# Positive Ion and Electron Emission from Cleaved Si and Ge

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Cleavage of Si and Ge wafers in a vacuum produces spontaneous positive ion and electron emission with durations ranging from tens of microseconds up to 1.8 ms. The onset of emission is synchronous with the start of cleavage. The electron emission is explained by an Auger process energized by electron capture by a positive ion. The ion emission is about $10^7$ cm$^{-2}$ and is due to a peak in the surface atom vibrational energy distribution, showing that considerable energy is available for forming various surface structures. [S0031-9007(98)05848-7]

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The act of cleavage in Si is involved in almost all semiconductor device fabrication. It is known from various experiments that cleavage causes an excited electron distribution, observed by both generation of electrical currents [1,2] and of recombination radiation at energies up to 2.7 eV [3]. In the case of Ge, atom emission was also reported, but not until several milliseconds after cleavage was completed, and was ascribed to a mobile dislocation mechanism [4]. There has also been a report of electron emission from cleaved Si [5].

The question of whether cleavage causes the emission of atoms, ions, and electrons is important in evaluating the magnitude of the structural agitation that occurs by the act of bond rupture, especially in brittle semiconductors where new surface structures are formed. In this paper we have detected the emission of positive ions from both cleaved Si and Ge, and shown that it is synchronized with the commencement of cleavage. We have also confirmed, using enhanced temporal resolution of 10 ns rather than the 0.1 ms bin width used previously [5], that electron emission occurs from Si, and we now report the detection of electron emission from cleaved Ge. In addition, electron emission from Si has been measured over the temperature range 20 to 520 °C. The electron emissions are also found to be precisely synchronized with the onset of cleavage.

Three different types of Si wafers were used in these experiments: 0.7–1.1 Ω cm *n*-type wafers, 0.5 mm thick with (100) surface orientation; 8–10 Ω cm *n*-type wafers, 0.4 mm thick with (100) orientation; and heavily doped *n*-type wafers, 0.005–0.02 Ω cm, (111), 0.6 mm thick. Two types of Ge wafers were used: *n*-type, 0.16 Ω cm, (111), 0.5 mm thick; and undoped, >30 Ω cm (100), 0.35 mm thick. All of the samples had dimensions of approximately 1 cm × 2 cm.

The experiments were performed in a vacuum of $10^{-9}$ Torr, although a few cleavages were carried out at pressures of up to $10^{-7}$ Torr. Because of the ms duration of the signals, these vacua were ample. The samples were clamped tightly between stainless steel plates, and were cleaved by bending with a lever attached to the end of a rotary feedthrough, as shown in Fig. 1. Several samples were also cleaved under tensile stress; one end of the sample was affixed to a post with epoxy glue and the other end to a linear motion feedthrough, which could be screwed out so as to slowly pull on the sample.

Some of the cleavages were performed at temperatures up to 520 °C. For heating, a current of several amperes was passed through the samples, and was switched off a few seconds prior to cleavage. The samples were clamped between steel plates and insulated from the sample holder by sheets of Macor, and were cleaved by bending. The 8–10 Ω cm Si wafers were used for these experiments to ensure sufficient power dissipation in the samples. The temperature of the samples was monitored using two pyrometers, one (Ircon MR-6015-03C) covering the range 120–300 °C and another (Ircon MR-6015-06C) covering the range 250–600 °C. The pyrometers were focused close to the crack, and their emissivities calibrated by comparison with values from a carefully placed thermocouple.

For a few of the samples, near-Ohmic contacts were made by attaching thin wires with silver paint to the ends of the sample. A small current of no more than 50 μA was passed through the sample to determine the instant of cleavage by the rise in resistance [6], and also to trigger an

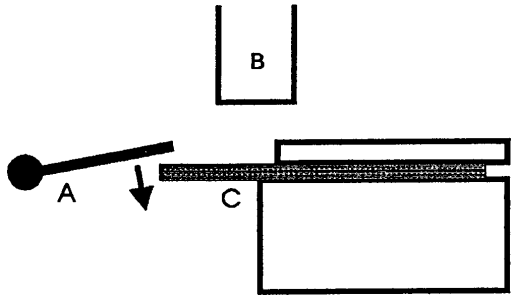


FIG. 1. Schematic diagram of cleavage apparatus. *A*: cleaving lever, actuated by rotary motion. *B*: electron multiplier. *C*: Si wafer protruding from stainless steel block clamp. Cleavage occurs close to the edge of the clamp.

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oscilloscope. The voltage across the sample was generally less than 50 mV.

