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Storage Effect in Photostimulated Exoelectron Emission from Scratched Aluminum

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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. This transient phenomenon has been studied in some detail as a function of the interval of the interruption and photon energy. To explain our data we propose a model, according to which there are two excitation processes competing during PSEE; one is the photoexcitation of the electrons at defect-related energy levels above the Fermi level, and the other is the thermal excitation of lower-energy electrons to the empty defect-related levels. Rate equations based on this model were found to be in satisfactory agreement with our observations.

§1. Introduction

Concerning the photostimulated exoelectron emission (PSEE) from the surface of scratched aluminum specimens, Ramsey and Arnott[1] reported as follows:

(1) Exoelectrons were not observed once photoillumination was interrupted. The emission began again immediately after the photoillumination was resumed.

(2) The exoelectron yield after resuming photoillumination did not depend on the interval of the interruption. The yield was essentially identical to that without the interruption.

These observations have led Ramsey and Arnott to believe that the basic mechanism of exoelectron emission should be independent from the photoexcitation process. A careful inspection of their results, however, has revealed that contrary to their conclusions the exoelectron yield does increase at the moment at which the photoillumination is resumed, and decays exponentially to the value that would be expected, were there no interruption of the photoillumination. This fact suggests that electrons are, during the intermission of photoillumination, accumulated at the sites from which the exoelectrons are excited.

The purpose of the present work is to investigate this momentary increase of PSEE and its decay in detail, and to interpret the phenomenon in terms of the electron accumulation in exoelectron emission sources.

§2. Experimental and Results

Figure 1 is a schematic of the experimental apparatus used. The system can be evacuated to 10^{-8} Torr. A 100 W Hg discharge lamp was used as an illumination source together with several optical filters. For the sake of convenience, the Hg light passing through filters a, b, c, d and e will be designated as light "a", "b", "c", "d" and "e", respectively.*

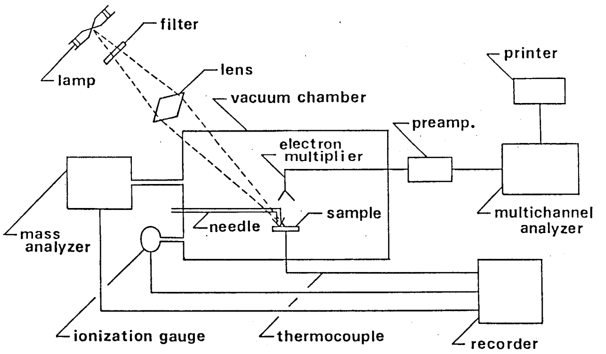

Fig. 1. Schematic diagram of the experimental arrangement.

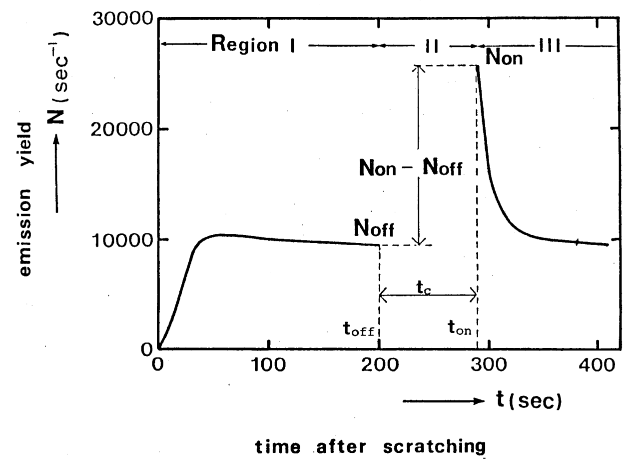

Fig. 2. PSEE yield from an Al specimen as a function of time after scratching the surface. The illumination was turned off at t_{off}, are resumed at t_{on}.

