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Time-of-Flight Study of the Compensation Mechanism in a-Se Alloys

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Arsenic is added to amorphous selenium to retard crystallization and to improve its mechanical properties. Arsenic in sufficient quantities acts as a weak hole trap that results in buildup of residual potential when subjected to charge–expose–erase cyclic conditions employed in electrophotography. A halogen, chiefly chlorine, that by itself acts as an electron trap in amorphous selenium is added to arsenic containing selenium to eliminate residual potential when operated in a positive charging mode (hole transport). Some selenium alloys contain 0.33-atom % arsenic and 30-ppm chlorine. Chlorine in excess of that required to compensate arsenic in bulk does not affect hole transport. However, excess chlorine decreases the electron range. When these alloys are employed as photosensitive elements for xeroradiography purposes in which x-rays are bulk absorbed and both hole and electron transports contribute to the sensitivity, the excess chlorine will have the effect of reducing the sensitivity. In this article, compensation of arsenic by chlorine has been explained in terms of structural considerations. These considerations and heat of formation data suggest that approximately 30-ppm chlorine is required to compensate 0.33-atom % arsenic. A technique has been developed to map the excess chlorine profiles. This is based on the principle that if a small electron current is injected into the film from a biased substrate in a time-of-flight setup, the electrons are selectively trapped at these excess chlorine sites. The resulting electric field profiles have been measured and related to the excess chlorine profiles. Experimentally, a film containing 0.33-atom % arsenic and approximately 40-ppm chlorine is ideally compensated, and excess chlorine is observed in films containing more than 40-ppm chlorine.

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Introduction

Amorphous-selenium (a-Se) photoreceptors consisting of vacuum-deposited 20- to 100-μm-thick films on aluminum drums were the first commercially used photosensitive elements in electrophotography and continue to be widely used. One type of amorphous-selenium alloy employed in electrophotography contains 99.67-atom % amorphous selenium, 0.33 % arsenic, and approximately 30-ppm chlorine. The evaporated films are compositionally graded in arsenic due to a fractionation that occurs during the evaporation of the alloy. A standard technique employing the electron microprobe exists to measure the arsenic profiles. Film produced by conventional open-boat evaporation techniques have an arsenic content of between 0.1% and 0.2% throughout most of the thickness, rising sharply to higher concentrations in the free-surface region of the film. However, precise information on the chlorine profiles is not available since existing methods of measuring chlorine content are very time consuming.

In this article, we have attempted to explain the chlorine compensation mechanism of arsenic based on experimental results with Raman spectroscopy, viscosity measurements, and charge-transport studies. Available heat of formation data on arsenic–selenium bonds seem to confirm that approximately 30-ppm chlorine is required to compensate the mild hole-trapping effect of 0.33% arsenic. Effect of dissimilarity between arsenic and chlorine profiles on charge transport under excitation by highly absorbed (visible light) and bulk absorbed (x-ray) radiation is discussed. The dissimilarity of arsenic and chlorine profiles results in some film regions having chlorine in excess of that required to ideally compensate the arsenic in that region.

A technique to measure excess chlorine profiles is described in the experimental section. This technique is a slightly modified version of the well-known time-of-flight (TOF) technique. The technique is based on the principle that if an electron injection current is maintained from the substrate in a time-of-flight (TOF) setup, the trapped electrons in any region would be proportional to the excess chlorine content because chlorine in a-Se is known to trap electrons. The electric field profile uniform across the film as soon as the voltage is turned on would change continuously as the electrons from the injection current from the substrate are trapped at excess chlorine sites. The electric field profile related to the trapped electron profile by Poisson's equation is monitored by the time-of-flight technique.

The section on results describes some of the electric field changes observed in amorphous selenium containing 0.33-atom % arsenic but varying amounts (in the range 20 to 140 ppm) of chlorine. Film containing 22-ppm chlorine is undercompensated, film containing 43-ppm chlorine appears ideally compensated, and film containing 51 ppm or more chlorine is overcompensated.

Background

Amorphous-selenium alloys containing arsenic and chlorine are employed as photoreceptor materials in some photocopiers. Arsenic is added to amorphous selenium to retard crystallization and improve mechanical properties.[1,2] Arsenic in sufficient quantities acts as a weak hole trap that results in a buildup of residual potential when subjected to positive charge—exposure to highly absorbed visible light—erase cycles. A halogen, chiefly chlorine, that by itself acts as a strong electron trap in selenium is added to arsenic containing selenium to improve hole range and eliminate residual potential. Some alloys of selenium contain about 0.33-atom % arsenic and about 20- to 30-ppm chlorine. Because the photoconductor is charged positive in all copying machine applications, hole

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transport is employed to discharge the film. Chlorine in excess of that required to compensate the arsenic in bulk does not affect hole transport. The only undesirable effect of excess chlorine is the increased dark decay of these materials. In most copier machine applications, this is not a serious problem.

On the other hand, if this alloy film with excess chlorine is used as the photoconductive element for xeroradiography purposes, the excess chlorine will have the effect of reducing sensitivity. Because x-rays are uniformly absorbed in the bulk of the photoconductor, the highest sensitivity would be attained if both holes and electrons have sufficient range to drift across the thickness of the film without getting trapped. The film thickness for use in xeroradiography are typically 150 μm. Chlorine in excess of that required to compensate arsenic will result in reduction of electron range thus lowering sensitivity.

