Production of Free Charge Carriers during Fracture of Single-Crystal Silicon

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(Received 28 August 1987)

Measurements of the time dependence and magnitude of fracture-induced changes in electrical conductivity in single-crystal Si are presented. A transient increase in conduction is observed during crack growth due to the production of free charge carriers. The presence and characteristics of this transient depend on the nature of the fracture.

PACS numbers: 72.20.Jv, 62.20.Mk, 72.80.Cw, 81.40.Np

During crack propagation, mechanical work of deformation is transformed into bond breaking in a relatively localized portion of the material. Energy-release processes at or near the fracture surface can have irreversible components, as evidenced by various fracto-emission phenomena,[1] including the emission of visible light (triboluminescence), electrons, ions, neutral species, and long-wavelength electromagnetic radiation. A number of these processes involve departures from equilibrium induced by fracture.

We have recently observed electron emission during the fracture of single-crystal Si in vacuum.[2] It seemed plausible that fracture might also create free charge carriers in the Si near or at the fracture surface. We present for the first time evidence of the production of fracture-induced charge carriers.

Commercial boron-doped $\{111\}$ silicon wafers, with one face polished and having resistivities of 10 to 20 Ω cm, were obtained from S.E.H. America, Inc. After an HF acid etch, the wafers were coated with about 50 nm of gold on each side and cleaved into oriented tensile specimens of dimensions $6 \times 25 \times 0.52$ mm^3. The gold-coating process resulted in Schottky-barrier contacts on the polished surfaces and Ohmic contacts on the unpolished surfaces. The Ohmic contacts were a consequence of the high density of recombination centers at the damaged surfaces. The specimens were epoxied to aluminum mounts and loaded in tension at an elongation rate of 0.01 mm/s. Contacts to the gold-coated surfaces of the sample were made with silver print. On occasion, samples were loaded in cantilever beam or torsional modes. In all cases, edge flaws created during preparation were the dominant loci of failure. These flaws were left untreated, resulting in a wide range of strengths.

The basic experiment involved the application of a small voltage across the Si sample and measurement of the current passing through the specimen before, during, and following failure. Measurements were carried out in air or in vacuum (10^{-7} Torr) at room temperature, or in streams of dry, cool N_2, which reduced the specimen temperature to approximately 200 K. A schematic diagram of a typical experiment is shown in Fig. 1. R_i in Fig. 1 is the input resistor of a fast amplifier or transient recorder. Both ac- and dc-coupled amplifiers were used, with typical gains of 6×. Digitization rates were either 10 or 320 ns/channel.

The current through the sample generally decreased during fracture. For the circuit of Fig. 1, this decrease was a consequence of cleavage along $\{111\}$ planes, which resulted in fracture surfaces which were not perpendicular to the wafer surfaces. Therefore, a small region of the wafer became less effective in conduction as fracture progressed. This current drop correlated well with the duration of fracture, as determined by simultaneous measurements of gold-foil conductivity. In many cases, crack bifurcation led to the removal of Si material from the circuit. Similarly, when only one end of the sample was connected into the circuit, fracture significantly reduced the amount of conducting Si. In these situations, a rapid, off-scale drop in observed current resulted. Because the fracture surfaces were not normal to the loading direction, the crack experienced shear as well as nor-

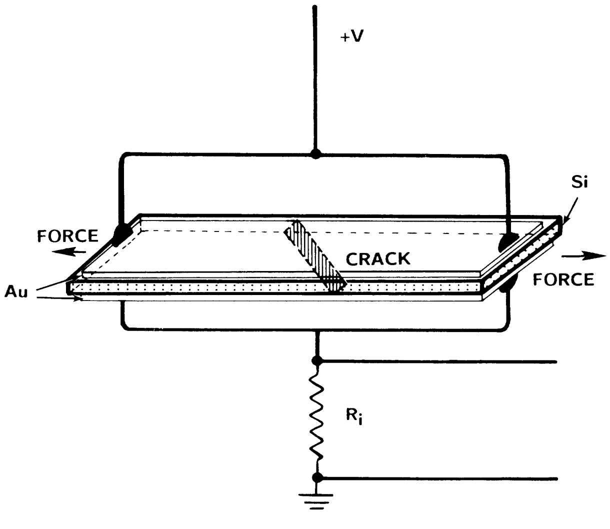

FIG. 1. Diagram of tensile specimen, showing the circuit used to measure sample current. The crack shown represents a typical $\{111\}$ cleavage plane. Samples broken in bending and torsional modes were supported at one end only.

mal stresses during loading. Therefore, even under tensile loading, mixed-mode fracture resulted.

