EVAPORATION CHARACTERISTICS OF Se/Te ALLOYS AS APPLIED TO PHOTORECEPTORS

Hideki Kina[a]; Hidetaka Yahagi[a]; Toshiyuki Iijima[a]; Mitsuru Narita[a]; Yasuo Nakaura[a]

[a] Fuji Electric Co., Ltd., Matsumoto, Nagano, Japan

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PHOTORECEPTORS

HIDEKI KINA, HIDETAKA YAHAGI, TOSHIYUKI IIJIMA,
MITSURU NARITA, AND YASUO NAKAURA
Fuji Electric Co., Ltd., 2666 Tsukama, Matsumoto, Nagano,
Japan

Abstract Xerographic devices obtained by vacuum deposition
of SeTe alloys have inhomogeneities in stoichiometry because
of the differences in vapor pressures of the individual
elements. As a result the concentration of Te on the top
surface of the devices is considerably higher than the rest
of the film. This is termed as "fractionation". It has
been observed that the fractionation characteristics of the
SeTe alloys are dependent on the quenching temperature
during the alloy preparation which in turn affects the
electrical properties of the photoreceptors.

INTRODUCTION

The structure of selenium depends to a great degree on the

quenching temperature when molten selenium is poured into pure

water. The content of 8-ring selenium, as opposed to chain

selenium, is inversely proportional to the quenching tempera-

ture.[1-2] However, the activation energy of crystallization of

selenium is directly proportional to the quenching temperature.[3]

These properties are the same for Se/Te alloys, and they affect

fractional distillation of selenium and tellurium when the alloys

are heated in an evaporation source for vacuum coating. The

fractional distillation level is inversely proportional to the

activation energy of crystallization. The electrical characteris-

tics of photoreceptors depend on the tellurium fractionation

levels.

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ALLOYING CONDITIONS

The high purity SeTe alloys with 5% and 10% by weight Te contents
were prepared at 400°C using quartz vessels equipped with stirrer.
The molten mass was quenched at temperatures ranging from 270°C
to 380°C by pouring into pure water held at 60°C. The materials
evaluated in this study include pure Se, SeTe alloy (5% by weight
Te) and SeTe alloy (10% by weight Te).

Evaluation of the Activation Energy of Crystallization

The activation energy of crystallization is calculated by
Kissinger's method[3-4] of analysis by using the data of DSC
(Differential Scanning Calorimetry) taken at the heating rates of
5, 10, and 50°C/min. The relationship between the temperature
of the peak of the exotherm (Tm in K) and the heating rate (ϕ in
K sec^{-1}) was fitted to the following formula;

$$d\,[\,\ln\,(\phi/Tm^2)\,]\,/\,d\,(1/Tm) = -\,E/k, \qquad (1)$$

where E is the activation energy and k is Boltzmann's constant.
Figure 1 shows the relation between the molten temperature of the
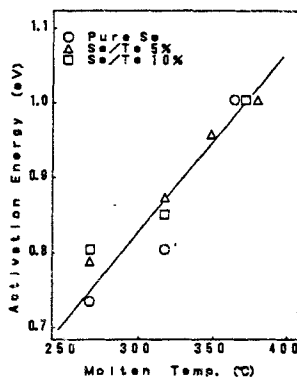alloys before quenching and the activation energy.

FIGURE 1   Molten temperature on quenching and activation
energy.

Evaluation of the Ratio of 8-Ring and Chain Se

The ratio of 8-ring Se to chain Se is evaluated from the rate of absorbant peak intensity of 8-ring Se, 254 cm^{-1}, and of chain Se, 140 cm^{-1}, by FT-IR (Fourier Transform Infrared)[5]. Figure 2 shows how the quenching temperature affects the structure.
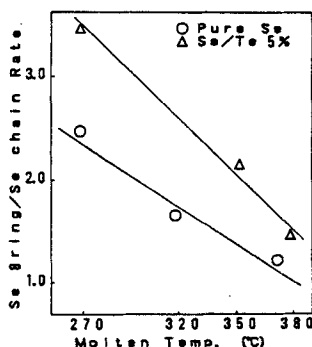

FIGURE 2   Quenching temperature and structure.

