Intensity vs Time Profiles of Photostimulated Exoelctron Emission from Scratched Aluminum

Hidemi Shigekawa and Shin-ichi Hyodo

Department of Applied Physics, The University of Tokyo, Bunkyo-ku, Tokyo 113 (Received April 4, 1983; accepted for publication July 23, 1983)

Aluminum sheets were scratched with steel needles of different diameters, and photostimulated exoelectron emission (PSEE) therefrom was studied. It was found that the PSEE change with time after scratching can be classified into five types, which differ in the number of intensity peaks, in t_m (the time required to reach the first peak), and in the mode of decay. Experiments showed that these five types were correlated with the type of scratching as well as with the surrounding gas pressure. The pressure dependence of t_m is explained in terms of the "two process model" previously proposed by the suthors.

§1. Introduction

In the present communication we describe experimental results, which show that the intensity change with time of PSEE from Al after scratching the surface is greatly influenced by the type of scratching. In our view, the lack of attention paid to this effect may have been responsible, at least partly, for the lack of good reproducibility often observed in PSEE experiments. We hope that the present results will throw some light on the various confusing results associated with PSEE from scratched metals.

§2. Experimental Procedures and Results

Polycrystalline aluminum sheets (99.99% purity), 75 μ m in thickness and 25 × 35 mm² in area, were used as specimens. Prior to experiments they were ultrasonically cleaned in acetone for 15 minutes, and some of them were annealed at 400°C for 30 minutes. The experimental arrangement employed was similar to that previously described.¹⁾

The speciemen was placed in a vacuum chamber. Gas constituents inside the chamber were analyzed with a mass spectrometer. Specimen temperatures, almost equal to room temperature, were monitored with a chromel-alumel thermocouple. The specimen surface could be scratched from outside the vacuum chamber with either of two stainless steel needles; one, about 0.2 mm, and the other, about 3 mm in diameter. (For convenience, we shall hereafter call the former a sharp, and the latter a blunt needle.) The needle pressure on the specimen could be controlled from outside the chamber. Using an optical system composed of a mercury arc lamp, a quartz lens and some filters, we illuminated the specimen surface by light with stimulation energy well below the work function of Al (4.2 eV²). To detect and record the exoelectrons emitted from the specimen, an electron multiplier (Murata EMS 6081) and a multichannel analyzer (Canberra 801) were

Figure 1 shows the results for the specimens scratched with the sharp needle under differnt atmospheric conditions. These results are very similar to those obtained by Ramsey for abraded aluminum.³⁾ However, when the specimens were scratched with the blunt needle, their PSEE intensity changed with time after scratching in various

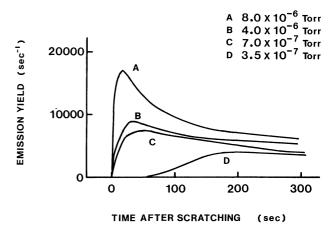


Fig. 1. Variation of photostimulated exoelectron emission with time after scratching at various background pressures.

manners; they can be classified into five types as shown in Fig. 2.

Type I: A single sharp peak in N, the PSEE intensity, appears within several seconds after scratching.

Type II: Within several tens or several hundreds of seconds, N reaches a peak and then monotonically decreases.

Type III: Within a few or several tens of seconds, N goes through the first peak and later, i.e. after several

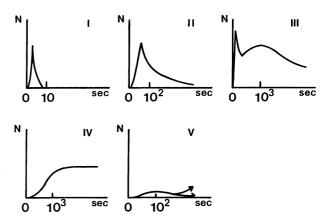


Fig. 2. Five time-dependences of photostimulated exoelectron emission caused by scratching with a blunt needle.

hundreds or thousands of seconds, reaches a second peak, whose height is much lower than that of the first.

Type IV: The intensity, N, increases slowly to saturation at several hundreds or thousands of seconds after scratching. The maximum emission can continue for a full day or longer.

Type V: A very low and dull peak appears at several hundreds of seconds or so. After passing the peak N may either decrease monotonically or change into type IV.

We measured $t_{\rm m}$, the time required for N to reach the first peak, and found that for each of the types I-V, $t_{\rm m}$ depends on the surrounding gas pressure. Some of the results are summarized in Table. 1.

