Proc. 8th Intern. Symp. on Exoelection Emission and Applications, Osaka, 1985
Japanese Journal of Applied Physics, Vol. 24 (1985) Supplement 24-4, pp. 122-124

PSEE-Related Phenomena Indicative of the Meaning of Two-Process Model Parameters for Mechanically Deformed Aluminum

Hidemi SHIGEKAWA, Yuichiro FUJIWARA, Yuji ANDO,
Akiko KUMAGAI and Shin-ichi HYODO

Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113

In order to examine the physical meaning of the parameters involved in the two-process model previously proposed by the authors, the following experimental studies were conducted for scratched Al specimens. (1) It was found that the statistical fluctuation in the PSEE yield obeys a Poisson distrubution. This indicates that not only the exo-emission process but also the process of reactivating inactive emission sources should be regarded as a stochastic process. (2) The rate of exo-activation was found to be insensitive to specimen temperatures between 100 and 300 K, and to agree well with the theoretical value obtained from a simple tunneling model. (3) Abrasion did not affect the frequency of the photoluminescence at peaks which were observed at 2.6, 3.0, 3.8 and 4.8 eV. The peak intensity, however, increased after abrasion and then gradually decreased. This is similar to the intensity change in a PSEE yield.

§1. Introduction

Exoemission from perturbed materials can sometimes last very long after a perturbation, *e.g.*, for a month or more. In this case, the total electron yield must be great enough to easily surpass the number of emission sources created by the perturbation, i.e., the number of crystal vacancies or the number of adsorbed sites. This further suggests that emission sources can be repeatedly activated, even after they have been inactivated by releasing electrons. From this viewpoint, we proposed the "two-process model (T-P model)",[1] which is effective in interpreting various time-related PSEE phenomena. The purpose of the present paper is to examine one of the underlying assumptions of the model and to clarify the microscopic meaning of the parameters used in the model on an experimental basis.

§2. Physical Meaning of the Parameters Used in the Model

Since we used mostly scratched or abraded aluminum sheets ($25 \times 25 \times 0.2$ mm^3, 99.99% purity) as specimens, only the case of PSEE from mechanically-excited aluminum will be discussed at first. Figure 1 schematically illustrates the exoelectron-emission mechanism for this kind of aluminum. When a surface oxide layer is removed by a mechanical treatment in an oxidizing environment, a fresh surface layer forms and is quickly oxidized. During this stage of oxidization, the defect-related trap levels of a donor type are likely to be created between the band gaps of the oxide layer.[2,3] An electron transfer will then occur so that the Fermi level of the bulk Al becomes equal to that of Al_2O_3 at the interface. This will cause a band bending and will result in not only a lowering of the vacuum level, but also a shift of trap levels to below the Fermi level. If the foregoing presumption is correct, electrons at the trap levels can be released by the application of a stimulation energy that is lower than the usual work function, i.e., the trap levels can be exoemission sources.

It is, however, obvious that exoelectrons can be emitted only from electron-filled trap levels. In other words, electron-vacant trap levels can no longer release electrons, even in the presence of sufficient stimulation. The trap levels without electrons are called inactive sources; those filled with electrons are calle active sources.

In Fig. 1 the basic concept of the T-P model is schematically illustrated; S' and S'' represent the number of active and inactive emission sources, respectively, and S_0 is the sum of S' and S''. The active sources are assumed to emit electrons and, consequently, to transform into inactive sources at a rate of α. Also, the inactive emission sources are assumed to be activated and to

