Atomic and Molecular Emission Accompanying Fracture of Single-Crystal Ge: A Dislocation-Driven Process

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We present evidence for the emission of atomic Ge and Ge_2 molecules accompanying dynamic fracture at room temperature of single-crystal Ge under flexure loading. The emission follows the completion of crack propagation by several milliseconds and occurs in bursts, typically 1–2 ms in duration. A dislocation-driven mechanism for this emission is presented suggesting that considerable dislocation activity is accompanying failure of these samples.

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The fracture of many materials in vacuum is accompanied by the emission of photons, charged particles, neutral atoms, and molecules,[1-3] collectively known as fracto-emission. In general, most fracto-emission intensities reach their peak *during* the fracture event and thereafter decay. Recent measurements of alkali and alkali-halide neutral emission accompanying the fracture of single-crystal NaCl and LiF show rapid, intense bursts of atomic and molecular emissions that arise *after* fracture, typically delayed 0.5–250 ms from the time of fracture,[1] with little detected neutral-particle emission during fracture. We presented evidence that these emissions are due to the ejection of atoms and molecular clusters accompanying the arrival of rapidly moving dislocations at the fracture surface. These neutral-emission bursts therefore probe the relaxation of metastable plastic deformation associated with fracture in the relatively ductile alkali halides. The presence of plastic deformation during crack growth in *brittle* materials is an open question. If this deformation were metastable rather than strictly irreversible, the apparent absence of fracture-related dislocations on fracture surfaces of more brittle materials would be explained. Single-crystal Ge, which is a covalent, monatomic solid with a diamond lattice, is quite brittle at room temperature. The goals of this particular study are to determine (a) if neutral emission occurs at all from fracture of such a material, and (b) if dislocation activity during and following fracture might explain the observed emission.

Samples of Ge were prepared from portions of a single boule. The samples were cut with a diamond saw to nominal dimensions of $10 \times 4 \times 2$ mm^3 and polished in successive stages; the final stage used 1-μm diamond paste. The samples were cleaned in ethanol, mounted in vacuum systems maintained at pressures below 1×10^{-6} Pa, and loaded to fracture in three-point bend. Samples of various orientation were prepared; however, fractographic characterization showed that fracture generally followed (111) cleavage planes. Generally, no significant differences were observed among samples of different orientations. Neutral-emission measurements were made with a UTI Model 100C quadrupole mass spectrometer (QMS). The masses of the Ge isotopes are well removed from typical vacuum-system contaminants, thus facilitating emission measurements with high sensitivity. The QMS ionizer was positioned 6 cm from the tensile surface of the sample.

Figures 1(a) and 1(b) show typical emissions at 74 amu (the most abundant atomic Ge isotope) for two different samples. The emission bursts were typically delayed 10–100 ms from the time of fracture (as determined by the drop in applied load). The time of fracture is indicated by the arrows on the time axis. (The duration of fracture is typically 1–2 μs.) Some shorter and longer delays were occasionally observed. The peak width was typically 1–2 ms FWHM, which is close to the limit of the response of the electronics at the sensitivity employed. Taking into account ionizer efficiencies, these peaks corresponded to $\sim 10^6$–10^8 atoms passing through the QMS ionizer. An estimate of the total neu-

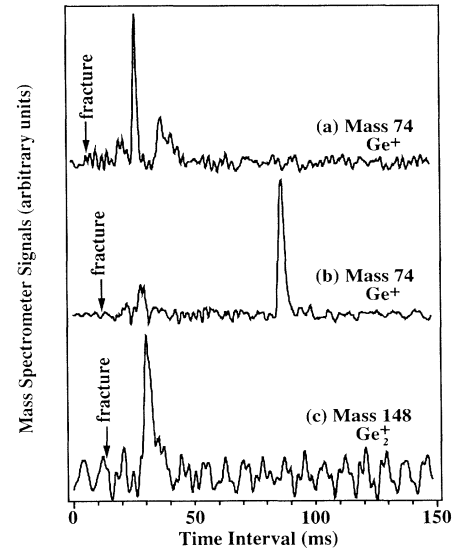

FIG. 1. Quadrupole-mass-spectrometer signals accompanying the fracture of single-crystal Ge. The signals of (a) and (b) are both for mass 74 and were acquired during two representative fracture experiments. They are primarily from the emission of atomic Ge. (c) A similar signal for mass 148 (Ge_2) from the fracture of a third (larger cross section) sample. The peaks have been normalized to a common height for presentation purposes. The peak electrometer currents were (a) 0.5 nA, (b) 0.6 nA, and (c) 4 nA.

