

## Two-Process Model for a Comprehensive Interpretation of Photostimulated Exoelectron Emission

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In order to explain several PSEE time-related phenomena regarding scratched metals, the authors have proposed a reaction-kinetic model (the Two-Process model), in which particular attention is given to activating inactivated emission sources. On the basis of this model the authors have succeeded in elucidating such PSEE phenomena (mostly observed for scratched aluminum) as a storage effect, the relation between the peak intensity and the ambient pressure, and the dependence of the intensity on the stimulation intensity. In a discussion regarding the parameters involved in the model it is suggested that glow curves produce useful information about the PSEE emission mechanism as well as TSEE measurements.

### §1. Introduction

In the thermodynamics sense exoelectron emission (EEE) is a result of the relaxation of various perturbations applied to materials. According to Glaefeke,<sup>1)</sup> EEE definitely differs from such stationary effects as photoemission emission since EEE is (i) nonstationary, (ii) present only after generation of a perturbation and (iii) governed by the relaxation of perturbation. In connection with (iii), he has written that the emission current,  $N(t)$ , is given by

$$N(t) \propto \frac{\partial p(t)}{\partial t} \quad (1)$$

where  $p(t)$  represents a summation over several kinds of perturbed states at time  $t$ .

If Eq. (1) is completely valid, one can see that the integration of  $N(t)dt$  from zero to infinity is proportional to  $p(0)$ , i.e., that the total emission yield observed for a sufficiently long time is a measure of the initially applied perturbations. There is, however, much experimental evidence that shows the approximate constancy of  $N(t)$  over a very long period, e.g., a few months. For that case, it appears very probable that the total emission yield is orders of magnitude greater than the number of exoelectron sources initially produced by the perturbations. This seems to indicate that not only the relaxation process of the perturbations, but also its reverse process, should be taken into account in order to precisely describe the EEE phenomenon. In other words,  $N(t)$  should not be regarded as a function of the time derivative of  $p(t)$  alone as in Eq. (1) but as a function of both  $p(t)$ , itself, and its time derivative.

Earlier, we proposed a model called the Two-Process (T-P) model for explaining the peculiar behavior of PSEE from scratched aluminum.<sup>2-7)</sup> The purpose of the present paper is to show that this T-P model is useful not only for interpreting various time-related PSEE phenomena of metals, but also for promoting a comprehensive understanding of PSEE and TSEE.

### §2. Basic Concept of the Two-Process Model

The T-P model is in itself a kind of reaction-kinetics and features in taking two competing processes into con-

sideration: one is the usual electron emission from (active) emission sites and the other the electron supply to (inactive or electron-deficient) emission sites. Below, for convenience, we list the symbols and notations used.

$S_0(t)$ : number of total emission sites in a specimen at  $t$ .

$S'(t)$ : number of exo-active sites in a specimen at  $t$ .

$S''(t)$ : number of exo-inactive sites in a specimen at  $t$ .

$N(t)$ : exo-emission yield (per unit time) from a specimen at  $t$ .

$\alpha$ : rate of exo-emission from exo-active sites (or from electron-filled trap levels).

$\beta$ : rate of activating exo-inactive sites (or of exciting low energy electrons to the higher unoccupied levels).

First, we assume that  $S_0(t)$  is always equal to a constant,  $S_0$ . Then, the following equation become apparent from the above definitions:

$$S_0 = S'(t) + S''(t) \quad (2)$$

$$\begin{aligned} \frac{dS'(t)}{dt} &= -\alpha S'(t) + \beta S''(t) \\ &= -(\alpha + \beta)S'(t) + \beta S_0 \end{aligned} \quad (3)$$

For an initial condition  $S'(0) = S_0$ , the solution of Eq. (3) is

$$S'(t) = \frac{\beta}{\alpha + \beta} S_0 + \frac{\alpha}{\alpha + \beta} S_0 \exp[-(\alpha + \beta)t]. \quad (4)$$

Also, the EEE intensity,  $N(t)$ , is given by

$$N(t) = \alpha S'(t). \quad (5)$$

It should be noted that the first term of the right-hand side of Eq. (4) corresponds to a stationary emission which can last a very long time; the second term corresponds to non-stationary emission such as that observed only immediately after perturbing specimens (e.g., by irradiation or mechanical treatments).