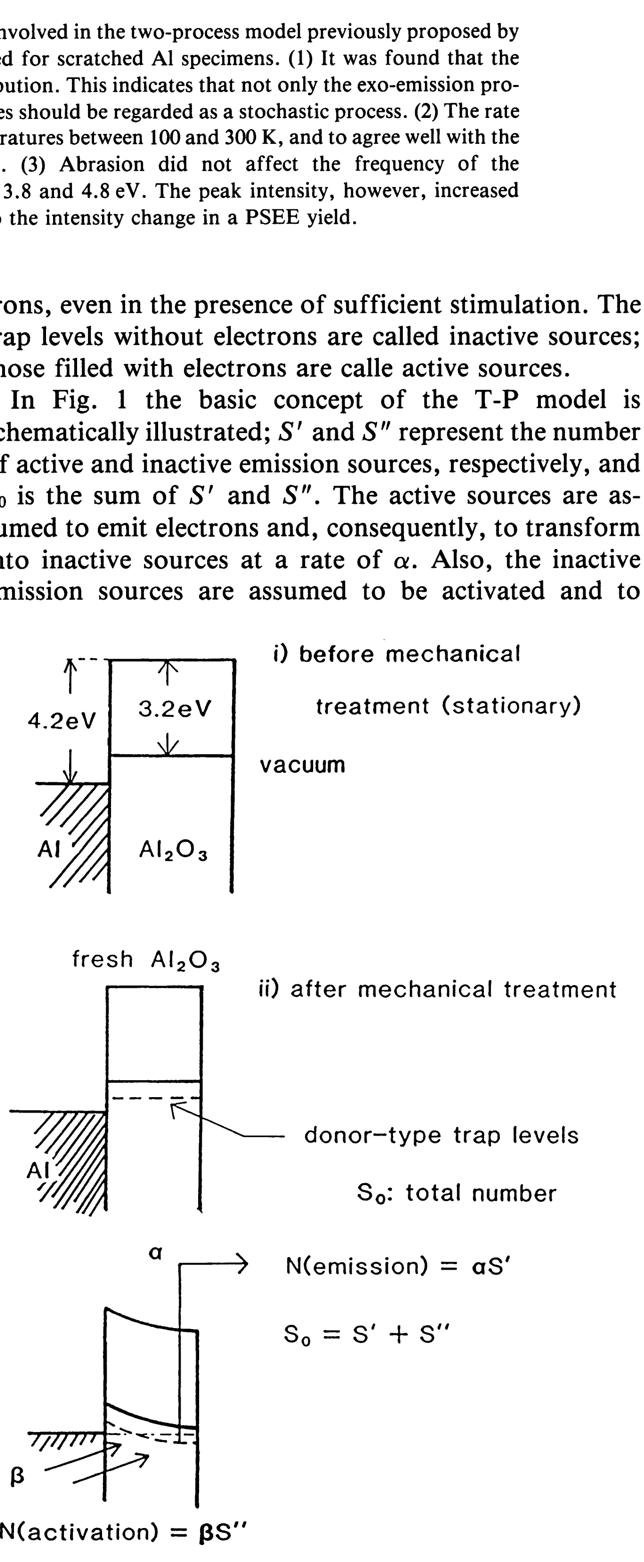

Fig. 1. A diagram illustrating the effects of mechanical processes on energy levels of surface-oxidized aluminum.

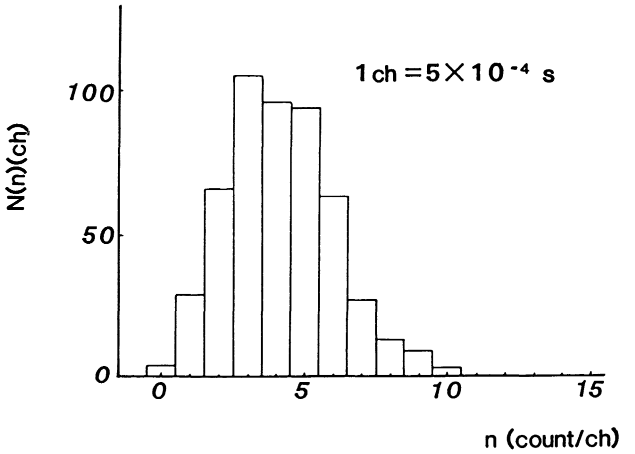

Fig. 2. Frequency Distribution of the PSEE yield per dwell time of each channel (5×10^{-4} 2).

transform into active sources at a rate of β. This reactivation process features the T-P model. The reactivation mechanism will be discussed in §4.

§3. Fluctuation of Exoemission Yield

It is implicitly assumed in the T-P model that both the emission from active sources and the reactivation of inactive sources take place independently, i.e., each source transfers at random from the exo-active state to the exo-inactive state at a rate of α and from the exo-inactive state to the exo-active state at a rate of β. From the stochastic theory concerning the Markov process, if both α and β are very small and mutually exclusive, the exoelectron yield per unit time must fluctuate so as to obey the Poisson distribution.

Thus, we conducted measurements to study the fluctuation in the PSEE yield from specimens scratched in a vacuum (5×10^{-6} Torr). The yield was counted with a combination of an electron multiplier and a multichannel analyser. (The analyzer had 512 channels, each of which had a 5×10^{-4} sec dwell time. Figure 2 shows the relation, thus determined, between the number of EE counts detected during the dwell time of each channel. Since for this distribution the ratio of its dispersion to its arithmetic mean was close to unity (precisely 0.87), it seems safe to state that the fluctuating PSEE yield during a brief period obeyed the Poisson distribution. This result evidently supports the stochastic approach of the T-P model.

