Cleavage Luminescence from Silicon

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(Received 26 July 1990; revised manuscript received 16 October 1990)

We report direct detection of light emission from single-crystal silicon cleaved in vacuum. The emission occurs in at least two wavelength regions, one above 1 eV energy (A) and the other between 0.25 and 0.36 eV (B). Intensities for about 0.1-cm^2 cleaved areas are in the region of 10^{12} photons in region A and 10^{11} photons in region B. The B radiation is of significantly longer duration than the A radiation. Some of the latter can be explained by radiative bulk band recombination, and the B radiation by radiative surface band recombination. The duration of the B radiation shows that the surface-state gap is indirect.

PACS numbers: 78.60.Mq, 73.20.At

We report direct detection of light emission from cleavage of single-crystal silicon. The light is of at least two wavelength groups in the infrared. A previous account[1] mentioned visible-light emission from silicon and other materials subjected to sandblasting but this appears to be unrelated to true cleavage luminescence which is extremely weak. This work appears to provide the first report and measurement of such.

The motivation for the work was to obtain information about the structure of the cleaved surface of silicon. Neither low-energy electron diffraction[2] nor scanning tunneling microscopy[3] can distinguish between the Pandey π-bonded chain reconstruction[4] or the three-bond-scission[5,6] (TBS) model, both of which feature surface-atom chains along $[\bar{1}10]$ directions that are consistent with optical and ion scattering data.[5] The models differ significantly, however, in subsurface structure and in the manner in which they arise.[5]

Upon cleavage, the surface-atom reconstructions that are known to occur from the ideal structure will involve changes in bond energies. Such changes may be radiative. The bulk band structure of silicon features an indirect band gap so that radiative transitions are much weaker and slower than from direct-gap materials. Nevertheless, they have been observed both in forward-biased *pn* junctions[7] and in reverse-biased junctions.[8] In the latter, microplasmas and high-energy radiation are involved, but in the former, which appears to be the more relevant case, band-gap radiation, less exciton and phonon energies, has been detected.

In the case of the cleaved surface, there may be radiation during the reconstruction process and subsequently when the surface band structure is established. A search for any such was undertaken. The radiation is expected to be in the range up to the bond-breaking energy which is about 2.1 eV, or half the heat of sublimation of crystalline silicon. No photon detector has its maximum sensitivity over the entire range so the first experiments were conducted with a liquid-nitrogen-cooled InSb photoconductive detector of peak detectivity about 10^{11} cm $Hz^{1/2} W^{-1}$, with peak sensitivity at about 0.3 eV and low-energy cutoff through the sapphire window at about 0.21 eV. Subsequently, 1-cm^2 Si photovoltaic detectors of peak detectivity about 10^{14} cm $Hz^{1/2} W^{-1}$ and low-energy cutoff at about 1 eV were also used, and later a 4-mm^2 mercury cadmium telluride (MCT) photoconductive detector with no window, peak detectivity of 10^{11} cm $Hz^{1/2} W^{-1}$ at 0.19 eV, and 50% sensitivity at approximately 0.38 and 0.19 eV. Detector decay times were less than 1 and 15 ms for the Si and MCT detectors, respectively.

Using a low-noise preamplifier and subsequent wide-band amplifier, care had to be exercised to avoid triggering of the signal analyzer by spurious signals due to mechanical vibrations and electrical pickup. The first experiments were conducted with the detector mounted close to a Si crystal subjected to continuous abrasion (mini cleavages), but after spurious sources were eliminated, no signal could be found. Subsequent trials were with n-type, 300-Ω cm silicon disks of (100) orientation, 0.52 mm thick and 19 mm in diameter. On cleaving these directly in air under the 4-mm^2 area InSb detector, signals were eventually found, of various intensities. There were some indications of stronger signals from

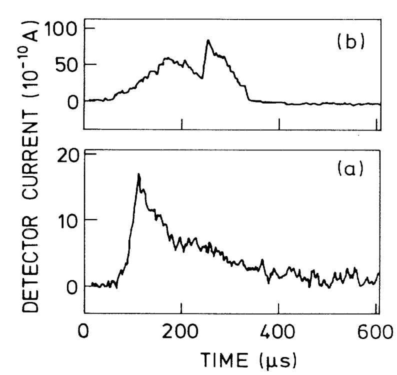

FIG. 1. Current pulse vs time from Si cleaved in vacuum received on (a) the Si detector and (b) the InSb detector.

noncrystallographic breaks, where more force had to be applied, than from cleavages directed along the preferred (111) planes. To reduce uncertainties, only the latter were carried out, and to avoid effects of oxidation, subsequent experiments were conducted in vacuum of about 10^{-5} torr, ample to avoid contamination in 1 ms.