If  $S_0(t)$  cannot be considered a constant, we can write a basic rate equation (corresponding to Eq. (3)) as

$$\frac{dS'(t)}{dt} = -(\alpha + \beta)S'(t) + \beta S_0 + \frac{dS_0}{dt}. \quad (6)$$

Usually, however, Eqs. (2) to (5) form the basis of our analysis for the phenomena to be discussed in the following sections.

### §3. Phenomena concerning PSEE from Scratched Metals

#### 3.1 Storage effect

Figure 1 is presented as direct evidence for the necessity of taking two competing PSEE processes into consideration: PSEE yields from an aluminum sheet were counted as functions of the time after scratching the sheet with a steel needle. Photostimulation was interrupted at  $t_{\text{off}}$  and an immediated extinction of yield followed. At  $t_{\text{on}}$ , the time from which the sheet was illuminated again, the PSEE yield quickly rose to a value that was distinctly higher than that at the plateau. It then gradually decayed to a stationary value that could be obtained by extrapolating the curve in Region I beyond  $t_{\text{on}}$ . Figure 2 shows that upon prolonging the interruption period of photostimulation,  $t_c (= t_{\text{on}} - t_{\text{off}})$ , the momentary PSEE enhancement,  $N_{\text{on}} - N_{\text{off}}$ , also increased to saturation.

This PSEE "storage" effect is very simple to interpret using the T-P model:<sup>2)</sup> Using Eqs. (3) and (4),  $S'(t_{\text{off}})$  and  $S'(t_{\text{on}})$  can be written as

$$S'(t_{\text{off}}) = \{\beta/(\alpha + \beta)\} S_0,$$

$$S'(t_{\text{on}}) = S_0 - \{\alpha/(\alpha + \beta)\} S_0 \exp(-\beta t_c).$$

Hence,

$$\begin{aligned} N_{\text{on}} - N_{\text{off}} &= \alpha[S'(t_{\text{on}}) - S'(t_{\text{off}})] \\ &= \{\alpha/(\alpha + \beta)\} S_0 [1 - \exp(-\beta t_c)]. \end{aligned} \quad (7)$$

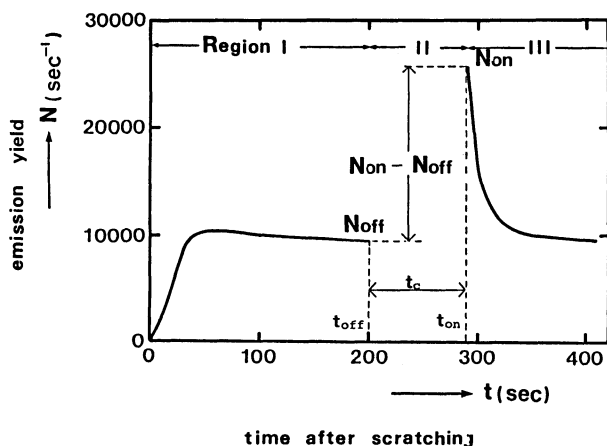


Fig. 1. PSEE yield from an Al specimen as a function of time after scratching the surface. The photostimulation was turned off at time  $t_{\text{off}}$ , and was resumed at  $t_{\text{on}}$ .

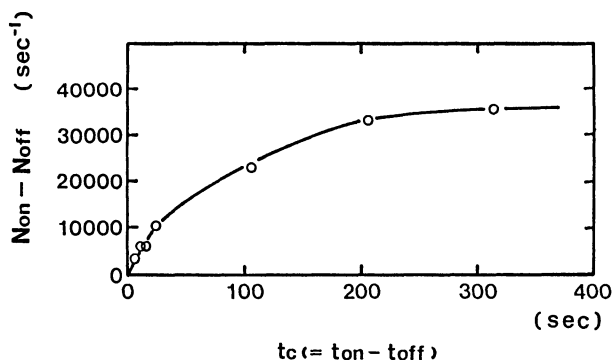


Fig. 2. Transient increase in the emission yield as a function of interruption length.

It is apparent from Eq. (7) that with increasing  $t_c$  the value  $(N_{\text{on}} - N_{\text{off}})$  tends to saturate (Fig. 2).

