

Change of Energy-Level Distribution of Photoemission Sources in Al and Zn Caused by Scratching

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Photoemission from Al (99.99% purity) specimens was measured for the photostimulation wavelength ranging from 190 to 700 nm. The specimens were scratched with a steel needle at temperatures from 77 to 290 K and at pressures from 10^{-5} to 10^{-7} Torr. Whereas prior to scratching the emission peaks from Al specimens appeared in a range from 250 to 290 nm, they shifted to a 290–350 nm range after scratching. Although this result is nothing but a manifestation of the so-called exoelectron emission, it has not been well recognized that scratching causes a change in the number of photoemission sources at various energy levels. The wavelength at the peak emission was influenced neither by the specimen temperature nor by the degree of vacuum. Similar results have been obtained for Zn specimens, though the yield observed was two orders of magnitude lower than that for Al.

§1. Introduction

In a previous paper,¹⁾ we presented a new model concerning PSEE (photostimulated exoelectron emission) from scratched aluminum: 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 the lower lying electrons to the empty defect-related levels. This "two process model" was adopted to interpret an observed "storage effect". The emission from those specimens to which the photoillumination had been turned off showed a temporary rise immediately after the illumination was resumed, and the emission rise became more apparent as the period of interruption was increased. Based on this model we further estimated the number and transition probabilities of the two kinds of sources.

The purpose of the present work is to study how the energy distribution of the emission sources is influenced by scratching and to directly verify our model by determining the levels of the new sources created.

§2. Experimental

The experimental setup of the equipment used is similar to that described earlier.¹⁾ Our specimens were Al and Zn polycrystalline sheets of 99.99% purity. They were kept at temperatures ranging from 77 to 290 K, and were scratched with a steel needle in a vacuum chamber at pressures from 10^{-5} to 10^{-7} Torr.

The specimens were subjected to photostimulation of variable wavelength by using a system comprising a deuterium lamp and a monochromator. It was possible for this system to automatically change the wavelength at rates from 2 to 100 nm/min. Since light for stimulation was introduced into the vacuum chamber from outside, photons with a wavelength shorter than 190 nm must have been completely absorbed by atmospheric air. To obtain the stimulating light of sufficiently high intensity, the resolving power of the monochromator was reduced as low as $\Delta\lambda = 10$ nm. The yield of PSEE (photostimulated exoelectron emission) from the specimen was then counted using an electron multiplier (Murata EMS 6081) and a

multichannel analyzer (Canberra 8100). Usually in the energy analysis of PSEE, attention has been paid to the energy distribution of emitted electrons and hence photostimulation at some fixed wavelength has been employed.^{2,3)} In the present experiment, however, the energy depth of emission sources is important and the apparent lowering of the work function is observed by changing the wavelength of photostimulation.

§3. Results and Discussion

Curve (a) in Fig. 1 shows the change of emission yield from a non-scratched Al specimen. The wavelength of photostimulation was scanned from 400 nm to the shorter at the rate of 20 nm/min. The threshold wavelength of electron emission is seen to be about 310 nm, the value almost equal to that derived from the work function of Al (4.2 eV^4). We conducted similar measurements just after irradiating the specimen by UV rays (250 and 230 nm in wavelength) for 10^3 seconds. The results are represented by the curves (b) and (c) in Fig. 1, where one can see that the total yield was very much reduced from that of curve (a) and the threshold wavelength shifted to about 270 or

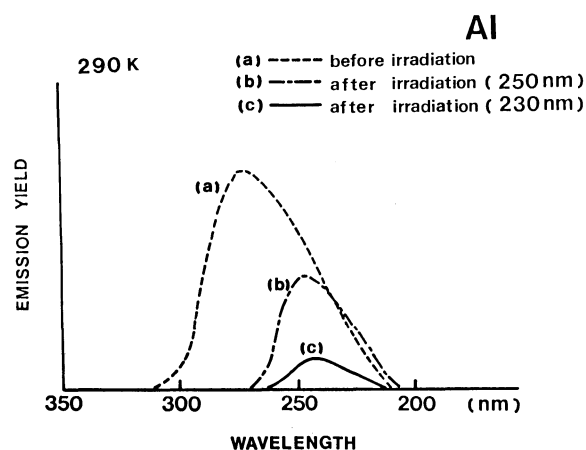


Fig. 1. Electron emission yield from Al as a function of photoillumination wavelength obtained before scratching the specimen. The distribution represented by curve (a) is the initial one, and those represented by curves (b) and (c) are the distributions obtained after irradiation with photoillumination wavelength of 250 nm and 230 nm, respectively.

