

The influence of deposition conditions and alloying on the electronic properties of amorphous selenium

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Electronic properties of *a*-Se as a function of the source (boat) temperature and as a function of As (up to 0.7%) and Cl (up to 40 wt.ppm) concentrations have been experimentally studied by carrying out conventional and interrupted field time-of-flight (IFTOF) transient photoconductivity measurements that provide accurate determinations of the drift mobility and the deep trapping time (lifetime). No variation in electron and hole lifetimes and mobilities for pure *a*-Se was observed with the source temperature, that is, no dependence was observed on the deposition rate nor on the vapor composition. The addition of As reduces the hole lifetime but does not change the hole mobility. At the same time As addition increases the electron lifetime while reducing the electron mobility. The electron range $\mu\tau$ however increases with the As content which means that the overall concentration of deep electron traps must be substantially reduced by the addition of As. Cl addition in the ppm range increases the hole lifetime but reduces the electron lifetime. The drift mobility of both carriers remains the same. We interpret the results in terms of a shallow trap controlled charge transport in which deep traps are due to potential under and overcoordinated charged defects that can exist in the structure.

1. Introduction

Renewed interest in amorphous selenium (*a*-Se) is motivated by its use as an *X*-ray sensitive photoconductor in recently developed direct-conversion, flat-panel *X*-ray image detectors [1,2]. In these devices, a layer (thick film) of *a*-Se is deposited over a thin-film transistor array. *X*-ray irradiation generates mobile charge carriers in the selenium layer that separate and drift due to a large applied electric field. With positive bias applied to the radiation receiving electrode, electrons are collected by the pixel storage capacitors. The amount of charge stored on each pixel is proportional to the radiation received by that pixel and represents a „pixel“ of the *X*-ray image. Sense amplifiers periodically read the stored charge row by row through the array's transistors thus forming the *X*-ray image. For more details the reader is referred to the review articles by Kasap and Rowlands [1,2]. Amorphous selenium satisfies three conditions that are necessary for use as an *X*-ray photoconductor in such an imaging system. First, it has good *X*-ray photosensitivity thus producing a strong signal. Second, its very high resistivity limits the background (dark) current. Third, it is easily evaporated to form large-area, thick films comparable in size to typical objects to be *X*-rayed, e.g. a human chest.

A large electric field is necessary because the amount of collected charge per unit absorbed radiation is a strongly increasing function of the field. Although the intrinsic dark conductivity of *a*-Se is small, the large field that is needed for good *X*-ray sensitivity tends to cause injection of charge from the metallic electrodes, which leads to a significant dark current. One way to minimize this undesired dark current is by adding thin layers that have small carrier lifetimes in order to trap the injected carriers, creating an

analog of a *p-i-n* structure [3]. In these advanced detector structures, control over the carrier mobilities and lifetimes is crucial.

There are a number of parameters that can potentially influence the structure and electronic properties of *a*-Se prepared by thermal evaporation such as the boat (or source) temperature, evaporation rate, and the substrate temperature. Post-deposition treatments such as annealing can also modify the sample's properties. In addition, the *a*-Se that is used in actual *X*-ray photoconductor applications is not simply „pure“ *a*-Se but *stabilized a*-Se, that is *a*-Se that has been alloyed with a small amount of As and doped with Cl in the parts per million (ppm) range. Over time, pure *a*-Se tends to crystallize even at room temperature, but this process is greatly retarded by the addition of As which forms cross-links between the selenium chains [4,5]. However, As addition also produces deep hole traps that reduce the hole lifetime. In order to obtain acceptably long hole lifetimes, Cl is added (or another halogen) [5–8]. In this paper, we systematically examine how the hole and electron drift mobility μ , the lifetime τ , and the product called the carrier range $\mu\tau$, depend on the amount of As and Cl addition to *a*-Se. The carrier range $\mu\tau$ is an important technological parameter that closely controls the sensitivity of the *X*-ray photoconductor [2]. It is therefore highly desirable to understand not only the experimental dependence of $\mu\tau$ on the exact composition of stabilized *a*-Se but also the reasons why such effects are observed.