The specimens, polycrystalline Al sheets of 99.99% purity, were annealed at 400°C for 30 minutes in vacuum prior to the experiments. The specimen surface, illuminated by light "a", "b", "c", "d" or "e", was scratched with a steel needle.** The electron emission yield was observed with the combination of an electron multiplier (MURATA EMS 6081) and a multichannel analyzer (CANBERRA 8100). These procedures were performed with the sample at room temperature.

Figure 2 shows typical results for the number of electrons emitted from the specimen as a function of time after scratching the surface. The electron yield increases ini-

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*Transmission characteristics of the filters a through e are shown in the right corner of Fig. 4.

**Unless otherwise noted, the specimens were excited by light "a", the maximum photon energy of which is lower than the work function of aluminum (4.2 eV).[2]

tially and reaches a plateau which tends to decrease very gradually (Region I). At $t_{\rm off}$, an arbitrary point in this plateau, the photoillumination is interrupted. The electron yield then drops to zero immediately (Region II).

At $t_{\rm on}$, the time from which the surface is illuminated again, the electron yield shoots up to a value markedly greater than that at the plateau, though Ramsey and Arnott noticed no difference between these two values. The yield then decays gradually to the stationary value that can be obtained by extrapolating the emission-time curve in Region I beyond $t_{\rm on}$ (Region III). We have found that the emission increment, $(N_{\rm on}-N_{\rm off})$, depends on $t_{\rm c}$, the time interval during which illumination is turned off. Figure 3 shows that this increment tends towards saturation with increasing $t_{\rm c}$.

In order to study the effect of photostimulation energy on this momentary increase in the emission yield, we conducted a series of experiments, using lights "a" to "d" in turn and setting $t_{\rm c}$ equal to 3500 s. The results are summarized in Fig. 4, where the results corresponding to photostimulation by lights "a", "b", "c" and "d" are represented by the curves A, B, C and D, respectively. The initial yield enhancement upon resuming photoillumination, distinctly observed in the curves A and B, cannot be recognized in the curves C and D. On the contrary the curve D shows a slight decrease in emission just after $t_{\rm on}$.

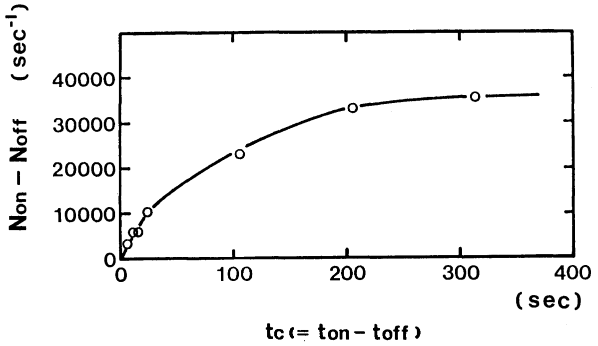

Fig. 3. Transient increase in emission yield as a function of intermission length.

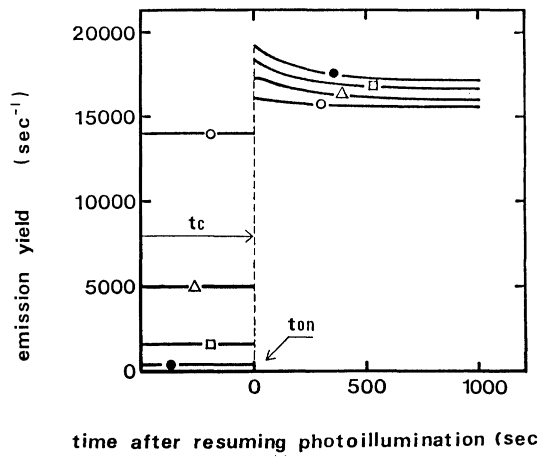

Fig. 5. The storage effect of electron sites as influenced by the degree of "darkness" during intermission ($t_{\rm c}$ = 1200 s) in which specimens were illuminated by lights "b" to "e". The curves ○, △, □ and ● correspond to the cases where lights "b" to "e" were used.