A dramatic, transient increase in current through the sample was often observed during crack propagation. Figure 2(a) shows the change in current for a sample tested in tension in dry, cooled N_2 at atmospheric pressure. The onset and completion of crack propagation are marked with vertical arrows. The total duration of crack propagation is 5 μs, which corresponds to an average crack velocity of 1200 m/s. The downturn in current immediately preceding the transient indicates that the instantaneous crack velocity during the transient is significantly higher.

Similar transients were observed whether fracture occurred in air, dry nitrogen, or vacuum, and appeared to be independent of the ambient temperature (room temperature to 200 K). When integrated, the detected current transients per unit cross-sectional area of the sample corresponded to 10^9 to 10^{11} free carriers/cm^2. The larger transient currents were most evident in samples exhibiting high strength and fast crack growth and in those fractured in a torsional mode. The surfaces of samples yielding large transients often displayed areas of unusual roughness. Transients were rarely detected in low-strength samples which often displayed very smooth fracture surfaces associated with slower crack growth. The change in current for such a specimen is presented in Fig. 2(b), which shows little evidence of increased conductivity during fracture. Here, the total duration of crack propagation is 8 μs, corresponding to an average crack velocity of 880 m/s. This observation lends further support to the hypothesis that free-carrier generation is associated with high crack velocities.

Current transients were also associated with highly damaged fracture surfaces, which are commonly produced in torsional and cantilever beam modes of loading. Typical results for a specimen loaded in torsion are shown in Fig. 2(c). The digitizer was driven off scale during the most intense portion of the current transient, suggesting a very strong response. The duration of crack propagation was about 7 μs.

These current measurements do not distinguish the sign of the participating charge carriers. However, under the conditions of bias used in this work, the depletion region near the Schottky interface served as a barrier to the transport of holes, but not to that of electrons. Further, the sample temperatures (200 K to room temperature) were sufficient to ensure that the acceptor impurities were fully ionized, ruling out the production of additional majority carriers (holes) by acceptor ionization. The minority-carrier (electron) mean free path in this material is expected to be on the order of 100 μm, a significant fraction of the sample thickness. Therefore, it seems likely that the observed current transients are due to minority carriers which have been promoted to the conduction band across the full width of the band gap.

