until cleavage occurred. The fracture stress was determined by



(a)



(b)

FIG. 1. (a) Crater produced by the discharge of a capacitor that yielded a spark energy of ~ 1 J. Crater was situated on the {110} surface of a Si single crystal. The visible ring located around the crater displayed the extent of the area in which the Ag surface film was removed by the action of the spark discharge. (b) Spark induced crack that was produced in the interior of the crater shown in (a). Crack (arrow) runs along the trace of the {111}-type cleavage plane which was situated perpendicular to the spark surface, {110}.

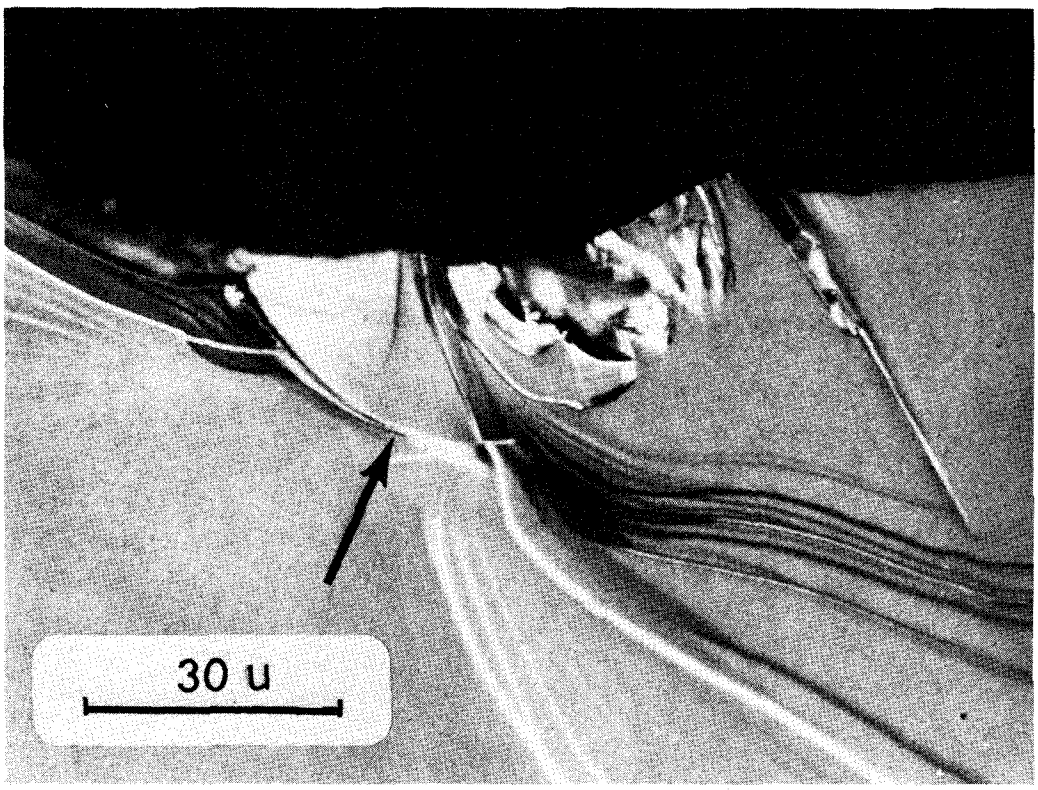


FIG. 2. Distinct semielliptical precursor crack (arrow) created by the spark discharge technique. The observation of the crack interface, which was located on the cleavage surface, was enhanced by the use of Nomarski contrast lighting.

dividing the load at the point of fracture by the cleavage surface area. The exact cleavage surface area was measured by using a compensating polar planimeter on a composite micrograph of the cleavage surface. The precursor crack length c was measured optically on the cleavage surface as viewed using Nomarski interference contrast which gave a direct indication of the sharpness of the precursor crack front (see Fig. 2). Most of the precursor cracks were semielliptical in nature (see Fig. 2). The fracture stress was subsequently corrected for this geometric shape following Irwin.[9] The corrected fracture stress σ_F coupled with the precursor crack length c responsible for the cleavage of Si $\{111\}$, Si $\{110\}$, GaAs $\{110\}$, and GaP $\{110\}$ are shown by the data points in Figs. 3–6.