The specimens used in the above-stated experiments were kept in complete darkness throughout the intermission of photostimulation. In another series of experiments the specimens were illuminated by lights "b" to "e" during the intermission ($t_{\rm c}$ = 1200 s) and by light "a" at all other times. As shown in Fig. 5, the initial emission increase at $t_{\rm on}$ becomes less apparent when the sample is illuminated with light of shorter wavelength, i.e., with lights "e" to "b", during $t_{\rm c}$. This result seems to suggest the presence of some sort of storage effect associated with PSEE.

§3. Discussion

To account for this anomalous transient phenomenon of PSEE observed immediately after resuming photoillumi-

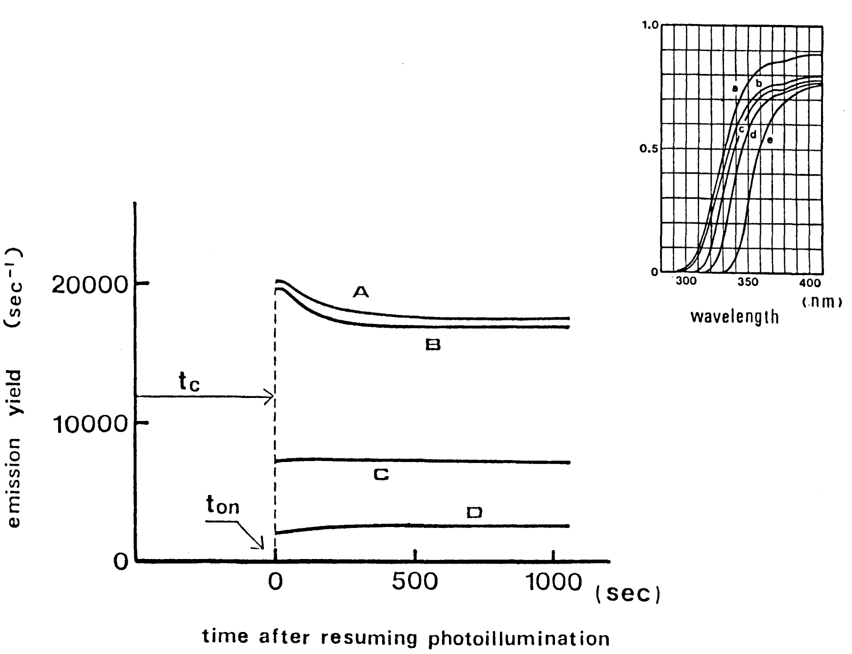

Fig. 4. The effect of photon energy on the storage effect of electron sites. The curves A to D correspond to the results where the lights "a" to "d" were used for photostimulation. The length of intermission $t_{\rm c}$ was 3500 s in all cases.

nation, we now propose a phenomenological model, assuming that there are two competing excitation processes; one is the photoexcitation process by which electrons at the filled levels are excited and emitted as exoelectrons and the other is the thermal excitation process, pumping low energy electrons to the empty higher levels.

Let S_0 be the total number of electron sites for exoelectron emission initially ($t=0$) created in a specimen by scratching its surface. From the foregoing assumption the sites should be composed of both filled and empty sites. Let $S'(t)$ be the number of filled sites at time t and $S''(t)$ be the number of empty ones.

Then

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

The filled sites are assumed to emit exoelectrons (i.e., to transform into empty sites) at a constant rate, α, during photostimulation. On the other hand, the empty sites are supposed to transform into filled ones at any time by thermal excitation at a constant rate β. The value of α should be zero during the intermission of photoillumination. Accordingly, we obtain a rate equation for electron sites in Region II ($t_{\text{off}} < t < t_{\text{on}}$), written as

$$\frac{\mathrm{d}S'(t)}{\mathrm{d}t} = \beta S''(t) = \beta(S_0 - S'(t)). \tag{2}$$

The solution of eq. (2) is

$$S'_{\text{II}}(t) = S_0 - (S_0 - S'(t_{\text{off}}))\exp(-\beta(t - t_{\text{off}})). \tag{3}$$

