Voltage Generation on Cleavage of Silicon

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Voltage pulses up to 0.39 V are generated on cleaving Si wafers in air or vacuum. Current pulses up to 5 mA are also generated between contacts on either side of the crack. The phenomena are explained in terms of dipole generation due to loss of centrosymmetric properties about a crack.

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We have found that significant voltage pulses are generated across the developing crack during cleavage of silicon single crystal wafers. The voltages can be as high as 0.39 V. There are also large current pulses, up to 5 mA, across the crack. The existence of such voltages, and their magnitude, is initially surprising since silicon, being a centrosymmetric cubic crystal, cannot generate piezovoltages, i.e., the high stresses associated with the initiation of cleavage should not cause any voltages. There is known to exist a piezoresistance effect, i.e., a change in specimen resistance as a function of stress [1,2]. This is referred to further below, but the effect does not appear to be directly implicated. Current bursts have been reported parallel to the crack [3], but they would not account for the present results across the crack, although they may be related. We comment on their significance below. An explanation of the generated voltage is given in terms of the formation of dipoles between the surfaces. It is shown by computations that these can occur.

The techniques of cleavage were similar to those described in detail previously [4–7] and involved the bending of a 0.5 mm thick Si wafer (n type, 1–10 Ω cm) over a sharp edge, either suddenly downward with a "paddle cleaver" or gently upward with a "block cleaver," illustrated in Fig. 1(a). The specimens were mostly 3 to 4 cm long, and 5 to 15 mm wide. They were provided with Ohmic contacts at each end prepared by diffusing previously evaporated Al in a vacuum furnace.

Experiments were carried out in both vacuum and air, but no consistent differences were noted. Great pains were taken to eliminate possible spurious effects. To reduce as far as possible any circuit effects, the initial amplifiers used were removed, and the voltages were recorded directly on a digital storage adapter (Thurlby DSA 524). Many dummy experiments, including ones where the low impedance across a high impedance voltmeter was suddenly increased, were carried out. These gave negligible effects. Deliberately induced vibrational shocks also gave negligible effects. We could not find a false origin for the voltage or current bursts on cleavage.

The simplest circuit for detecting time-resolved voltages was that shown in Fig. 1(a), involving a DSA connected across two electrical contacts on the specimen, one on either side of the crack. Figure 1(b) shows the circuit for measurement of current. Care was taken to avoid parallel capacitative impedances, due to the fast onset times of the signal. Therefore, the specimen was mounted between 1 mm thick glass slides. The cleaving force was also applied through a similar piece of glass. The assembly was clamped between Al blocks, and checks were made that no spurious voltages were generated from any portion of the assembly. Confirmation of reliability of this aspect was the occasional finding from some cracks, of voltages that were very small, of order of tens of mV, indicating that voltage sources other than the specimen were not present.

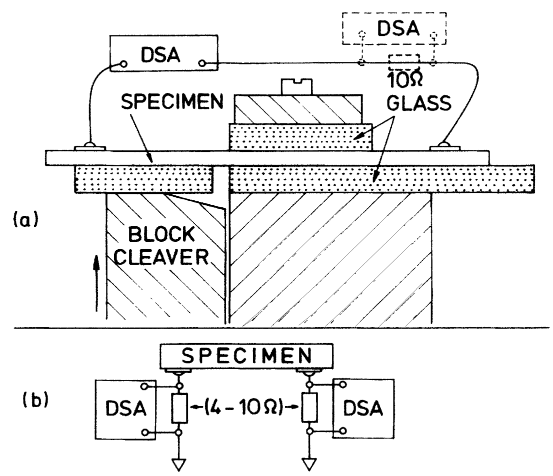

FIG. 1. (a) Schematic diagram of cleavage arrangement using "block" cleaver and circuit for voltage pulse measurement. A low-value series resistor was sometimes inserted for simultaneous current measurements. (b) Circuit used for current pulse measurement.

Voltages were often of magnitude 0.3 to 0.4 V. An example is shown in Fig. 2. The upper curve (a) shows how the signal is lengthened if the glass packing is not used to reduce capacitances. The lower curve (b) shows an example of two cracks occurring, a not infrequent occurrence. The integrated charge during the voltage pulse was of order 10^{-9} C. This number corresponds to that for a charge of about 1 electron in 2×10^4 atomic sites on a cleaved surface.

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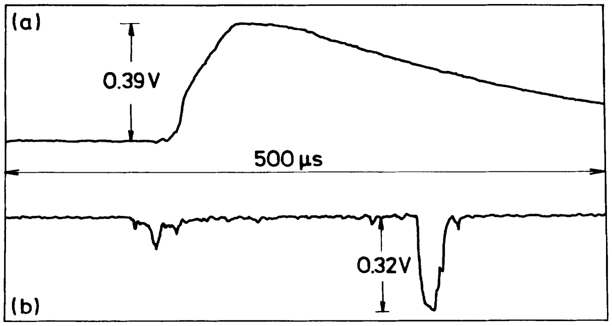

FIG. 2. (a) Graph of voltage versus time after cleavage of Si wafer, 33 mm long × 13 mm wide × 0.5 mm thick, in air. Glass spacers not used. (b) Voltage pulses from specimen in air where two cracks occurred. Glass spacers used.