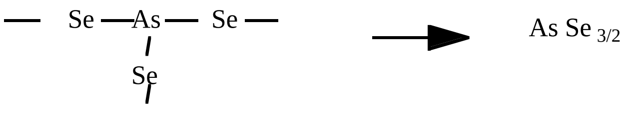
Considerable speculation exists regarding the relation between charge transport and atomic structure of selenium. Amorphous selenium contains both polymeric chains and Se_8 rings molecules.[3] Viscosity measurements indicate that the addition of chlorine leads to a decrease in chain lengths and these short chains are terminated by chlorine atoms. Transportwise, we observed that the presence of chlorine does not affect the hole range if the hole range starts large ($>2 \times 10^{-6}$ cm^2/V). However, if the hole range is short, addition of chlorine sometimes causes an increase in the hole range. This presumably happens because chlorine compensates for impurities that caused the short hole range in the first place. The presence of chlorine by itself in a few parts per million range severely reduces the electron range by causing heavy trapping because chlorine acts as an electron trap.[4,5] An alternative explanation of dopant effect on charge carrier range is based on the effect of the dopant on the population of native defects valence alternation pairs (VAPS).[6] It has been suggested on the basis of chemical arguments that VAPS consists of a one-fold coordinated negatively charged Se atom and a three-fold coordinated positively charged Se atom.[7] A strong electronegative additive like chlorine by interacting with native defects increases the positive charge defects to maintain charge neutrality. The increase in the population of the positive charge defects results in electron trapping. The reverse situation occurs when a-Se is doped with a strong electropositive additive like sodium.

Infrared and Raman spectroscopy studies indicate that incorporation of arsenic in amorphous selenium reduces the ring population, which reaches a zero value when the arsenic concentration is 20 atom %.[8–10] The characteristic Raman spectroscopic peak corresponding to the molecular species As-$Se_{3/2}$ increases linearly with arsenic concentration in the range 0% to 40 % arsenic. The glass transition temperature varies linearly with arsenic concentration in the 0% to 8 % range, and this is attributed to a random concentration of As-$Se_{3/2}$ branch points.[3] The reduction of hole life time (or range) for low arsenic concentration (below 8 %) is associated with arsenic branch points acting as hole traps. If a hole trap is associated with each of the arsenic atoms, then unless the capture cross section of the trap is extremely small, expecting the presence of a few parts per million arsenic atoms to reduce the hole life time drastically would be reasonable. This does not happen. Also, selenium alloy containing 0.33 % (3300-ppm) arsenic is compensated by about 30-ppm chlorine resulting in a material with excellent hole and electron ranges. If each chlorine atom compensates for the presence of one arsenic atom, the effect of adding about 30-ppm chlorine in amorphous selenium containing 3300-ppm arsenic should be insignificant.

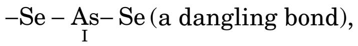
Therefore, any explanation of compensation of arsenic by chlorine should reconcile with the three experimentally observed phenomena: (1) presence of arsenic leads to a very slight reduction of hole range, (2) the majority of arsenic atoms produce branch points, and (3) only 30-ppm chlorine is required to compensate the hole-trapping effect of 3300-ppm arsenic.

Defects in Amorphous State

The Raman spectroscopy studies and measurements of glass-transition temperature indicate that a majority of arsenic atoms produce As-$Se_{3/2}$ branch points.[8,9] The result in this study that only about 40-ppm chlorine is required to compensate the effect of 3300-ppm arsenic suggests that only a small fraction of arsenic atoms act as hole traps, and these could not be As-$Se_{3/2}$ branch points shown below.



Heat of formation data suggest the existence of species other than As-$Se_{3/2}$ branch points. Raman measurements may not permit the observation of peaks that are as a result of other possible species such as



$$-Se-\underset{|}{As}-Se \text{ (a dangling bond),}$$

and so the absence of a peak corresponding to this specie does not preclude their existence in small numbers. In this section, a procedure to calculate the defect density on the basis of thermal entropy and data on heat of formation is discussed. A procedure for calculating the heat of formation for any specie knowing the atomic bond energies is also outlined.

According to thermodynamics, the equilibrium of a solid is determined by the free energy F that reaches a minimum value. The free energy F is also called the Helmholtz free energy of the system and is given by the expression

$$F = E - TS, \tag{1}$$

where E is the internal energy of the solid, S is the total entropy, and T is the temperature of the solid.[11] It is well known that to satisfy this criterion, a certain number of defects exist in the solid. Entropy S is a sum of S_{th} the thermal entropy and S_{cf}, the configurational entropy. The thermal entropy is determined by the number of ways W_{th} in which total vibrational energy of the solid can be distributed over the possible vibrational modes and is given by the relation

$$S_{th} = k \log W_{th} \tag{2}$$

where k is the Boltzman constant. The configurational entropy S_{cf}, on the other hand, is determined by the number of ways W_{cf} in which the atoms could be arranged on the available lattice sites. If the number of atoms is N and the number of vacancies or defects is n, the number of possible arrangements over $(N + n)$ sites is given by

$$W_{th} = \frac{(N+n)!}{N!\,n!} \tag{3}$$

and from the Boltzman relation,

TABLE I. Cleavage Energies of Single Bonds

	S	Se	As	Sb	O	I
S	65					
Se	57	49				
As	61	52	46			
Sb	62	51	44	42		
O	86	82	105	109	60	
I	46	38	42	42	X	26

$$S_{\mathrm{th}} = k \log \frac{(N+n)!}{N!\,n!}. \tag{4}$$

The free energy of the solid is given by

$$F(n,T) = F_0 + n\Phi_v - nT\Delta S_{\mathrm{th}} - kT \log \frac{(N+n)!}{N!\,n!}, \tag{5}$$

where F_0 is the free energy before the defects are introduced, ΔS_{th} is the increase in thermal entropy as a result of introducing a defect, and Φ_v is the formation energy of a defect. In equilibrium $(\delta F/\delta n) = 0$. Solution of Eq. 5 results in

$$\frac{n}{(N+n)} \approx \frac{n}{N} = \exp\left(\frac{\Delta S_{\mathrm{th}}}{k}\right)\exp\left(-\frac{\phi_v}{kT}\right). \tag{6}$$

Clearly, defining a "defect state" is necessary, especially in an amorphous material. If the perfect amorphous material is defined as one in which all bonds are satisfied, a defect is an unsatisfied or dangling bond. Based on this definition, an amorphous material consists of a random network in which most of the bonds are satisfied but in which a certain statistical fraction of bonds are unsatisfied.

