Thermal View on Fracture-Induced Electron Emission and Electronic Excitation

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Abstract: The fracture of many materials causes electronic excitation near fracture surfaces. This electronic excitation was reported to be observed as the electron emission from fractured metal surfaces and as the increase in electrical conduction in fractured semiconductors. However, the mechanism of electronic excitation near fracture surfaces has been hardly studied to date. In the present paper, we give theoretical consideration to fracture-induced electronic excitation in metals and semiconductors in terms of thermal excitation near fracture surfaces. It is shown that the reported electron emission from fractured metal surfaces corresponds to thermoelectronic emission at about 1000 K. It is estimated that the reported increase in electrical conduction in fractured semiconductors also corresponds to thermal excitation of carriers at about 1000 K. Excited states near fracture surfaces are discussed on the basis of the present estimations.

Key words: Fracture, Electron emission, Electronic excitation, Fractoemission, Metals, Semiconductors

1. INTRODUCTION

When solid materials are fractured, particles such as electrons, ions, molecules and photons are emitted from the fracture surface. This fracture-induced particle emission is called fractoemission. Fractoemission was observed for a variety of solid materials including glass, ceramics, polymers, metals and rocks [1-10]. Fracture by different kinds of mechanical loads, for example, by tension, bending, torsion, friction, crushing, exfoliation and indentation, causes fractoemission. Observation of fractoemission was made in various environments including in vacuum, in air, in specific gas such as oxygen or nitrogen, and in oil.

Because fractoemission is one of the energy release processes by fracture, as well as acoustic emission, it is fundamentally important in understanding the microscopic process in fracture. Also fractoemission has technological potentialities in the future. For example, the precise in situ measurements of fractoemission may lead to the development of methods to monitor the cutting process of materials. Understanding the excited states near fracture surfaces through fractoemission may lead to the positive use of fracture surfaces for chemical reactions.

Although measurements of fractoemission were made by several authors, the mechanism of fractoemission is not yet well understood. This is partly because experimental information on the excited states near fracture surfaces is not sufficient, and also because there is few theoretical studies of the mechanism. In the present situation, a proper theoretical estimation of electronic or atomic excitation near fracture surfaces is needed to explore the mechanism of fractoemission.

In this paper, we pay attention to fracture-induced electronic excitation in metals and semiconductors. We estimate the electron emission from fractured metal surfaces and the increase in electrical conduction in fractured semiconductors in terms of thermal excitation near fracture surfaces. Based on the estimations, we discuss the excited states near fracture surfaces.

2. EXPERIMENTAL REPORTS

There have been several experimental reports on fractoemission or fracture-induced excitation. Experimental studies showed that electrons were emitted from fracture surfaces in metals and an increase in electrical conduction was observed in fractured semiconductors. We here refer to some experimental reports on the electron emission from fractured metals and the electronic excitation in fractured semiconductors, and point out open subjects.

2.1. Electron Emission from Fractured Metals

Nakayama et al. [11] reported on the measurement of electron emission from different metal surfaces (Ti, W, Mo, Fe, Al, Ni, Cd, Zn and Pb) in the cutting process. The metals were cut in oxygen gas, in nitrogen gas, or in vacuum. The observed intensity of electron emission during and after cutting depends on the combination of metal and surrounding gas species. They concluded that the electron emission from the cut metal surface is caused by the interaction of the fresh metal surface with the surrounding gas.

Nakahara et al. [12] measured the electron emission during fracture along a metallic Mg/glass interface in oxygen gas. Localized ductile deformation in the metallic phase exposes metallic Mg to the reactive oxygen atmosphere and produces intense electron
emissions. They also concluded that the observed electron emission is due to chemisorptive electron emission from metal surfaces.

2.2. Electronic Excitation in Fractured Semiconductors

Langford et al. [13] measured the fracture-induced change in electrical conduction in single-crystal Si. A transient increase in electrical conduction was observed during crack propagation. This was considered to be due to the fracture-induced production of free charge carriers near fracture surfaces. They suggested thermal generation of charge carriers during fracture as one of possible explanations of the transient increase in electrical conduction.

2.3. Open Subjects

The electron emission from fractured metal surfaces was attributed to chemisorptive electron emission because the emission intensity in the surrounding gas is much higher than that in vacuum [11,12]. On the other hand, the fracture-induced electron emission was also observed in vacuum though the emission intensity is weak. The fracture-induced electron emission in vacuum was also observed in other materials such as glasses [3]. Fracture surfaces are imagined to be excited in high energy states and to relax by losing a part of those energy as the electron emission. What excitation and relaxation processes take place near fracture surfaces in metals is an open subject.

The transient increase in electrical conduction in fractured semiconductors is an intriguing issue in connection with a probe of fracture-induced electronic excitation [13]. However, how free charge carriers are excited and how many carriers are produced by fracture in semiconductors are not yet well known. This is also an open subject.