§3. Discussion

The results so far described will be discussed in terms of our "two-process model"¹⁾: There are two excitation processes competing during PSEE; one is the photo-excitation (occurring at a rate of α) of the electrons at defect-related energy levels above the Fermi level, and the other the thermal excitation (occurring at a rate of β) of the lower-lying electrons to the empty defect-related levels.

Let S'(t) be the number of filled emission sites at time t, S''(t) the number of empty ones, and $S_0(t)$ (= S'(t) + S''(t)) their total number. In a previous work, 10 measurements were performed after the emission had stabilized, so that $S_0(t)$ was assumed constant. In the present case, however, we assume that $S_0(t)$ grows to saturation and can be written as

$$S_0(t) = S_0(1 - \exp(-\gamma t))$$
 (1)

where γ is the creation rate of emission sites. Since γ should

Table 1. Pressure-dependence of the time necessary for the emission yield to achieve the maxima shown in the five PSEE types caused by scratching with a blunt needle.

Туре	Pressure (Torr)	<i>t</i> _m (s)
Ι -	7.5×10^{-6}	6
	7.5×10^{-7}	14
и -	6.0×10^{-6}	30
	6.0×10^{-7}	140
III -	1.0×10^{-6}	10
		900
	6.0×10^{-7}	25
		6000
IV -	7.0×10^{-6}	5000
	7.0×10^{-7}	7000
v -	4.0×10^{-7}	1200
	2.5×10^{-7}	1800

be associated with the oxidization of fresh metal surfaces, it seems natural to assume that γ is pressure dependent. In addition, α and β are dependent on the structure of the emission surfaces; but in this experiment (with pressures ranging from 10^{-5} to 10^{-7} Torr), no marked dependence on pressure was observed. We further assume that all the sites created in accordance with eq. (1) are the ones filled with electrons. Under these assumptions we obtain a rate equation for emission sites as given by

$$\frac{dS'(t)}{dt} = -\alpha S'(t) + \beta (S_0(t) - S'(t)) + \frac{dS_0(t)}{dt}.$$
 (2)

Case 1 $(\gamma \gg \alpha, \beta)$:

In this case, using eq. (1), we can write the approximate solution of eq. (2) as

$$S'(t) = \left(\frac{1}{\alpha + \beta} (\alpha \exp(-(\alpha + \beta)t + \beta) - \exp(-\gamma t)\right) S_0. \quad (3)$$

In accordance with the definition of α , N(t), the observable emission intensity, should be written as

$$N(t) = \alpha S'(t). \tag{4}$$

Equation (4) indicates that the intensity peak appears at the time when the number of filled sites, S'(t), reaches maximum. By differentiating eq. (3), we can see that S'(t) has a single maximum, and we obtain an expression for t_m

$$t_{\rm m} = \frac{1}{\gamma} \ln \left(\frac{\gamma}{\alpha} \right). \tag{5}$$

One may see from Eq. (5) that $t_{\rm m}$ decreases monotonically with increasing γ , since ${\rm d}t_{\rm m}/{\rm d}\gamma$ is negative. The results (summarized in Table 1), that the pressure increase caused $t_{\rm m}$ to decrease, are very consistent with our model, if γ is increased with increasing atmospheric pressure. We firmly believe that this assumption holds; by combining eqs. (3) and (4), one may see that N(t) increases with increasing γ for any value of t. This was always observed, whenever we raised the atmospheric pressure.

The term $\exp(-\gamma t)$ in Eq. (3) can be neglected at $t = t_m$, and Eq. (4) can be approximately written as

$$\alpha S'(t_{\rm m}) = \frac{\alpha S_0}{\alpha + \beta} (\alpha \exp{(-(\alpha + \beta)t_{\rm m})} + \beta). \tag{6}$$

Equation (6) indicates that the intensity peak is lowered exponentially with increasing $t_{\rm m}$, which is also consistent with our observations. Equation (6) can be modified to

$$\ln\left(\alpha S'(t_{\rm m}) - \frac{\alpha \beta S_0}{\alpha + \beta}\right) = \ln\left(\frac{\alpha^2 S_0}{\alpha + \beta}\right) - (\alpha + \beta)t_{\rm m}. \tag{7}$$

Since $\alpha S'(t_m)$, the peak emission intensity, and $\alpha \beta S_0/(\alpha + \beta)$, the stationry intensity (at $t = \infty$), can be experimentally determined, the observed data (Fig. 1) are plotted against t_m in Fig. 3, where the results of Ramsey³⁾ for abraded Zn are also emloyed. Figure 3 indicates the validity of eq. (7) clearly.