Applying Eq. 6 for the case of arsenic-doped amorphous seleniu, N and n would be the atoms in the $\mathrm{AsSe}_{3/2}$ specie and in the defect state

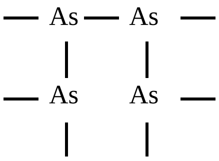
$$-\mathrm{Se} - \underset{\mathrm{I}}{\mathrm{As}} - \mathrm{Se}\,,$$

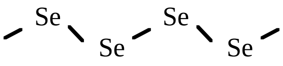
respectively. The value Φ_v is the difference in the energy of formation between the two species. To calculate the relative ratios of $\mathrm{AsSe}_{3/2}$ and

$$-\mathrm{Se} - \underset{\mathrm{I}}{\mathrm{As}} - \mathrm{Se}\,,$$

it is necessary to calculate the energy of formation using the bond energies[12] given in Table I. This is accomplished in the following manner:

Schematically pure As and pure Se have the following bond arrangements:





To form any As–Se specie, one must first determine the number of As–As bonds that must be severed and the number of As–Se bonds that must be reformed. The energy of formation of a specie is the difference between the sum of the severed bond energies and the sum of the reconstructed bonds. To form $\mathrm{AsSe}_{3/2}$ one must break three As–As bonds and four Se–Se bonds and form three As–Se bonds.

$$\mathrm{As} + 3\mathrm{Se} \rightarrow \mathrm{AsSe}_3.$$

Substituting from Table I,

$$3(46) + 4(49) \rightarrow 3(52) + \Delta H_2$$

$$\Delta H_2 = 178 kcal / mole$$

where ΔH_2 is the energy of formation of the $\mathrm{As{-}Se}_{3/2}$ species. To form

$$-\mathrm{Se} - \underset{\mathrm{I}}{\mathrm{As}} - \mathrm{Se}\,,$$

it is necessary to break three As–As bonds and three Se–Se bonds and to form two As–Se bonds.

$$\mathrm{As} + 2\mathrm{Se} \rightarrow \mathrm{AsSe}_2$$

$$3(46) + 3(49) \rightarrow 2(52) + \Delta H_1$$

$$\Delta H_1 = 181 kcal / mole$$

where ΔH_1 is the energy of formation of the

$$-\mathrm{Se} - \underset{\mathrm{I}}{\mathrm{As}} - \mathrm{Se}\ \text{ species.}$$

The value Φ_v is the difference between ΔH_1 and ΔH_2 and is 3 kcal/mol. This value is used in conjunction with Eq. 6 to calculate the relative ratios of these two species,

$$\frac{n}{N} = 0.01 \tag{7}$$

Based on this calculation, 1% of arsenic alloyed with selenium possesses unsatisfied or dangling bonds. Due to the unavailability of data on the increase in the thermal entropy as a result of introducing a defect, the term exp $(\Delta S_{\mathrm{th}}/k)$ in Eq. 6 has been set equal to unity which means that ΔS_{th} is small. For glasses for which the entropy data are available, the ΔS term in general is smaller than the $\Delta H/T$ term.[11] In the event that the ΔS_{th} term cannot be neglected, the ratio n/N will be larger than 1%. It is easily seen that because of the small value of $\Delta H_2 - \Delta H_1$, any changes in the value of either ΔH_2 or ΔH_1 would have a profound effect on the value of n/N. It is not unusual to find values for cleavage energies that are different from those shown in Table I. The thrust of this study is the consideration of possible defect states in amorphous materials and the illustration of a technique to calculate their density.

Similar calculations can be carried out for larger Se chain lengths but this does not change the energy difference between the specie with all the As bonds satisfied and the specie with one unsatisfied arsenic bond. The relative ratio of a specie containing two dangling bonds,

$$-\mathrm{Se} - \underset{\mathrm{I}}{\mathrm{As}} -$$

to the $\mathrm{AsSe}_{3/2}$ specie as determined by a set of calculations similar to those carried out above is 0.0001. The concentration of a defect with two dangling bonds is small.

TABLE II. Average Chlorine Content in the Starting Material and Films

Film #	Starting material	Film content
1	20	22
2	50	43
3	75	51
4	100	93
5	125	108
6	150	116
7	200	137

Experimental Procedure

The samples used in this study are evaporated from chrome-plated crucibles. The alloy is a mechanically blended alloy of 2 parts of an alloy containing 99.5% selenium and 0.5% arsenic and 1 part of an alloy containing selenium doped with chlorine. A series of samples containing increasing amounts of chlorine are prepared. The evaporation is carried out at 280°C onto Nesa substrates (slightly electron injecting) maintained at 55°C. The chlorine content of the starting material and the average chlorine content in the film as determined by neutron activation analysis are shown in Table II. Arsenic profiles carried out by electron microprobe show the arsenic fractionation is small with about 0.8% arsenic near the top surface. The measurements are carried out by a modified TOF technique on a sandwich structure with the a-Se alloy film sandwiched between the Nesa electrode and a semitransparent gold electrode.

