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EFFECT OF VARIOUS IMPURITIES ON ELECTROPHOTOGRAPHIC PROPERTIES OF Se AND Se-Te ALLOYS

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Abstract Effect of various impurities and additives on electrophotographic properties of Se and Se-Te alloys has been systematically investigated by the xerographic measurement technique. It was found that oxygen has a profound effect on the residual potential of pure Se. In order to find Se-Te alloys with the residual potential as low as possible, various quarternary alloys with V group elements (Bi, Sb) and halogens have been prepared and evaluated. Se-Te-Sb-Cl alloy showed the best electrophotographic properties with the lowest residual potential and dark decay. The experimental results are explained by modifying the structural defect model developed by Kastner et al.

INTRODUCTION

Pure Se and Se-Te alloys are materials which are very important for photoreceptors in xerography. Despite this importance, little attention has been paid to the purification of selenium and the effect of various impurities on the electrophotographic properties of Se-Te alloys. It has also been very difficult to explain theoretically their electrophotographic properties since Se and Se-Te alloys are amorphous semiconductors.

From the viewpoint of xerographic application, Se-As alloys have been used for copiers for a long time because they have an excellent sensitivity for long wavelength light and resistance to crystallization. However, Se-As alloys have a shortcoming in that arsenic is toxic. Se-Te alloys are therefore expected as

good alternatives for Se-As alloys except that they are susceptible to crystallization.

In our laboratory, we have been systematically studying the purification of selenium, and the effect of impurities on electrophotographic properties of selenium^{1,2} and Se-Te alloys.^{3,4} We have also applied the structural defect model developed by Kastner et al.⁵ to explain theoretically the effect of impurities on the electrophotographic properties of Se and Se-Te alloys. In this paper, we report comprehensively our experimental results on Se-Te alloys which show the best properties as photoreceptors.

EXPERIMENTAL

For the purification of selenium, we optimized not only the final vacuum distillation process, but also the previous processes, such as the SO₂ reduction, ion exchange and SeO₂ sublimation. The purity of selenium was determined by various techniques which include atomic absorption spectroscopy, solid mass spectroscopy, absorptiometry and neutron activation analysis. By the optimization of the purification process selenium of 5N purity level as shown in Table 1 can be prepared.

TABLE 1 Typical purity of highly purified selenium.

Te	<0.01 ppm	Mn	<0.01 ppm
As	0.02-0.05 ppm	Cr	<0.01 ppm
Sb	<0.01 ppm	Bi	<0.01 ppm
Cu	0.02 ppm	Mg	<0.03 ppm
Pb	<0.01 ppm	Ag	<0.01 ppm
Zn	<0.03 ppm	Tl	<0.01 ppm
Fe	0.05-0.20 ppm	Hg	<0.05 ppm
Ni	<0.01 ppm	S	<0.2 ppm
Al	<0.07 ppm	Cl	<0.04 ppm
Cd	<0.01 ppm	Br	0.01-0.03 ppm
Sn	<0.01 ppm	I	<0.02 ppm
Co	<0.01 ppm		

Unspecified: atomic absorption spectroscopy

*Absorptiometry

**Neutron activation analysis

The purified selenium was doped with various impurities in the range between 0.1 ppmw to 1 wt.%. The selenium was also alloyed with Te, Bi or Sb, and halogens. For doping and alloying, pyrex ampoules containing the materials were vacuum-sealed under 10^{-5} Torr, heated at 450°C for 5 hr in a rocking furnace and were rapidly cooled to room temperature.

Doped specimens were then vacuum-deposited on aluminum substrates of the dimension of 50x50x1 mm³. The substrates were ultrasonically cleaned in ethyl alcohol, acetone, neutral detergent Extran MA-02 and deionized water and then oxidized before the deposition. The deposition of selenium was performed with a source temperature of 270°C, a substrate temperature of 70°C and a deposition rate of 0.2 µm/min. The thickness was controlled to about 50 µm.

The electrophotographic properties of the samples prepared as mentioned above were measured by conventional xerographic technique. The instrument used for the measurements was the SP-428 of Kawaguchi Electric Corp. The instrument consists of a corotron, a sample rotating mechanism, a light-exposing mechanism and a surface-potential measuring apparatus. In order to control the temperature at which the measurement was performed, an electronic cooler and a heater were provided in the system with a temperature controller. As light source, a tungsten lamp or a xenon lamp was used depending on the light intensity needed. The measurement parameters like the dark decay time, the light decay time and the charge-exposure repeating number can be controlled by an electronic system.

