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TWO-PROCESS MODEL OF PSEE FROM SCRATCHED METALS

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When photoillumination is interrupted, the exoelectron emission from scratched metal samples decays quickly. When the illumination is resumed, however, the recovered exoelectron emission shoots up to a value significantly higher than before and then decreases gradually – a fact overlooked by previous researchers. To explain this "storage effect" in PSEE (photostimulated exoelectron emission), the authors have proposed a model, according to which there are two excitation processes competing during PSEE; one is the photoexcitation of the electrons at energy levels within the band gap of surface oxide layers, and the other is the tunneling transition of electrons in bulk metals to occupy the vacant levels of the oxide layers. From the rate equations based on this model and also from the PSEE data obtained for scratched aluminum and zinc, three kinds of quantities, i.e., the number of exo-active sites, the emission rate from the sites and the rate of activating exo-inactive sites, are successfully estimated. Other PSEE phenomena such as the peculiar emission intensity versus time profiles can also be elucidated in view of this model.

1. Introduction

Exoelectron emission (EEE) is known to be a concomitance of the relaxation of perturbations of various thermodynamic equilibria [1]. In contrast to the case of thermally stimulated exoelectron emission (TSEE), however, relaxation-kinetic studies seem to have scarcely been carried out on photostimulated exoelectron emission (PSEE). The aim of the present paper is to show that some of the confusing time-dependent PSEE phenomena can successfully be described by relaxation kinetics, if the competition between two processes of electron excitation is taken into consideration.

2. Two-process model of PSEE

To explain our data, which are presented below, we have proposed a PSEE model in which such symbols and notations as listed below are used:

$S_0(t)$: number of total emission sites in a specimen at time t (the origin of which is taken at the moment of scratching).
$S'(t)$: 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.
α: rate of emission from exo-active sites (or rate of photoexcitation of electrons at occupied levels).
β: rate of activating exo-inactive sites (or of exciting low energy electrons to the higher unoccupied levels).
γ: creation rate of emission sites.

The concept of our model is illustrated in fig. 1. It is the essential assumption of the model that there are two competing exciting processes relevant to PSEE. One is the photoexcitation by which electrons are emitted as exoelectrons at a rate α. The other is the excitation of lower energy electrons at a rate β. Eqs. (1) to (4) described below form the base of our analysis:

$$S_0(t) = S'(t) + S''(t) \ , \tag{1}$$

$$N(t) = \alpha S'(t) \ , \tag{2}$$

$$\frac{\mathrm{d}S'(t)}{\mathrm{d}t} = -\alpha S'(t) + \beta S''(t) + \frac{\mathrm{d}S_0(t)}{\mathrm{d}t}$$

$$= -\alpha S'(t) + \beta\{S_0(t) - S'(t)\} + \frac{\mathrm{d}S_0(t)}{\mathrm{d}t} \ , \tag{3}$$

$$S_0(t) = S_0[1 - \exp(-\gamma t)] \ . \tag{4}$$

The meaning of eqs. (1) and (2) should be obvious from the definitions of

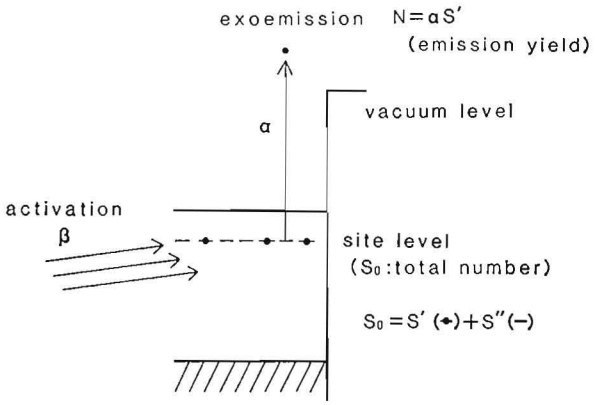

Fig. 1. Schematic exoelectron emission from exo-active sites at a rate α and electron supply to exo-inactive sites at a rate β.

the notation. Eq. (3), a rate equation, is central to the present treatment, while eq. (4) has been derived from a somewhat arbitrary assumption that the number of exo-emission sites grows to S_0, a constant, exponentially with time after scratching; this is probably in accordance with the oxidation of a freshly scratched metal surface.