The conventional electroded time-of-flight technique has been one of the most useful techniques for measuring properties of highly insulating materials such as disordered and noncrystalline solids characterized by high dark resistivity with low dark carrier density and mobility. Those factors result in a long dielectric relaxation time; and hence, a sheet of excess electrons or holes created by a light flash survives for a long time without being neutralized. A block diagram of the traditional electroded TOF measurement setup is shown in Fig. 1. A voltage is applied across the sample sandwiched between two blocking contacts from a calibrated power supply in series with a resistance R_L to ground. In the absence of light, the entire voltage appears across the film, that acts as a capacitor. A short light flash from a laser light source is employed to photogenerate free carriers. The transit across the sample of a sheet of charge of appropriate polarity produces a measurable current in the external circuit. To time resolve the current transient, the duration of the light pulse must be short compared to the shortest measurable transit time and the absorption coefficient of the material must be sufficiently large so that the light is absorbed in a narrow region close to the top electrode. The amount of charge injected from the photogeneration region into the bulk of the sample must be small compared to the applied charge producing the electric field across the sample. For the voltage polarity shown in Fig. 1, the motion of holes across the film with a velocity $\mu_d E$ induces a current through R_L. Here μ_d is the hole drift mobility in units of cm^2/volt second and E is the applied electric field. The transient voltage across R_L is monitored on an oscilloscope or a transient recorder. The signal across the load resistance depends on the RC time constant of the circuit, R_LC, where $C = \varepsilon A/L$ is the capacitance of the film with A the area of the electrode and L, the thickness of the film.

For the case where R_LC is short compared to the transit time t_T (= $L/\mu_d E$), the current through the resistance R_L is given by

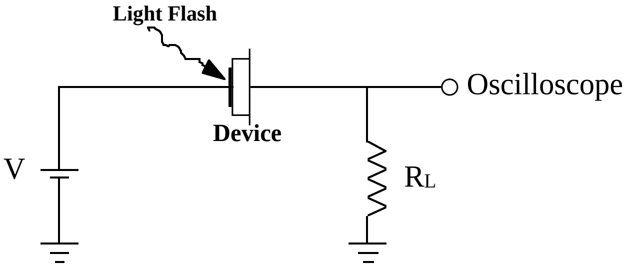


Figure 1. Schematic diagram of an electroded time-of-flight setup.

$$i = \frac{\Delta Q}{t_T} = e\eta F \frac{\mu_d E}{L} \quad \text{for } t < t_T \qquad (8)$$
$$= 0 \quad \text{for } t > t_T$$

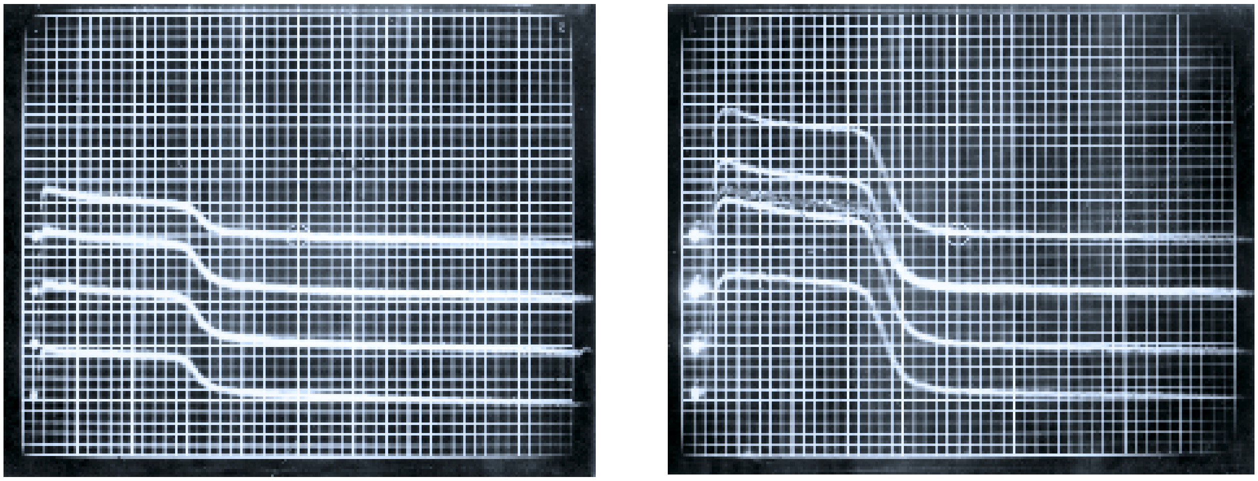
where η is the quantum efficiency of photogeneration, F is the number of absorbed photons from the flash, and ΔQ is the number of charges in the drifting sheet. The current reaches its final amplitude in a short time (with a time constant R_LC) and stays constant at that value as the charge sheet is swept through the sample. At a time corresponding to the transit time t_T, the sheet reaches the counter-electrode and the current drops to zero. The Coulombic repulsion of the charges in the transiting sheet results in a rounding off of the current transient at $t = t_T$

For the case where R_LC is large compared to the transit time, a ramp-type signal appears across the resistance and is given by

$$\Delta V(t) = \frac{\Delta Q(t)}{C} = \frac{\eta Fe}{C}\frac{t}{t_T} \quad \text{for } t < t_T,$$
$$\Delta V(t) = \frac{1}{C}\eta Fe \quad \text{for } t > t_T \qquad (9)$$

The short-time-constant measurements (Eq. 8) are employed to measure transit times and, hence, mobilities, and the long-time-constant measurements (Eq. 9) are employed to integrate the current signal to measure quantum efficiency of photogeneration η. In amorphous selenium η is electric field dependent.[13]