Vacuum Coating

The alloys were evaporated onto an aluminum substrate in a vacuum to form photoreceptors which are called photoconductive drums. Vacuum coating conditions were as follows; the vacuum was set at 10^{-5} torr, temperature for evaporation was 350°C, substrate temperature was 50°C and the evaporation source was an indirect heating Knudsen type. The resulting film thickness was approximately 50 μm.

Evaluation of the Fractional Distillation Level

In order to evaluate the fractional distillation level, a depth profile of the film was analyzed by EPMA (Electron Probe Microanalysis). For EPMA, a cross-sectional sample was taken and coated with epoxy resin to hold it in place and then polished to a mirror finish. A typical depth profile of tellurium is shown in Figure 3. The fractional distillation can be determined

quantitatively. In Figure 3, there are three distinctive changes
of tellurium concentration, P1, P2 and P3. The authors suggest
that the fractional distillation be defined as P3/P2 because in
the region between P2 to P3 there exists the highest rate of
fractional distillation. Figure 4 shows how the activation energy
of crystallization (A.E.C.) and the ratio of 8-ring and chain Se
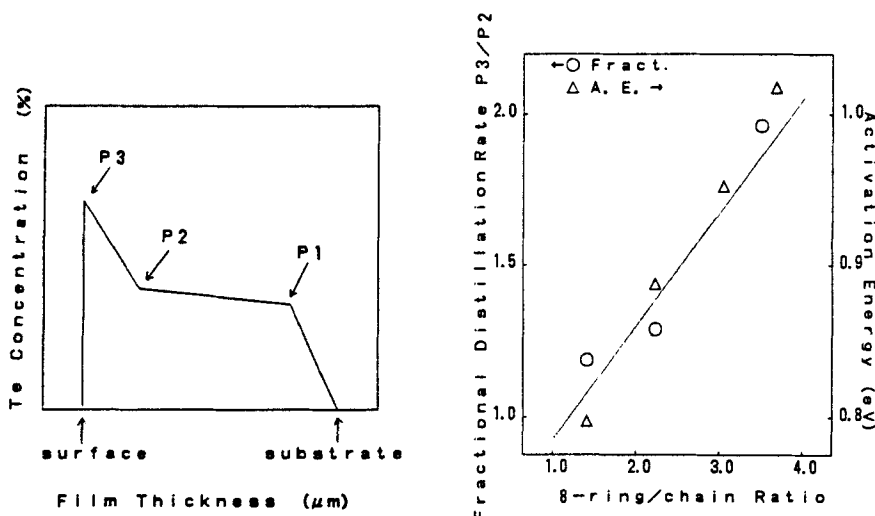affect the fractional distillation level (F.D.).

FIGURE 3   Te depth profile   FIGURE 4   F.D. vs structure
              by EPMA.   and A.E.C.

It is concluded that when the concentration of 8-ring Se is
higher, since the binding energy is as follows; Se-Se 184.1
$KJmol^{-1}$, Se-Te 169.9 $KJmol^{-1}$, Te-Te 138.0 $KJmol^{-1}$ as calculated
by L. Pauling's equation,[6] and the vapor pressure of Se, 417 K at
10^{-5} torr, is higher than that of Te, 527 K at 10^{-5} torr, frac-
tional distillation becomes larger.

ELECTRICAL CHARACTERISTICS

To investigate the effect of how the fractional distillation
level affects the electrical characteristics of photoreceptors,

the following techniques were used; Xerographic spectroscopy[7-8] which is used for the evaluation of gap state and Depletion discharge[9] which is used for the evaluation of dark decay.

