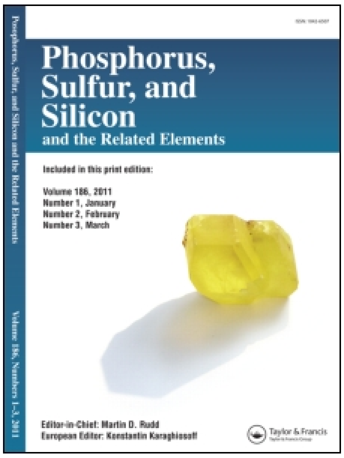

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APPLICATION OF SELENIUM-TELLURIUM PHOTOCONDUCTORS TO THE XEROGRAPHIC COPYING AND PRINTING PROCESSES

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Abstract For reasons having to do with overall copying machine and laser printer design, as well as customer-driven improvements in overall copy quality, the most common inorganic photoreceptors used in the xerographic process today are constructed of Selenium alloyed with Tellurium and/or Arsenic. These materials and their xerographic properties will be briefly described. The remainder of the talk will focus on unsolved problems which are of both academic and practical interest. These problems have to do with opto-electronic properties which are influenced by chemical doping and by interaction with the operating environment. The presentation will be largely descriptive in order to display the range of phenomena encountered in working with the subject materials.

INTRODUCTION

Alloys of selenium with tellurium and/or arsenic are being used for a variety of practical purposes in such devices as solar cells, optical discs, fibre optics, simple photodetectors and ion selective electrodes. Many of these uses are still in the exploratory stage. Another class of usage of these materials is as additives for such diverse materials as glass, pigments, rubber, steel, fertilizers and catalysts. An equally exotic use from the perspective of 50 years ago is as large area photoconductors which are at the heart of today's copying and printing machines. They are usually constructed as a film, approximately 60 micron thick on a cylindrical substrate. A typical area is $0.1m^2$ but objects of $1m^2$ are used in the largest such machines. Several million of these devices are manufactured world-wide each year and use up some 10^6kg of high purity Se and about a factor of 200 less of high purity Te each year. Yet even with what seems like a well-established manufacturing base, and the focus of solid-state physics attention on amorphous materials in the 1970's, a lot is yet to be learned about these materials from both a pure and applied science point of view. This paper will concentrate on the uses of alloys of Se and Te as photoconductors for image reproduction machines, especially why they are used and what our areas of ignorance are.

Today's customer expects that his or her copying machine will reproduce in a clearly legible fashion whatever document is presented to it. The range of documents covers not only black and white type-written sheets, but photographs or graphics containing shades of gray, originals containing colour, and material printed on an overall coloured background. An image of the original document is formed by a lens on the machine's photoconductor by illuminating the original with a broad-band source. It is both the need to copy a variety of originals, and the need to accomodate to cheap, low power, stable lamps biased toward the red end of the visible spectrum which has dictated the shift to Se:Te alloys from Se as the photoconductor of choice. As Te is added to Se the material becomes more photosensitive for a given wavelength. That is, the free charge created per photon increases, and thus more voltage discharge occurs for a given exposure energy. It is the variation in the amount of voltage discharge caused by the variation in illumination level from the original that is developed by a dry ink process in a typical copying machine. The typical amount of broad-band energy used to discharge the photoconductor is in the 10-20mJ/m^2 range. The typical amount of voltage discharge at these levels of exposure is about 600 volts. In other words, it takes about 6 or 7 photons to produce one useable electron. At this level of efficiency, which falls rapidly the longer the wavelength, it is important to gain as much efficiency as possible. For example, at 500nm a Se:Te alloy containing about 6.5% Te is about an order of magnitude more efficient than pure Se in this regard.

Another demand comes from the use of HeNe lasers as exposure sources. In this case the image produced is digitized (the laser is either on or off) as opposed to continuous. The wavelength of the laser is such that about 13.5 at % Te is required to produce efficiencies such as those noted above. It is even possible to produce photoconductors which are sufficiently sensitive to diode laser wavelengths (about 780nm); this requires the use of about 25 at % Te. Systems incorporating lasers are used as printers for any kind of computer, and as facsimile machines.

