ON TRIBOEMISSION FROM THE SLIDING CONTACT OF Si AND Ge

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ABSTRACT

Experimental research work is presented seeking a better understanding of triboemission of negatively-charged particles from sliding contacts. Previous research by the authors found significant emission of electrons from diamond-on-alumina, diamond-on-sapphire and alumina-on-alumina during sliding contact and after contact ceased, while no emission was detected from diamond-on-aluminum systems.

This study explores negative-charge intensity from the semiconductors silicon and germanium when they are scratched by a diamond pin in high vacuum. While significant triboemission was always detected during the sliding contact, emission was undetectable when contact ended. Emission intensity is substantially higher for diamond-on-Si than for diamond-on-Ge. Decreasing emission is observed when the same wear track is scratched in repeated passes. These results are discussed with a focus on surface mechanisms that have been postulated to explain triboemission.

KEYWORDS: triboemission, exoemission, semiconductors.

1. INTRODUCTION

Triboemission is defined as the emission of electrons, ions, neutral particles, photons, radiation and acoustic emission under conditions of tribological damage. Triboemission of electrons is a particular case of the general phenomenon of exoelectron emission, which is observed when a material surface is disturbed and whose origin is still unclear. Triboemitted electrons are thought to play a significant role in tribochemical reactions under boundary lubrication conditions [1].

Early research in the field of triboemission was carried out by Nakayama et al. [2] on using a Faraday-cup type assembly to detect bursts of electric current - either charged-particle emission or surface-charge variation - from scratching diamonds on metals and insulators. More recently Dickinson et al. [3] investigated photon emission and electron emission intensities and electron kinetic-energy from reciprocating scratching of MgO with diamond. The work of Molina et al. [4-6] characterized triboemission of electrons from diamond-on-alumina, diamond-on-sapphire, alumina-on-alumina, and from diamond-on-aluminum. The first three pairs of materials consistently showed burst-type negatively-charged triboemission during contact at constant load and speed, while the aluminum system produced no significant emission [4-6]. Decaying emission after the contact ceased also was detected from the three ceramic systems for durations exceeding the minute-range [6]. For the cases of diamond-on-alumina and diamond-on-sapphire, energy spectrometry showed that a large fraction of the triboemitted negative-charges were of low-energy (e.g., 1-5 eV) [4, 6].

A mechanism for charged-particle triboemission, however, is still lacking. Although a correlation was demonstrated in the fractoemission field [7] between the onset of fracture of surface oxides and the emission of electrons and photons, proving a connection between ceramic-scratching surface features and the observed triboemission can be experimentally difficult [8]. Creation of new surface by scratching can yield complex combinations of several surface structures and defects at microscopic level [9], while at the atomic level surface reconstruction for ceramics is a very complex and not yet fully known process [10].

Silicon behavior when new surface is created by fracture has been extensively studied (and to less extent, for germanium). Fracture of Si and Ge occurs by brittle cleavage after microcracking in a few crystallographic planes [11], and surface reconstructions for Si and Ge surfaces reduce to a few well-known stable structures [12, 13]. In addition to possessing simpler structures than those of ceramics,
semiconductors present the advantage for triboemission studies that their surface-charging is negligible in comparison with charge-effects on insulators [3].

Fractoemission from semiconductors was investigated by Dickinson et al. [14], who used a channel electron multiplier (CEM) in pulse-counting mode to detect electron-emission outputs from bending fracture of single-crystal Si. They also measured atomic and molecular Ge emission from Ge fracture [15]. Kaalund and Haneman [16] studied in-vacuum emission during cleavage by bending of Si and Ge. They observed burst-type electron emission starting at the onset of cleavage with durations ranging from tens of microseconds to 1.8 milliseconds. The signals were independent of dopant concentrations, of high-vacuum levels and of temperature. Maxima of integrated signal intensity were up to three times higher for Si cleavage than for Ge under the same conditions. All the reported fractoemission outputs were substantially longer than the typical fracture durations (e.g., 2-10 microseconds). This paper presents a study of the triboemission outputs and wear-track profile measurements and SEM observations from the diamond scratching of Si and Ge.

2. EXPERIMENTAL

The triboemission instrument developed by Molina et al. [4,6] was employed for negative-charge intensity measurements from diamond-on-Si and diamond-on-Ge in a vacuum of 10^-4 Pascal or better. A CEM detector in the pulse-counting mode was operated at 1,750V and +200V input bias for negative-charge capture. Background-noise was reduced to less than 0.1 count/sec. Computer data-acquisition was carried out for a 10msec-window. Instrument features, its ranges and measurement and acquisition capabilities are presented by Molina et al. [4,6].