3. Application of the two-process model

3.1. Storage effect of PSEE

Previously the authors [2] performed experiments in which EEE yields from polycrystalline aluminum sheets of 99.99% purity were counted in a vacuum (about 10^{-8} Torr) as a function of time after scratching the sheets with a steel needle. The Al specimens were photostimulated using a mercury discharge lamp and optical filters, the latter being selected so that photon energies of the stimulating light would be sufficiently below 4.2 eV, the work function of aluminum. Fig. 2 illustrates the typical yield behavior after scratching the specimens: at t_{off}, the photoillumination is interrupted and the immediate extinction of yield follows. At t_{on}, the time from which the specimen surface is illuminated again, the PSEE yield shoots up to a value distinctly higher than that at the plateau, and then decays gradually to the stationary value that can be obtained by extrapolating the curve in Region I beyond t_{on}. Fig. 3 shows that the transient increment of emission at the moment photoillumination is resumed (i.e., $N_{on} - N_{off}$ at t_{on} in fig. 2) is a function of t_c, the interval of interruption, and tends to saturation with

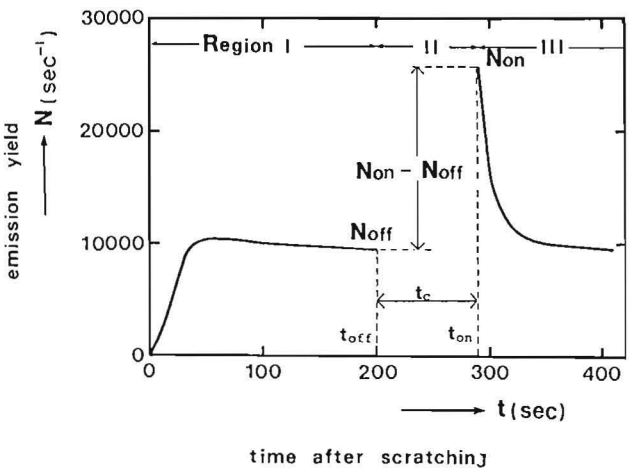

Fig. 2. PSEE yield from an Al specimen as a function of time after scratching the surface.

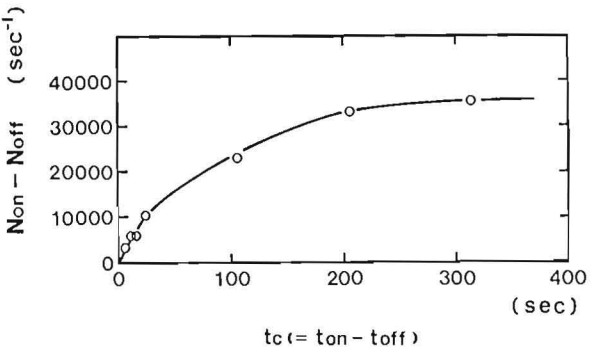

Fig. 3. Transient increase in emission yield as a function of intermission length.

increasing t_c. (Although Arnott and Ramsey [3] once conducted similar experiments, they did not notice such a storage effect of PSEE as described here, probably because t_c was too brief in their case.)

This effect is interpreted in terms of our "two-process" model as follows: Since the emission yield was almost stationary at t_{off}, $S_0(t)$, α and β are all assumed to be constants. Hence, the number of exo-active sites at t_{off}, $S'(t_{off})$, should be equal to $\beta S_0/(\alpha+\beta)$. Solving eq. (3) for Region III in fig. 2, we obtain

$$S'(t_{on}) = S_0 - \frac{\beta}{\alpha+\beta} S_0 \exp(-\beta t_c) \ , \tag{5}$$

$$N_{on} - N_{off} = \alpha[S'(t_{on}) - S'(t_{off})]$$

$$= \frac{\alpha}{\alpha+\beta} S_0[1 - \exp(-\beta t_c)] \ . \tag{6}$$

From eq. (6) it is apparent that with increasing t_c the value $(N_{on} - N_{off})$ tends to saturate, as shown in fig. 3.

3.2. Determination of excitation ratios

Eq. (5) indicates that for t_c long enough the experimental value of N_{on}, i.e., $\alpha S'(t_{on})$, will be equal to αS_0. Once αS_0 is known, it is possible to determine β on an experimental basis, since $-\beta$ is the slope of the $\ln[\alpha S_0 - \alpha S'(t_{on})]$ versus t_c relation, as shown in fig. 4.