An electron multiplier (ETP AF150H) was positioned 2 cm above the sample. It was operated at 1.8 kV. The input was biased at $+200$ V for detection of electrons and $-2400$ V for positive ions. The multiplier signal was amplified by a high bandwidth amplifier (Stanford SR445) and captured with a digital storage oscilloscope (LeCroy LS140) with 50 $\Omega$ across the input in order to match the amplifier output impedance. The time base on the oscilloscope was set to 0.02 ms/division, with a corresponding resolution of 10 ns, although some signals were acquired on a longer time base of 0.2 ms/division. For the high temperature experiments a pulse counter (Stanford SR430) was used to capture the signals with a long time base of 5.3 s, since triggering could not be performed as with the oscilloscope. The resolution in this case was 164 $\mu$s.

To check that the signal was due to the emission of ions or electrons and not small fragments, several trials were performed without a bias on the input dynode of the multiplier, since the electric field would have little influence on the motion of fragments. There was no signal in these cases. Negative ion emission is not expected to occur since negative Si and Ge ions are unstable.

A typical ion emission signal due to cleavage of Ge is shown in Fig. 2, along with the current through the sample. At 0 $\mu$s, the current through the sample begins to drop, indicating the moment at which cleavage begins. After 25 $\mu$s the current is zero, indicating the completion of cleavage. Ion emission is most intense during cleavage, and, thereafter, is followed by sporadic bursts of single or multiple ions. The multiplier was operated at high gain so that current pulses are clearly visible.

Figure 3(a) is a plot of the number of ions and electrons emitted from cleaved Ge versus signal duration for all of the room temperature experiments performed in which the sample was cleaved by bending. Figure 3(b) is the corresponding graph for Si. The variations in intensity and duration could be due to variations in the force required to cleave the sample. There was no correlation between signal intensity or duration with the magnitude of the current applied through the samples or the voltage across the samples, both of which were small. The signal was also independent of the degree of high vacuum in the vacuum chamber and the dopant concentration. Table I is a summary of the experimental results, showing the maximum intensities and durations of the signals for charged particle emission for Si and Ge, cleaved at room temperature. It includes the cleavage luminescence data of Ref. [7] for comparison. This table presents raw data; the actual emission intensities are much greater than observed when the geometry of the crack is considered. Following cleavage, the two halves of the sample move apart by about 5 $\mu$m in 1 ms, assuming that the cleaver applies a force of 10 N. Since the sample is 500 $\mu$m thick, this corresponds to an opening angle of 0.01 rad. Therefore, the actual total emission is about $0.5 \times 10^6$ ions or electrons.

In order to check the possibility that the observed emissions are due to the scraping together of the two portions of a cleaved wafer, three Si wafers were cleaved in tension so that they could not scrape. The signals obtained had durations of 20 $\mu$s, 240 $\mu$s, and 1.8 ms, within the range of results for the bending experiments. Scraping, therefore, cannot account for the results.

A graph of electron emission duration versus temperature for cleavage of Si is shown in Fig. 4. The data is rather scattered, showing no general trend. Only two

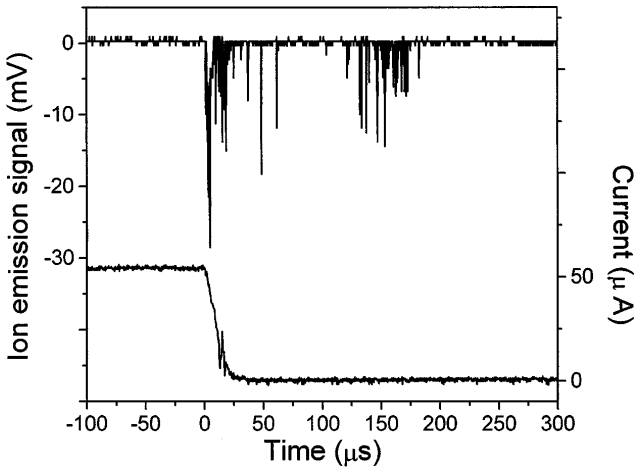


FIG. 2. Upper: typical ion emission signal from Ge. Lower: current through specimen. Onset of drop shows onset of cleavage. The right-hand scale refers to the lower diagram.