260 nm; the work function of the specimen appeared to be raised. However, about half an hour after stimulating the specimen by UV rays, we found that the emission yield vs wavelength relation recovered its initial profile shown in curve (a). All of these results so far stated seem to indicate the following: Photoemission sources in the oxide-covered Al specimen are not restricted to a single energy level but distributed to some levels separated by gaps. When the specimen is photostimulated, only those sources at levels not deeper than the incoming photon energy emit electrons one by one. To fill them with electrons again, a considerable period, *e.g.* several tens of minutes, is required.

We irradiated the non-scratched specimen by UV rays of 280 and 250 nm in wavelength, and counted their electron emission as a function of time (Fig. 2). Whereas the emission showed a simple exponential decay for 280 nm, the yield vs time curve was well approximated by the sum of two exponential terms for 250 nm. Since it seems natural to assume that photoemission sources at different energy levels have different rates of electron emission, Fig. 2 may indicate that the sources in the specimen had at least two energy levels, below that corresponding to 250 nm UV rays, one between 250 and 280 nm and the other below 280 nm. Since for pure metals having numerous conduction electrons such a photoemission decay is not conceivable, such a decay as observed under constant UV irradiation should be related to the draining of active emission sources in oxide layers.

Figure 3 shows the yield vs wavelength relation for an Al specimen kept at 290 K and at 1.0×10^{-6} Torr. Before scratching the emission peak was found at 280 nm in the photostimulation wavelength, but after scratching it shifted to about 330 nm; the stimulation energy well below the work function of Al could induce an electron emission of a considerable amount—a phenomenon known as PSEE. In the case of Fig. 3 we decreased the photostimulation wavelength from 700 nm, but found no other peaks than that located at 350 nm, although Grunberg and Wright⁵⁾ reported an emission peak at

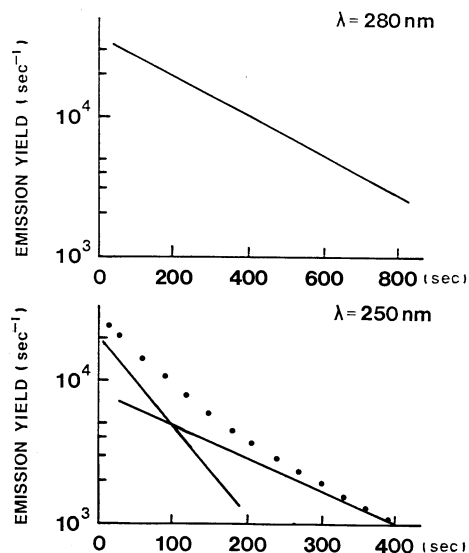


Fig. 2. Decrease in the electron emission yield from Al during the irradiation of the specimen by UV rays.

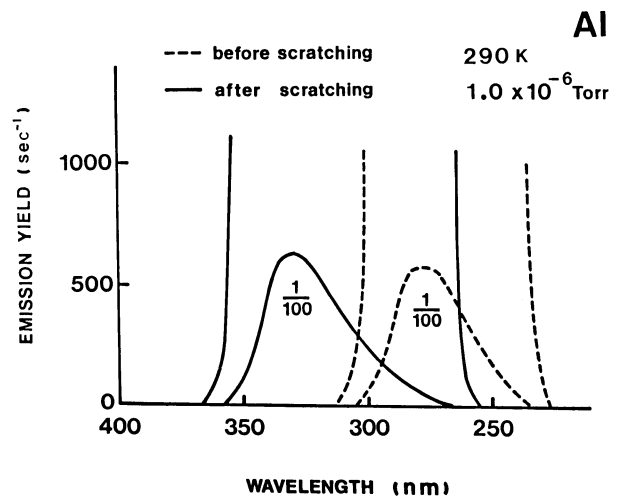


Fig. 3. Electron emission yields from an Al specimen as a function of photoillumination wavelength obtained before and after scratching at 290 K and at 1.0×10^{-6} Torr.

470 nm and a lower one at about 520 nm for abraded aluminum.*

Next we increased the wavelength from 150 nm at the rate of 20 nm/min. The results for a scratched specimen at room temperature are compared in Fig. 4 with those obtained when the wavelength was reduced from 400 nm at 20 nm/min. When the wavelength was increased, no electron yield was observed for photostimulation shorter than 190 nm in wavelength, because of UV adsorption by the surrounding air. When the wavelength exceeded 250 nm, the yield became null again. This result indicates that, by the time when the stimulation wavelength reached 250 nm, all the emission sources with energy levels equal to or shallower than the level corresponding to 250 nm had emitted their electrons. This result can well explain the reason why previous workers did not notice such an energy distribution shift of photoemission sources due to mechanical damage as observed here: They measured the kinetic energy of electrons emitted under the illumination of light with wavelength equal to or shorter than the value