The main difference between the traditional TOF and the technique used for this study is that the substrate is made slightly injecting. The bias voltage is applied and kept on continuously as the TOF signals are monitored every few seconds. At $t = 0^+$ after turning on the voltage source, the electric field across the film is uniform because the small electron current from the substrate will not have had sufficient time to trap the charge at the excess chlorine sites. For $t > 0$ after turning on the voltage source, electron trapping proceeds at excess chlorine sites, changing the field profile within the film which in turn alters the shape of the transient current and voltage signals. The electron-trapping proceeds until a quasi steady state is reached. The electron-trapping efficiency of any region of the film depends on excess chlorine (more than that required for ideal compensation of arsenic). In the absence of bulk trapping of photogenerated holes in the TOF experiment, the shape of the transient current reflects the electric field profile inside the film. The increase in electric field in the photogeneration region (about 1000 Å of the top region of the film) leads to an increase in the photogeneration efficiency.[13] This should reflect itself as an increase in the amplitude of the signal in the voltage mode.



(a) **(b)**

Figure 2. (a) Electroded time-of-flight current signals in an amorphous-selenium film containing 0.33% arsenic and 22-ppm chlorine. Film thickness is 100 µm, applied voltage is 120 V, and the scale of the x axis is 2 µs/cm. The four transients are recorded at $t = 0$ (bottom transient), 60, 120, and 360 (top transient) s after the application of the potential. The four transients are displaced along the y axis for clarity; (b) Electroded time-of-flight current signals in an amorphous-selenium film containing 0.33% arsenic and 43-ppm chlorine. Film thickness is 100 µm, applied voltage is 120 V, and the scale of the x axis is 2 µs/cm. The four transients are recorded at $t = 0$ (bottom transient), 60, 120, and 360 (top transient) s after the application of the potential. The four transients are displaced along the y axis for clarity.

From the experimentally observed transient current TOF signal and the transient signal in the voltage mode, the electric field and, hence, the charge profiles can be obtained. The procedure is outlined below. In the analysis to follow, the top surface of the film is at $x = 0$ and is positive and the bulk space charge is due to trapped electrons. If in the TOF experiment, the photogenerated TOF signal arrives at a distance x in time t,

$$x = \int_0^{x(t)} \frac{dx}{dt} dt = \int_0^{x(t)} \mu E(t) dt. \qquad (10)$$

Multiplying both sides by $(1/C)\,(eN_0/L)$, where $N_0 = \eta F$ is the number of holes generated by the light flash and is a function of the electric field in the photogeneration region,

$$\frac{1}{C} eN_0 \frac{x}{L} = \frac{1}{C} \int_0^{x(t)} \frac{eN_0}{L} \mu E(t) dt = \frac{1}{C} \int_0^{x(t)} i(t) dt = \Delta V(t). \qquad (11)$$

Rearranging,

$$\frac{x}{L} = \frac{\Delta V(t)}{(\frac{eN_0}{C})} = \frac{\Delta V(t)}{\Delta V(\infty)}. \qquad (12)$$

The relationship between the space-charge density $\rho(x)$ and the electric field $E(x)$ is given by the Poisson's equation,

$$\frac{\partial E}{\partial x} = \frac{\rho(x)}{\varepsilon}. \qquad (13)$$

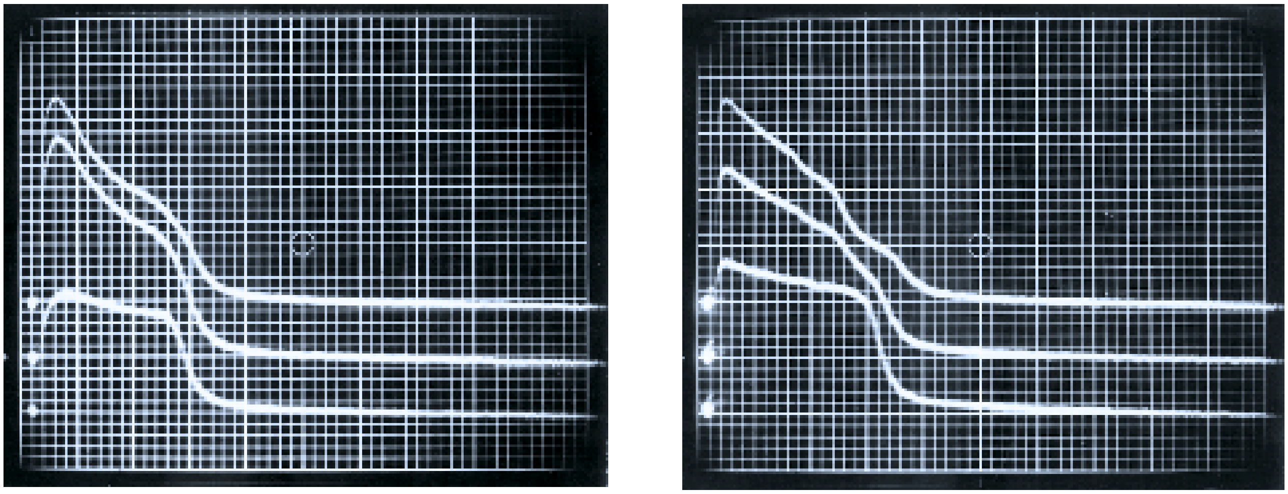
Integrating, the electric field at any point x is given by,

$$E(x) = E(L) + \int_x^L \frac{\rho(x)}{\varepsilon} dx \qquad (14)$$

Therefore, the procedure for constructing the charge profile from the transient current pulse $i(t)$ and the transient voltage pulse $\Delta V(t)$ involves three steps: (1) the term $i(t)$ is first converted to $E(t)$ employing the expression $[i(t) = (eN_0/L)\, \mu E(t)]$ and $[N_0 = (C/e)\, \Delta V(\infty)]$, (2) the term $E(t)$ is converted to $E(x)$ from Eq. 12, and (3) the term $E(x)$ is converted to $\rho(x)$ employing the Poisson's relation (Eq. 13).