In order to assess the amount of plastic energy associated with the measured γ_c $\{hk\,1\}$ values, dislocation etch pit and Berg-Barrett x-ray topography were used to reveal possible dislocation substructure prior to, and following, the cleavage process. In this study, the following chemical etching techniques were used to reveal dislocation etch pits: Si,[5,10] GaAs,[11] and GaP.[12]

III. RESULTS AND DISCUSSION

The γ_c for a specific $\{hk\,1\}$ of a material can be obtained from the modified Griffith equation for an edge crack ten-

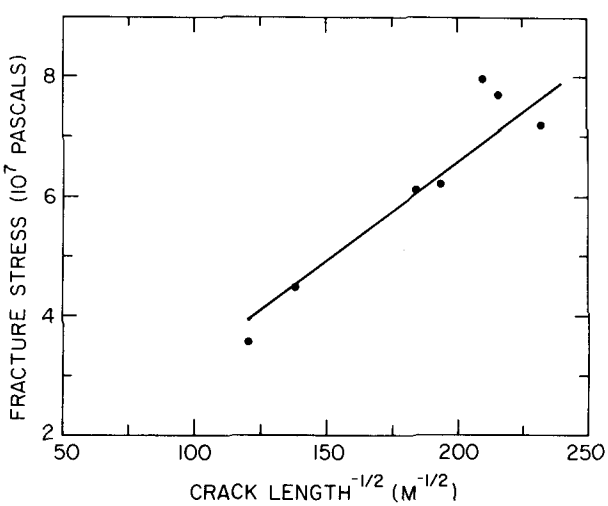


FIG. 3. Linear regression plot of the fracture stress, σ_F vs (crack length)$^{-1/2}$, $c^{-1/2}$, obtained from the $\{111\}$ cleavage of Si single crystals.

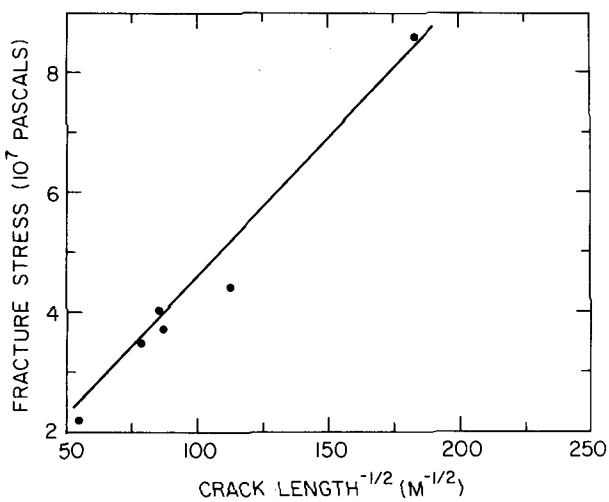


FIG. 4. Linear regression plot of the fracture stress, σ_F vs (crack length)$^{-1/2}$, $c^{-1/2}$, obtained from the $\{110\}$ cleavage of Si single crystals.

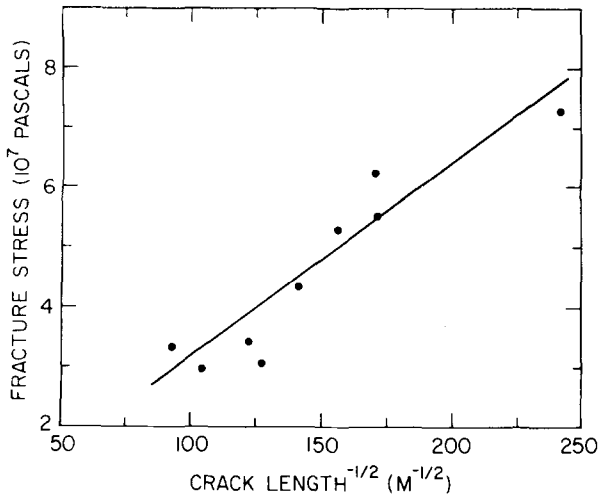


FIG. 5. Linear regression plot of the fracture stress, σ_F vs (crack length)$^{-1/2}$, $c^{-1/2}$, obtained from the $\{110\}$ cleavage of GaAs single crystals.