There is, however, a serious drawback encountered as the at % of Te in the alloy is increased. This drawback is related to the fact that the propensity to generate charge in the dark increases as the Te content increases, and to the fact that optical and thermal fatiguing occurs more readily and relaxes more slowly as Te is added to the alloy. Both of these effects cause the photoconductor to operate in an unstable manner when used repetitively for long periods of time i.e. when making hundreds of copies at a time rather than tens of copies or prints.

PROPERTIES OF SE:TE ALLOYS

From studies of the molten alloy[1] it has been determined that for a Te content less than 50 at %, the Te atoms are predominantly 2-fold coordinated (as is Se) and are simply randomly substituted in the Se chains. The photoconductive films are produced by quenching such melts and subsequently vacuum evaporating the solid to form the film. Thus the films also have Te randomly substituted in the Se structure. The effect of adding Te is to increase Tg, Tx, and Tm as shown[2] roughly in Fig. 1 where the values for added Te have been normalized to the value for pure Se.

The optical properties have been studied much more extensively. The next two figures show properties which are relevant to the use of the alloys as photoconductors. Figure 2 shows[3] the photoefficiency at two wavelengths as a function of composition measured at 10^7V/m, a value typical of those encountered in copying machines. 500nm represents an energy above the band-gap for all concentrations and exhibits a relatively linear increase with Te content. 600nm is below the band-edge for Se and very close to the band-edge for 2.5 at % Te. At 600nm, the absorption coefficient changes by an order of magnitude over the indicated concentration range. In copying machines Te contents less than 10 at % are typically used, and this figure clearly shows that wavelengths beyond about 600nm are not useful for the discharge process. Such light is, however, still quite strongly absorbed. Figure 3 shows[4] the optical band-gap and the glass-transition temperature, both as functions of Te content. The band-gap can be viewed as a measure of what wavelengths will give useable discharge. The Tg curve gives information on useable operating temperatures. Typically, less stable behaviour will begin to be observed within 10°C of Tg.

The final electrical properties which have some relevance are the charge carrier mobilities and the trap states in the gap. Broadly speaking,[5,6] over the range of Te concentrations discussed so far, the hole mobility decreases by one order of magnitude and the electron mobility by two orders of magnitude. The trap states are less well studied. The major change in transport properties, including trap states,[4,5,7] as the Te content increases is a broadening of distributions in energy space. The most obvious manifestation of this is the fact that transport in Se:Te alloys is dispersive.

OUTSTANDING PROBLEMS

A. Evaporation Kinetics

To make the photoconductive films, the alloys are vacuum evaporated. Due to the non-equilibrium situation pertaining in this process, Te concentration gradients are produced in the film. The species which evaporate from the molten liquid are poorly understood as are their evaporation coefficients. As can be seen from the foregoing figures, Te gradients will produce gradients in other properties. Thus controlling evaporation kinetics is a most important step in controlling photoconductive film properties.

B. Surface Reactions

Apart from the problem of surface variations in Te content due to the evaporation kinetics, the environment in a copying machine is particularly harsh. It is abrasive and oxidative and can be some 10-15°C above room temperature. Should the film crystallize it no longer will hold a charge. Crystallization in pristine conditions has been studied[8] but we have very