Xerographic Spectroscopy

Figure 5 shows a measuring system of Xerographic spectroscopy. In this system, charge and exposure were repeated as the photoconductive drum was revolved until the amount of dark decay and the build-up of residual voltage were saturated as shown in Fig. 6. After saturation, the drum was stopped and the residual voltage decay was measured and evaluated by using the following formula;[8]

$$Pt(Em) = (2 \, e_0 \, e_s/qL^2kT) \cdot |dV_R(t)/dt|, \qquad (2)$$

$$Em(t) = kT \ln (\nu t), \qquad (3)$$

where $Pt(Em)$ is distribution of local state density, e_0 is dielectric constant in a vacuum, e_s is dielectric constant of samples, L is film thickness, k is Boltzmann's constant, T is sample temperature, $V_R(t)$ is residual voltage at time t, $Em(t)$ is trap level above valence band and ν is attempt-to-escape frequency. Thus Gap state as measured by Xerographic spectroscopy is evaluated as shown in Figure 7.
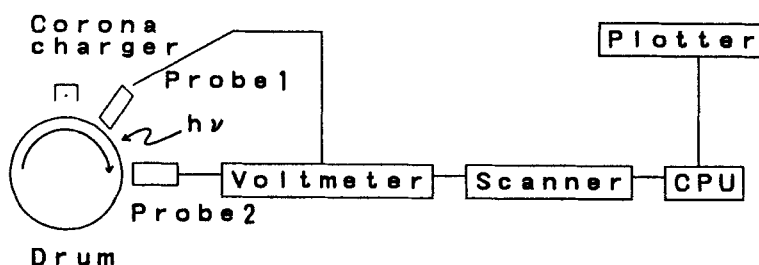

Figure 5   Xerographic spectroscopy.

The relationship between the fractional distillation rate and the energy above valence band and the gap state density are

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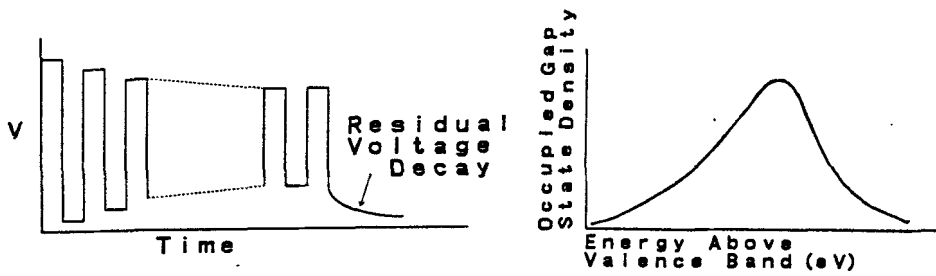

FIGURE 6   Data of Figure 5.   FIGURE 7   Gap state.

shown in Figure 8 and Figure 9, respectively. From our research,
we theorized that the sharp slope of the Te depth profile indi-
cates some structural defects. These defects lead to an increased
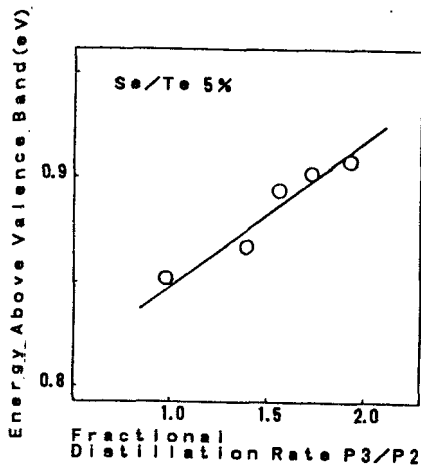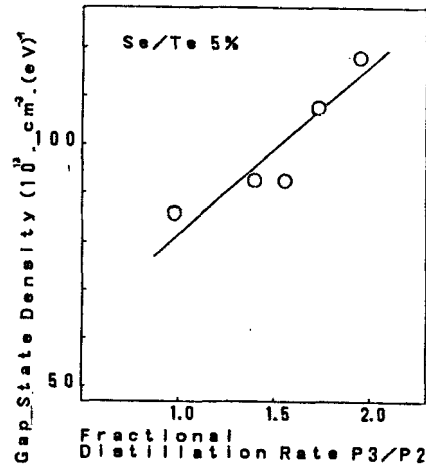gap state density and a deeper trap level.