§4. The Exoactivation Process

We determined the exoactivation rate, β, as a function of temperature (100 to 300 K).[4,5] Though the values determined for different specimens varied from 10^{-1} to 10^{-4} sec^{-1} for each specimen, the rate was considered to be almost constant (Fig. 3). We have another type of evidence which shows that β is also independent of atmospheric conditions. Based on these results, we believe that electrons are supplied from bulk metals to electron-vacant sources in the surface oxide layer.

In the case of an electron transfer from bulk to a surface emission source, two processes are considered to be possible: a thermal process and a tunneling process.

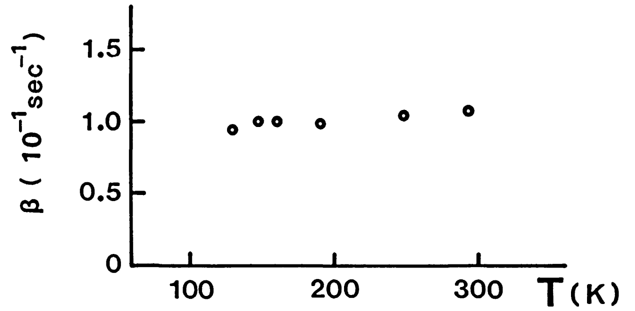

Fig. 3. The exoactivation rate determined as a function of temperature.

When electrons are thermally supplied, the activation rate is strongly influenced by specimen temperature. Since the barrier height between the Al and the surface oxide layer is about 1 eV. For example, the value of β at 100 K has been calculated to be about 10^{30} times smaller than that at 300 K. It is, however, apparent that if electron transfers are dominated by tunneling, the temperature effect should be much smaller. By applying the WKB method to a simple model (Fig. 4), we calculated the probabilities of electron transfers due to tunneling. For tunneling widths between 10 and 50 Å, the calculated probabilities were 10^{-1} and 10^{-3} sec^{-1}, respectively. These are in good agreement with the experimental values. For this reason we believe that electrons are supplied to electron-deficient trap levels through quantum mechanical tunneling.

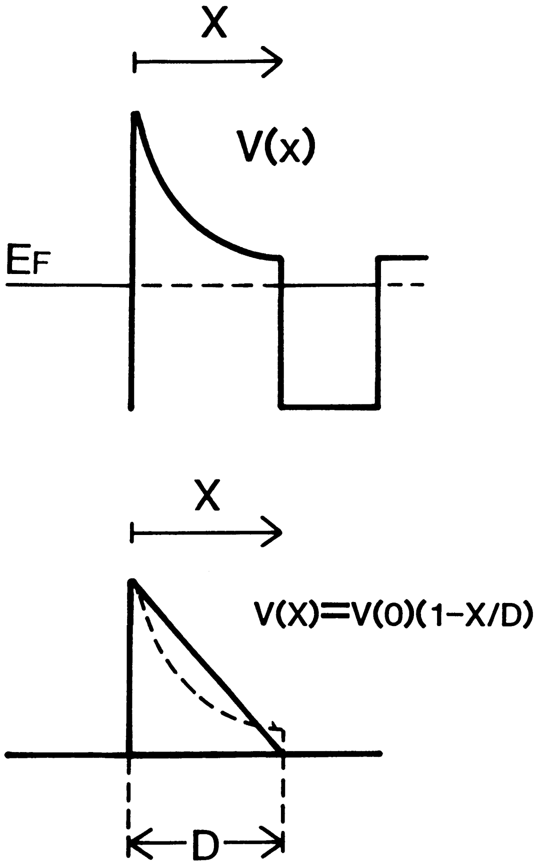

Fig. 4. The potential model used for calculating the tunneling frequency in order to estimate the exoactivation rate.