FIGURE 1

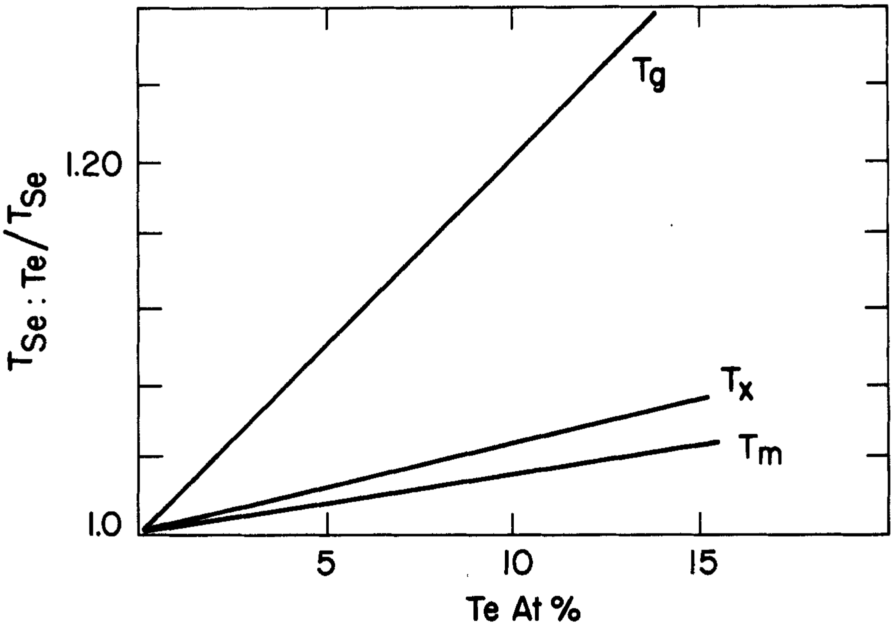


FIGURE 2

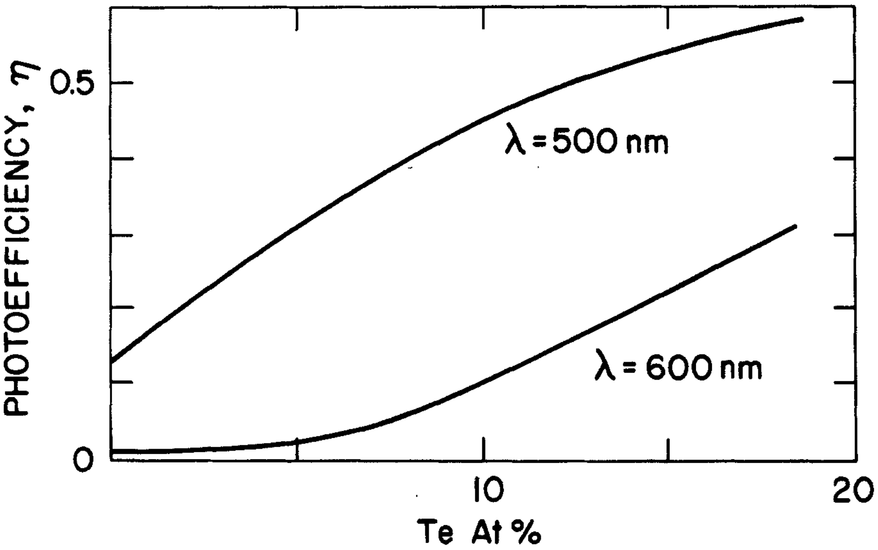
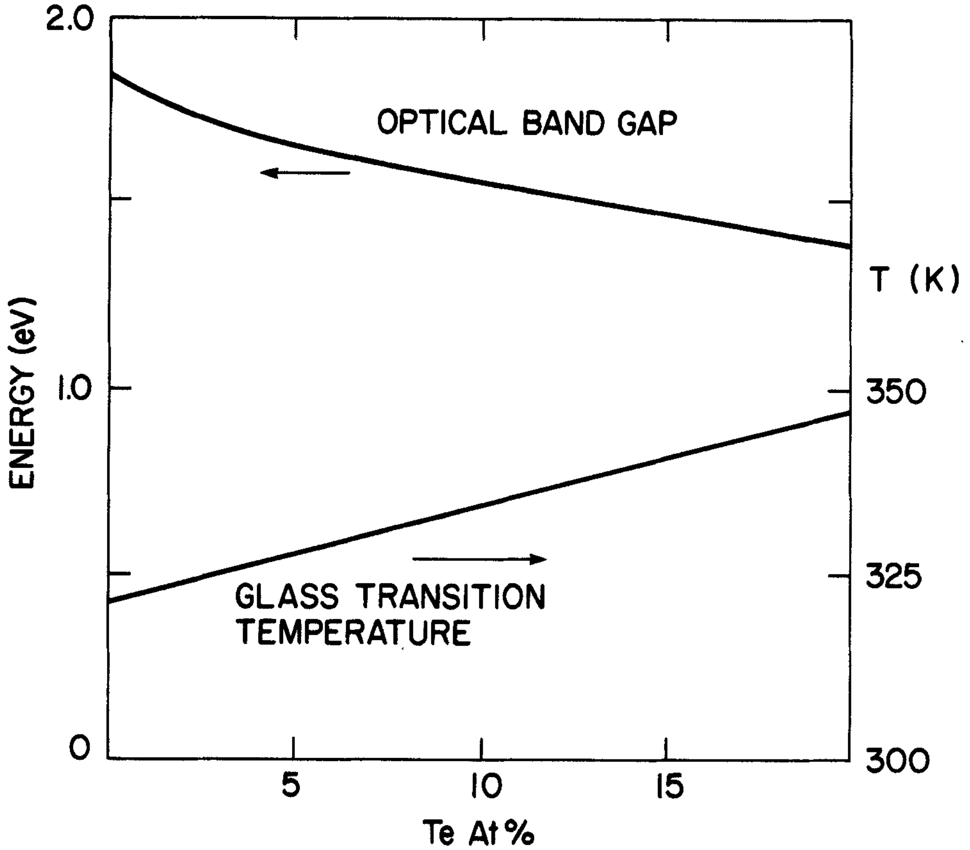