For evaluating the ease of crystallization, a differential thermal analysis system (Rigaku Denki Corp., DTA-10A) was used with a heating rate of 5°C/min. For each measurement, 0.1 g of a sample material was charged in a platinum crucible and heated in a nitrogen gas flow.

EXPERIMENTAL RESULTS

1. Effect of Various Impurities on the Electrophotographic Properties of Selenium

Effect of various impurities on the electrophotographic properties of pure selenium has been examined systematically. In the present paper, we report the effect of impurities briefly on the residual potential of selenium. For the measurement of the residual potential, low charge-discharge cycles and high charge-discharge cycles have been performed. In the case of low charge-discharge cycles, the residual potential is formed by the space charge due to the carriers trapped at deeper levels and in the case of high charge-discharge cycles, the residual potential is formed by the space charge not only due to deep levels but also due to shallower levels because the charge-discharge cycle is sufficiently high for the carriers trapped at shallower levels not to be released.

Figure 1 shows the effect of oxygen on the residual potential measured by low charge-discharge cycles. During our purification study, the residual potential measurement was routinely applied to evaluate purification process. It was surprising to note that the residual potential varied greatly from lot to lot. For instance, the negative residual potential varied between 20 to 200V from lot to lot even though selenium meets the purity requirements as shown in Table 1. Assuming that the cause of this variation in residual voltage is because of oxygen impurity levels, selenium was further purified in order to reduce the oxygen content. It was found that the most purified selenium showed a residual potential value that was nearly the same for positive charging and negative charging. From this observation, we concluded that pure selenium has donor and acceptor type deep traps with nearly the same concentration. This conclusion is also theoretically supported as explained later.

It may be discerned from Figure 1 that it is quite important

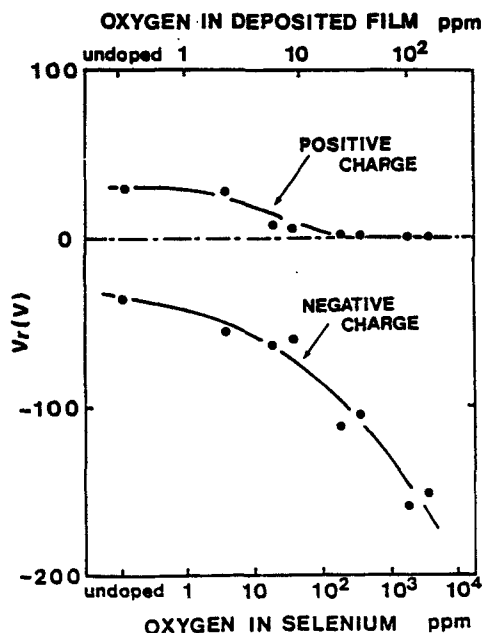


FIGURE 1 Effect of oxygen on the residual potential of pure selenium. Oxygen content in deposited film was measured by FT-IR.

to control the oxygen content in pure selenium because, if it is not controlled exactly, the starting selenium material will already have a different residual potential and the effect of impurities cannot be precisely evaluated. This observation can explain the difference in reported values of residual potentials for pure selenium by various investigators.

In Figure 2, the positive residual potential for various impurities measured by low charge-discharge cycles is summarized. Even though Bi, Sb and S have the same effect as oxygen, higher content is necessary to decrease the residual potential. Contrary to O, Bi, Sb and S, As and P have an effect to largely increase the residual potential.