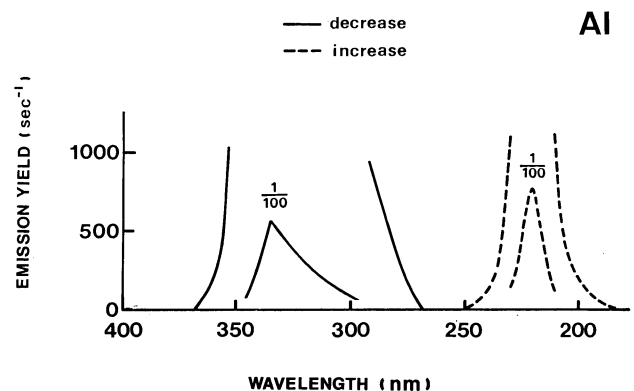


Fig. 4. Comparison of electron emission yields from a scratched Al specimen between the cases when photoillumination wavelength was decreased from 400 nm at 20 nm/min and was increased from 150 nm at the same rate.

*Grunberg and Wright attributed the peak at 470 nm to excited F-centers (oxygen ion vacancies occupied by two electrons). According to them, the centers return to their ground states, inducing emission from shallow sources near the surface.⁵⁾

corresponding to the work function of their specimens. Accordingly, all the sources with levels shallower than the photoexcitation must have become empty of electrons at the time of measurement.

Similar results as shown in Fig. 3 were obtained under different specimen temperature and atmospheric pressure conditions. They are summarized in Table I, which shows that, while before scratching the stimulation wavelength at peak emission is found in the range, 240–290 nm, it moves to 290–350 nm after scratching. The wavelength shift, however, appears to have no temperature dependence in agreement with the view that the emission peak after scratching corresponds to the defect-related levels in the oxide layers created. According to Table I, atmospheric pressures also appear to have no effect on the wavelength shift. To make this point clear, experiments at higher vacuum conditions should be carried out.

The photoemission increase with decreasing wavelength was studied at various times after scratching. As shown in Fig. 5, the emission increased more rapidly and seemed to reach higher peaks at longer than shorter waiting times, but the threshold wavelength for the emission occurrence was always constant. This result supports our view that exoelectrons are emitted from the defect-related sources created in oxide layers by scratching, but seems to disagree with the ordinary view that the gradual change of work function of metals causes PSEE to vary with time after mechanical treatments.

We repeated many measurements on the photoemission vs wavelength relation of aluminum at times up to about

Table I. Stimulation wavelength at peak emission from Al specimens before and after scratching.

Temperature (K)	Pressure (Torr)	Wavelength at Emission peak (nm)	
		Before scratch	After scratch
290	1.0×10^{-6}	280	330
288	1.4×10^{-6}	290	350
284	5.3×10^{-6}	280	310
284	6.0×10^{-7}	250	300
134	5.5×10^{-6}	240	290
121	3.1×10^{-6}	290	350
87	9.0×10^{-7}	270	330
77	3.5×10^{-6}	270	350

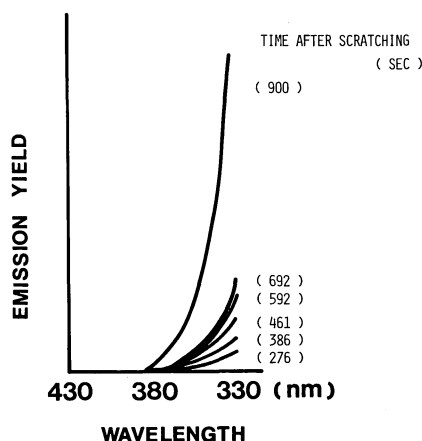


Fig. 5. Approach to scratching-induced emissions peak for various time of observation after scratching.

10^4 s after scratching. The wavelength corresponding to the peak emission was time-independent, although the peak height was much influenced by the time of observation after scratching.* These results agree well with a model we previously presented;¹⁾ the PSEE change with time after scratching is associated with the change in the number of total emission sources. In other words, the change is not due to a change in the intrinsic mechanism of PSEE.**

Figures 7 and 8 present results similarly obtained for a Zn specimen kept at 290 K and at pressures 7×10^{-6} Torr. Though the emission yield was two orders of magnitude

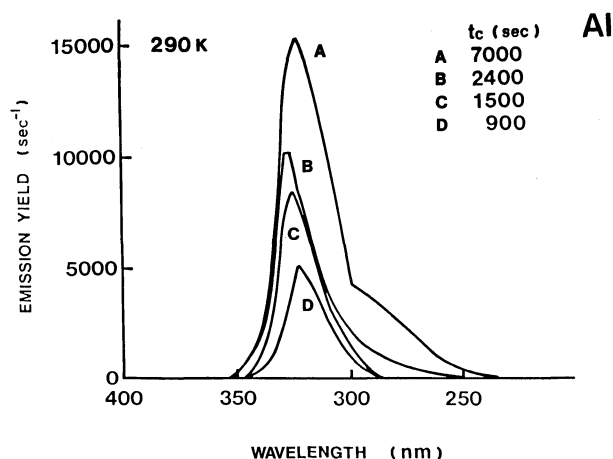


Fig. 6. Variation of the electron emission yield from an Al specimen as a function of the photoillumination wavelength. The parameter t_c represents the period of intermission of illumination. The curves A, B, C and D correspond to the cases where t_c was set for 7000, 2400, 1500 and 900 sec, respectively.