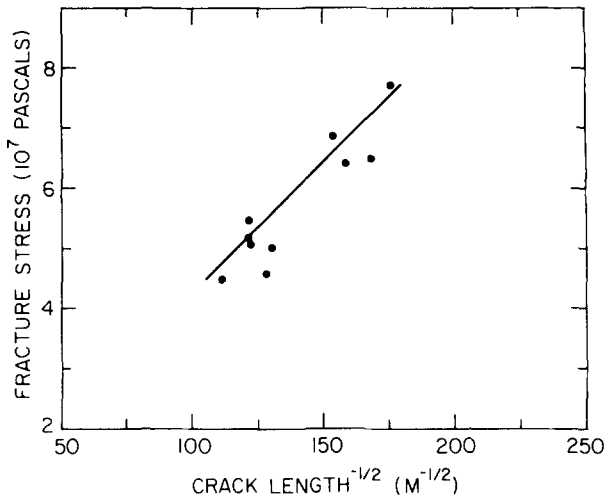


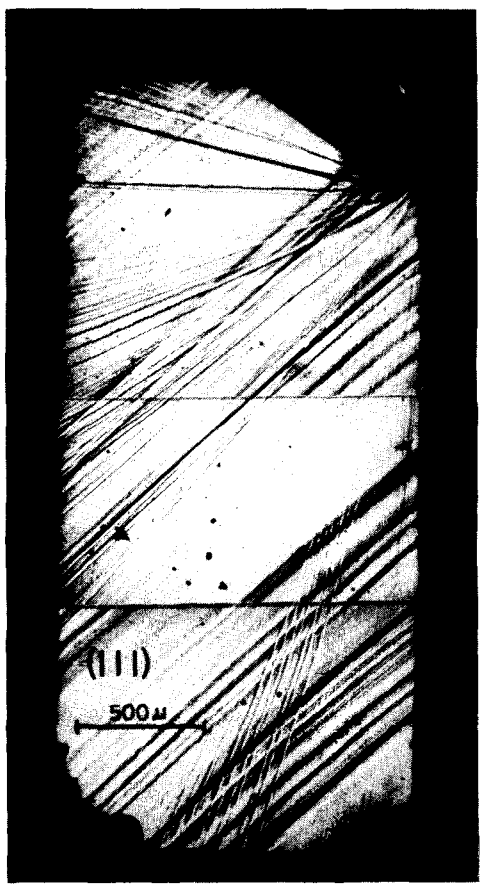
FIG. 6. Linear regression plot of the fracture stress, σ_F vs (crack length)$^{-1/2}$, obtained from the $\{110\}$ cleavage of GaP single crystals.

sion test, in which

$$\sigma_F = [2E_{hk1}\gamma_c\{hk1\}/(1-\nu^2)\pi c]^{1/2}, \quad (1)$$

where σ_F = corrected fracture stress, E_{hk1} = elastic constant in $\{hk1\}$ direction, $\gamma_c\{hk1\}$ = cleavage surface energy of $\{hk1\}$ plane, ν = Poisson's ratio, and c = precursor crack length.