§5. Identification of Emission Sources

Since photoluminescence is known to have an intimate relation with PSEE, photoluminescence studies were performed for Al specimens with an emphasis on the effect of abrasion. The specimens were abraded with a steel brush in a room atmosphere,* and stimulated by UV light from a deuterium lamp (200 W). The luminescence emerging from the specimens was analyzed using a combination of a photomultiplier and a spectrometer with a resolution of 2 Å. The results which are summarized in Fig. 5 indicate that luminescence peaks always appeared at 2.6, 3.0, 3.8 and 4.8 eV for the Al specimens and that no abrasion effect was observed at these peak energies. However, each peak intensity was observed to increase just after abrasion and then to gradually decrease. This situation is very similar to that of the PSEE yield. Since the peaks at 3.0, 3.8 and 4.8 eV are known to arise from F and F^+ centers in Al_2O_3, it seems very probable that in the case of Al, the trap levels which have been so far assumed to be the exoemission sources are caused by these color centers.[6] The peak observed at 2.6 eV (Fig. 5) is possibly identical with the one observed by Grunberg.[7] While studying the PSEE yield from abraded aluminum, he found a very strong exoemission for a stimulation energy of 2.6 eV and ascribed the anomalous emission to excited F′ centers in the surface oxide layers. In the present case, however, no anomalous exoelectron emission could be detected, similarly to the case of Sujak[8].

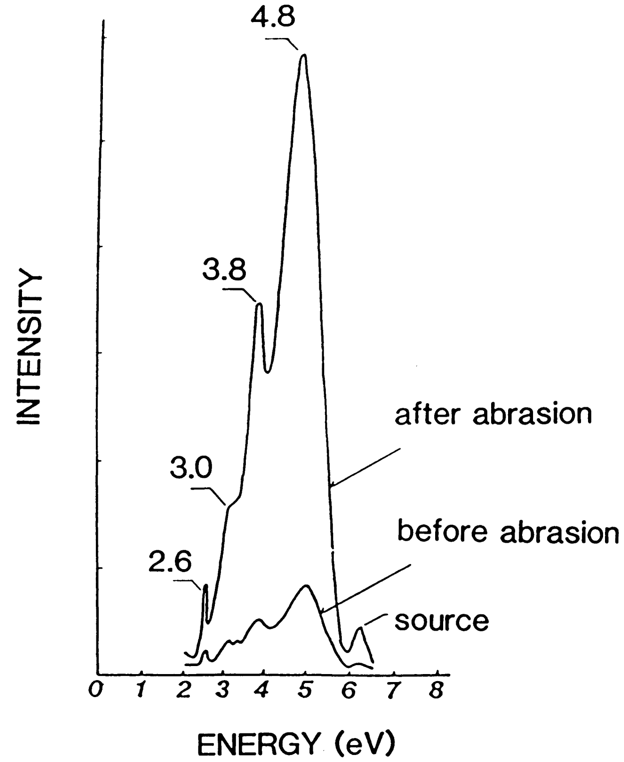

Fig. 5. Spectral changes in the photoluminescence from aluminum due to abrasion.

§6. Conclusion

We have confirmed from the PSEE intensity of scratched aluminum that the exoelectron fluctuation obeys the Poisson distribution. This indicates the validity of our stochastic approach to the study of the PSEE mechanism. On the basis of a photoluminescence study, the exoemission aluminum sources can be ascribed to F and F^+ centers created in the surface oxide layers. Within the scope of the present results, the reactivation of exoemission sources (electron supply to electron-deficient trap levels) appears to occur principally through a quantum mechanical tunnling from bulk metals to surface oxide layers.

References

1) H. Shigekawa and S. Hyodo: Jpn. J. Appl. Phys. **21** (1982) 1278.
2) H. Shigekawa and S. Hyodo: Jpn. J. Appl. Phys. **22** (1983) 42.
3) H. Shigekawa and S. Hyodo: Jpn. J. Appl. Phys. **22** (1983) 1493.
4) H. Shigekawa and S. Hyodo: Jpn. J. Appl. Phys. **22** (1983) 1627.
5) H. Shigekawa, Y. Fujiwara and S. Hyodo: Jpn. J. Appl. phys. **23** (1984) 1146.
6) K. H. Lee and J. H. Crawford Jr.: Phys. Rev. B **19** (1979) 3217.
7) L. Grunberg and K. H. R. Wright: Proc. Roy. Soc. (London) **232** (1955) 403.
8) B. Sujak: Brit. J. Appl. Phys. **10** (1959) 102.

---

*The PSEE yield from metals abraded in air is usually thought to arise from a lowering of the work function induced by water adsorption on specimen surfaces. From the viewpoint that this may be dominant but that other mechanisms must also operate, as is explained in this paper, we carried out measurements in a room atmosphere for simplicity.