For Region III ($t_{\text{on}} < t$), a rate equation is similarly derived as

$$\frac{\mathrm{d}S'(t)}{\mathrm{d}t} = -\alpha S'(t) + \beta(S_0 - S'(t)). \tag{4}$$

The initial condition of eq. (4) is given by

$$S'(t_{\text{on}}) = S_0 - (S_0 - S'(t_{\text{off}}))\exp(-\beta t_{\text{c}}). \tag{5}$$

Hence, eq. (4) can be solved to give

$$S'_{\text{III}}(t) = \frac{\beta}{\alpha+\beta}S_0 + \left(S'(t_{\text{on}}) - \frac{\beta}{\alpha+\beta}S_0\right) \times \exp(-(\alpha+\beta)(t - t_{\text{on}})). \tag{6}$$

Since t_{off} is always in the plateau region where the emission is fairly constant, we may assume

$$S'(t_{\text{off}}) = \frac{\beta}{\alpha+\beta}S_0. \tag{7}$$

Substituting eq. (7) into eq. (3), we obtain

$$S'_{\text{II}}(t) = S_0 - \frac{\alpha}{\alpha+\beta}S_0 \exp(-\beta(t - t_{\text{off}})). \tag{8}$$

Combining eqs. (5), (6), and (7), we have

$$S'_{\text{III}}(t) = \frac{\beta}{\alpha+\beta}S_0 + \frac{\alpha}{\alpha+\beta}S_0(1 - \exp(-\beta t_{\text{c}})) \times \exp(-(\alpha+\beta)(t - t_{\text{on}})). \tag{9}$$

$$S'(t_{\text{on}}) = S_0 - \frac{\alpha}{\alpha+\beta}S_0 \exp(-\beta t_{\text{c}}). \tag{10}$$

Since the filled sites have been assumed to lose their electrons at a rate α, $N(t)$, the electron yield observed at time t, should be written as

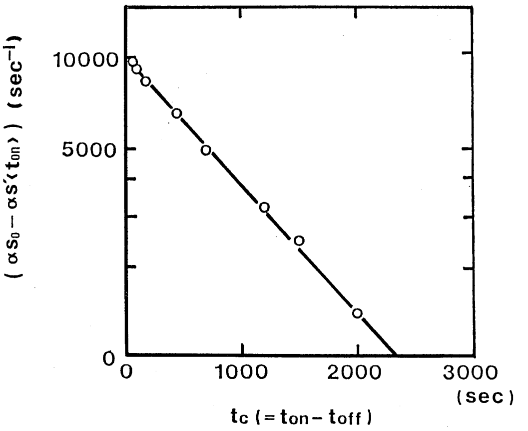

Fig. 6. The observed relation between $\alpha S_0 - \alpha S'(t_{\text{on}})$ and t_{c}, the length of intermission. Note that αS_0, equal to N_{on} for t_{c} long enough, corresponds to the yield when all of the electron sites are filled and that $\alpha S_0 - \alpha S'(t_{\text{on}}) = \alpha(S_0 - S'(t_{\text{on}}))$, where $(S_0 - S'(t_{\text{on}}))$ represents the number of empty sites at t_{on}.

$$N(t) = \alpha S'(t). \tag{11}$$

From eq. (10) one can see that $\lim_{t_{\text{c}}\to\infty} S'(t_{\text{on}}) = S_0$, which means that for t_{c} long enough the experimental value of N_{on}, such as shown in Fig. 2, should be equal to αS_0. Equation (10) also indicates that, once αS_0 is known, it is possible to determine β on an experimental basis, since $-\beta$ is the slope of the $\ln(\alpha S_0 - \alpha S'(t_{\text{on}}))$ vs t_{c} relation, as shown in Fig. 6.