Hence, $\gamma_c\{hk1\}$ is obtained by plotting the corrected fracture stress σ_F as a function of the inverse square root of the initial crack length $c^{1/2}$. The data points on Figs. 3–6 each represent a separate fracture experiment of the specific material tested. The crystals that were fractured adhered to the Griffith criterion, that is, there was a linear dependence between σ_F and $c^{1/2}$ within experimental error. The slope of this lin-



(a)

(b)

FIG. 7. (a) $\{111\}$ cleavage surface of Si crystal chemically etched to reveal dislocation etch pits. (b) Magnified view of the precursor crack area of the etched cleavage surface shown in (a). Notice the lack of any significant increase in dislocation etch pits around the precursor crack interface.

ear regression line is being directly proportional to $\gamma_c\{hk1\}$ by

$$m_i = [2E_{hk1}\gamma_c\{hk1\}/(1-\nu^2)\pi]^{1/2}, \quad (2)$$

where m_i = slope of the linear regression line of σ_F vs $c^{1/2}$. From the data obtained from these experimental curves, Figs. 3–6, cleavage surface energies of 1.14 ± 0.15 J/m^2 and 1.9 ± 0.2 J/m^2 were determined respectively for the $\{111\}$ and $\{110\}$ planes of the Si single crystals tested. For the $\{110\}$ planes in GaAs and GaP, $\gamma_c\{110\}$ were 0.86 ± 0.15 J/m^2 and 1.96 ± 0.2 J/m^2, respectively.

Errors associated with these values are due mostly to difficulties arising from the measurements of crack lengths and of the presence of slight bending moments during tensile loading. The existence of a subtle interface at the crack front and its distance to the edge of the specimen, which has been degraded due to the spark discharge crater, was the main cause of uncertainty in the accurate measurement of crack lengths. Slight bending moments are always present to some degree in the tensile loading of brittle materials due to difficulties in accurately aligning the grips for such small gage sections.[3] These two effects are random in the nature of the experimental technique used and accounts for some of the spread in the data exhibited in the fracture energy curves, Figs. 3–6.

In order to determine $\gamma_s\{hk1\}$ from the measured $\gamma_c\{hk1\}$ of these brittle materials, two energy processes which are unrelated to direct interplanar bond rupture must be taken into account. First, plastic energy dissipation during cleavage was analyzed by dislocation etch pit analysis and reflection x-ray topography. In the case of metallic crystals, plastic energy dissipation is evidenced by increases in dislocation substructure around the precursor crack front. The extent of this deformation zone being related to the amount of plastic energy associated with the measured $\gamma_c\{hk1\}$ values.[8] Figure 7 shows the area around an initial crack or a cleavage surface which has been etched to reveal dislocation etch pits. No distinct increases in the dislocation substructure around the precursor crack front was observed for any sample. Only typical grown-in dislocations were present on all the cleavage surfaces examined by chemical etch pit analysis. Berg-Barrett topographs of the cleavage surface displayed a similar dislocation substructure. These results indicated that fracture was predominantly brittle in nature occurring when the stresses at the crack front satisfied the Griffith criterion. These findings agreed quite well with the experimental evidence[11,13–20] of the energetics of plastic deformation in semiconductor materials, that is, dislocations play no significant role in the fracture process of the materials at 293 °C.

A significant problem in calculating $\gamma_s\{hk1\}$ from $\gamma_c\{hk1\}$ values could arise from deviations of the cleavage plane from the appropriate $\{hk1\}$ at the precursor crack front. Such deviations cause the local stresses at the crack-tip to become so complex that the modified Griffith equation for an edge-crack tension test no longer applies. The classical cleavage surfaces, Si$\{111\}$, GaAs $\{110\}$, and GaP $\{110\}$, showed no such deviations in the specimens tested in this study, these all fractured in a brittle manner and exhibited a mirror-type fracture surface, Fig. 8. Cleavage started at a point along the precursor crack front and fanned out across the sample in a series of river lines. Only the fracture surface Si $\{110\}$ showed any deviations from the $\{110\}$ plane. In this case, the surface showed the appearance of a rapid, highly unstable crack propagation as observed in Fig. 9. Fracture initiated on $\{110\}$ plane perpandicular to the tensile axis but as the crack propagated across the sample, the cleavage plane shifted from a $\{110\}$ to a $\{111\}$-type surface in a series of cleavage steps. This is what one would intuitively expect to happen since the intrinsic energy to separate the $\{111\}$ planes in Si is less than the surface energy of the $\{110\}$. Cleavage initiates on $\{110\}$ due to the orientation of the test specimen which maximizes the stress concentration of the precursor crack along the $\{110\}$ and not on $\{111\}$ planes. During crack propagation, any irregularity (i. e., bending moments) causes the crack to divert into its lowest energy