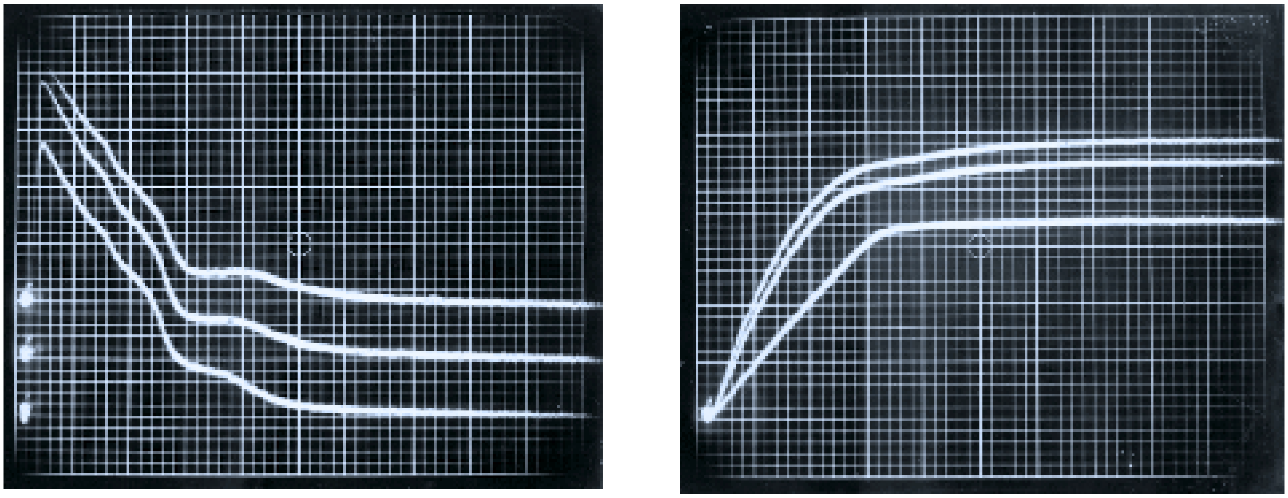
Results and Analysis

The transient current TOF signals are shown in Fig. 2(a) and 2(b) for films containing average chlorine contents of 22- and 43-ppm chlorine, respectively. Each film is 100 µm thick and contains arsenic content of 0.33%. Each figure shows four transients taken at times 0+, 60, 120, and 360 s after the application of 120 V across the film with the bottom Nesa electrode biased negative and the light flashes incident through the positively biased top gold electrode. The four transients are displaced slightly along the vertical axis for clarity . The bottom transient is the first one obtained soon after the application of the voltage and the top transient is obtained 360 s after the application of the voltage source. Although, the Nesa electrode injects a slight electron current, the transients show that the electric field remains uniform across both the films, suggesting the absence of electron trapping within the film. The transient current TOF signals for films containing average chlorine contents of 51- and 108-ppm chlorine are shown in Fig. 3(a) and 3(b) respectively. In Fig. 3(a) the transients are obtained at 0+, 60, and 120 s after the application of the voltage source. In Fig. 3(b) the transients are obtained at 0+, 10, and 20 s after the application of the voltage source. Again, as in Fig. 2, the transients are displaced slightly along the vertical axis for clarity. In Fig. 3(a), the first transient (bottom curve) shows the electric field as uniform across the film when the voltage source is applied. The electric field profile changes as a result of electron trapping. In 60 s, the field profile suggests uniform trapping of electrons within the bulk of the film. Similarly, the initial transient (bottom curve) in Fig. 3(b) shows the field uniform soon after the application of the potential. The field pattern changes continuously as electrons are trapped at the excess chlorine sites. Figure 4(a) shows



(a) (b)

Figure 3. (a) Electroded time-of-flight current signals in an amorphous-selenium film containing 0.33% arsenic and 51-ppm chlorine. Film thickness is 100 μm, applied voltage is 120 V, and the scale of the x axis is 2 μs/cm. The three transients are recorded at $t = 0$ (bottom transient), 60, and 120 (top transient) s after the application of the potential. The four transients are displaced along the y axis for clarity; (b) Electroded time-of-flight current signals in an amorphous selenium film containing 0.33% arsenic and 108-ppm chlorine. Film thickness is 100 μm, applied voltage is 120 V, and the scale of the x axis is 2 μs/cm. The three transients are recorded at $t = 0$ (bottom transient), 10, and 20 (top transient) s after the application of the potential. The three transients are displaced along the y axis for clarity.



(a) (b)

Figure 4. (a) Electroded time-of-flight current signals in an amorphous-selenium film containing 0.33% arsenic and 108-ppm chlorine. Film thickness is 100 μm, applied voltage is 120 V, and the scale of the x axis is 2 μs/cm. The three transients are recorded at $t = 50$ (bottom transient), 65, and 85 (top transient) s after the application of the potential. The three transients are displaced along the y axis for clarity; (b) Electroded time-of-flight voltage signals in an amorphous-selenium film containing 0.33% arsenic and 108-ppm chlorine. Film thickness is 100 μm, applied voltage is 120 V, and the scale of the x axis is 2 μs/cm. The three transients are recorded at $t = 0$ (bottom transient), 65, and 110 (top transient) s after the application of the potential.

further changes in this film at 50, 65, and 85 s after the application of the voltage source. The transient TOF signals suggest some structure to the electric field pattern. During the time the electric field profile changes within the film due to electron trapping, the field increases at the front of the film and because the applied voltage is held constant a decrease occurs in the bottom of the film (near the Nesa substrate). Figure 4(b) shows the integrated voltage signal for the film containing 108-ppm chlorine at $t = 0$, 65, and 110 s, respectively. The increase in electric field in the front portion of the film results in an increase in photogeneration efficiency as shown by the increase in the amplitude of the voltage signal in Fig. 4(b).