2. Samples preparation and experimental details

Samples of *a*-Se were prepared by thermal evaporation of selenium pellets from a molybdenum boat using a Norton NRC3117 vacuum system with a base pressure

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of $(5-9) \times 10^{-7}$ Torr. The deposition rate was measured by a Sigma Instruments SQM-160 rate monitor. A shutter protected the substrates until steady evaporation conditions had been established and also during cool-down following deposition. For depositions using boat temperatures lower than the melting point of selenium, the pellets were first melted at 230°C and then cooled to the desired temperature. Numerous samples were prepared with the boat temperature T_B kept constant at a value in the range 190–250°C. The substrate temperature was typically 60–65°C, above the glass transition temperature of pure and stabilized *a*-Se. The pellets used for the starting material were either high-purity (photoreceptor grade) selenium or high-purity selenium alloyed with various concentrations of arsenic and chlorine. In referring to alloyed samples below, the concentration listed is that of the starting material; because of fractionation, the concentration of a particular vacuum deposited films will be somewhat different than the bulk material. Substrates were either intentionally oxidized aluminum plates or Corning 7059 glass with pre-deposited aluminum, platinum, or gold electrodes. The top electrodes were semitransparent films of sputtered gold or platinum. Samples were rested at least 24 h before depositing the top electrode. Sample thicknesses ranged from 50 to 200 μm and were measured by a precision micrometer (to 0.1 μm).

Electron and hole drift mobilities and deep-trapping lifetimes were determined by time-of-flight (TOF) and interrupted-field time-of-flight (IFTOF) transient photoconductivity experiments [9,10]. The samples were rested at least 24 h in the dark prior to measurement. To avoid the build up of trapped charge within the selenium film, a measurement consisted of a single light pulse rather than an average over multiple pulses. The samples were shorted and rested in dark between measurements.

3. Results and discussion

Evaporation of pure selenium avoids the issue of fractionation which can occur with alloys, leading to a non-uniform composition across the thickness of the sample (this effect, for example, has been well studied and modeled for Se-Te alloys [11]). For pure *a*-Se, the relevant deposition parameters include the temperature of substrate T_S and the temperature of evaporating boat T_B . Most samples were prepared with T_S in the range 60–65°C, just above the glass transition temperature, which is known to lead to electronic quality *a*-Se films [5]. T_B influences the deposition in two ways. Firstly, T_B simply controls the rate of deposition and, secondly, T_B also determines the composition, that is the distributions of different molecular species, in the vapor phase [12]. For selenium, increasing T_B from 190 to 250°C results in Se_5 to increase and be the predominant species in the gas-phase instead of Se_6 [12]. We have investigated pure *a*-Se samples deposited by using various boat temperatures in this range. Fig. 1 summarizes the mobility and lifetime values as a function of T_B and shows that the lifetimes