FIGURE 3



poor detailed knowledge of what changes occur in the presence of an oxidized and abraded surface. Also of interest is the effect of various dopants such as halogens, arsenic, phosphorous, and germanium on crystallization kinetics.

Likewise, we have very poor knowledge of the oxidation kinetics of the surface and its dependence on Te content. What we do know is that oxidation of the surface, mainly the Te component, occurs to a depth of about 10nm quite readily, especially in the presence of greater than band-gap light. This oxidation also affects the photo-efficiency of the film.

C. Fatigue Effects

As already mentioned, stable operation of the photoconductor is one of the major requirements for xerography. Electrically there are two effects which cause instability. One is dark-generated charge (DD) and changes in this generation rate; the other is the "Residual Potential" (RP). RP is the potential below which the film cannot be discharged due mainly to charge trapping in the bulk of the film; this effect is also subject to changes.

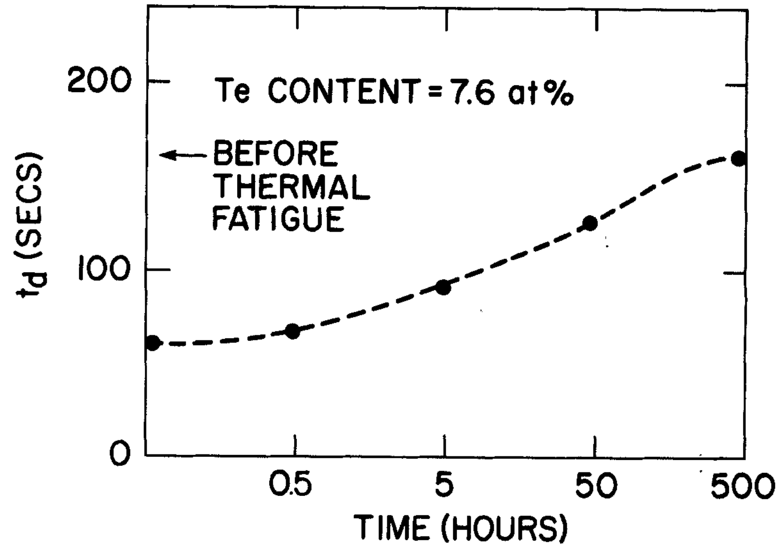
DD is caused by generation of holes from states some 0.1 - 0.3eV above the valence band. Obviously, then, temperature changes will cause significant shifts in this parameter. There is another, more complicated, effect which is related to the dynamic population of these shallow states as the photoconductor is used repetitively. These population shifts are brought about by light which penetrates the bulk and by re-trapping events during discharge. As the Te content is increased, these states increase in number and broaden in energy space such that Se:Te alloys are much more susceptible to changes in temperature and light exposure (or fatigue) than is pure Se.

The position in energy-space, the number density, and the release and capture rates of these states are all poorly understood quantitatively as functions of the Te content of the alloys. Some fraction of these states are also thought to govern charge carrier transport properties. The dispersive character of charge transport in the alloys is but one indication that these states are considerably broadened in energy as Te is added to Se.