#### 3.2 Intensity versus time profiles of PSEE

When aluminum specimens are scratched under various ambient pressures (i.e., different partial pressures of oxygen), the PSEE intensity, therefrom, changed with time in such a manner as is exemplified in Fig. 3. Here one can see that there is a peak in each curve. Let the time for the intensity to reach the peak be denoted by  $t_{\text{max}}$ , and the time for a clean surface to be covered by a monolayer at given ambient pressures by  $t_{\text{ox}}$ . It is experimentally known that  $t_{\text{max}}$  is much longer than  $t_{\text{ox}}$ , and that an increase in the ambient pressure generally causes a yield enhancement of the PSEE. An explanation of these phenomena is given in terms of the T-P model:

The scratching of a metal causes old oxide layers to be removed and fresh surfaces to be exposed to an oxidizing atmosphere (if present). We rather arbitrarily assume that along with the progress of the oxidation of fresh layers, the number of exoemission sites vary exponentially with time and obey the relation

$$S_0(t) = S_0[1 - \exp(-\gamma t)]. \quad (8)$$

By substituting Eq. (8) into Eq. (6) and assuming that  $\gamma$  is much greater than either  $\alpha$  or  $\beta$  under the given ambient condition (see Table 1), we obtain<sup>4)</sup>

$$\begin{aligned} S'(t) &= \{[1/(\alpha + \beta)]\} \{\alpha \exp(-(\alpha + \beta)t + \beta) \\ &\quad - \exp(-\gamma t)\} S_0. \end{aligned} \quad (9)$$

Equation (9) indicates that a yield peak should sometimes appear after scratching and that, because of the  $\exp(-\gamma t)$  term, the peak should grow higher upon in-

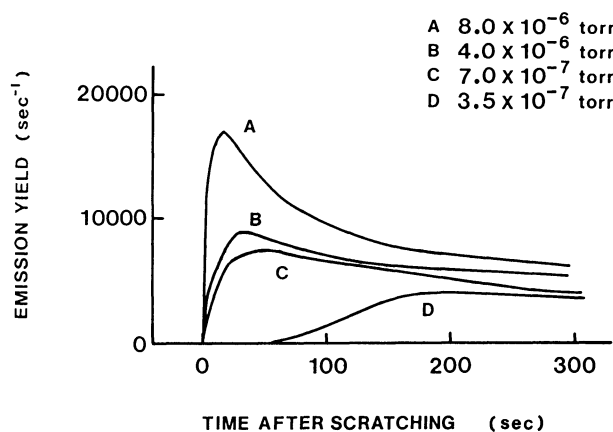


Fig. 3. Effect of ambient pressure on the PSEE yield behavior after scratching aluminum specimens.

Table I. Values of two-process model parameters determined for PSEE from scratched aluminum at various ambient pressures.

$P(\text{Torr})$	$S_0$	$\alpha(\text{sec}^{-1})$	$\beta(\text{sec}^{-1})$
$5.5 \times 10^{-5}$	$1.62 \times 10^7$	$2.86 \times 10^{-3}$	$5.19 \times 10^{-3}$
$2.4 \times 10^{-5}$	$1.73 \times 10^7$	$2.40 \times 10^{-3}$	$2.03 \times 10^{-3}$
$8.5 \times 10^{-6}$	$4.82 \times 10^5$	$5.31 \times 10^{-2}$	$3.22 \times 10^{-2}$
$2.5 \times 10^{-6}$	$5.56 \times 10^6$	$3.06 \times 10^{-2}$	$2.44 \times 10^{-2}$
$6.0 \times 10^{-7}$	$3.42 \times 10^6$	$1.87 \times 10^{-2}$	$1.33 \times 10^{-2}$
$1.1 \times 10^{-7}$	$4.06 \times 10^7$	$4.80 \times 10^{-4}$	$1.33 \times 10^{-3}$