Figure 5 shows the transient current TOF traces for the film containing 108-ppm chlorine at $t = 0$ and 60 s after the application of the voltage source. Figure 6 shows the transient voltage signals at $t = 0$ and 60 s. The transient current shape is idealized by ignoring the dispersive tail. The current trace at $t = 0$ is flat indicating that the electric field is constant and equal to 1.2×10^4 V/cm (120 V across 100-μm-thick film). The transit time of 5.6 μs is the time at which the probing hole sheet exits the system. The voltage signal of Fig. 6 at $t = 0$ is the integral of the current pulse and is a ramp. Between $t = 0$ and 60 s, the electron injection current from the substrate traps electrons at the excess chlorine sites, giving rise to bulk space charge. Under the conditions of this altered field profile, the time (approximately 9 μs) at which the probing hole sheet exits the system is much longer than the transit time of 5.6 μs under uniform field conditions. The electric field profile

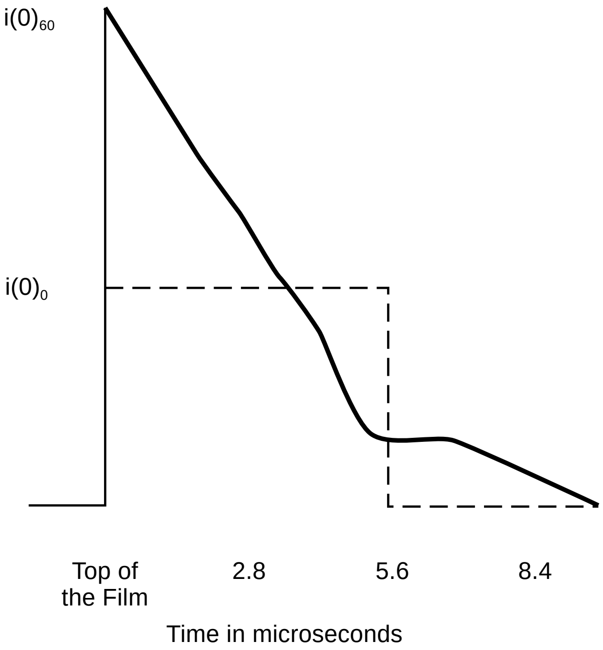


Figure 5. Electroded time-of-flight current signals in an amorphous-selenium film containing 0.33% arsenic and 108-ppm chlorine. The two transients are recorded at t = 0 and 60 s after the application of the potential.

in Fig. 5 at t = 60 s is obtained as a time function, and this has to be converted as a function of space. This is done by the procedure indicated in Fig. 6. If the amplitude of the voltage pulse at t = 60 s is assumed to be 100 (same magnitude as the film thickness of 100 µm), the amplitude at any other time is proportional to the location of the probe sheet at that time (Eq. 12). For example, the pulse amplitude at 2.8 µs is 67.5 µm into the film. The space function of $E(x)$ is then converted to a space-charge profile by the application of Poisson's equation and is shown in Fig. 7. A correction is applied to convert the space-charge profile into an excess chlorine profile. This correction takes into consideration that the electron-trapping probability in any region depends not only on the excess chlorine concentration but also on the velocity of the electrons. Given two regions of identical excess chlorine, the probability of capture is higher in the region with lower electric field. The excess chlorine profile of Fig. 8 is obtained from the trapped bulk space-charge profile of Fig. 7 after correcting for the differences in electric field in the various regions of the film. The excess chlorine profile of Fig. 8 is in arbitrary units. The changes in excess chlorine content between various regions are not as abrupt as those indicated in the figure. The technique employed here does not distinguish between regions that are undercompensated or ideally compensated because neither traps electrons. The 5-µm region between 90 and 95 µm is one such region.

Discussion

Arsenic when alloyed with amorphous selenium is a weak hole trap that results in a residual voltage buildup when films of arsenic-doped selenium are subjected to fast cyclic mode operation consisting of positive charge–expose–erase steps. The residual buildup in a-Se alloy containing 0.33% arsenic drops considerably when chlorine in the 20- to 30-ppm range is added to the film. The residual buildup caused by hole trapping drops to a negligible value if chlorine content is increased to 100 ppm. These results suggest that

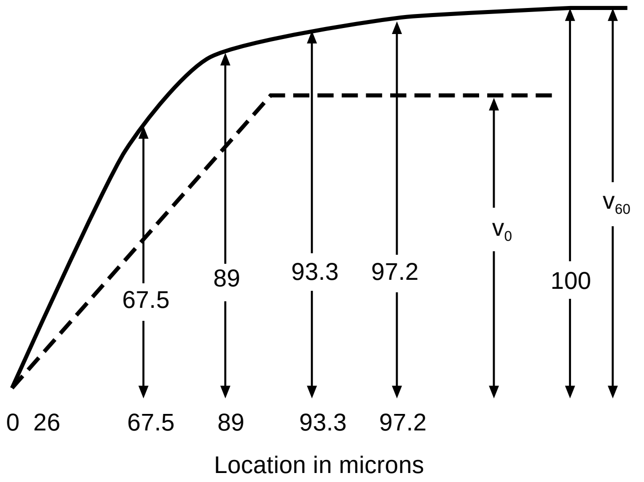


Figure 6. Electroded time-of-flight voltage signals in an amorphous-selenium film containing 0.33% arsenic and 108-ppm chlorine. The two transients are recorded at t = 0 and 60 s after the application of the potential.