Figure 3 shows the residual potential measured by high charge-discharge cycles. In this case, the residual potential is formed not only because of carriers trapped at deep levels

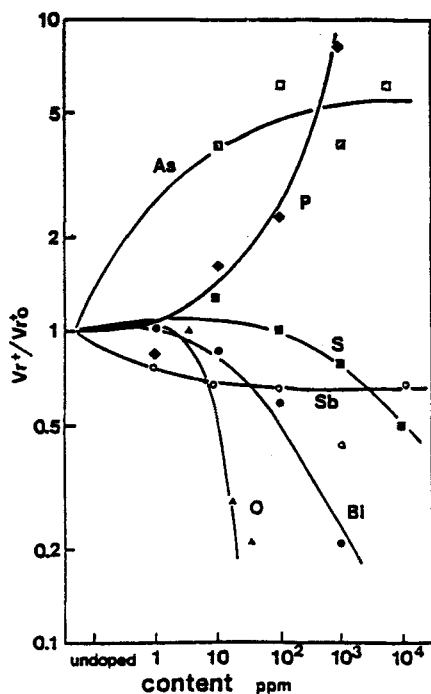


FIGURE 2 Effect of various impurities on the residual potential in positive charging, measured by low charge-discharge cycles. Residual potential (V_{r+}) is normalized by the value of pure selenium (V_{r0+}).

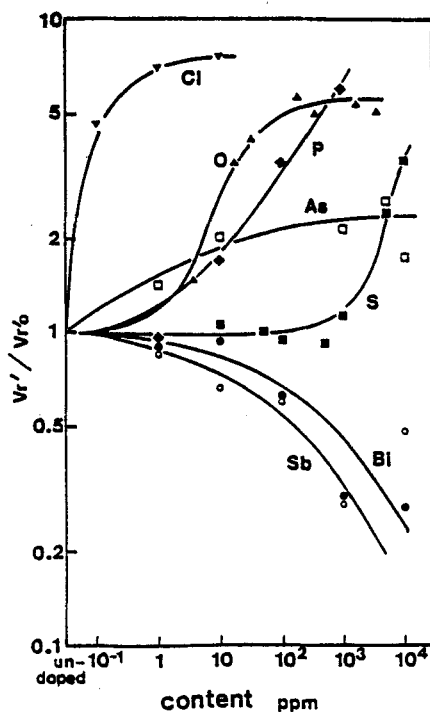


FIGURE 3 Effect of various impurities on the residual potential in positive charging, measured by high charge-discharge cycles. Residual potential ($V_{r'}$) is normalized by the value of pure selenium ($V_{r0'}$).

but also because of carriers trapped at shallower levels. It can be concluded that impurities with large electronegativity such as Cl, P, O, S and As have a large effect on increasing the residual potential whereas impurities with smaller electronegativity such as Sb and Bi have an effect on decreasing the residual potential.

2. Exploitation of Se-Te Alloys

Se-Te alloys are very attractive since they have good photosensitivity at long wavelength lights like Se-As alloys. However, in order to apply Se-Te alloys as main photoreceptors in copiers, two shortcomings should be overcome, namely large residual potential and ease of crystallization. In order to improve the shortcomings of Se-Te alloys, we have examined the electrophotographic properties of crystallization of Se-Te alloys doped with one of V group elements and with one of halogens.

Figure 4 shows the residual potential measured by low charge-discharge cycles. It can be known that, by alloying with Te, the residual potential is increased and that it is increased further when Sb or Bi is added to Se-Te alloys. However, the chlorine addition is quite effective in reducing the residual potential for every case. The residual potential becomes nearly zero for all alloys with the chlorine content of more than 10 ppm.

Figure 5 shows the dark decay properties of various Se-Te alloys. Surface potential, V_{10} , means the surface potential measured after holding in dark for 10 sec after surface charging. It can be seen that the dark decay becomes very large in the case of Se-13wt.%Te alloys and Se-13wt.%Te-0.1wt.%Bi when the chlorine content is increased while in the case of Se-13wt.%Te-1wt.%Sb, the surface potential is held at a certain value even if the chlorine content is increased.

Figures 6 and 7 show the residual potential measured by high charge-discharge cycles. It can be known that the residual potential is decreased in the case of Se-Te-Bi and Se-Te-Sb alloys as the content of halogens are increased. It should also be noted that the decrease of the residual potential is larger in the order of Cl, Br and I. This effect of halogen is probably due to the compensation of defects induced by Sb or Bi so that the effect of the residual potential decrease is larger when the

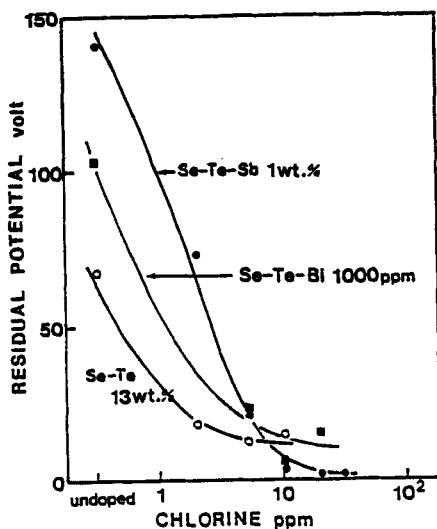


FIGURE 4 Effect of chlorine on the residual potential in positive charging measured by low charge-discharge cycles for various Se-Te alloys.