RP is also governed by a set of traps, but deeper in energy. These states are thought to straddle the Fermi energy and are from 0.4 - 0.8eV from either band-edge.[4] Again, the observed RP depends upon the kinetics of trapping and release of carriers into and out of these states as the photoconductor is exercised repetitively.[9] The number density of these states also plays a major role. The number density is believed to be "frozen-in" by the fabrication process and the states are connected with defects inherent in the structure. Quantitatively, there are about 10^{15} cm^{-3} eV^{-1} of these states.[4,10] The actual density seems not to be influenced so much by Te content as by thermal and light fatigue.[11] The density can be readily increased by a factor of two by less than a 20°C increase in temperature, or by absorption of near band-edge light. The relaxation rate after fatigue is very slow, varying from hours to many days depending on stress level and Te content. It is clear that these states areassociated with structural modifications on the molecular level, but a systematic study has yet to be undertaken, and a full explanation arrived at, especially for the case of dynamic, equilibrium existing during repetitive operation.

Figure 4 shows a single manifestation of thermal fatigue. On the vertical axis is plotted the time for a given fraction of the surface charge to release from bulk traps. The horizontal axis is the time after the temperature of the sample has been reduced from 308K to 295K. The curve is a convolution of a reduction in the number of states with time and position in energy space.

FIGURE 4



D. Impurities

Before discussing the effect of specific impurities on electrical properties, it is necessary to briefly describe what the currently accepted model is for the deep trapping states. The model begins by considering possible bonding configurations of Se atoms in pure Se. Generally speaking, Se atoms can exist singly, doubly, or triply coordinated in the amorphous film. The normal condition is two-fold coordination. By electron transfer and some positional shifting of the atoms (configurational change), pairs of singly and triply coordinated atoms are created such that the first is net negatively charged and the second positively charged. The reaction is believed to be exothermic and is represented as follows

$$2C_2 \rightarrow C_3^+ + C_1^-.$$

The whole system remains electrically neutral, so one can write

$$c_3c_1 = k^2c_2^2 \text{ and } c_3 = c_1 = kc_2,$$

where the lower case "c" represents the number density of the various atomic states. The constant k^2 is the reaction rate coefficient which is temperature dependent in such a way that as temperature increases c_3, c_1 also increase. It is believed that the C_1^- state is responsible for the hole trapping which gives rise to the residual potential (RP). If we now add Te, further bonding configurations can arise in the form of Se-Te and Te-Te bonds which can undergo similar configurational reactions. This in turn broadens the distribution of the deep traps and moves them closer to the band-edges. Each combination will have its own characteristic activation energy and coefficient so that temperature effects will also be altered, in particular relaxation back to an equilibrium condition.

There are two types of impurities to be considered; those which can exist in a negatively charged state such as halogens or oxygen, and those which can exist in a net positively charged condition such as alkali or other metals. A majority of these impurities remain neutral and in their lowest energy state; a fraction will ionize by electron transfer with either Se or Te[12]. Roughly speaking the number of charged defect states, kc_2, remains constant. If the number of dopants, A, which become ionized, via a thermal activated process such as