FIGURE 8   Trap level.   FIGURE 9   Trap density.

Depletion Discharge

Figure 10 shows a measuring system of Depletion discharge. After
a charge is applied on the photoconductive drum, when the charged
point reaches the Probe which measures the surface voltage of the
drum, the drum revolution is stopped and the dark decay voltage
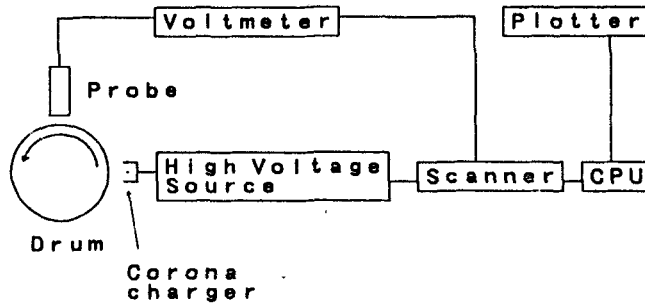is measured. Figure 11 shows the dark decay curve. Depletion

FIGURE 10   Measuring system of depletion discharge.

time, Td, is acquired by log-log plotting of dark decay time
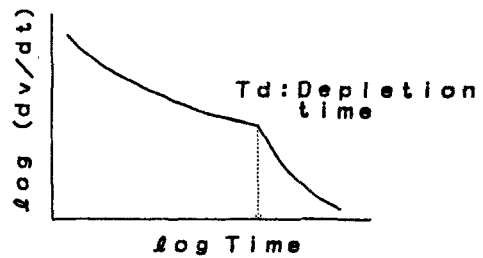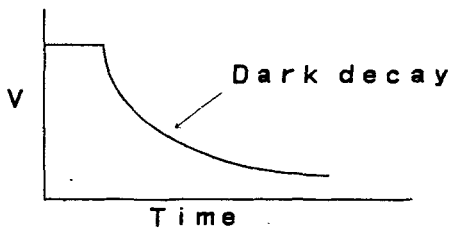against a derivative of dark decay voltage over decay time

FIGURE 11   Dark decay curve.   FIGURE 12   Depletion time.

Figure 13 shows that when the fractional distillation level is
higher, the depletion time is shorter. It is concluded that when
the tellurium concentration is higher toward the surface due to
fractional distillation, the band gap of the surface is narrower
and the ability of charge acceptance is less.

SUMMARY

In summary, the first point is that the activation energy of
crystallization is proportional and the ratio of 8-ring to
chain Se is inversely proportional to the quenching temperature.
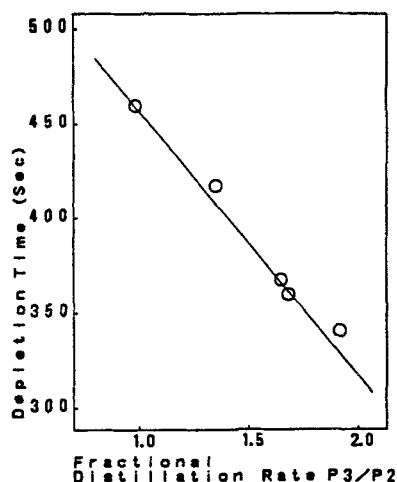Second, the fractional distillation level is proportional to the

FIGURE 13   Depletion time against fractional distillation.

activation energy of crystallization, but inversely proportional
to the ratio of 8-ring to chain Se.   Third, the less the frac-
tional distillation level, the shallower the trap level and the
less the trap density, and further the longer the dark decay time.
Therefore the quenching temperature determines the structure
which affects the fractional distillation rate.   Consequently,
electrical characteristics are varied.

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