The contact geometries consisted of a 90 degree-angle cone diamond-pin sliding on rotating-disks of the semiconductors Si and Ge (of disk thickness of 2mm and 3mm respectively). The 25.4mm-diameter disks were supplied by Infrared Optical Products as plane mirror-polished windows of IR-reflecting quality (optical grade Si and Ge, resistivity: 5-40 Ohm-cm, n-type).

For constant rotational speed of 2 rpm two different wear-track radii were set (e.g., 4.8mm and 9.0mm, which corresponded to sliding speeds of 1.0mm/s and 1.9mm/s). Such low speeds and the load (5N) used in this study prevented thermionic emission from sliding contacts. In each record of acquired data, a 15-second period without contact was initially set for background reference. The contact was then applied for a single turn on the circular wear-track (corresponding to 30 seconds at the used speed of 2 rpm), after which the contact ceased and data acquisition continued for a total acquisition time of 10 min 55 seconds. This long period without contact after each turn allowed careful investigation of any post-contact emission. This schedule of data acquisition was repeated for consecutive turns on the same wear track. The starting point of contact for each turn was not controlled and can be different for consecutive turns. Figure 1 shows plots of negatively-charged triboemission measurements for diamond-on-Si and diamond-on Ge under same conditions of sliding contact.

Figure 1 (next page) shows that significant negatively-charged triboemission was detected clearly associated with sliding contact, while emission was undetectable when contact ended. Data post-processing allows the presentation in figure 2 of a single plot for the first-four-turns (contact periods only) on the same wear track.

The largest bursts of negatively-charged triboemission from Si and Ge occur during these first-four turns of contact for the used loads and sliding speeds. The difference between the measured average triboemission rates for diamond-on-Si and diamond-on-Ge is statistically significant to a 99.5% confidence level. Figure 2 (next page) suggests a decrease of triboemission intensity as sliding progresses. To explore this emission trend, measurements were carried out for diamond-on-Si and diamond-on-Ge in the first 25 turns on the same wear track.

Figure 3 shows a plot of the average rates of emission (computed for each turn) in the first 25 turns.

![Average rate of negatively-charged triboemission](image)

Fig. 3. Average rates of negatively-charged triboemission for first 25 turns in diamond-on-Si and diamond-on-Ge measurements. Load: 5N. Speed: 1.9mm/s.
Fig. 1. Negatively-charged triboemission from diamond-on-Si and diamond-on Ge sliding contact. Acquisition window: 10msec. Load: 5N. Speed: 1.0mm/s.
Fig. 2. Negatively-charged triboemission for first-four turns of contact from diamond-on-Si and diamond-on-Ge. Acquisition window: 10msec. Load: 5N. Speed: 1.0mm/s.

Figure 3 shows a clear decreasing trend of the triboemission intensity as contact progresses on the same wear track for diamond-on-Si and diamond-on-Ge. Table 1 summarizes most relevant triboemission data obtained for the investigated material systems and their statistical analysis. It also presents for comparison some relevant triboemission data from alumina system obtained by Molina et al. [4, 5].

Average rates of triboemission for diamond-on-Si are in a similar range of those for diamond-on-alumina systems. The latter, however, were obtained for longer contact-periods and higher speeds [4] and the contact geometry was different in the case of...
Table 1. Ranges of negative-charge emission and statistical significance with respect to measurement background for different material systems.

<table>
<thead>
<tr>
<th>Sliding contact material system</th>
<th>Emission ranges during contact (in counts/sec)</th>
<th>Statistically significant (c) (Confidence level in %)</th>
<th>Negative-charge post-contact emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond-on-Si</td>
<td>38-86 (a)</td>
<td>Yes (95%)</td>
<td>None</td>
</tr>
<tr>
<td>Diamond-on-Ge</td>
<td>0.5-1.0 (a)</td>
<td>Yes (88%)</td>
<td>None</td>
</tr>
<tr>
<td>Diamond-on-alumina [4, 6]</td>
<td>8.5-13 (b)</td>
<td>Yes (86%)</td>
<td>Yes, lower level</td>
</tr>
<tr>
<td>Diamond-on-sapphire [4, 6]</td>
<td>11-36 (b)</td>
<td>Yes (86%)</td>
<td>Yes, lower level</td>
</tr>
<tr>
<td>Alumina-on-alumina [5, 6]</td>
<td>15.9-710 (b)</td>
<td>Yes (98%)</td>
<td>Yes, lower level</td>
</tr>
</tbody>
</table>

(a) Average rates for two different wear-tracks on same specimen in 120 sec-contact (four turns). Load: 5N. Speed: 1-1.9 mm/s. (b) Average rates for different specimens in 320 sec-contact. Load: 2-5N. Speed :1.4-4.8mm/s [4, 5]. (c) For differences between average triboemission count and CEM background. Sample size: 2 (3 for alumina-on-alumina) [4, 6].