We can determine the value of $(\alpha + \beta)$ from the slope of the lines in Fig. 3. We are also able to obtain the experimental values of αS_0 and $\alpha \beta S_0/(\alpha + \beta)$, since from eq. (6) αS_0 can be taken as $\alpha S'(0)$ and $\alpha \beta S_0(\alpha + \beta)$ as $\alpha S'(\infty)$.

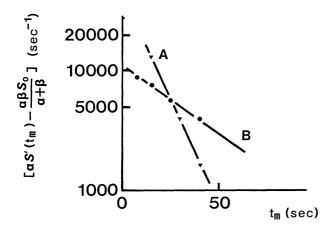


Fig. 3. The relation between the maximum emission yield to the stationary value, $\left(\alpha S'(t_{\rm m}) - \frac{\alpha \beta S_0}{\alpha + \beta}\right)$, and the time necessary for the emission yield to achieve the maximum, $t_{\rm m}$. While Curve A represents our results, Curve B is obtained by modifying Ramsey's normalized data on emission yield on the assumption that they should become equal to our data.

The values of α and β , thus determined, are typically about $10^{-2} \, \mathrm{s}^{-1}$.* Since in our experiments t_{m} for Type I ranged from 5 to 20 s (Table 1), we estimate from eq. (5) the value of γ to be typically $\sim 1 \, \mathrm{s}^{-1}$ at 10^{-5} Torr and $\sim 10^{-1} \, \mathrm{s}^{-1}$ at 10^{-6} Torr.

Type I and Type II are very similar to the profile for the specimens scratched with the sharp needle (Fig. 1). This sugests that the blunt needle can sometimes cause damages similar to those produced by the sharp needle. Also, the first peak in Type III may be associated with this effect. Since $t_{\rm m}$ for Type II is much longer than that for Type I, γ for Type II should be considerably smaller than that for Type I. We believe, however, that Type II should be included in Case 1, i.e., the relation $\gamma \gg \alpha$, β holds for Type II, too. Type II is considered to occur when the damage caused by scatching resembles that caused by tensile deformation:⁴⁾ the PSEE intensity from elongated Al speci-

mens is usually much lower than that from scratched or abraded specimens, and $t_{\rm m}$ for the former is much longer than that for the latter.

Case 2 $(\gamma \sim \alpha + \beta)$:

In this case the approximate solution of Eq. (2) is

$$S'(t) = \frac{\beta}{\gamma} S_0 + \alpha \left(t - \frac{\beta}{\alpha \gamma} \right) S_0 \exp(-\gamma t). \tag{8}$$

By differentiating Eq. (8), we obtain

$$t_{\rm m} = \frac{1+\beta}{\alpha} \sim \alpha^{-1}.\tag{9}$$

and become aware that, when α is as small as $\sim 10^{-3}$ s⁻¹, there may appear a 2nd peak in the intensity vs time profiles (Type III). The first peak of Type V is considered to be included in Case 2, too.

Case 3 $(\gamma \ll \alpha, \beta)$:

In this case, the approximate solution of Eq. (2) can be written as

$$S'(t) = \frac{\beta}{\alpha + \beta} S_0(1 - \exp(-\gamma t)). \tag{10}$$

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

§4. Conclusion

The PSEE intensity from Al sheets scratched with blunt needles were measured as a function of time after scratching. In contrast to the case when specimens were scratched with a sharp stylus, the intensity vs time profiles had several features and were classified into five types. These emission types were discussed in terms of a previously proposed "two-process model", under the assumption that fresh emission sites are created in the specimens at a pressure-dependent rate. Good agreement was obtained between the model and the experimental results.

References

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^{*}As reported earlier, the "storage effect" of PSEE also enables us to determine the values of α and β on an experimental basis. The previous experiments have shown fairly good consistency in the values of α and β .