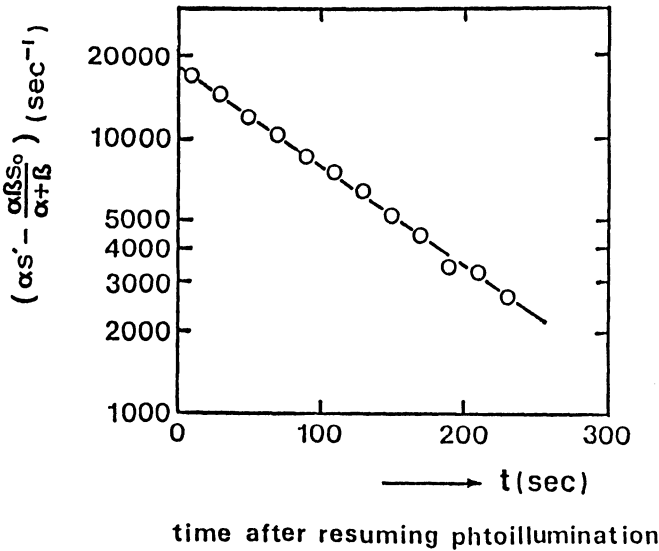


Fig. 4. The transient increase in emission yield,  $\alpha S$ , from the stationary value,  $\alpha \beta S_0 / (\alpha + \beta)$ , observed after resuming photostimulation.

creasing the ambient pressure. Also, the differentiation of Eq. (9) with respect to  $t$  leads to

$$t_{\max} = \frac{1}{\gamma} \ln(\gamma/\alpha). \quad (10)$$

One can see from Eq. (8) that  $1/\gamma$  gives a measure of (or a little greater than)  $t_{\text{ox}}$ . Also,  $\gamma$  has been determined to be much larger than  $\alpha$  (Table I). Hence, Eq. (10) seems to explain the experimental result that  $t_{\max}$  was much longer than  $t_{\text{ox}}$  (Fig. 3) fairly well.

By differentiating Eq. (10), we find that

$$dt_{\max}/d\gamma < 0. \quad (11)$$

This relation makes it reasonable that at higher ambient pressures the PSEE intensity reaches its maximum faster than at lower pressures.

Because  $\gamma t_{\max}$  is much greater than unity at  $t = t_{\max}$ , the second exponential term in the right-hand side of Eq. (9) can be neglected. Then a slight modification of Eq. (9) results in

$$\begin{aligned} & \ln [\alpha S'(t_{\max}) - \{\alpha \beta S_0 / (\alpha + \beta)\}] \\ & = \ln [\alpha^2 S_0 / (\alpha + \beta)] - (\alpha + \beta) t_{\max}. \end{aligned} \quad (12)$$

Equation (12) implies that a value equal to the peak yield subtracted by the stationary yield decreases exponentially with  $t_{\max}$  and that if the values are plotted on a semi-logarithmic scale, the line slope is given by  $-(\alpha + \beta)$ . Figure 4 shows that this relation holds for the observed PSEE data on scratched aluminum not only regarding the present research but also that of Ramsey *et al.*<sup>9)</sup>

### 3.3 Dependence of PSEE intensity on stimulation intensity

The PSEE intensity from scratched metals can be considerably high at an early stage after scratching; however, it then decreases to reach a quasistationary value much weaker than the initial emission. Denoting the emission current at this quasistationary stage by  $N_s$ , we obtain

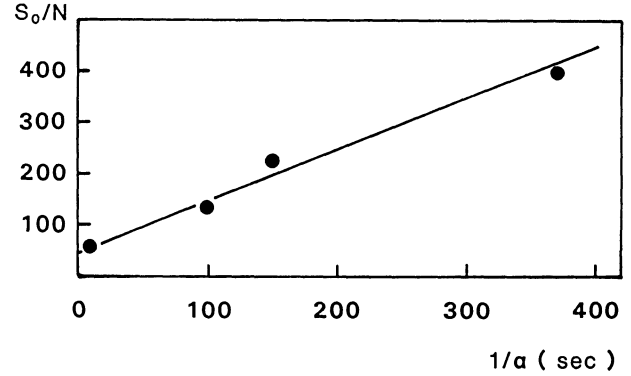


Fig. 5. Effect of the photostimulation intensity on the quasistationary intensity of PSEE from scratched aluminum.

from Eq. (4)

$$N_s = \alpha \beta S_0 / (\alpha + \beta) = S_0 / \{(1/\alpha) + (1/\beta)\}. \quad (13)$$