Table 2. Average values of wear-track depth, width and computed cross-section area from 20 profile measurements for diamond scratching on Si and Ge. Load: 5N.

<table>
<thead>
<tr>
<th>Wear track from diamond-on-</th>
<th>Speed [mm/s]</th>
<th>Path length [mm]</th>
<th>Average [micrometers] Depth</th>
<th>Width</th>
<th>Average computed area [micrometers$^2$]</th>
<th>Volumetric wear [mm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Si (*)</td>
<td>1.0</td>
<td>121</td>
<td>146</td>
<td>16</td>
<td>1,272</td>
<td>0.0384</td>
</tr>
<tr>
<td>- Si (**)</td>
<td>1.9</td>
<td>1,414</td>
<td>258</td>
<td>19</td>
<td>3,352</td>
<td>0.189</td>
</tr>
<tr>
<td>- Ge (*)</td>
<td>1.0</td>
<td>121</td>
<td>422</td>
<td>37</td>
<td>8,079</td>
<td>0.244</td>
</tr>
<tr>
<td>- Ge (**)</td>
<td>1.9</td>
<td>1,414</td>
<td>393</td>
<td>64</td>
<td>11,931</td>
<td>0.675</td>
</tr>
</tbody>
</table>


alumina-ball on alumina [5]. Profilometry and SEM observations were carried out for wear tracks. Table 2 summarizes the profile measurements.

For measurements in table 2 there was significant variability in the profile traces at different positions along the wear track. Although hardness data for semiconductors is very scarce and comparisons are difficult, a literature search led to the conclusion that optical grade Si (Vickers hardness ~10GPa) is harder than same grade Ge (Vickers hardness ~7GPa). The computed volumetric wear values in Table 2 agree with such conclusion, because they consistently show more wear for Ge than for Si under the same scratching conditions. However, these wear values do not fit in with Archard’s wear law.

3. DISCUSSION

The measurements of negative-charges from diamond-on-Si and diamond-on-Ge showed emission clearly associated with sliding contact. This burst-type electron emission was not substantially different from those previously reported with diamond-on-ceramics and alumina-on-alumina sliding [4-6]. Although SiO$_2$ and other oxides are known to emit tristoelectrons [2, 3], the triboemission levels measured from Si and Ge cannot be explained by emission from oxide surface layers. Molina et al [4,6] found that triboemission from thin oxide layers was not significant (e.g., in triboemission measurements from diamond-on-aluminum).

A significant difference was found between triboemission rates from diamond-on-Si and diamond-on-Ge. Kaalund and Haneman [16] found that maxima of integrated electron-emission intensity were up to three times higher for Si cleavage than for Ge under the same in-vacuum conditions. The difference found between triboemission outputs from these materials can be related to their different hardness. Nakayama et al. [2] found that increased material hardness corresponded to higher negative-charge currents from diamond scratching. The triboemission data reported by Molina et al. [4, 6] (included in table 1) for sliding of diamond-on-alumina and diamond-on-sapphire is consistent with such conclusion, because the measured triboemission-range for the former are higher than that for softer alumina in same sliding conditions. Accordingly, triboemission from harder Si must be higher than that from Ge.

Decreasing emission is also observed from the semiconductors when the same wear track is scratched in repeated passes. Measurements of negative-charge triboemission from diamond-on-insulators [4-6] suggested similar behavior. Figures 4...
and 5 show examples of Si and Ge wear-tracks after four turns of contact. While the edges of the wear tracks suggest brittle fracture, the center of the tracks shows some plastic deformation that likely occurred after repeated pass of the diamond tip on the surface. This is compatible with a wear transition from brittle fracture to plastic deformation in Si that may be related to a thermal activation of dislocations for a local temperature increase [18]. However, no data about wear transitions was found for Ge. The authors believe that decreasing triboemission can relate to decreasing semiconductor wear. SEM micrographs of the diamond pins after repeated passes on Si or Ge revealed important diamond-wear, but no conclusions should be drawn from such limited observation.

![Fig. 4. SEM micrograph of Si wear-track from scratching by diamond tip.](image)

**Load**: 5N, **speed**: 1.9mm/s, 25 turns on same wear track. **Magnification**: 500X.

![Fig. 5. SEM micrograph of Ge wear-track from scratching by diamond tip.](image)

**Load**: 5N, **speed**: 1.9mm/s, 25 turns on same wear track. **Magnification**: 500X.

An important finding of this work regards the absence of emission after the contact ceased for diamond-on-semiconductor in comparison to significant post-contact triboemission from insulators. This paper presents the first clear evidence of such different behavior, although Dickinson et al. [14] noticed the shorter duration of Si fractoemission bursts when compared to those from wide band-gap materials (e.g., from MgO), which seemed to extend in the millisecond range and well beyond typical fracture duration. Four surface mechanisms have been postulated to explain triboemission: (i) surface-charge effects, (ii) surface microfracture and charge-separation, (iii) reduction of surface work function, and (iv) interaction of new reactive surface with atmospheres. The latest mechanism would not apply to the presented results of triboemission from Si and Ge under high vacuum. The first three mechanisms are discussed with a focus on the post-contact triboemission and its absence for insulators and semiconductors, respectively.