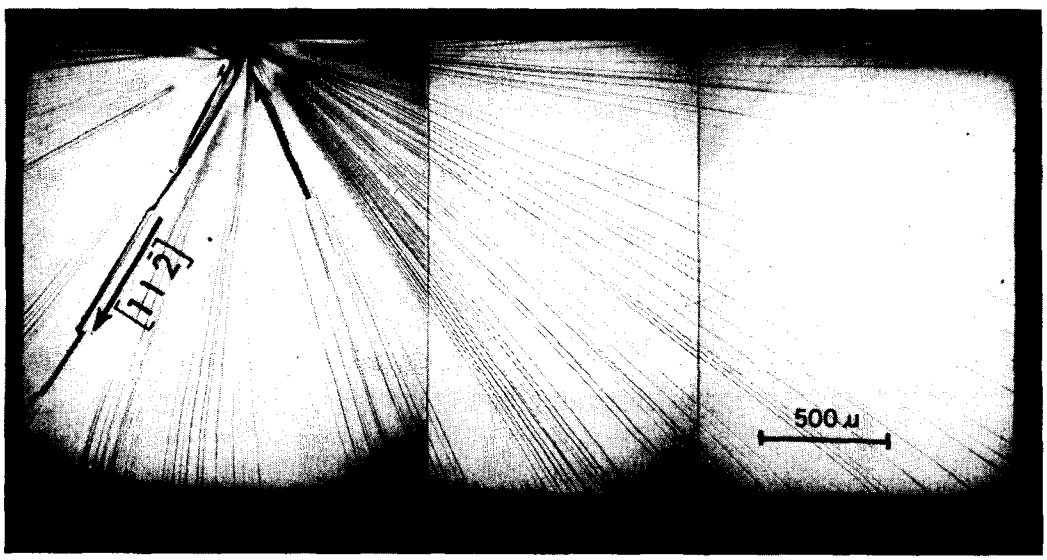


FIG. 8. $\{111\}$ cleavage surface of a Si single crystal. Surface was produced by HBV method of determining cleavage surface energy of crystal. This mirror-type fracture surface was exhibited by all of the classical cleavage specimens: $\{111\}$ cleavage in Si, $\{110\}$ cleavage in GaAs and GaP. Arrow indicates initial crack area on cleavage surface.

FIG. 9. {110}-cleavage surface of a Si single crystal. Arrow indicates initial crack area. The surface shows the appearance of a rapid, highly unstable crack propagation fracture initiated on {110} plane (light areas), but as the crack propagated across the specimen, the cleavage plane shifted from a {110} type (light areas) to a {111} type (dark areas) in a series of cleavage steps.

path, that is, along the {111} plane. Because deviations in the cleavage surface occurred in areas away from the initial crack front, thus the modified Griffith criterion was still valid at the onset of fracture which is required in order to measure $\gamma_c\ \{hk1\}$.

Since both the effects of plastic energy dissipation and crack branching were determined to be minimal in the cleavage process of these materials, the $\gamma_c\ \{hk1\}$ values measured were considered to be close to the intrinsic surface energy values.

In comparing the measured value for the $\gamma_c\ \{hk1\}$ of Si with those or previous mechanical measurements, it seems that this value was in good agreement with the lower values that were previously reported [Gilman[2] (~ 1.24 J/m^2) and Jaccodine[21] (~ 1.23 J/m^2)]. The disagreement with the value found by St. John[13] (~ 2.5 J/m^2) can be explained by the differences in the testing procedure used to obtain $\gamma_c\ \{hk1\}$ of Si. St. John used a tapered DCB test which enabled him to obtain repetitive crack propagations and arrests which varied up to eight fractures per specimen. The $\gamma_c\ \{111\}$ of Si that was measured by this technique was calculated to be considerable higher than that of the other measured values that contained only one fracture per specimen. A possible reason for this effect could be traced to the static positions of the crack front in St. John's tests, where it was reported that changes in the cleavage-surface elevation of ~ 1000 Å were observed. Also, St. John used a wedge method for precracking, which caused deviations of the precrack plane from the {111} cleavage plane to the order of several degrees. This deviation of the precursor plane coupled with the changes in elevation at the static crack positions could have had the effect of decreasing the stress concentration experienced on the {111} in Si.