Equation (13) indicates that if one can freely vary the rate of exoemission,  $\alpha$ , the limiting values of  $N_s$  will be given by

$$\lim_{\alpha \rightarrow 0} N_s = \alpha S_0, \quad \text{and} \quad \lim_{\alpha \rightarrow \infty} N_s = \beta S_0. \quad (14)$$

Since  $\alpha$  is considered to have a positive correlation with the photoillumination intensity,\* the following deduction from Eq. (13) appears reasonable: As long as the intensity of the stimulating light is comparatively low, nearly all of the exoemission sources will be active ( $S_0 \doteq S'$ ); hence, the quasistationary emission current  $N_s$  will be proportional to the intensity. When the intensity is very high, on the other hand, nearly all of the sources will be inactive ( $S_0 \doteq S''$ ) and the current will be dominated by the rate of source activation,  $\beta$ .

A mere transformation of Eq. (13) leads to

$$S_0/N_s = (1/\alpha) + (1/\beta). \quad (15)$$

On the basis of this relation, we conducted an experiment to measure  $N_s$  under the condition that the varying photostimulation intensity was always maintained at very low levels. The results shown in Fig. 5 seem to confirm the validity of Eq. (15).

### §4. TSEE and PSEE Glow Curves

Glow curve determination is very important and, hence, common in TSEE measurements. Although an elevation of specimen temperature can obviously be replaced by changing the wavelength of the stimulating light from longer to shorter wavelengths, PSEE glow curves have seldom been determined. In the present section it will be shown in view of the T-P model that a PSEE glow curve can provide information about emission mechanisms that is as useful as that of TSEE.

From now on it will be convenient to assume that the rate of emission from exo-active sites,  $\alpha$ , is the product of two factors,  $\eta$  and  $\alpha_0$ . Here,  $\alpha_0$  represents the probability that an electron occupies an excited state, while  $\eta$  denotes the probability that an electron in an excited

\*As will be seen in Eq. (22),  $\alpha$  corresponds to the probability of photoelectric emission.

state escapes into the vacuum. Hence, Eq. (5) should be rewritten as

$$N(t) = \eta \alpha_0 S'(t). \quad (16)$$

#### 4.1 TSEE glow curves

According to Holzapel and the other workers,<sup>10-12</sup>  $\eta$  is usually taken to be a constant (unity in most cases), and  $\alpha_0$  is given by

$$\alpha_0 \propto \xi \exp(-E/kT), \quad (17)$$

where  $E$  is the activation energy,  $k$  the Boltzmann constant,  $T$  the absolute temperature and  $\xi$  a frequency factor. Since at glow peaks the time derivative of  $N(t)$  should be null, from Eqs. (3) and (16)

$$\left[ \frac{d}{dt} (\eta \alpha_0) - \eta \alpha_0^2 \right] S'(t) + \eta \alpha_0 \beta (S'(t) - S_0) = 0. \quad (18)$$

In the case of TSEE experiments where ionic crystals with wide band gaps are mostly used as specimens, emission is usually regarded to be stationary. This implies that the process of activating inactivated emission sources can be neglected in TSEE, i.e.,  $\beta$  can be taken as null. On the assumption that  $\beta$  is zero and  $\eta$  is a constant, the above equation reduces to

$$\left( \frac{d\alpha_0}{dt} - \alpha_0^2 \right) S'(t) = 0. \quad (19)$$

During TSEE measurements the heating rate often influences the observed glow peak temperatures, and the following equation is widely adopted for determining the activation energy  $E$ ,

$$E = \frac{k \ln [(q_1/T_{1m})/(q_2/T_{2m})]}{(T_{1m})^{-1} - (T_{2m})^{-1}}. \quad (20)$$

where  $q_1$  and  $q_2$  represent different heating rates, and  $T_{1m}$  and  $T_{2m}$  are glow peak temperatures that corresponds to  $q_1$  and  $q_2$ , respectively. It should be noted here that if one assumes Eqs. (19) and (17), Eq. (20) can be derived without great difficulty. Also, using Eqs. (19) and (17) it can be seen that

$$\frac{d \ln q}{dT_m} = \frac{E}{kT_m^2} + \frac{2}{T_m} > 0 \quad (21)$$

where  $T_m$  is the glow peak temperature at a heating rate of  $q$ . On the basis of Eq. (21) it is natural that the increase of heating rates during TSEE measurements should generally cause glow peaks to shift to higher temperatures.