$$A_n + C_2 \rightarrow A_n^- + C_3^+$$

or

$$A_p + C_2 \rightarrow A_p^+ + C_1^-,$$

is included in the charge balance equation, then we find

$$a_n + c_1 = c_3$$

or

$$a_p + c_3 = c_1$$

Focusing on the number of C_1^- (the hole traps) in each case we have

$$2\,c_1 = -a_n + (a_n^2 + 4k^2c_2^2)^{1/2} \tag{1}$$

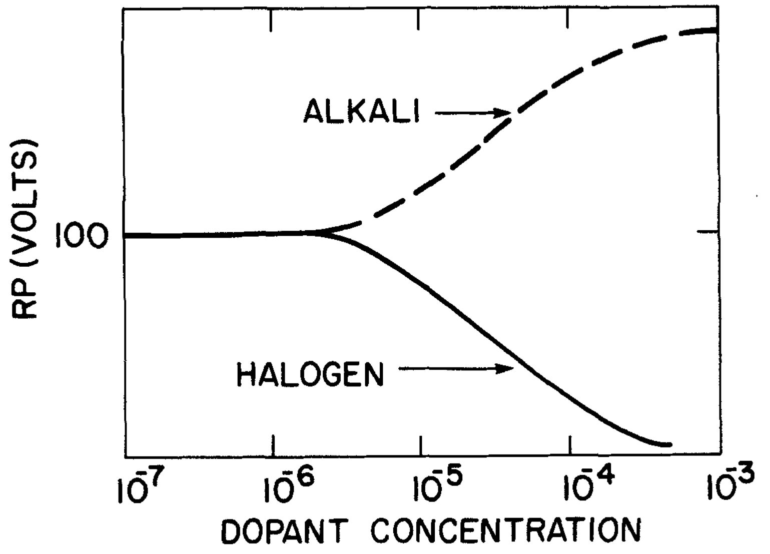
and

$$2\,c_1 = a_p + (a_p^2 + 4k^2c_2^2)^{1/2} \tag{2}$$

Equation (1) corresponds to halogen doping and (2) to alkali metal doping. It is immediately apparent that, since the C_1^- center is believed responsible for trapping holes (and C_3^+, electrons) and ionized dopants are too shallow to trap significantly, that halogens will decrease RP and alkali metals will increase it. The opposite effect will occur if electrons are passed through the film.[13] This situation is sketched in Fig. 5.

Typically, only 5-20% of the additives become electrically active and only when the ionized population becomes comparable to kc_2 are large effects observed. The exact mechanisms involved are not known, nor, more

FIGURE 5



importantly are the positions of the various states which result from doping in the gap.[14] The presence of Te complicates the situation quite considerably both theoretically and experimentally, since the gap has been narrowed and the distribution of all states in the gap broadened.

SUMMARY

The figures display the broad shifts in properties which occur as Te is added to Se. The references are the best sources for specific details. Our current understanding of SeTe alloys comes largely from studies on Se itself and optical measurements. The major areas where detailed understanding is lacking are:

(i) thermodynamic equilibration processes, including vacuum evaporation;
(ii) the kinetics and bonding configurations of defect states and impurity states;
(iii) the distribution in number density and energy space of states in the gap of the material.

Most of our understanding has come since 1980, and coincides with the widespread introduction of SeTe alloys as photoconductors in xerographic copiers, and a lot of this understanding has come from xerographic measurements and earlier work on selenium.

REFERENCES

1. R. Bellissent and G. Tourand, J. Non-Cryst. Solids 35 & 36, 1221 (1980).
2. S.O. Kasap, C. Juhasz, and J.R. Hardwick, Proc. 3rd Int. Symp. on Industrial Uses of Selenium & Tellurium, Selenium-Tellurium Development Association, Darien, CT (U.S.A. 1984), p.307.
3. S.H. Hagen and P.J.A. Derks, J. Non-Cryst. Solids 65, 241 (1984).
4. L. Cheung, G.M.T. Foley, P. Fournia, and B.E. Springett, Photo. Science and Eng. 26, 245 (1982).
5. S.M. Vaezi-Nejad and C. Juhasz, Thin Solid Films 148, 251 (1987).
6. T. Takahashi, J. Non-Cryst. Solids 34, 307 (1979).
7. M. Abkowitz and S. Maitra, J. Appl. Phys. 61, 1038 (1987).
8. A.H. Abou El Ela, M.K. Elmously, and K.S. Abdu, J. Mat. Science 15, 871 (1980).
9. M. Okuda, K. Motomura, H. Naito, T. Matsushita, and T. Nakau, Jap. J. Appl. Phys. 21, 1293 (1982).
10. H. Naito, M. Nakaishi, H. Nakayama, M. Okuda, T. Nakau, A. Suzuki, and T. Matsushita, Jap. J. Appl. Phys. 22, 1818 (1983).
11. M. Abkowitz and J. Markovics, Phil. Mag. B49, L31 (1984).
12. H. Fritzsche and M. Kastner, Phil. Mag. B37, 285 (1978).
13. A. Onozuka, O. Oda and I. Tsuboya, Thin Solid Films 149, 9 (1987).
14. M. Abkowitz, F. Jansen and A. Melnyk, Phil. Mag. B51, 405 (1985).