Surface electrostatics-charge, which has been measured during triboemission from insulators under vacuum [3], can remain after sliding ceases and may account for post-contact emission from insulators by acceleration of free-charge. For Si, however, Zharkikh et al. [17] showed that surface-charging which is observed in atmosphere relates to a weak form of water adsorption, which is not possible under high vacuum. The absence of post-contact emission from semiconductors could be explained by a corresponding absence of surface-charge on semiconductors under vacuum.

Creation and growth of surface microfracture has been linked to the origin of triboemission and in particular of fractoemission from insulators [3, 7] and from Si and Ge [14-16]. A “conceptual mechanism” for fractoemission was postulated by Dickinson et al. [19] based on charge separation due to fracture and building of an electric field on charged nascent surfaces. In the case of fracture in atmosphere, charge separation will be accompanied by desorption of gases in the crack tip, and gas breakdown producing local electron-discharge and photon emission; experimental evidence of these processes was presented by Dickinson et al. [3]. The same mechanism would proceed for secondary events by electron bombardment of newly created surfaces producing electron-hole pairs, followed by electron-hole recombination yielding an emitted electron or a photon, and emitted electrons striking positive charges, emitting them as either positively-charged or neutral particles. Statistical models analyzing fractoemission and triboemission in frequency-domain are reviewed by Molina et al. [20], and they suggest that secondary events occur following primary emissions. Dickinson et al. [14] also proposed that fractoemission for Si may not involve charge separation and discharge, but it would proceed by surface-defect recombination and reconstruction in open fractures, similar to the creation of free electrons during chemisorption.

Important surface-fracture structures were observed after diamond scratching of Si and Ge in this experimental work: SEM micrographs are shown in figures 6 and 7 of wear-tracks for diamond scratching...
on Si and Ge, respectively, after only 4 turns of sliding at speed of 1.0mm/s.

SEM observations in figures 6 and 7 show that the edges of the wear tracks are ragged, suggesting that flake and plate-like portions were worn by brittle fracture at starting of contact. The observed brittle behavior in the scratching of Si and Ge by diamond therefore compatible with fast microfracture growth which completes in the microsecond range when contact ceases. Kaalund and Haneman [16] suggested that the bond rupture in brittle semiconductors leaves weakly-bonded surface atoms which supply the energy for exoemission (e.g., 1.98 and 1.85eV per bond respectively for Si and Ge) and that the surface vibrations for such dangling bonds can be present for milliseconds.

There is extensive proof that triboemitted electrons are of low energy (e.g., 1 to 5eV) [1, 3, 4, 6] and that suggests that a reduction of surface electron work-function (WF) due to strain and deformation is needed for triboemission to occur. Experimental [21, 22] and theoretical [22, 23] evidences are available for metal wear that plastic deformation and increased dislocation density during sliding reduce WF, and that stable WF-values lower than for unworn surface are measurable from the onset of plasticity. Changes of WF during wear have been reported for Si and alumina, although WF is difficult to measure on insulators, because the surface-charge dominates [24]. The authors believe that the reduction of WF and the action of surface charging are essential to electron triboemission from insulators and semiconductors.

4. CONCLUSIONS

The authors carried out experimental work to compare the negatively-charged triboemission process from semiconductors with previous triboemission results from selected insulators (e.g., alumina and single crystal sapphire) and one conductor material (e.g., aluminum). This paper presents the first-known evidence that negative-charges are emitted from diamond-on-Si and diamond-on-Ge during sliding contact. This burst-type electron emission is not substantially different from those shown in diamond-on-insulators sliding. A significant difference was found between triboemission rates from diamond-on-Si and diamond-on-Ge, and the possibility is discussed that such difference relates to the material hardness. Decreasing triboemission is also observed from the semiconductors when the same wear track is scratched in repeated passes, and such decreasing triboemission may relate to decreasing semiconductor wear.

Clear evidence for a new finding is presented that no emission is produced after the contact ceased for these semiconductors, while significant post-contact triboemission was previously detected for insulators (e.g., alumina and sapphire) under vacuum. These findings are discussed with a focus on surface mechanisms which have been postulated to explain triboemission. The presence or absence of three dry-sliding effects, e.g., surface-charge, surface microfracture with charge-separation and reduction of surface work-function during plastic deformation may explain some of the observed features of the triboemission outputs from insulators or semiconductors.

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