tral emission would require knowledge of the angular distribution of the emissions and the escape probabilities associated with the crack geometry at the time of emission. Estimation of these factors is problematic at this point and will not be attempted here. However, it is clear that the emissions can be substantial. Given the sample geometry, the emission represents a minimum of 10^{-9}–10^{-7} of the Ge atoms in the first monolayer of the fracture surface (ignoring surface roughness).

Some measurements were also made at 148 amu, the mass of the most abundant Ge_2 dimer. Relatively intense emission bursts of the dimer were also observed; a typical result is shown in Fig. 1(c). Based on a limited sample set (eight bursts), the intensities of the bursts at 148 amu are very similar in intensity to those at 74 amu after correcting for the relative transmission and detection efficiencies at these two masses. The delays in the dimer bursts are also comparable to those of the monomer bursts. The relative intensities of the dimer and monomer bursts suggest that most of the emission at 74 amu is due to emission of Ge atoms from the fracture surface, and not due to dissociation of the dimer in the QMS ionizer. The existence and relative intensity of the dimer peak is also inconsistent with a thermal-emission mechanism. First, we found no discussion in the literature of thermal emission (vaporization) of Ge_2 directly from a liquid Ge surface. Furthermore, Knudsen-cell–QMS studies of *equilibrium* Ge vapors at temperatures of 1400–2200 K yield typical Ge_2/Ge ratios <0.01,[4] far below the observed ratio from fracture (on the order of unity).

The chief potential source of artifacts in the emission measurements is the vaporization of small Ge fragments (ejecta) striking the quadrupole ionizer. Depending on the stress at fracture, the ejected particles can be numerous, and their velocities are often sufficiently low to account for a significant delay from fracture. Fairly large pieces of ejecta were only occasionally observed to strike the ionizer filament (W at ~2200 K). This resulted in long, intense signals at 74 amu which decayed over some minutes. These signals are readily distinguished from the sharp bursts shown in Fig. 1. Furthermore, the detection of the dimer is inconsistent with such an artifact. If ejecta were captured by the ionizer filament, it is highly unlikely that dimers would be directly emitted from the hot W surface.

To further test for such artifacts, several fracture experiments were performed with a fine Ni mesh between the sample and the ionizer. The mesh openings were 6 μm square and yielded a net "transparency" of 25%. The presence of the grid had little if any effect on the number of observed bursts, but did reduce the average intensity. These observations are consistent with atomic emissions, but do not rule out the presence of ejecta smaller than 1 μm.

To unambiguously rule out the possibility that the detected emissions were due to small Ge fragments, Ge emitted during fracture was deposited on an alumina substrate and subsequently thermally desorbed in front of the QMS ionizer. The substrate was a thin-walled alumina ceramic tube heated with a Mo filament running through its center. Temperature estimates were obtained by fixing an Alumel-Chromel thermocouple to the substrate during a separate experiment and applying a heating cycle identical to that used in the desorption runs. For comparison purposes, thermal desorption of Ge evaporated onto the substrate from a Knudsen cell was also performed. The QMS filter was again tuned to 74 amu and the detected signal digitized at regular time intervals. Figure 2 shows typical desorption-induced emissions for Ge deposited by fracture and by evaporation. The approximate temperature is noted along the horizontal (time) axis. The desorption of fracture-deposited Ge shows a peak at the same temperature and with time behavior similar to the desorption of Knudsen-cell–deposited Ge. This is strong evidence for the atomic (or molecular) nature of the fracture-related emission. The low temperature at which desorption takes place is further evidence for atomic or molecular Ge. The vapor pressure of Ge in this temperature range is exceedingly low, totally ruling out evaporation of captured ejecta as a source of these emissions.