3. THEORETICAL ESTIMATION

Very little is known about the electronic excitation and relaxation processes near fracture surfaces. We can imagine that the fracture surfaces just after fracture are in highly excited states because part of fracture energy is expended to excite atoms and electrons near the fracture surfaces. We here assume that electrons near the fracture surfaces are in excited states corresponding to high temperature and estimate the electron emission from fractured metal surfaces and the increase in electrical conduction in fractured semiconductors.

3.1. Electron Emission from Fractured Metals

When electrons near fracture surfaces in metals are in excited states corresponding to high temperature, part of the electrons can be emitted as thermoelectronic emission. There have been a number of studies of thermoelectronic emission from metal surfaces reported in the literature. We here use a simple formula well known as the Richardson-Dushman equation, which is, for the number of electrons emitted from unit area per second, given by

\[ N = AT^2 \exp \left( -\frac{W}{kT} \right), \quad (1) \]

where \( A \) is the constant, \( T \) is the absolute temperature, \( W \) is the work function, and \( k \) is the Boltzmann constant.

We have estimated the intensity of electron emission, \( N \), for Al, Ti, W and Ni, as a function of temperature using Eq.(1). Here the value, \( A = 7.48 \times 10^{20}\text{cm}^{-2}\text{s}^{-1}\text{K}^{-2} \), has been used ignoring the electron reflection at the surface. Figure 1 shows the estimated result of \( N \) vs. \( T \) for the four metals, where \( T \) is regarded as the temperature near fracture surfaces. Because the work function of these metals is 4 to 5 eV, appreciable electron emissions are expected if electrons near the fracture surfaces are in excited states corresponding to about 1000 K. The intensity at 1000 K is about \( 10^6\text{cm}^{-2}\text{s}^{-1} \) for Al and about \( 10^2\text{cm}^{-2}\text{s}^{-1} \) for Ni.

The energy distribution of emitted electrons is given by

\[ f(E)dE = \frac{1}{kT} \exp \left( -\frac{E}{kT} \right) dE, \quad (2) \]

where \( E \) is the kinetic energy of electrons for the motion perpendicular to the fracture surface and \( f(E)dE \)
Fracture-Induced Electron Emission and Excitation

Fig. 2. Energy distribution of electrons emitted from fracture surfaces corresponding to $T = 1000$ and $1500$ K.

represents the rate of electrons with the energies between $E$ and $E + dE$. Figure 2 shows the relation between $f(E)$ and $E$ at $T = 1000$ and $1500$ K. The mean value of the energy is given by

$$
\langle E \rangle = \int_0^\infty E f(E) dE = kT. \tag{3}
$$

So the mean value of the energy is about $0.1 \text{ eV}$ at $T \approx 1000$ K.

3.2. Electronic Excitation in Fractured Semiconductors

The transient increase in electrical conduction for fractured single-crystal Si was attributed to the production of free charge carriers [13]. This transient increase will be considered to be the following process. After electrons near fracture surfaces are excited to the conduction bands near the surfaces, they will diffuse to the conduction bands inside bulk. And then these electrons will lose their energy through electron-lattice interaction and electron-hole recombination.

We here estimate the increase in electrical conduction in fractured semiconductors using a simple model.

Let us consider that a sample of the length $L$ is cleaved into two parts and the region of the width $d$ near the fracture surface is in excited states corresponding to high temperature, as shown in Fig. 3. When the temperature of bulk is $T_b$ and that of the fracture surface region is $T_f$, the conduction electron density after fracture, $n_c$, is given by

$$
n_c = \left(1 - \frac{d}{L}\right) n_b + \frac{d}{L} n_f, \tag{4}
$$

where $n_b$ and $n_f$ are the electron densities in bulk and in the fracture surface region, respectively. Because $d \ll L$, the ratio of the electron density after fracture to that before fracture is given by

$$
\frac{n_c}{n_b} = 1 + \frac{d}{L} \frac{n_f}{n_b}. \tag{5}
$$

In intrinsic semiconductors with the energy gap, $E_g$, the electron and hole densities, $n$ and $p$, are given by

$$
n = p = 2 \left( \frac{kT}{2\pi \hbar^2} \right)^{3/2} (m_e m_h)^{3/4} \exp \left(- \frac{E_g}{2kT} \right), \tag{6}
$$

where $m_e$ and $m_h$ are the effective masses of electrons and holes, respectively. The ratio of Eq.(5) can be estimated by using Eq.(6). The electron density in bulk, $n_b$, is estimated by substituting $T_b$ in $T$ of Eq.(6).
and the electron density in the fracture surface region, \( n_f \) is estimated by substituting \( T_f \) in Eq. (6). We have calculated the ratio of Eq. (5) as a function of temperature of the fracture surface region, \( T_f \).

Figure 4 shows the ratio, \( \frac{R_{nc}}{n_b} \), as a function of \( T_f \) for two different bulk temperatures, \( T_b = 250 \) and 300 K. Here we have used \( d/L \approx 10^{-6} \) in Fig. 3, and \( E_g = 1.1 \text{eV} \) for Si. The ratio \( \frac{n_c}{n_b} \) becomes 10 to \( 10^3 \) when the temperature of the fracture surface region rises up to about 1000 K.