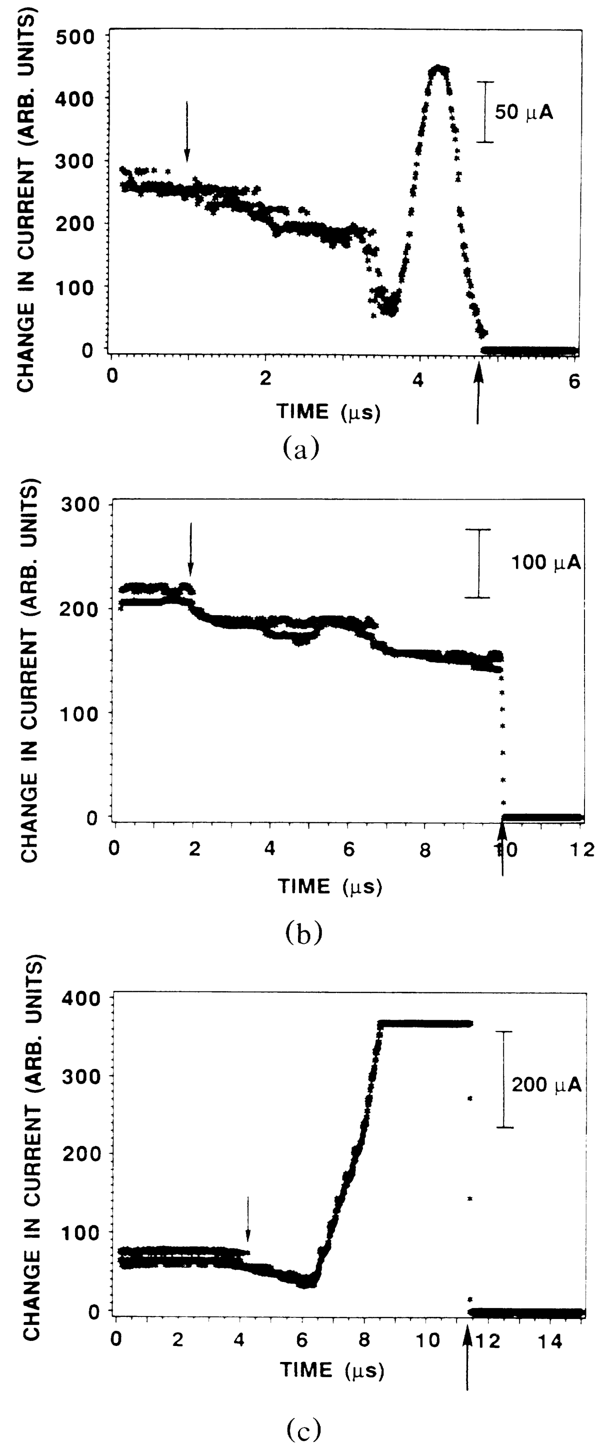

FIG. 2. Fracture-induced current changes observed from (a) a strong specimen loaded in tension, (b) a weak specimen loaded in torsion, and (c) a strong specimen loaded in torsion. The fracture of (a) was performed in a cold, dry nitrogen atmosphere, while the fractures of (b) and (c) were performed in air at room temperature. Arrows mark times of crack initiation and completion.

The excitation mechanism is not clear at this time, but may be electronic, thermal, or chemical in character.

Electronic excitations resulting in charge-carrier production would most likely be associated with localized states of energy greater than or equal to that of the conduction band. Localization reduces the probability of recombination with valence-band holes and thus increases the probability of transitions to the conduction band. The relatively low acceptor concentration in the material used also limits the recombination rate. The states involved in the excitation would probably be associated with surface defects or other localized phenomena.

As Si atoms are drawn away from each other in an advancing crack tip, the decreasing wave-function overlap across the crack may result in localized states. Anderson localization is expected to result from variations in crack width and from mismatch across the crack due to shear displacements. Decreasing wave-function overlap is generally associated with increasing electron energy. If the energies of these localized states approach that of the conduction band, transitions to the conduction band via tunneling would be possible, creating minority carriers. These transitions may be further facilitated by shifts in the conduction-band energy due to high stress fields near the crack tip.

Lemke and Haneman have identified localized states which they associate with wave-function overlap across narrow indentation cracks in Si.[3] Their electron-spin resonance measurements indicate the presence of about 10^{14} spins/cm^2 of crack area. In contrast, well cleaved surfaces show very low spin densities. The high density of paramagnetic states suggests that "normal" surface relaxation is hindered while the crack width is less than about 0.5 nm. In crack propagation, particularly involving mixed fracture modes where crack opening displacements immediately behind the crack tip are small, a similar hindrance may increase the probability of high-energy excitations.

Thermal generation of charge carriers during fracture could also explain the transients. Thermal generation of electron-hole pairs by excitation across the band gap would require temperatures in excess of 700 K to produce the observed current transients, if we assume that 1 nm on each side of the crack tip was heated during fracture. This heating could be the result of irreversible processes in the region of the crack tip. Although the fracture of Si is generally not associated with macroscopic plastic deformation,[4] surface relaxation behind the crack tip may yield significant energies. The energy of the relaxed surface is about 0.36 eV per surface atom lower than that of the ideal, truncated bulk.[5] Some of this energy may be available for surface heating, as seems to be the case for various glasses. Rough measurements of the temperature rise during the fracture of glass and quartz have yielded values in excess of 2000 K.[6] The intensity and duration of the thermal pulse is limited by conductive cooling. The high thermal diffusivity of Si relative to glass suggests that the temperature rise in Si is much less than in glasses. However, rapid crack growth would be associated with rapid heating and higher final temperatures, and thus higher carrier concentrations.

Other energetic processes occur on fracture surfaces, including the production of defects such as vacancies and adatoms.[7] The density of such defects is expected to be a strong function of crack velocity and fracture mode. Recombination reactions involving these species could lead to the creation of charge carriers, similar to the creation of free electrons during chemisorption of reactive gases on some surfaces.[8]

We are currently exploring several unresolved issues concerning the production of charge carriers during fracture. For instance, the crack tip experienced significant shear stresses in each of the fracture modes employed in this work. Thus the influence of fracture mode is not clearly demonstrated, although it appears that shear stresses are important. The effects of crack velocity and microcracking remain to be quantified. Carrier generation is also expected to be affected by the electronic properties, e.g., band gap, of the fractured material.

We have demonstrated that a fundamental electronic excitation, the production of free carriers in a semiconductor, can accompany fracture under certain conditions. Free-carrier generation, being a lower-energy process than the previously mentioned electron emission, may serve as a probe of lower-energy electronic processes induced by deformation and fracture. Such measurements may provide new insight into the process of dynamic crack growth in semiconducting materials.

The authors wish to thank Richard Hoaglund, Washington State University, for helpful discussions, and S.E.H. America, Inc., for providing the Si wafers. This work was supported by the Ceramics and Electronic Materials Division of the National Science Foundation under Grant No. DMR 8601281 and the Office of Naval Research, Contract No. N00014-87-K-0514.

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