Typical luminescence results from the InSb detector are shown in Fig. 1(b) and from the Si detector in Figs. 1(a) and 2. The response from the InSb detector could be greatly weakened if a glass slide was interposed (low-energy cutoff at about 0.48 eV). Therefore the emission energies are in the range of about 0.2 to 0.5 eV. There was some variability in signal duration, and it was of interest to determine if there was a relation between the signals received by the two kinds of detector. Eventually we were able to detect signals from the one cleave on both the (liquid-nitrogen-cooled) MCT detector and the Si detector. These were from 20-mm-long samples of 0.365 mm thickness. Typical data are shown in Fig. 3. Note the simultaneous onset. Either signal could be used as trigger. When a 3.4–5-μm filter was placed over the MCT detector, a signal was still detectable, but was stopped by a glass slide. This shows the radiation was in the range 0.25–0.36 eV. It was considerably longer in duration than that recorded by the silicon detector, both in Fig. 3 and in the other trials.

In considering the results one must take into account the configuration during cleavage. If the surface cracks across its whole length simultaneously, the downward motion of the crack could be completed in as little as a few microseconds, according to measurements of cleavage on similar specimens.[9] In that period the cleaver end, under a force of about 10 N, has hardly moved. In 1 ms it has moved downward by about 5 μm. Therefore there is only a very narrow gap of order microns between the two surfaces. For the 0.25 to 0.36 eV (B) radiation, the absorption coefficient of Si is small so that much of it will penetrate the bulk crystal pieces to reach the InSb and MCT detectors. However, the radiation to the Si detector will be strongly absorbed in thicknesses greater than about 0.1 mm, and only the narrow solid angle emerging from the crevice could reach the detector directly.

Taking into account these factors and the reduced Si detector sensitivity for threshold radiation, we estimate the total number of emitted photons as in the region of 5×10^{12} for the silicon detector (A) band-gap radiation and 10^{11} for the B radiation. The signal durations for the A radiation were 0.22 to near 1 ms and for the B radiation were 0.28 to near 2 ms.

We now interpret the data. There are some 10^{14} surface atoms on the two cleavage surfaces of about 0.1-cm^2 area each. Therefore the radiation, if originating directly from electron rearrangements at the surface, represents only a small fraction of the decay events. There is however, a more general description possible. It was found by Langford, Doering, and Dickinson[9] that a pulse of current is induced in silicon by the cleavage process; i.e., electrons are excited into the conduction band by some mechanism associated with the energy expended during the bond breaking. These represented 10^9–10^{10} free carriers per cm^2, but presumably were concentrated initially around the crack sides. They are sufficient to account for at least some of the radiation and, in particu-

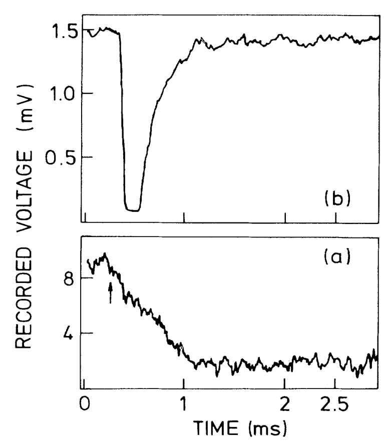

FIG. 2. Voltage detected by Si detectors from vacuum-cleaved Si using (a) a high-impedance input and (b) a shunt resistor across the input. In (b) a particularly large signal was obtained, which saturated the detector. In (a) the signal detection mode (the most sensitive) results in a changing base line while light is being received and a very slow recovery thereafter. The trigger time is shown with an arrow.

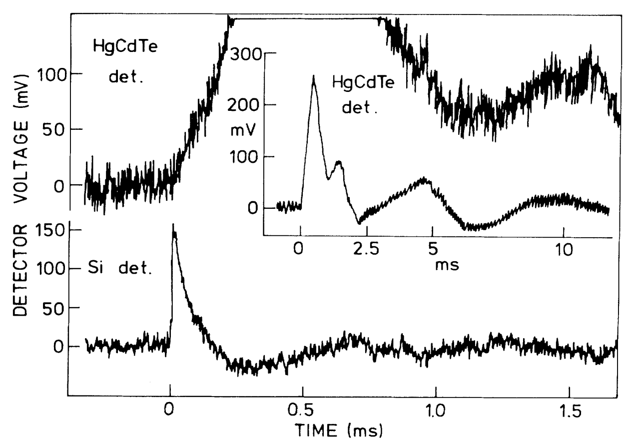

FIG. 3. Voltages detected simultaneously by the Si detector and a HgCdTe detector from cleavage of Si. Inset: A different (longer) time scale. The slow oscillatory behavior of the signals after the initial peak is due to mechanical vibrations from the cleavage shock, affecting the detectors. Use of longer specimens, and the need to mount both detectors as close as possible to the cleavage, caused lesser vibration isolation than in Fig. 2. Mounting of either detector singly could be performed to give the displayed peaks without oscillations. For the Si detector, the voltage is across a feedback resistor.

lar, explain the otherwise surprisingly long duration of the emission, of order 1 ms. Since the bulk gap of Si is indirect, minority-carrier lifetimes are long, around 2 ms. Hence the radiative recombination of excited electrons is expected to have a similar duration, accounting for the observed temporal extent of the A emission. It should be noted that cracks are variable and can start at one or more points. For crack velocities of around 100 m/s, a crack traveling sideways across the 14–25-mm-wide slices could take hundreds of microseconds to complete. In principle, one could argue that the whole time for the A radiation might be due to the sideways crack progression and that the radiation is in fact very prompt. However, this seems very unlikely because some of the total times appear too long for crack progression. Emission times of hundreds of microseconds for the indirect radiation are reasonable for Si. The variations in observed times are believed to be due to variations in the crack types. In any case the key point is that the B radiation is of significantly longer duration than the A radiation.