As t_{c} increases to infinity, eq. (9) is reduced to

$$S'_{\text{III}}(t) = \frac{\beta}{\alpha+\beta}S_0 + \frac{\alpha}{\alpha+\beta}S_0 \exp(-(\alpha+\beta)(t - t_{\text{on}})). \tag{12}$$

Hence, at $t = t_{\text{on}}$,

$$S'_{\text{III}}(t) = \frac{\beta}{\alpha+\beta}S_0 + \frac{\alpha}{\alpha+\beta}S_0 = S'(t_{\text{off}}) + \frac{\alpha}{\alpha+\beta}S_0. \tag{13}$$

By rewriting eq. (13), we obtain

$$\frac{S'_{\text{III}}(t_{\text{on}}) - S'(t_{\text{off}})}{S'(t_{\text{off}})} = \frac{\alpha}{\beta}. \tag{14}$$

Since $\alpha S_{\text{III}}(t_{\text{on}})$ corresponds to the maximum exelectron yield in Region III and $\alpha S'(t_{\text{off}})$ to the yield at the plateau in Region I, both $\alpha S_{\text{III}}(t_{\text{on}})$ and $\alpha S'(t_{\text{off}})$ can be experimentally determined. Equation (14) thus provides us with a means for estimating α. By using the obtained values for αS_0, S_0 can be determined.

So far we have assumed that all three of the quantities α, β, S_0 are constant. If this assumption holds, the electron yield $N(t)$ should be constant in the pleateau of Region I, since $N(t) = \alpha S'(t)$ is equal to $\alpha\beta S_0/(\alpha+\beta)$ in Region I (cf. eq. (7)). Actually, however, the yield decays gradually, i.e., $N(t)$ is, to be exact, not constant but variable. It is thus necessary to determine to what extent α, β and S_0 actually are constant.

Multiplying both sides of eq. (12) by α, one sees that it is possible to determine $-(\alpha+\beta)$, obtained as the slope of the $\ln(\alpha S_{\text{III}}(t) - \alpha(\beta/\alpha+\beta)S_0)$ vs $(t - t_{\text{on}})$ relation which is shown in Fig. 7. In Fig. 8 the values thus obtained are shown over a wide range of t, together with the observed electron yield $N(t) = \alpha S'(t)$. In Fig. 9 the ratio α/β determined by using eq. (14) is plotted against t. Figures 8 and 9

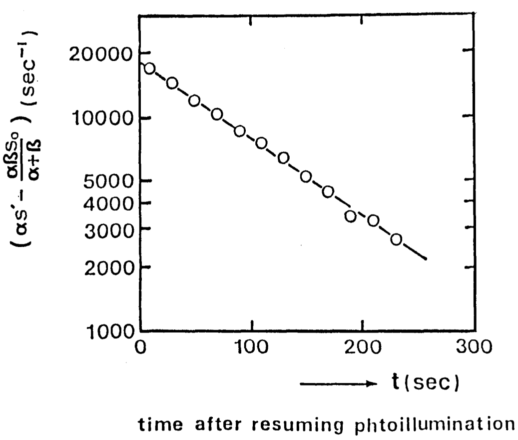

Fig. 7. The transient increase of emission yield, $\alpha S'$, from the stationary value, $\alpha\beta S_0/(\alpha+\beta)$, observed after resuming photo-illumination.

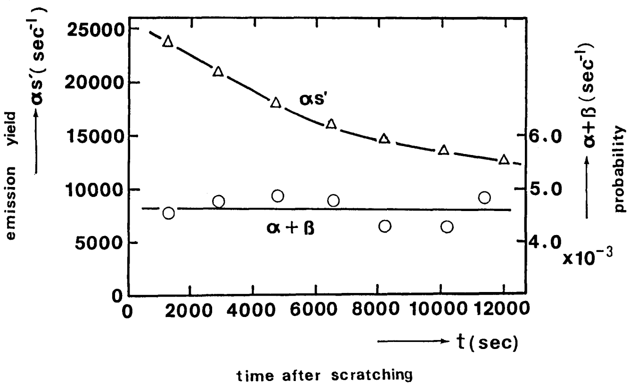

Fig. 8. The observed PSEE yield, $\alpha S'$, and the ratio of the two rates of electron site transformation, α/β, as a function of time after scratching the surface.

obviously indicate that, 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 decay of exoelectron emission after scratching the sample surface 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 sources, i.e., S_0.