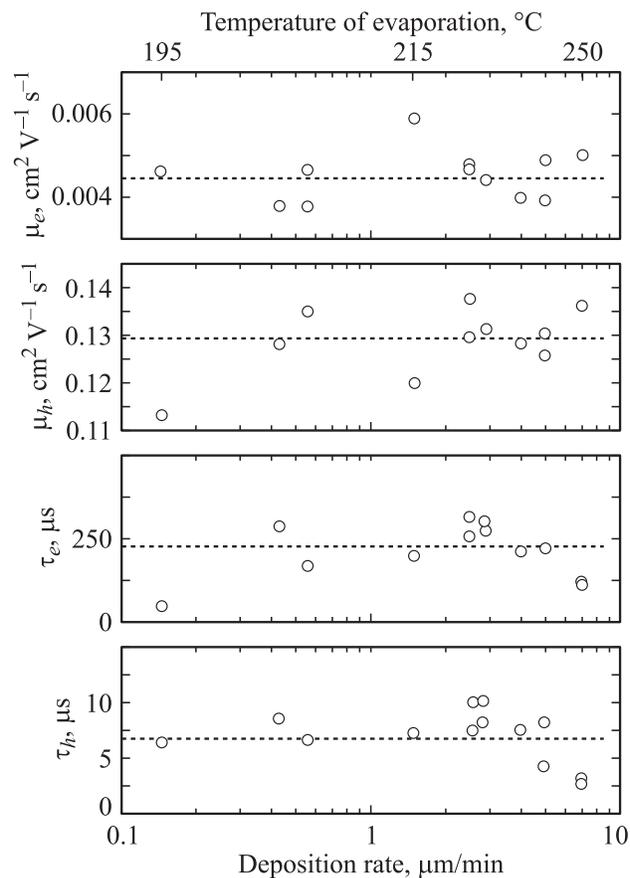


Figure 1. The influence of evaporation temperature and deposition rate on the electronic properties of *a*-Se. The source material is high purity photoreceptor grade selenium.

and mobilities of both electrons and holes are relatively independent of T_B even though the deposition rate varied by nearly two orders of magnitude. The lack of any change in the electronic properties despite the change in the vapor-phase composition implies that all arriving species either are decomposed or are incorporated into the growing film in a uniform way regardless of the particular vapor-phase composition. Maintaining T_S above the glass transition temperature during film deposition enhances the surface atomic mobility of deposited species and allows them to find the optimal positions. In contrast, our attempt to deposit *a*-Se at room temperature led to samples with very poor electronic properties that improved only marginally with subsequent annealing.

The structure of *a*-Se is believed to consist of ring-like and chain-like molecular regions [5]. Ring-like Se regions are various fragments of Se_8 -rings found in α -monoclinic Se which has good electron transport but exhibits poor hole transport. Chain like Se regions are fragments of Se_n chains found in trigonal Se which has good hole transport but poor electron transport. There is an intuitive argument that the relative fraction of atoms in chain-like and ring-like regions may control the relative importance of hole and