So far we have assumed that all the three quantities α, β and $S_0(t)$ are constant. To see to what extent this assumption holds, the authors [4], using equations derived from eq. (3), determined $(\alpha+\beta)$ and α/β as a function of time after scratching as shown in figs. 5 and 6, which obviously indicate that,

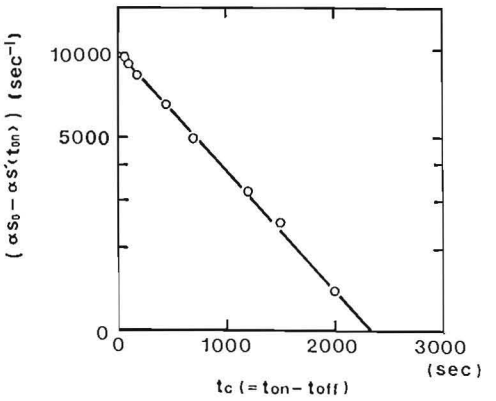

Fig. 4. The observed relation between $\alpha S_0 - \alpha S'(t_{on})$ and t_c.

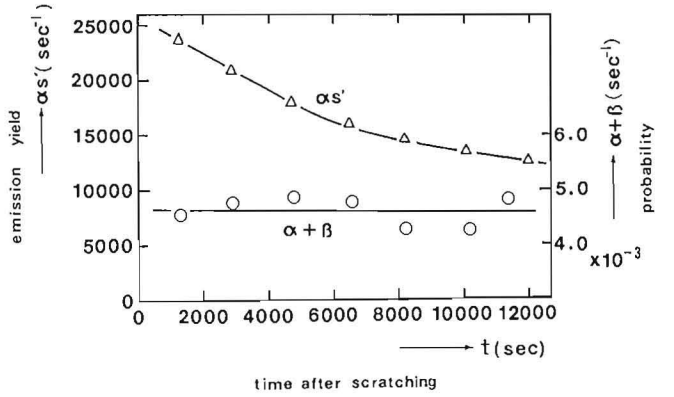

Fig. 5. The observed $\alpha S'$ and $(\alpha + \beta)$ as a function of time after scratching the specimen surface.

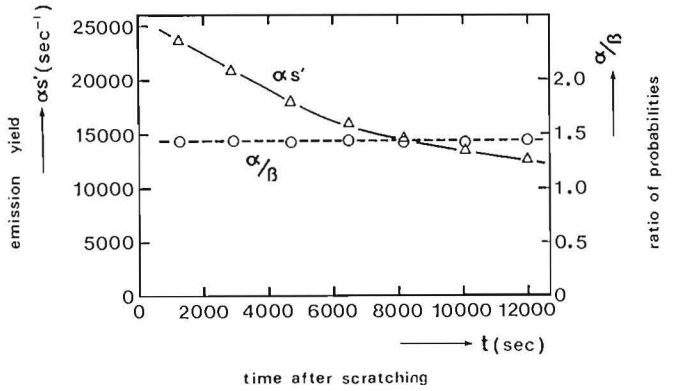

Fig. 6. The observed $\alpha S'$ and α/β as a function of time after scratching the specimen surface.

Table 1
Experimentally determined values of excitation rates and site population

P (Torr)	S_0	α (s^{-1})	β (s^{-1})
5.5×10^{-5}	1.62×10^{7}	2.86×10^{-3}	5.19×10^{-3}
2.4×10^{-5}	1.73×10^{7}	2.40×10^{-3}	2.03×10^{-3}
8.5×10^{-6}	4.82×10^{5}	5.31×10^{-2}	3.22×10^{-2}
2.5×10^{-6}	5.56×10^{6}	3.06×10^{-2}	2.44×10^{-2}
6.0×10^{-7}	3.42×10^{6}	1.87×10^{-2}	1.33×10^{-2}
1.1×10^{-7}	4.06×10^{7}	4.80×10^{-4}	1.33×10^{-3}

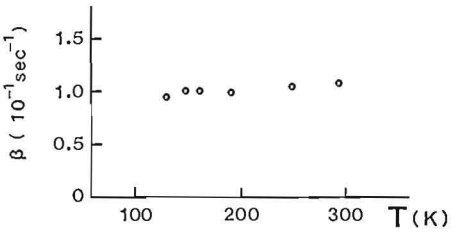

Fig. 7. Exo-activation rate β determined as a function of temperature.

while the yield $\alpha S'$ decays considerably during the period of observation, both $(\alpha+\beta)$ and α/β (hence α and β) remain constant. This result further indicates that the observed gradual yield decay after scratching is principally due, not to a change in the PSEE mechanism, i.e., a change in α or β, but to the change in the number of emission sites, i.e., in $S_0(t)$. Table 1 summarizes the values of α, β and S_0 obtained under several different vacua. All of the values are considerably scattered and there is no obvious pressure dependence. (To determine α, β and S_0, the authors [4] conducted a series of experiments, in which the photoillumination was not shut off but changed in intensity or in wavelength, a new method which is quite time-saving.)