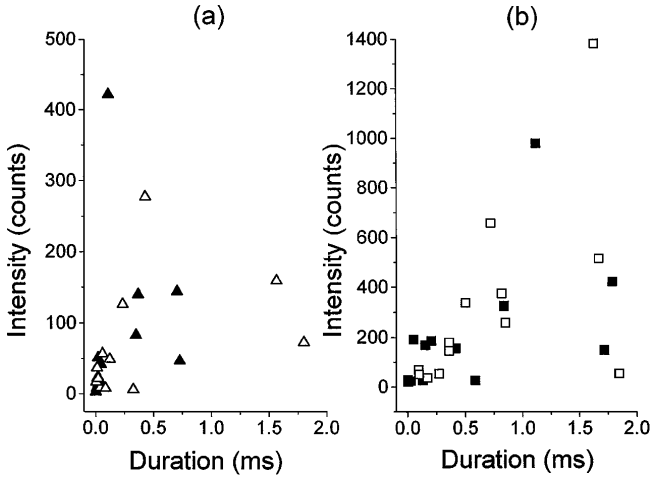


FIG. 3. Graph of the summed signal intensity, or total number of electrons or ions emitted, versus the signal duration for room temperature cleavages using the bending method to cleave the specimens. (a) Ion emission (closed triangle) and electron emission (open triangle) from Ge. (b) Ion emission (closed square) and electron emission (open square) from Si.

TABLE I. Maximum intensities and durations of fracto-emission signals from Si and Ge at room temperature. Cleavage was performed by bending the specimens in each case.

| | Si | | Ge | |
|---|---|---|---|---|
| Emission | Duration ($\mu$s) | Intensity (counts) | Duration ($\mu$s) | Intensity (counts) |
| Electrons | 1845 | 1377 | 1803 | 276 |
| Positive ions | 1785 | 979 | 727 | 422 |
| Photons[a] | $\sim$2000[b] | $\sim 10^8$ | 500 | $\sim 10^8$ |

[a] From Ref. [7]. The Si signal was detected in the wavelength range 1.1–2.7 eV and the Ge signal in the range 0.73–1.46 eV.
[b] The duration of 300 $\mu$s quoted in Ref. [7] is the $T_1$ time, defined in Ref. [14]. The actual total duration is up to 2000 $\mu$s.

signals were longer than 2 ms, and so we conclude that temperature has no marked effect on electron emission durations.

We now consider mechanisms for ion emission. An atom or ion will be emitted only if the bonds between it and surrounding atoms on the surface are broken. Bond enthalpies for Si and Ge are 1.98 and 1.85 eV per bond, respectively [8]. If four bonds are broken, the energy required to remove an atom from the surface is roughly 4 times the bond enthalpy, that is, 7.9 eV for Si and 7.4 eV for Ge. For weakly bonded surface atoms the energy can be less than half this value. Examples of weakly bonded atoms include those at kink sites and on antiphase boundaries, as predicted in Ref. [9] and observed by scanning tunneling microscopy (STM) [10]. We, therefore, presume that it is the partially bonded atoms that are emitted, and further propose that the energy required for emission is available from surface vibrations. Such vibrations are present for milliseconds [11,12], consistent with the observed durations. These

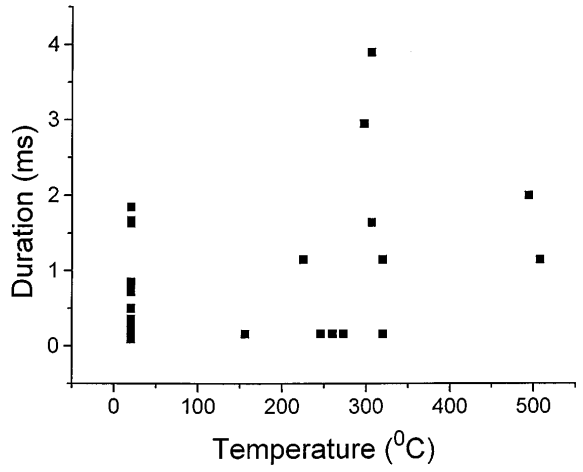


FIG. 4. Graph of the duration of electron emission from Si versus the temperature of the sample. This graph also includes the room temperature data.

long vibrational lifetimes are, as explained in Ref. [12], a consequence of the stretching that occurs throughout the material prior to cleavage. When rupture occurs, strong bulk vibrations, lasting several ms, are excited throughout a large region behind the cleavage plane as the bulk relaxes. Ion emission is also facilitated by cleavage-excited valence band holes at the surface. The density of surface atoms is $\sim 10^{15}$ cm$^{-2}$ and photon emission from Si is up to $10^{12}$ cm$^{-2}$ [7], but since the nonradiative recombination rate is much greater than the radiative recombination rate the number of surface holes must exceed this value by a few orders of magnitude. The presence of a hole will weaken a surface bond, increasing the likelihood of direct ion or atom emission. Ion emission could also be enhanced by energy dissipation due to multiphonon recombination at surface defect sites, as described in Ref. [13]. Phonon coupling to the bulk is inefficient at a defect site, allowing thermal energy to build up at the site until it exceeds the potential barrier for ion or atom emission. This mechanism is viable, since it is known from cleavage luminescence experiments that there is a large nonequilibrium concentration of electrons and holes at the surface following cleavage [3], and it also accounts for the similar durations of ion and photon emission, as given in Table I.