Table I summarizes the values of α, β and S_0 obtained under several different vacuums.*

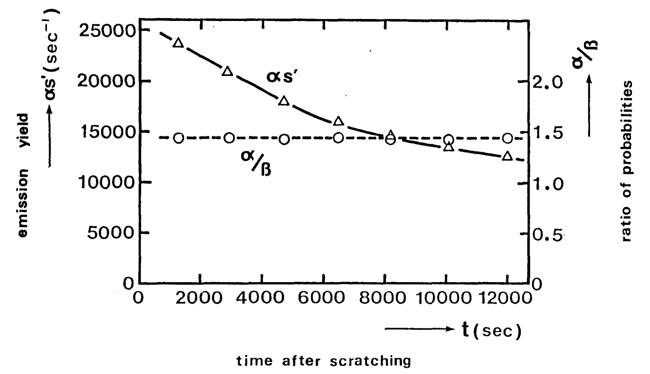

Fig. 9. The observed PSEE yield, $\alpha S'$, and the sum of the two rates of electron site transformation, $(\alpha+\beta)$, as a function of time after scratching the surface.

Table I. Experimentally estimated values concerning electron sites for exoelectron emission.

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}

α, emission rate of filled sites; β, excitation rate of empty sites; S_0, number of total electron sites initially produced.

All of the values are considerably scattered and there is no obvious pressure dependence. This is considered to be due mainly to the difficulty in producing very similar scratches in different specimens and to the time interval required for PSEE to become stable after scratching; the interval, ranging from 10^2 to 10^3 s, must be long enough to grow thick oxide layers on the scratched surface of aluminum. In Table I it should be noted that, in spite of the scattering, the values of α are of the same order of magnitude as values observed in ordinary photoemission yields. This model can be applied to elucidate PSEE phenomena other than those treated here, such as the temperature effect observed by Pimbley and Francis$^{3)}$ or the pressure and time dependences of the yield reported by Ramsey$^{4)}$ and Lohoff.$^{5)}$ The extension of this model in these directions will be reported elsewhere.

§4. Conclusion

1) During the observation of PSEE from scratched aluminum, the interruption of photostimulation has been found to cause the transient enhancement of the electron yield, which indicates some sort of storage effect in emission sources.

2) To explain this phenomenon, a "two-process model" has been proposed, in which S_0 (the number of total emission sites produced in specimens at the initial emission peak), α (the rate of exoelectron emission from higher-energy sites) and β (the rate of thermal excitation of lower-energy sites) are assumed constant for given experimental conditions. It has been found that, whereas S_0 cannot be regarded as constant for a long period of observation, α and β are quite constant. The values of α determined for several experiments are on the order of 10^{-2}–10^{-4} sec^{-1}, i.e., comparable to the rates observed for photostimulation yields.

3) From the results of experiments using light of various wavelength for stimulation, the electron sites responsible for the storage effect studied here seem to lie at rather deep energy levels.

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*Since S_0 cannot be considered unchangeable, the values of S_0 shown in Table I correspond to the maximum emission just after scratching. When S_0 varies considerably during the period of observation, it is difficult to determine β experimentally in the way illustrated in Fig. 6. However, β can be obtained by modifying eq. (5) to

$$1-\exp(-\beta t_c)=\frac{S'(t_{on})-S'(t_{off})}{S_0-S'(t_{off})}=\frac{S'(t_{on})/S'(t_{off})-1}{S_0/S'(t_{off})-1}$$

since the ratios $S'(t_{on})/S'(t_{off})$ and $S_0/S'(t_{off})$ depend only on α and β.

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