#### 4.2 PSEE glow curves

In the case of PSEE,  $\alpha_0$  can be written as Eq. (22). This is nothing but the result of an analogy with quantum-mechanical treatments of photoelectric effects, i.e.,

$$\alpha_0 \propto |\langle f | H_{int} | i \rangle|^2 \cdot \rho_f \cdot n, \quad (22)$$

Here,  $\langle f |$  and  $| i \rangle$  represents the wave functions of an electron corresponding to its final and initial states, respectively;  $H_{int}$  is a Hamiltonian indicating the interaction between the electron and photons;  $\rho_f$  is the state density for the final state; and  $n$  is the number of photons.

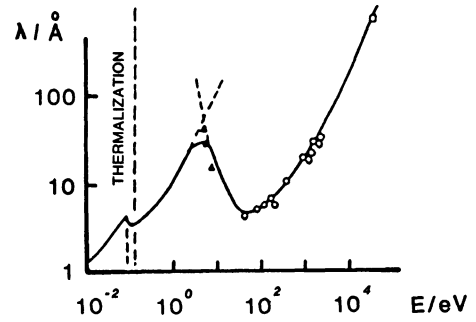


Fig. 6. Relation between the mean free path of low-energy electrons and their energies.

With regard to  $\eta$  for aluminum, we assumed the existence of the relation

$$\eta \propto \exp[-A/(v - v_0)] \quad (23)$$

where  $v$  represents the frequency of the stimulating light ( $v_0$  its threshold value) and  $A$  is a constant. This results from an extrapolation of an actually observed relation between the mean free path of low-energy electrons in aluminum and their energy (Fig. 6).

With assumptions that (1)  $\beta$  is close to zero, (2)  $\alpha_0$  is constant for a constant illumination, and (3)  $\eta$  varies with the light frequency as described in Eq. (23), we derived (from Eqs. (19), (22) and (23)) a relation between the glow peak frequency,  $\nu_{max}$ , and the rate of changing light frequency,  $dv/dt$ , written as

$$\nu_{max} - \nu_0 = \sqrt{(A/\alpha)(dv/dt)}. \quad (24)$$

( $\nu_0$ : threshold frequency)

It can be seen from Eq. (24) that, similar to the case of Eq. (21), the glow-peak frequency tends to shift to the higher energy side upon increasing the rate of changing light frequency. Figure 7 shows sample PSEE glow curves obtained for scratched aluminum by changing the rate of decrease in the photostimulation wavelength. Figure 8 indicates that a linear relation holds when the data (shown in Fig. 7) regarding both  $\nu_{max} - \nu_0$  and  $dv/dt$  are plotted on logarithmic scales. A slight deviation from linearity in Fig. 8 seems to indicate that  $\beta$  cannot wholly be neglected in the case of PSEE from metals.

In order to give a somewhat quantitative explanation

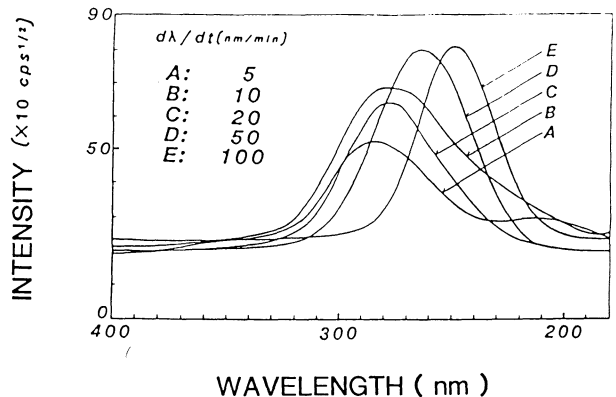


Fig. 7. PSEE intensity peaks as a function of the wavelength of stimulating light for different values of  $d\lambda/dt$  (the rate of changing wavelength).