The excited electrons would also occupy surface states. It is known from direct measurements of surface reflectivity[10] and surface absorption[11] on cleaved Si surfaces with polarized light that there is a band gap between the surface states with a peak optical-absorption coefficient at approximately 0.45 eV. Hence the observed emission B in the range 0.25–0.36 eV could well be due to transitions across the surface-state gap. Since the duration of B is hundreds of microseconds, we infer that the radiative recombination must be indirect. Inspection of surface-band-structure calculations shows that indeed the minimum band gap turns out to be indirect. A calculation for the Pandey model based on the pseudopotential approximation within the local-density-functional formalism[12] gave a valence-band peaking at the K' point in the Brillouin zone and a conduction-band minimum just off the J point towards K', as shown in Fig. 4. The J-K' ($[\bar{2}11]$) region is the one excited by light polarized along the surface chains (of either surface model), namely, $[0\bar{1}1]$, due to optical selection rules determined by the reflection symmetry through the $(0\bar{1}1)$ plane.[13] In this calculation, the indirect gap is only about 0.05 eV and the minimum direct gap is 0.15 eV. In another calculation[14] using the self-consistent pseudopotential method, the surface-state band edges occur at the same points as before, but the indirect gap is about 0.16 eV, and the minimum direct gap about 0.21 eV. Both these calculations were for optimized versions of the Pandey model. Although neither gives a good fit to the experimental optical-absorption data[10,11] showing maximum around 0.45 eV, it is known that local-density theory is usually unable to predict correct excited-state energies.[15] The calculations along Γ-J ($[0\bar{1}1]$) did fit the angle-resolved photoemission data of Uhrberg *et al.*[16] for the filled valence surface band. The size of the

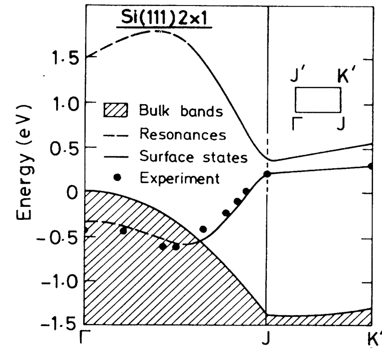

FIG. 4. Calculated (Ref. 12) dispersion of surface states for the optimized Pandey model. Experimental points (Ref. 15) have been shifted by 0.3 eV to match theory. Hatched area, bulk bands. Dashed lines, surface resonances. Solid lines, surface states. Inset: The two-dimensional Brillouin zone.

surface band gap is very sensitive to chain buckling,[13] so that apparently the buckling taken by minimizing the energy does not agree with that needed for optical data on the Pandey model. It may also be noted that for the two calculations, the absorption peak width should be about 0.1 eV, which is much less than the experimental one[10] of 0.3 eV at $\frac{1}{5}$ maximum, even allowing for instrument broadening. In the case of the TBS model, a surface-state calculation has not been performed; however, the surface possesses π-bonded chains along $[0\bar{1}1]$ and the dispersion along Γ-J is expected to be similar. For example, a calculation for an isolated such chain[17] gave 0.6-eV dispersion (compared with about 0.8 eV found[16]) along Γ-J.

Our B-emission data can thus be interpreted as arising, at least in part, from conduction-band electrons dropping to the surface-state conduction-band minimum and there making transitions to the surface-state valence band. The lowest-energy transitions are indirect, requiring phonons of almost the entire zone-width momentum, and thus accounting for the long observed durations.

The data thus support the feature of the surface-state theories in that there is an indirect gap. This would not be detected by surface-state optical absorption since it would be too weak. The magnitude of 0.25–0.36 eV is somewhat larger than that calculated for the Pandey model but the accuracy of the gap calculations is limited. We stress that these interpretations may not account for all the emission. We also mention that there are other discrepancies between the calculated bands and data. Thus the calculated band dispersion in the Γ-J' direction was 0.35 eV (Ref. 12) or 0.32 eV (Ref. 14) downward, compared with experimental dispersions[16,18] of less than 0.1 eV. Hence there is room for further study of these matters and it would be of interest to test the various features on the TBS model.

In conclusion, we have detected radiative emission from cleavage of silicon in vacuum. The radiation is in at least two wavelength regions, with durations of hundreds of microseconds and low intensities. It can be accounted for, at least in part, by radiative indirect transitions across the bulk band gap and across the surface-state gap.

This work was supported by the Australian Research Council.

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