The intensity of the ion emission must depend on the number of surface atoms that have the least bonding to the surface. From analysis of large scale STM images [14], kink sites are not expected to contribute more than 0.1% to the surface layer, and probably much less. Using this figure, the observed ion emission intensity of about $0.5 \times 10^6$ ions from 0.05 cm$^2$, or $10^7$ ions cm$^{-2}$, therefore, corresponds to a maximum of about $10^{-5}$ of the density of such sites. This figure represents the high energy peak in the initial surface atom vibrational energy distribution. In principle, the energy of surface vibrations can be deduced from a knowledge of the maximum energy, provided one knows the statistical distribution function. Using as a trial a Boltzmann distribution, one calculates that most of the surface atoms have an energy of about 1–2 eV, which seems too high, and suggests that the distribution is more strongly peaked than Boltzmann. This may also be because equilibrium has not been achieved. In any case, it is clear that the surface must be in a state of considerable agitation. This is consistent with previous indications of temperature rises on freshly cleaved surfaces [11,12,15], and has implications for the formation of surface reconstructions. There are several alternative structural models for the cleaved Si(111)-(2 $\times$ 1) surface: the modified Pandey model, the triple-bond scission (TBS) model, and reverse-buckled versions of both these models [16]. STM and other experimental techniques have failed to determine unambiguously the model which best describes the surface. Very recent LEED calculations, however, show that a mixture of both models is possible [17]. According to total energy calculations the TBS model is 0.25 eV per surface

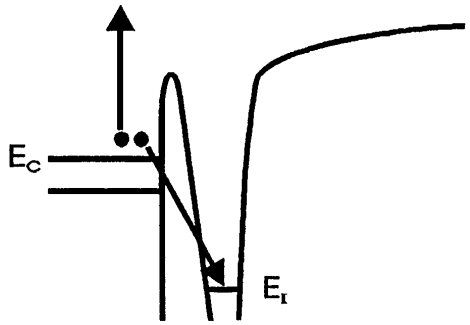


FIG. 5. Illustration of electron emission mechanism. $E_c$ is the minimum conduction band energy level and $E_I$ the energy of the unoccupied state of an emitted ion.

atom higher in energy than the Pandey model [16]. Total energy calculations seek a minimum energy configuration. The present ion emission experiments show that the surface is in a state of energetic disturbance following cleavage, suggesting that there is plenty of energy available for the formation of surface reconstructions other than minimum energy ones.

We now consider mechanisms for electron emission. We first considered a simple interband Auger mechanism. Although it could explain electron emission from Si, using the peak of the excited electron distribution in the conduction band, it was not viable for Ge since the excited electron distribution was insufficient for enough energy to be available to excite an electron over the work function barrier. Therefore, we propose the following mechanism, illustrated in Fig. 5, which is energetically viable. When an ion is emitted, its electronic states will relax to those of a free ion, resulting in unoccupied energy levels at about $-8.15$ eV for Si and $-7.90$ eV for Ge relative to the vacuum level, being the first ionization energies [18]. If an electron in the conduction band tunnels through to the ion's unoccupied state while the ion is still close to the surface, it may transfer its energy to another conduction band electron via an Auger interaction. Such an electron will have sufficient energy to overcome the surface potential barrier, reported as 4.05 eV for Si and 4.0 eV for Ge [18], and some will subsequently be emitted. This mechanism explains the similar duration of the electron and ion emissions, as shown in Fig. 3. Furthermore, a simple calculation confirms that the above mechanism is consistent with the observed temperature data of Fig. 4, which shows little variation of electron emission duration with temperature. Note also that the durations do not depend on the degree of doping, since carrier concentrations at the surface are determined by the cleavage-excited hot electron distribution.

In conclusion, we have detected positive ion and electron emission due to cleavage of both Si and Ge, with durations ranging from tens of microseconds up to 1.8 ms. The onset of emission is synchronous with the act of cleavage. The experiments show that vibrational agitation occurring on a freshly cleaved surface is sufficient to result in the emission of about $10^7$ ions $cm^{-2}$. There is clearly energy available to form various structures other than minimum energy ones. An Auger mechanism coupled with tunneling of a conduction band electron to an emitted ion could explain electron emission from both Si and Ge.

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