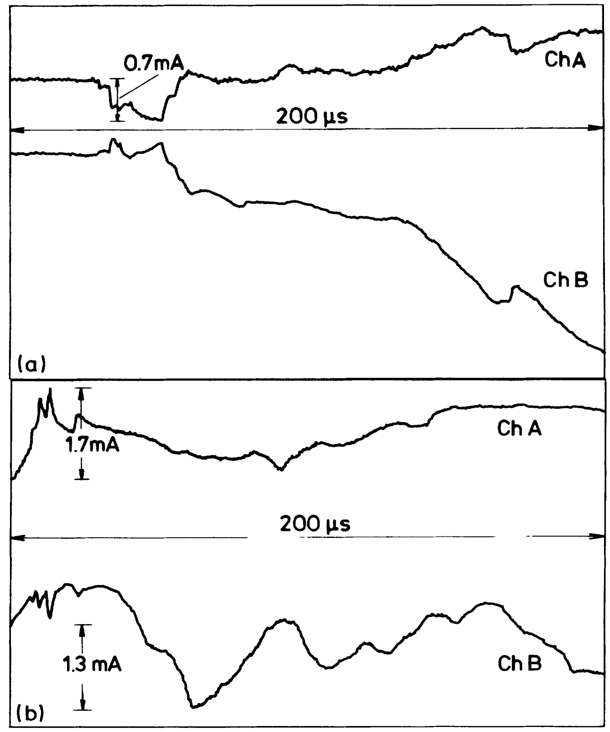

FIG. 3. (a) Current pulses from specimen cleaved (in air) showing (nearly) equal and opposite currents to ground from each cleaved side of specimen. (b) Current pulses from specimen cleaved (in vacuum of 10^{-4} torr) showing almost no correspondence between currents to ground from each cleaved side of specimen.

In order to measure the maximum currents that could flow across the crack during cleavage, a low impedance circuit, as shown in Fig. 1(b), was mostly used. The current was determined from the time-resolved voltage, measured with a DSA, appearing across a 4 or 10 Ω resistor placed between ground and each contact on either end of the wafer.

These current data were also of great interest. One would expect that any temporary current flowing from one broken piece of specimen to ground would be equal and opposite to that flowing from the other piece to ground, in order for charge to be conserved. In some instances of the over 30 experiments this occurred, as shown in Fig. 3(a), but in other cases the currents after the first one or few microseconds appeared unrelated as to integrated charge, to sign, and to time variation. An example is shown in Fig. 3(b).

We first discuss the phenomena of the currents. As mentioned, it had previously been found [3] that short bursts of current, sometimes of up to nearly 1 mA, flowed in silicon wafers similar to ours during cleavage. These currents were measured between contacts on the front and back of a specimen, i.e., they flowed within each cleaving piece in a direction roughly parallel to the crack and not across it, as in our measurements. The bursts were shorter, usually several microseconds in duration, with magnitudes sometimes up to nearly 1 mA. In our measurements, the current flows initially from one side of the crack to the other and is clearly related to the appearance of a voltage across the crack. Magnitudes were mostly several mA and up to 5 mA.

The currents flowing parallel to the crack are presumably due to electrons having gained energy from the bond rupture process. This energy gives rise to various phenomena, including even delayed atom emission in the case of Ge [8], and various luminescence signals in the cases of Si, Ge, GeSi alloys, GaAs, and InP [4–7]. Whereas the currents parallel to the crack flowed for only a few microseconds, related to the crack times, we have found in our experiments that currents flowing from the separating pieces can survive for many tens of microseconds so that the individual pieces are still sending carriers to ground for such times after complete scission has occurred.

The relatively long times can be explained as follows. There are surface states on the surface, both when it is clean for a short time if cleaved in vacuum and also when it is contaminated if cleaved in air. The upper levels of these state distributions, namely above the Fermi level, can become partly occupied due to the cleavage excitation of electrons. Similarly, lower levels can have excess holes. These carriers are localized at the surface; hence such temporarily occupied states act as carrier traps, with various time constants to empty, depending on whether the states occur on flat terraces, or on step edges or other irregularities such as vacancies and crevices [9–15]. If there are no net extra carriers, excited or otherwise, in a specimen then this effect will not account for a current flow after cleavage is complete. However, if there has been a net transfer of charge between two cleaved surfaces, and/or a loss of carriers by electron emission to surroundings, then the imbalance of charge will cause currents to flow, with time constants determined by the kind of surface traps and the emission processes. Therefore, the current can show both positive and negative signs as the surface traps discharge. It has been reported that electrons are emitted from cleaved Si for up to 2 ms after cleavage [16].