### 4. DISCUSSION

We here discuss fracture-induced electronic excitation by comparing our estimations with experimental reports. Table 1 lists the intensity of electron emission \( N \) from fractured metal surfaces of Al, Ti, W and Ni. The experimental values in Table 1 have been obtained from data measured by Nakayama et al. [11]. They measured the intensity of electrons emitted from fresh metal surfaces exposed during the cutting process of a rotating metal disk surface, as counts per second. We have calculated the intensity per unit area per second from the area of fresh metal surfaces exposed per second in the cutting process. The theoretical values in Table 1 are the thermoelectronic emission at 900 K in Eq. (1). Also Table 1 includes the values of the work function \( W \) and the melting temperature \( T_m \) for the four metals.

The intensities of the thermoelectronic emission are in fair agreement with the experimental intensities if the fracture surfaces correspond to about 1000 K. This agreement should be regarded as qualitative because the experiment counted electrons detected only at the place of an electron detector above the metal disk and because the theory ignores the electron reflection at the surface. Thus the electron emission from fractured metal surfaces in the experimental report corresponds to thermoelectronic emission at about 1000 K. The fact that the intensities for Al and Ti are higher than those for W and Ni can be attributed to the difference in the work function. This suggests that electrons are possibly emitted from fresh metal surfaces by overcoming the potential barrier of the work function.

The transient increase in electrical conduction in fractured single-crystal Si was reported to be 10 to 100 times [13]. If the effective masses and the relaxation times of carriers are assumed to be the same before and after fracture, then the increase in the electrical conductivity after fracture is due to the increase in the number of carriers. From Fig. 4, if the fracture surfaces are in excited states corresponding to about 1000 K, then the increase in the electrical conductivity is the same order of magnitude as experiments. Thus the reported increase in electrical conduction in fractured Si corresponds to the thermal excitation of carriers at about 1000 K.

Temperature measurements near fracture surfaces have not yet been reported for metals and semiconductors. However, some reports on molecular dynamics simulations insist that a temperature rise up to about 1000 K can be caused by a wearing or cutting process. Iso and Tanaka [14] performed molecular dynamics simulations of cutting Ni surfaces. They reported that the cutting process can cause a rise of local temperature up to more than the melting temperature. Also Maekawa [15] reported that molecular dynamics simulations of cutting Cu surfaces show a temperature rise up to about 1000 K. Thus fracture can cause a temperature rise up to about 1000 K.

It should be noted that we cannot define strictly the temperature near fracture surfaces because the surface just after fracture is not always in thermal equilibrium states. The temperature in molecular dynamics simulations is also only a measure of the excited states of particles when the simulations are applied to non-equilibrium processes such as fracture. Therefore the temperature near fracture surfaces should be regarded as a measure of excited states near the surfaces. The fracture surfaces can be in the excited states corresponding to about 1000 K.

At present, we have little detailed experimental information on the microscopic process of electronic excitation near fracture surfaces. For example, fracture-emission continues for such a fairly long time as several seconds or more, which suggests that the excited states near fracture surfaces have a long life-time. The relaxation process of excited states near fracture surfaces is one of open subjects in fracture-emission. The interaction between fracture surfaces and surrounding gas is also left for future studies. Many experimental and theoretical investigations will be necessary to understand fracture-induced electronic excitation and relaxation.

### 5. CONCLUSION

Fracture-induced electronic excitation has been discussed in terms of thermal excitation of electrons near fracture surfaces. The present study is summarized as follows:

1. The electron emission from fractured metal surfaces in the experimental report corresponds to thermoelectronic emission from the fracture surfaces at about 1000 K.

2. The increase in electrical conduction in fractured semiconductors in the experimental report also corre-

<table>
<thead>
<tr>
<th>( W[\text{eV}] )</th>
<th>( T_m[\text{K}] )</th>
<th>( N(\text{Ex.}) )</th>
<th>( N(900\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.20</td>
<td>934</td>
<td>1000</td>
</tr>
<tr>
<td>Ti</td>
<td>4.33</td>
<td>1946</td>
<td>1250</td>
</tr>
<tr>
<td>W</td>
<td>4.54</td>
<td>3695</td>
<td>( \sim 20 )</td>
</tr>
<tr>
<td>Ni</td>
<td>4.96</td>
<td>1728</td>
<td>( \sim 20 )</td>
</tr>
</tbody>
</table>
Fracture-Induced Electron Emission and Excitation

responds to thermal excitation of carriers near the fracture surfaces at about 1000 K.

Although fracture surfaces will not always be in thermal equilibrium states, the excited states corresponding to about 1000 K can cause the electron emission and the increase in electrical conduction as observed.

Acknowledgment — This work was supported by Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology.

REFERENCES