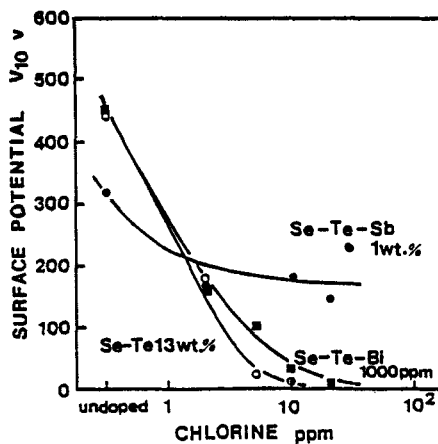


FIGURE 5 Effect of chlorine on the surface potential measured at 10 sec after charging for various Se-Te alloys.

3. Crystallization

Even if the electrophotographic properties of Se-Te alloys are satisfactory as photoreceptors, it is necessary that the material is adequately resistant to crystallization. Figure 8 shows the crystallization properties measured by differential thermal analysis. As seen in the figure, Se-Te alloy and Se-Te-Bi alloy show a distinct crystallization at about 150°C while in the case of Se-Te-Sb alloy, no crystallization was observed. We can therefore conclude that the Se-Te-Sb-Cl alloy is the best photoreceptor material among all Se-Te alloys investigated in the present work.

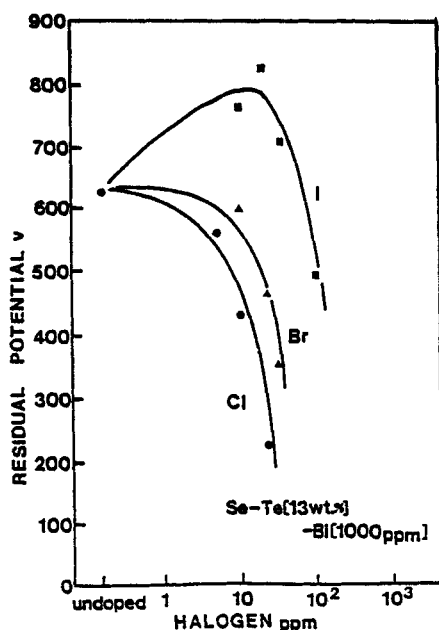


FIGURE 6 Effect of halogens on the residual potential of Se-Te-Bi alloys. The residual potential was measured by high charge-discharge cycles.

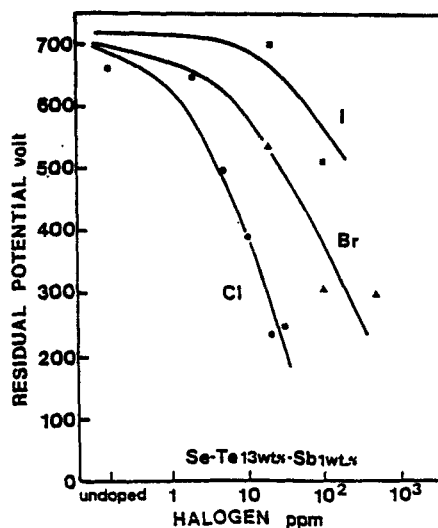


FIGURE 7 Effect of halogens on the residual potential of Se-Te-Sb alloys. The residual potential was measured by high charge-discharge cycles.

4. Explanation by the Structural Defect Model

Since Se and Se-Te alloys are amorphous materials, it has been very difficult to explain the experimental results theoretically so that the exploitation of new photoreceptor materials has been carried out according to experiences. However, Mott⁶ and Kastner et al.⁵ proposed structural defect models in which they postulated that dangling bonds are polarized to positively and negatively charged defects. By purifying Se, we found that the purest selenium showed nearly the same residual potential for positive and negative charging. This experimental fact proves that the structural defect model is a reasonable one.