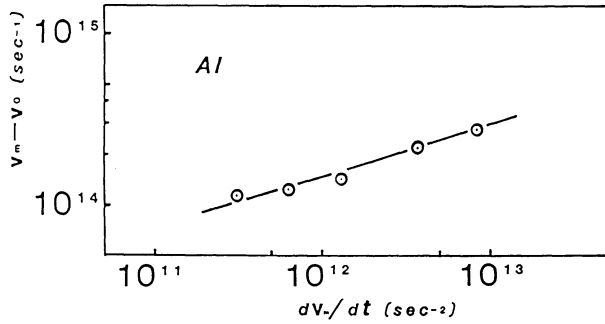


Fig. 8. Linear relation between  $\nu_m - \nu_0$  (the peak frequency shift) and  $d\nu_m/dt$  (the rate of changing frequency) for PSEE from scratched aluminum.

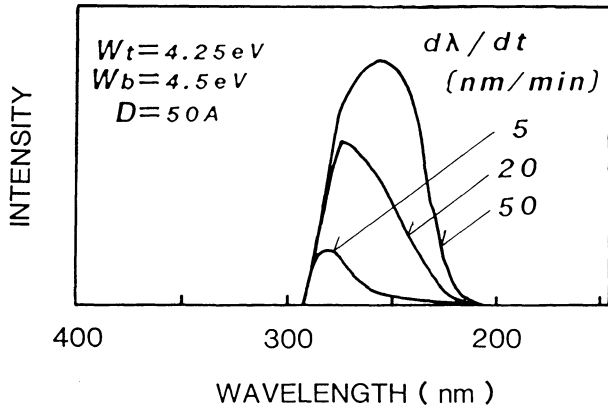


Fig. 9. Calculated profiles of PSEE glow curves for three kinds of decreasing rate in the wavelength of stimulation light.

for the changes in the peak height and peak frequency (wavelength) shown in Fig. 7, we performed a numerical calculation (Table II). This was principally an energy integration over the volume of a specimens, using Eqs. (5), (6) and (23) as well as the values  $\alpha$  and  $\beta$  (which we determined by a method to be mentioned in the next section). For this calculation we had to assume several values for the oxide layer thickness on scratched aluminum and for the width of the energy level dispersion of the values that were found in the best agreement with the observed peak change in height and wavelength (Fig. 9). It should be mentioned here that this PSEE glow peak can be used for estimating both the surface depth and the energy width of the exoemission sources.

##### §5. Methods for Determining T-P Model Parameters.

In Table I examples are given of the observed values of  $\alpha$ ,  $\beta$ , and  $S_0$ . Here, we would like to describe how these parameters were determined.

As can be seen in Eq. (4), the PSEE intensity which

was equal to  $\alpha S_0$  initially after perturbation decayed exponentially with time and reached the stationary value  $N_s$  given by Eq. (13). Equation (4) also indicates that, if one alters the condition by an abrupt stimulation, an exponential change in the emission intensity will follow and the time constant of the change will be a measure of the quantity  $(\alpha + \beta)$ . Since  $N_s$  is linearly related to  $S_0$ , it is possible to determine all of the parameters,  $\alpha$ ,  $\beta$  and  $S_0$ , on an experimental basis if either  $\alpha$  or  $\beta$  can be independently determined.

The PSEE storage effect, stated in the previous section, appears convenient for this purpose. As is evident from Eq. (7), the increase in emission yield tends to saturate for a long interruption of photostimulation. This indicates that for a large  $t_c$   $N_{on}$  is no longer a function of  $t_0$ , but is equal to  $\alpha S_0$ . If this saturated value of  $N_{on}$  is denoted by  $N_0$ , we can easily derive the relation

$$N_{on} - N_{off} = [1 - \exp(-\beta t_c)](N_0 - N_{off}).$$

This equation is identical to

$$1 - \exp(-\beta t_c) = \frac{(N_{on}/N_{off}) - 1}{(N_0/N_{off}) - 1}. \quad (25)$$

Since all of the quantities on the right-hand side of Eq. (25) are measurable, the right-hand side can be plotted against  $t_c$ . If this is done on a semi-logarithmic scale, the slope of the line should be equal to  $\beta$ . (In the right-hand side of Eq., (25) the ratios of the emission intensity are used so as to lessen the influence of a change in the number of total emission sources,  $S_0$ .) Figure 10 shows