TABLE I. Comparison of surface energy values measured by this study with those calculated from various theoretical models.

Surface Energies (J/m^2)			
Si	GaAs	GaP	Reference
(110)~1.90	(110)~0.86	(110)~1.96	This study
(111)~1.14			
(100)~1.34	(100)~0.91	(100)~1.04	22
(110)~1.23	(110)~1.23	(110)~1.04	
(111)~0.84	(111)~1.08	(111)~0.74	
(Bulk)~1.69	(Bulk)~1.51	(Bulk)~1.73	23
(100)~2.53	(100)~3.17	(100)~4.00	24
(110)~1.78	(110)~2.24	(110)~2.82	
(111)~1.46	(111)~1.81	(111)~2.31	
(Bulk)~1.86	(Bulk)~1.20	(Bulk)~2.06	25
(100)~2.53	(100)~2.20	(100)~2.90	26
(110)~1.78	(110)~1.50	(110)~2.00	
(111)~1.46	(111)~1.30	(111)~1.70	
(Bulk)~1.56	(Bulk)~1.97	(Bulk)~2.50	27
(Bulk)~1.90	(Bulk)~1.78	(Bulk)~2.50	28

There have been numerous theoretical models proposed[22–28] to estimate the $\gamma_s\ \{hk1\}$ for various planes in a material. Table I summarizes these estimations of $\gamma_s\ \{hk1\}$ along with the values of $\gamma_c\ \{hk1\}$ measured by this study. The measured $\gamma_c\ \{hk1\}$ values are consistently lower than those of the theoretical values, but are well within the range expected by the theories. The tendency for γ_S(GaP) > γ_s (Si) > γ_s(GaAs) predicted by the theoretical models is supported by the $\gamma_c\ \{hk1\}$ values obtained here. The only discrepancy occurs in the compound semiconductors where the {110} classical cleavage plane does not have the lowest intrinsic surface energy as predicted by the theoretical models. From theory one would expect that the {111} planes in the diamond and zinc-blende structures would be the easiest cleavable plane due to the fact that it is the one with the lowest interplanar bond density. But it must be emphasized that the theoretical models were developed for elements with either pure covalent or pure metallic bonding. Discrepancies in the theoretical values of $\gamma_s\ \{hk1\}$ for GaAs and GaP could be traced to the differences in atomic masses and mixed nature of bonding associated with these compound crystals.[22] None of the existing theories takes into account these two conditions.

IV. CONCLUSIONS

Cleavage surface energies of the following crystallographic planes were measured in Si, GaAs, and GaP.

Si: $\gamma_c\ \{111\} = 1.14 \pm 0.14$ J/m^2,

$\gamma_c\ \{110\} = 1.90 \pm 0.20$ J/m^2,

GaAs: $\gamma_c\{110\} = 0.86 \pm 0.15\ \mathrm{J/m^2}$,

GaP: $\gamma_c\{110\} = 1.96 \pm 0.20\ \mathrm{J/m^2}$.

The cleavage process was found to be independent of the dislocation structure and occurred only when the stress field at the precursor crack-tip satisfied the Griffith criterion. Since both the effects of plastic energy dissipation and crack branching were determined to be minimal in the cleavage process of these materials, the $\gamma_c\{hk1\}$ values measured may be regarded as the "intrinsic" crystalline values. These measured $\gamma_c\{hk1\}$ are well within the range of the calculated $\gamma_s\{hk1\}$ values obtained from the various theoretical models[22–28] reported above. Differences between the $\gamma_c\{111\}$ of Si measured by this study and those of past mechanical measurements[2,13,21] can be explained by the differences in testing procedures employed by each study.

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