The structural defect model can be modified easily for

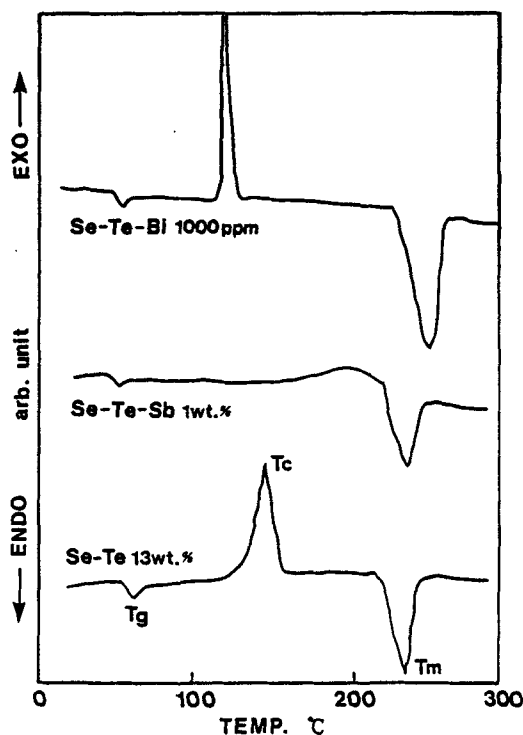


FIGURE 8 Differential thermal analysis data for various Se-Te alloys.

selenium doped with impurities and for selenium alloy added with various impurities.

According to Mott⁶ and Kastner et al.⁵, because of its non-crystallinity, structural defects such as dangling bonds and/or trivalently bonded selenium atoms are not stable in its neutral state. They are rather stable when polarized to positively and negatively charged defects. The densities of these defects can be deduced by the law of mass action.

$$2C_3^0 = C_3^+ + C_1^- \quad K = (C_3^+) \times (C_1^-) / (C_3^0)^2 \quad (1)$$

These structural defects are believed to form localized energy levels in the band gap of selenium and to act as deep traps for carrier transport.

In the case of pure selenium, the neutral condition for charged defects is

$$(C_3^+) = (C_1^-) . \quad (2)$$

This explains why in the case of pure selenium the residual potential shows nearly the same value for positive and negative charging.

In the case of one kind of impurity which is contained in selenium, the above mentioned model is easily modified. According to the electronegativity of the contained impurity, this impurity atom is charged negatively or positively. In the case of oxygen, since the electronegativity of oxygen ($x=3.5$) is larger than that of selenium ($x=2.4$), oxygen atoms can be supposed to be negatively charged. The existence of oxygen then affects the neutral condition of the structural defects as follows.

$$(C_3^+) = (C_1^-) + (O^-) \quad (3)$$

By inserting eq. (3) into eq. (1), the densities of the structural defects can be represented as follows

$$(C_3^+) = ((O^-) + \sqrt{(O^-)^2 + 4K'}) / 2 \quad (4)$$

$$(C_1^-) = (\sqrt{(O^-)^2 + 4K'} - (O^-)) / 2 \quad (5)$$

In Figure 9, the densities of structural defects are shown as a function of oxygen content according to the above equations by changing the equilibrium constant, K' . Here, K' is $Kx(C_3^0)^2$. It can be seen that by increasing the oxygen content the density of C_1 begins to decrease and that of C_3^+ begins to increase linearly with the content of oxygen when the content exceeds a threshold value. This theoretical prediction clearly explains the experimental result shown in Figure 3. The increase of (C_3^+) increases the residual potential in the negative charge and the decrease of (C_1^-) decreases the residual potential in the positive charge. The experimental result is in good agreement with this

theoretical prediction.