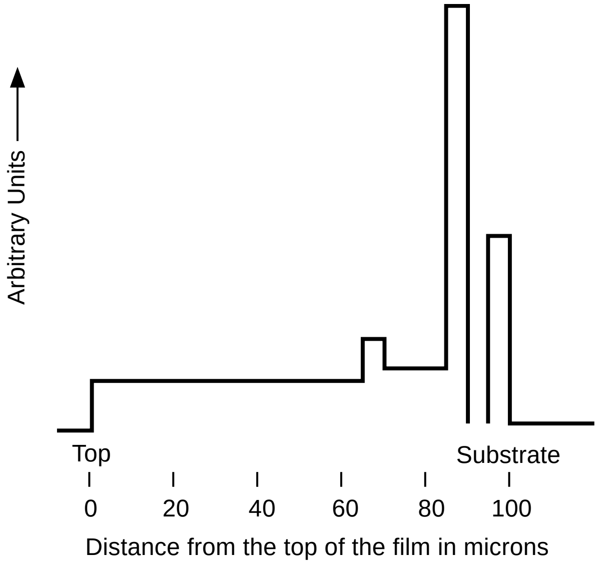


Figure 7. Electron space-charge profile generated from the current and voltage transients of Figs. 5 and 6.

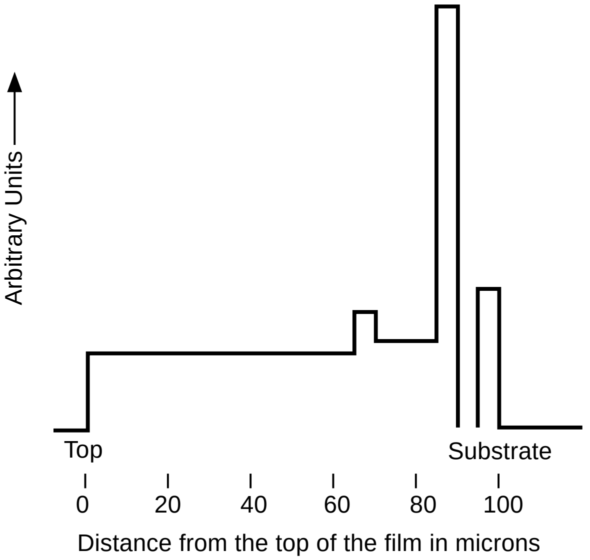


Figure 8. Excess chlorine profile generated from the space-charge profile of Fig. 7.

addition of 20- to 30-ppm chlorine in arsenic-doped selenium compensates for the hole-trapping effect of arsenic. On the other hand, chlorine when doped in amorphous selenium by itself (in the absence of arsenic) is a strong electron trap. The summary of the results from the current study are: (1) in amorphous selenium doped with 0.33% arsenic, chlorine in concentrations less than 40 ppm do not introduce electron traps (Fig. 2); (2) in films containing 50-ppm chlorine or more, electron traps are observed (Fig. 3); (3) in films containing excess chlorine, the electron-trap distribution is nonuniform (Fig. 7); and (4) the nonuniform electron traps can be converted into excess chlorine profiles (Fig. 8). These results suggest that in amorphous films containing 0.33% arsenic, the amount of chlorine required to ideally compensate the effect of arsenic is around 40 ppm.

The calculations in the section on defects in the amorphous state indicate that approximately 1% of arsenic in As–Se glass is associated with a glass defect (an unsatisfied bond). Based on this study, we postulated that this defect

$$-\mathrm{Se}-\underset{|}{\mathrm{As}}-\mathrm{Se}$$

is a hole trap. The addition of an electronegative dopant such as chlorine has been experimentally demonstrated as a method of eliminating this hole trap. The results from this study seem to indicate that the addition of chlorine ties up the unsatisfied bond in

$$-\mathrm{Se}-\underset{|}{\mathrm{As}}-\mathrm{Se}\,.$$

The concentration of chlorine required to satisfy the dangling bonds of these defects in selenium containing 0.33% arsenic would be 1% of 0.33% (3300 ppm).

The experimental results in this study on a series of films containing 0.33% arsenic and chlorine varying from a low of 22 ppm to a high of 137 ppm confirm that chlorine in excess of 30 to ~40 ppm behaves differently than chlorine in quantities less than about 30 to ~ 40 ppm. Chlorine in excess of 30 to ~ 40 ppm appears as electron traps. No effort has been made in this study to determine the peculiar chlorine profiles in films containing higher concentration (> 40 ppm) of chlorine.

Conclusions

Compensation of arsenic by chlorine in selenium alloys has been explained with structural considerations. Using bond cleavage energies to calculate the energy of formation of different species, approximately 1% of the arsenic atoms is shown to form the species

$$-\mathrm{Se}-\underset{|}{\mathrm{As}}-\mathrm{Se}$$

and the rest, As $\mathrm{Se}_{3/2}$. The presence of the latter has been inferred from the study of data on Raman spectroscopy. The experiment showed that approximately 40-ppm chlorine is required to compensate 0.33% arsenic. Chlorine in excess of 40 ppm appears as electron traps. It is suggested that chlorine compensates the dangling bond of

$$-\mathrm{Se}-\underset{|}{\mathrm{As}}-\mathrm{Se}\,.$$

A technique was developed to measure these chlorine profiles.

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