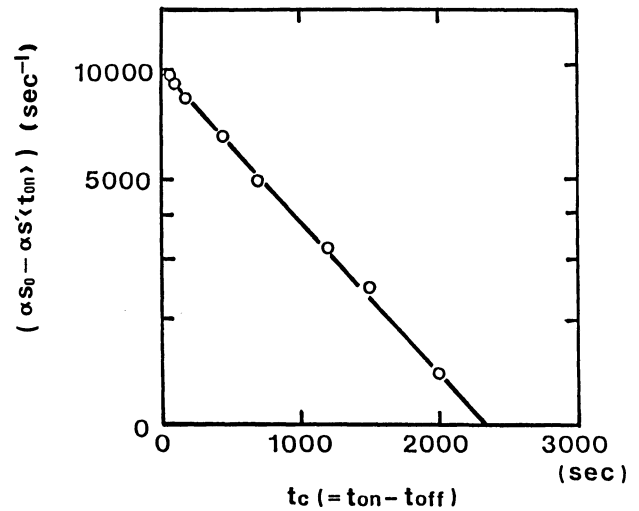


Fig. 10. The observed relation between  $\alpha S_0 - \alpha S'(t_{on})$  and  $t_c$ , the length of intermission. Note that  $\alpha S_0$ , equal to  $N_{on}$  for  $t_c$  long enough, corresponds to the yield when all of the mission sites are filled and that  $\alpha S_0 - \alpha S'(t_{on}) = \alpha(S - S'(t_{on}))$ , where  $(S_0 - S'(t_{on}))$  represents the number of inactivated sites at  $t$ .

Table II. Estimated values of the energy depth of exoemission sites and of the thickness of an oxide layer; they were determined so that, as shown in Fig. 7, best fits to observed values would be obtained.

Threshold (nm)	$\alpha$ ( $\text{sec}^{-1}$ )	$\beta$ ( $\text{sec}^{-1}$ )	$d\lambda/dt$ (nm/min)	peak wavelength		peak intensity ratio		sourceb width (eV)	oxied layer (Å)
				exp.	cal.	exp.	cal.		
310	0.015	0.0002	5	285	283	0.24	0.22	0.25	~ 50
			20	277	277	0.57	0.67		
			50	264	260	1	1		

an example of a determination of  $\beta$ . The good linearity of the plotted data appears to support the present view regarding the Two Process model.

### §6. Conclusion

The Two Process model is intended to draw attention of exoemission researchers to the presence of a process which enables the reactivation of emission sources once inactivated. This process does not seem to have been seriously considered by other researchers. As was stated in the text, however, the model has proved to be useful in explaining various PSEE phenomena, mostly related to scratched aluminum. It is suggested that this model is not limited to PSEE but can be applied to various TSEE phenomena.

### References

- 1) H. Glaefeke, in: *Topics in Applied Physics*, Vol. 37, edited by P. Bräunlich (Springer, Berlin, 1979) p. 225.
- 2) Y. Saito, Y. Shinada, Y. Hasegawa: *J. Jpn. Inst. Metals.* **38** (1974) 1006.
- 3) H. Shigekawa and S. Hyodo: *Jpn. J. Appl. Phys.* **21** (1982) 1278.
- 4) H. Shigekawa and S. Hyodo: *Jpn. J. Appl. Phys.* **22** (1983) 42.
- 5) H. Shigekawa and S. Hyodo: *Jpn. J. Appl. Phys.* **22** (1983) 1493.
- 6) H. Shigekawa and S. Hyodo: *Jpn. J. Appl. Phys.* **22** (1983) 1627.
- 7) H. Shigekawa and S. Hyodo: *Jpn. J. Appl. Phys.* **23** (1984) 1146.
- 8) H. Shigekawa and S. Hyodo: *Appl. Surf. Sci.* **22/23** (1985) 361.
- 9) D. R. Arnott and J. A. Ramsey: *Surf. Sci.* **28** (1977) 1.
- 10) G. Holzapfel: *phys. stat. sol.* **33** (1969) 235.
- 11) G. Holzapfel and M. Krysted: *phys. stat. sol. (a)* **37** (1976) 303.
- 12) W. Schelenk: *phys. stat. sol. (a)* **33** (1976) 217.