A final test for atomic and molecular emission utilized the setup shown in Fig. 3, where the emission was detected using *two* mass spectrometers at distances of 3 and 9 cm from the sample. Figure 3 shows the leading edges of two sequential bursts acquired at mass 74. The time difference at half maximum shown here is ~100 μs; an average value of 85 μs was observed. A time delay of 85 μs indicates that atoms in this portion of the emission curve have a velocity of about 700 m/s, which corresponds to a kinetic energy of 0.2 eV. Interpreting the data as a shift in the leading edge of a Maxwellian time-

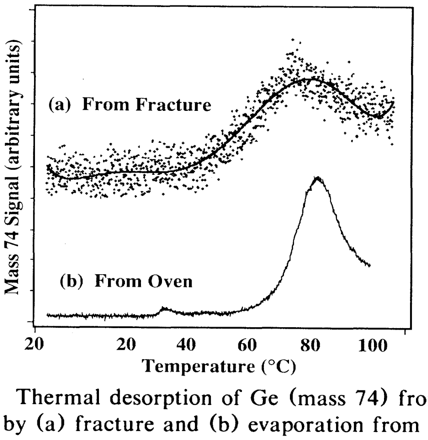

FIG. 2. Thermal desorption of Ge (mass 74) from alumina deposited by (a) fracture and (b) evaporation from a Knudsen cell. The temperature scale along the horizontal axis was established in a separate experiment with a thermocouple attached to the alumina substrate. The peaks heights have been normalized for presentation purposes. The peak electrometer currents were (a) 20 pA and (b) 400 pA.

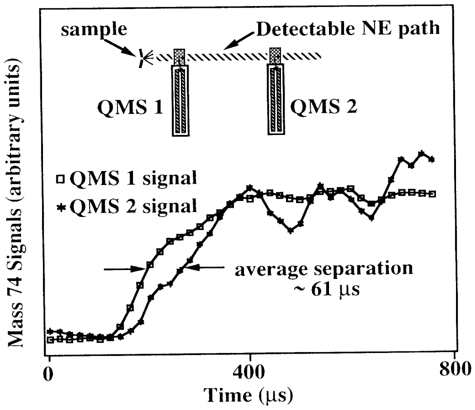

FIG. 3. Mass-selected emissions at 74 amu (principally Ge atoms) detected by two consecutive quadrupole mass spectrometers. The experimental geometry is shown in the inset, showing two quadrupole mass spectrometers (QMS1 and QMS2) tuned to the same mass (mass 74) at different distances from the sample. Because of the long duration of the signals on this faster time scale, only the leading edges of the signals are shown.

of-flight distribution, the corresponding temperature is about 750 K. This is consistent with a nonthermal-emission mechanism, since reasonable vapor pressures of Ge require $T > 1200$ K.

The velocity associated with this peak shift is far greater than that expected for particles ejected from the surfaces. Upper limits for ejecta translational speeds are given by the maximum particle speed associated with a longitudinal wave incident on the fracture surface, Δu. The most intense longitudinal waves would be associated with stress oscillations equal in magnitude to the tensile stress at fracture, Δp. Under these conditions, $\Delta u = \Delta p/\rho c$, where c is the longitudinal sound speed in Ge.[5] In this work $\Delta p < 360$ MPa, so that $\Delta u < 14$ m/s. Thus, the observed mass-74 bursts are traveling far too fast to be attributed to ejecta. We therefore conclude that the observed bursts seen in the QMS tuned to masses 74 and 148 are due to principally Ge atoms and Ge_2 molecules.

Similar emission bursts of atomic and molecular species accompanying the fracture of single-crystal NaCl and LiF were attributed to the emergence of dislocation structures (e.g., loops, pileups, and slip bands) at the fracture surface.[1] Dislocations are produced in the fracture of alkali halides and are readily observed by etching the fracture surfaces.[6,7] Shallow dislocations and dislocation structures are attracted to the surface by the image force which decreases as 1/(distance from the surface). Dislocations are readily generated during the fracture of alkali halides, being driven into the bulk by the high-stress field near the crack tip. After fracture, mobile dislocations close to the surface will be accelerated back to the surface. Numerical models of dislocation motion in LiF suggest that shallow dislocation loops $\lesssim 2$ μm from the surface take long enough to reach the surface to explain significant delays from fracture (on the order of ms to s).[1] The kinetic energy delivered by such a dislocation loop at "popout" can be high, on the order of several keV. Because of the great number of atoms and molecules observed in a typical emission burst from the alkali halides, we proposed that dislocation structures, such as dislocation pileups and slip bands, are involved.