Fig. 7 shows the results of our experiment to determine β as a function of temperature [5]. Contrary to our expectation, β was found to be practically temperature-independent. Since the height of the energy barrier for the interface between Al and Al_2O_3 is known to be about 1 eV, it is very unlikely that this temperature change would exert no influence on β. Hence, this result suggests that the electron supply to exo-inactive sites occurs not through thermal excitation but through quantum-mechanical tunneling.

3.3. Intensity versus time profiles of PSEE

PSEE intensity from scratched metal specimens changes with time after scratching the surface. The authors [6] noticed that, when a needle with a

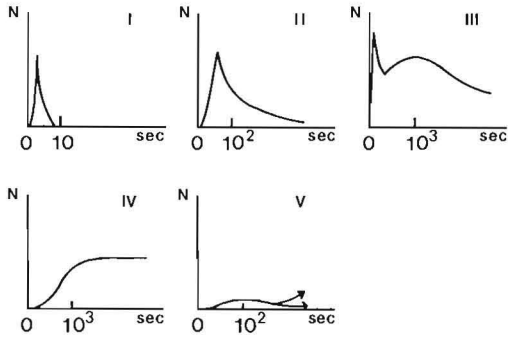

Fig. 8. Five profiles of time-dependent PSEE caused by scratching aluminum with a blunt needle.

blunt tip was used for scratching, the intensity versus time profile was not very reproducible but variable and could be classified into five types as schematically shown in fig. 8. This difference in the profile can be explained also in terms of the "two-process" model on the assumption that eq. (4) can describe the change in the number of total emission sites with time, $S_0(t)$.

Case 1 ($\gamma \gg \alpha$, β): In this case, using eq. (4), we can write the approximate solution of eq. (3) as

$$S'(t) = \left[\frac{1}{\alpha+\beta}\{\alpha \exp(-(\alpha+\beta)t+\beta)\} - \exp(-\gamma t)\right] S_0 \ . \tag{7}$$

By differentiating eq. (7), we can see that $S'(t)$ has a single maximum at t_m which is given by

$$t_m = (1/\gamma)\ln(\gamma/\alpha) \ . \tag{8}$$

One may see from eq. (8) that t_m decreases monotonically with increasing γ, since $dt_m/d\gamma$ is negative. This appears consistent with our observation that the pressure increase caused t_m to decrease, if γ is increased with increasing ambient pressure.

Setting further detailed discussion aside, we point out that both Types I and II are included in Case 1.

Case 2 ($\gamma \sim \alpha + \beta$): In this case the approximate solution of eq. (3) is

$$S'(t) = \frac{\beta}{\gamma} S_0 + \alpha\left(t - \frac{\beta}{\alpha\gamma}\right) S_0 \exp(-\gamma t) \ . \tag{9}$$

By differentiating eq. (9), we obtain

$$t_m = (1+\beta)/\alpha \sim \alpha^{-1} \ , \tag{10}$$

and become aware that, when α is a small as $\sim 10^{-3}\,s^{-1}$, there may appear a second peak in the intensity versus time profile, as observed in Type III. The first peak of Type V is also considered to be included in Case 2.

Case 3 ($\gamma \ll \alpha, \beta$): The approximate solution of eq. (3) is written as

$$S'(t) = \frac{\beta}{\alpha + \beta} S_0[1 - \exp(-\gamma t)] \ . \tag{11}$$

Since $S'(t)$ has no maximum but tends to saturate monotonically, this case is believed to correspond to the emission Type IV.

4. Conclusion

In the PSEE studies hitherto carried out, the rate β has tacitly been assumed to be null; i.e., the process of activating exo-inactive sites has been neglected. Through the present study the importance of the process has been clarified, particularly in elucidating the time-dependent PSEE phenomena. Although the present results are concerned only with PSEE from scratched aluminum, we hope that similar reasoning will be helpful in understanding other related relaxation phenomena such as TSEE, photoluminescence (PL) and thermally stimulated conductivity (TSC).

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