One might in principle expect a difference between vacuum and air cleavage, as the surface states would be quite different. However, from a number of trials in vacuum and air, we could not establish any consistent differences. The spread of results in each set of experiments was too great, and this is related to the difficulty of producing cleavages that are similar on the atomic scale, despite similar general appearance. It has been shown by various studies that cleavage surfaces of dimensions 100 μm and more are topographically very inhomogeneous [10–15].

We now discuss the very interesting finding of substantial voltages occurring between the cleaved pieces. As mentioned, the Si lattice is centrosymmetric and cannot develop piezovoltages, i.e., as a result of stress. An effect would, however, be possible if the inversion symmetry were destroyed. This happens to the region of crystal surrounding the leading edge of a crack. Here the lattice on either side of the crack is distorted differently from that just ahead of the crack.

Cleavage occurs along (111) planes. However, there are two such in the diamond structure, the so-called shuffle plane [with single bonds between atoms, orthogonal to the (111) plane] and the glide plane [with three bonds between atoms, at oblique angles to the (111) plane]. It is not known along which planes cleavage progresses [17]. In an infinite undistorted lattice, there is inversion symmetry about a point at the center of a bond in the shuffle plane. For the glide plane, the inversion center is at a point in space between three nearest-neighbor atoms.

As far as cleavage energy is concerned, calculations have shown that shuffle plane cleavage has lower energy but by only about 0.17 eV per surface atom [18–20]. The role of ever-present shear stresses in causing cleavage to occur at glide planes has been calculated and discussed [21].

We have examined the possibility of dipole generation with an *ab initio* quantum chemistry computational package DMOL [22] applied to various Si atom clusters. DMOL calculates variational self-consistent solutions to the local density functional equations, expressed with a numerical atomic orbital basis. As a structure is deformed, the program calculates the new wave functions for each configuration and the electronic and net dipole moments.

No net dipole moment was found when any centrosymmetrically shaped cluster was stretched about the plane containing the center of inversion symmetry, whether that occurred in a shuffle plane or in a glide plane. This is in agreement with the symmetry argument above. For the calculations, the dangling bonds of clusters were terminated with H atoms in the usual way. Clusters used ranged from Si_8H_{18} up to $Si_{42}H_{46}$. Details of the various computations, including the effects of introducing shear, will be given separately, but the key result is that a dipole moment only developed when a crack distortion was introduced into the cluster. An example of a cluster where a crack was introduced into the glide plane is shown in Fig. 4 for $Si_{14}H_{20}$.

It may also be relevant to note that the plateaus on cleaved surfaces are small, with atomically flat planes rarely exceeding about 10 or 20 nm in the smaller dimension [10–15]. Therefore, the finite cluster calculations, in addition to establishing the principle, have some quantitative relation to reality.

For the cluster in Fig. 4, we took a crack on the central glide plane, from one side to the center, having an opening angle of approximately 6°, similar to that taken in the theoretical computations of crack properties by Huang *et al.* 20]. The other side of the cluster was unstretched. The dipole moment orthogonal to the cleavage plane, for this stretch at one edge of the cluster of 0.0413 nm, was computed by the program as 0.0025 D. For clusters symmetric about a shuffle plane, similar results were obtained. Thus for a cluster $Si_{26}H_{30}$, a crack with the same angle, penetrating halfway across the cluster gave a dipole moment of 0.007 28 D. Because the area is roughly 3 times that of the cluster of Fig. 4, the moment per unit area is similar. From these numbers, a rough comparison with the experiment is possible.

Thus from the experimental figure given above, the transferred integrated charge over an area of approximately 0.05 cm^2 was generally a small integer times 10^{-9} C. From the calculated dipole moment, taking an effective dipole length of about 0.04 nm for the first example above, one obtains a charge of 2.1×10^{-22} C over an area of unit mesh of 0.1275 nm^2. This gives 8.2×10^{-9} C over 0.05 cm^2. The agreement with the experimental value above is not unreasonable, considering

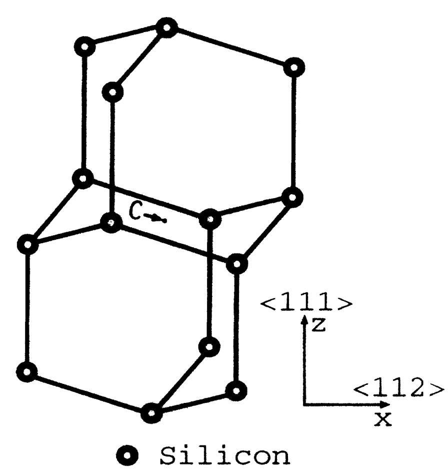

FIG. 4. Atomic model of Si atom cluster having center of inversion symmetry C in a glide plane. All dangling bonds were closed with hydrogen.

the various uncertainties, such as dipole length and small size of cluster used in the computation.

It is, of course, possible to propose other reasons for the appearance of a voltage, such as some kind of unspecified electrostatic effect, but pending establishment of any such reason, the dipole effect appears to be at least a contributory possibility.

In conclusion, we have found that significant voltages and currents appear across cleavages in thin Si wafers. One explanation is the development of dipole moments due to breaking of inversion symmetry about the (moving) crack edge.

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