However, dislocation motion at room temperature in Ge is severely hindered relative to the alkali halides. The activation energy for "low-temperature" dislocation motion is on the order of 1.4–1.7 eV,[8,9] due to the energy required for the nucleation of double kinks. In the absence of kinks, dislocation motion would require stresses on the order of the Peierls stress, which is estimated to be 2–3 GPa.[10] Fracture stresses in excess of this (at least 3.8 GPa) have been observed in carefully prepared, chemically etched Ge samples.[11,12] Stresses at the crack tip can be up to twice this high before reaching the limit imposed by crack branching.[13] These stresses are sufficient to create large numbers of dislocations and to move them into the bulk material, as shown by etch-pit studies of fracture surfaces of very strong samples.[11] However, the image stresses driving dislocations back to the surface are well below the Peierls stress at depths greater than a few lattice spacings, implying that long, straight dislocations in the bulk would be trapped.

However, curved dislocations geometrically require high kink densities to accommodate their curvature. These kinks are quite mobile, even at room temperature. (The activation energy for kink motion in Ge is on the order of 0.04 eV.) TEM observations indicate that curved dislocations are *much* more mobile than straight segments in Ge.[9] Since dislocations produced by fracture must begin and end on the surface and therefore require curvature, we expect dislocations produced by fracture to be similarly mobile. The geometry of such a loop is shown in Fig. 4. If a curved dislocation is not pinned, these kinks provide a low-stress mechanism for motion toward the surface which is not available to long, straight segments.

In the alkali halides, numerical models indicate that dislocations may arrive at the surface with substantial kinetic energies in addition to their nominal line energy.[1] Similar models of dislocation motion in Ge may be difficult to construct, given the "nonequilibrium" density

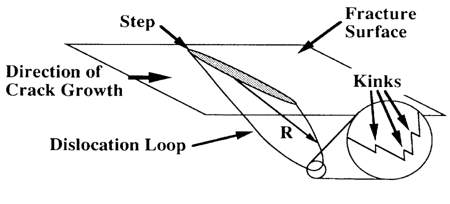

FIG. 4. Geometry of a dislocation loop of radius R relative to the fracture surface. The curvature of the loop requires kinks along its length, as shown in the inset.

of kinks along a dislocation loop. However, the elastic strain energy associated with dislocations in Ge is quite high; the energy of a dislocation loop 1 μm in radius is in excess of 100 keV, which corresponds to ~5.1 eV per atomic length (estimated from $E = Gb^3$).[10] This is well in excess of the sublimation energy of Ge, about 3.6 eV/atom.[14] Additional energy may be available in the form of dangling or strained bonds in the dislocation core (about 0.5 eV per dangling bond for Si). Although it is overly optimistic to assume that all this energy will be available for emission, this is sufficient for the emission of perhaps 10^4 Ge atoms. As in the case of the alkali halides, the intensity of the observed emissions requires the participation of many dislocations in any given emission event. We suggest that *the concerted emergence of such dislocations is responsible for the bursts in neutral Ge and Ge_2 emission described above,* where the required energy is supplied by release of both lattice strain and kinetic energies associated with moving dislocations.

Localized plastic deformation may result from rapid crack growth in a number of brittle materials. X-ray line-broadening measurements and selected-area electron-channeling measurements on alumina fracture surfaces have shown features attributed to plastic deformation.[15,16] Similar evidence for plastic deformation at cleavage surfaces of Ge formed in compression is provided by x-ray diffraction.[17] This deformation need not represent slip *per se,* but perhaps deformation twinning[17] or imperfect healing of microcracklike structures.[18] Although the popout of dislocation pileups may be the most likely source of the observed emissions, a number of other structures can be produced by inelastic deformation during rapid crack growth. Again, *catastrophic* relaxation of such deformation, e.g., via dislocation popout or a related process, could yield bursts of neutral emission.

To conclude, we have presented evidence that accompanying the fracture of single-crystal Ge under flexure loading, low-energy Ge atoms and Ge_2 molecules are released from the fracture surface at times ranging from 10 to 100 ms after fracture. We have attributed this emission to the emergence of dislocations from the fracture surface, where these dislocations are created by dynamic crack growth. Our results strongly suggest that production of dislocations from dynamic crack growth in Ge is more extensive than might be expected. Measurements of atomic and molecular emission serve as a useful probe of these processes, particularly in light of the time scales (ms) that are involved.

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