The above structural defect model can also be modified for Se-Te alloys doped with various impurities. As an example, the case of Se-Te-Sb-Cl alloys is considered. Since Te and Sb have smaller electronegativity than Se, they are expected to act as positively charged defects while chlorine is expected to act as a negatively charged defect because the electronegativity of chlorine is larger than that of Se. The neutral condition can therefore be rewritten as follows.

$$(C_3^+) + (Te^+) + (Sb^+) = (C_1^-) + (Cl^-) \quad (6)$$

By inserting eq. (6) into eq. (1), using a constant K' and a variable $Ci(Ci = (Te^+) + (Sb^+) - (Cl^-))$, the densities of structural defects can be represented as follows.

$$(C_3^+) = (\sqrt{(Ci)^2 + 4K'} - (Ci))/2 \quad (7)$$

$$(C_1^-) = ((Ci) + \sqrt{(Ci)^2 + 4K'})/2 \quad (8)$$

Structural defect concentrations can then be calculated as in the case of oxygen doping except that the variable is changed from (O^-) to Ci as shown in Figure 10. From Figure 10, it can easily be known that if the concentration of Te and Sb is increased the concentration of (C_1^-) is increased while if the concentration of Cl is increased, the concentration of (C_1^-) is decreased. This theoretical prediction is very coincident with the experimental results. As shown in Figure 4, the residual potential is increased when the content of Te and Sb is increased and it is decreased when the content of chlorine is increased. In this way, the structural defect model is very useful to predict the electrophotographic properties of Se-Te alloys doped with various impurities. However, the model is not yet complete from the viewpoint of the quantitative prediction of the electrophotographic properties. For this purpose, it is needed to modify the model considering quantitatively the electronegativity

and the ionization ratio of each element in Se. This improvement is now under research.

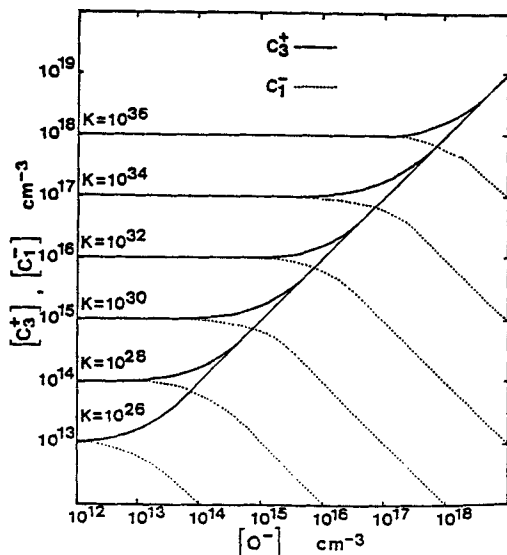


FIGURE 9 Theoretical calculation of defect concentrations as a function of oxygen.

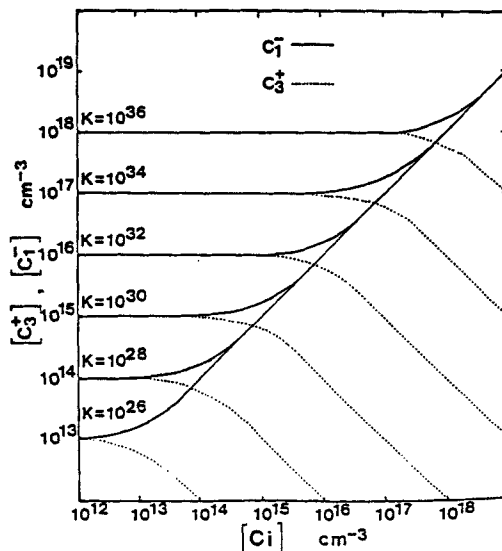


FIGURE 10 Theoretical calculation of defect concentrations as a function of the difference of various impurity content, C_i .

CONCLUSION

In the present work, we have examined the effect of various impurities contained in pure selenium and various additives contained in Se-Te alloys on the electrophotographic properties.

It was found that among various impurities in pure selenium, oxygen is one of the most important since it is difficult to control and it greatly affects the residual potential of pure selenium.

As for Se-Te alloys, the best material is Se-Te-Sb-Cl alloy, not only from the viewpoint of the electrophotographic properties but also from the viewpoint of crystallization.

In the present work, the theoretical explanation was also given by modifying the structural defect model developed by Kastner et al. The model could be well applied not only for the case of impurities in pure selenium but also for Se-Te alloys with added impurities. The modified model is useful for the exploitation of Se-Te alloys but for the quantitative prediction of the electrophotographic properties, further improvement of the model is desired.

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