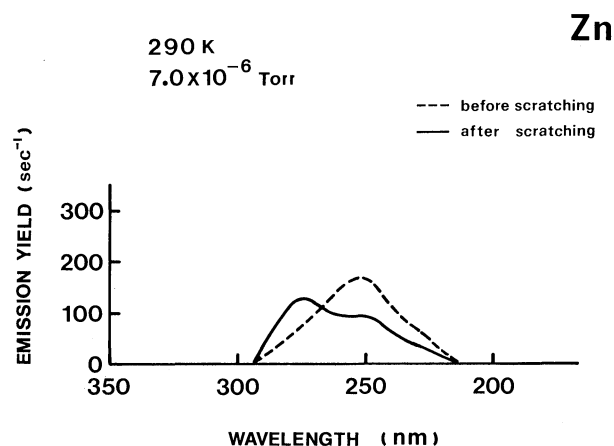


Fig. 7. Electron emission yields from a Zn specimen obtained before and after scratching.

*Similar results were obtained, when we, after irradiating the scratched specimen with UV rays of 230 nm in wavelength for 10^3 sec and turning off the illumination for the period of t_c sec, counted the electron emission from the specimens irradiated with light decreasing in wavelength from 400 nm. As shown in Fig. 6, the wavelength corresponding to the peak emission was stable, i.e., not influenced by the value of t_c , although the peak height increased distinctly with increasing t_c . This result shows storage effect¹⁾ directly.

**We determined two kinds of transition rates related to PSEE. One is the rate of exoelectron emission from higher-energy sites, and the other the rate of thermal excitation of lower-energy sites. Both of them proved to be actually constant, while the sum of emission sites could not be regarded constant for a long period of observation.

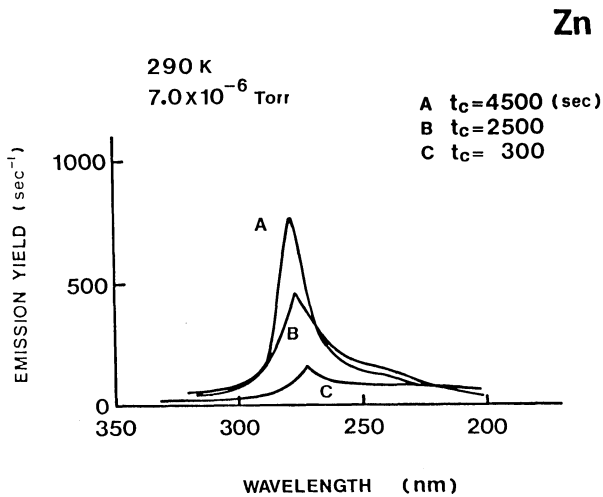


Fig. 8. Variation of the electron emission yield from a Zn specimen as a function of the photoillumination wavelength. The parameter t_c represents the period of intermission of illumination. The curves A, B and C correspond to the cases where t_c was set for 4500, 2500 and 300 sec, respectively.

lower than that for Al, it is apparent that the emission peak, first located at about 250 nm in photostimulation wavelength, moves to 280 nm after scratching. We con-

sider that this peak shift is, as in the case of Al specimens, also associated with creation of shallow energy sites in oxide layers.

§4. Conclusion

Photoemission from Al and Zn specimens was measured by continuously decreasing the stimulation wavelength from the visible to UV region. The yield vs wavelength relation was considerably different before and after scratching the specimen surfaces. After scratching, the emission peak was observed at longer wavelength than the critical one corresponding to the work function of Al or Zn, in agreement with the fact usually recognized as exoelectron emission. The wavelength of light producing the maximum electron emission was found very independent of the time after scratching or of the intermission period of photoillumination.

References

- 1) H. Shigekawa and S. Hyodo: *Jpn. J. Appl. Phys.* **21** (1982) 1278.
- 2) T. K. G. Swami and Y. W. Chung: *Surf. Sci.* **99** (1980) 373.
- 3) G. C. Allen and P. M. Tucker: *Surf. Sci.* **102** (1981) 207.
- 4) R. M. Eastman and C. H. B. Mee: *J. Phys. F* **3** (1973) 1738.
- 5) L. Grunberg and K. H. R. Wright: *Proc. R. Soc. A* **232** (1955) 403.