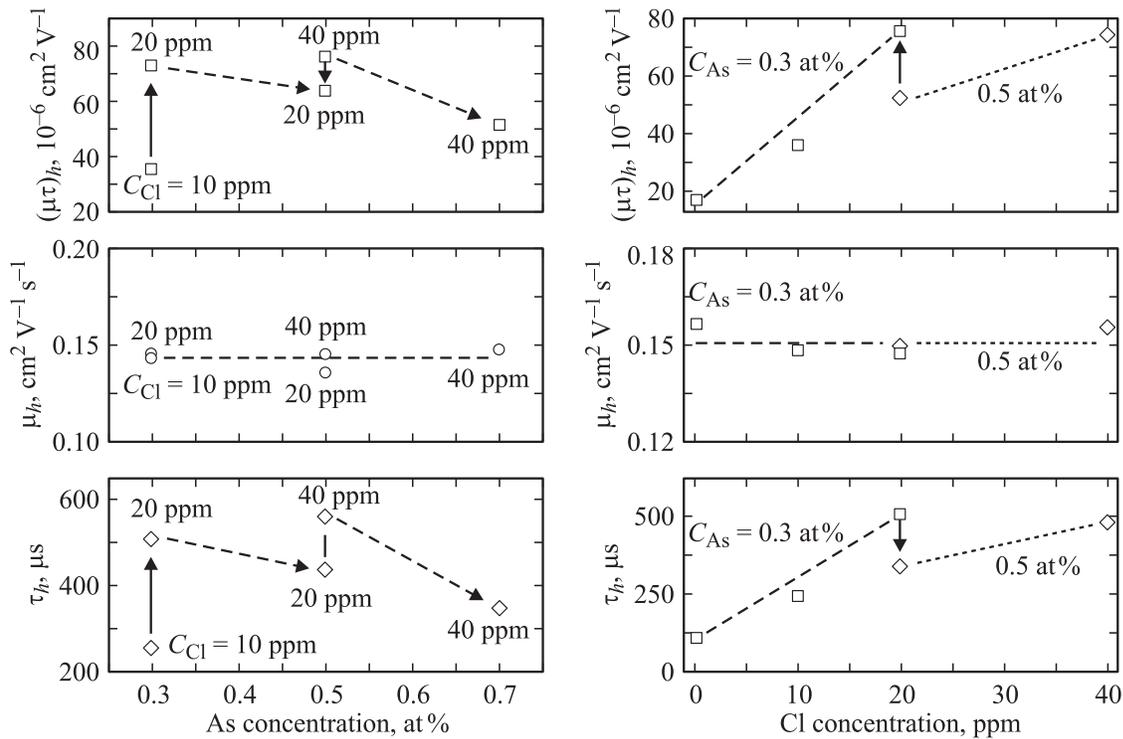


Figure 2. The influence of As and Cl doping on hole lifetime, mobility and hole range in *a*-Se.

electron transport in *a*-Se respectively. The fact that we see no dependence of electronic properties on the Se vapor composition implies that the deposited *a*-Se structure does not seem to depend on the vapor-phase molecular species.

In the past, the effects of As and Cl addition had been studied by either xerographic measurements or by conventional TOF experiments. Xerographic experiments involve measuring the first residual potential V_{r1} that results from fully photodischarging an electrostatically charged *a*-Se film. V_{r1} can only provide a value for the product $\mu\tau$, and the $\mu\tau$ determination depends of the actually model used to interpret V_{r1} , [13,14]; hence $\mu\tau$ values tend to be only estimates, or only approximate at best. Further, since *a*-Se cannot always be charged negatively to high voltages, xerographic measurements provide $\mu\tau$ for holes only. In conventional TOF measurements, one relies on decreasing the electric field until the carrier transit time t_t ($t_t = L/\mu E$; E is the field) is comparable with the lifetime τ , and the photocurrent decays exponentially with a time constant τ that represents the deep trapping time, i.e. the lifetime. (This method was used previously to measure τ in stabilized *a*-Se [6,7]). There are various problems with this technique as well. First, in *a*-Se alloys, photogeneration depends on the field and if we reduce the field too much we effectively extinguish the photocurrent. Long lifetimes therefore cannot be measured reliably. Secondly, the composition of alloyed *a*-Se is not totally uniform across the film, which means that the shape of the photocurrent will be influenced by this fractionation effect. Further, any net bulk space charge in the sample due to trapped carriers will result

in a nonuniform field profile $E(x)$ which will lead to a photocurrent shape $i(t)$ that depends on this field profile rather than the effect trapping. Thus, the determination of τ from the shape $i(t)$ of the conventional TOF photocurrent is not reliable. In IFTOF experiments, on the other hand, the drift of the photoinjected carriers is suddenly halted at time t_1 corresponding a particular location x_1 , usually near the middle of the sample, by removing the field. The carriers then gradually become trapped at x_1 , and the concentration of free carriers decreases exponential with a time constant τ equal to the lifetime. When the field is reapplied at time t_2 , the carriers restart drifting and give rise to a photocurrent i_2 that is less than the photocurrent i_1 at time t_1 just before interruption. The lifetime τ is obtained from the slope of the $\ln(i_2/i_1)$ vs $(t_2 - t_1)$ plot. This technique has been widely used by Kasap and coworkers to obtain accurate measurements of τ for both electrons and holes in a wide range of *a*-Se alloys [15].

We have used the IFTOF technique to investigate the effects of adding As (up to 0.7%) and Cl (up to 40 wt.ppm) to *a*-Se. The results for hole transport are presented in Fig. 2. It is apparent from the latter figures that the hole lifetime and also the hole range both decrease with As addition whatever the Cl content. Every time the Cl content is increased, there is a corresponding increase in τ and $\mu\tau$. Every time the As content is increased, there is a corresponding decrease in τ and $\mu\tau$. The As and Cl additions have *opposite* effects on the hole lifetime and range. The hole drift mobility is unaffected by either As or Cl addition. The most important technological conclusion

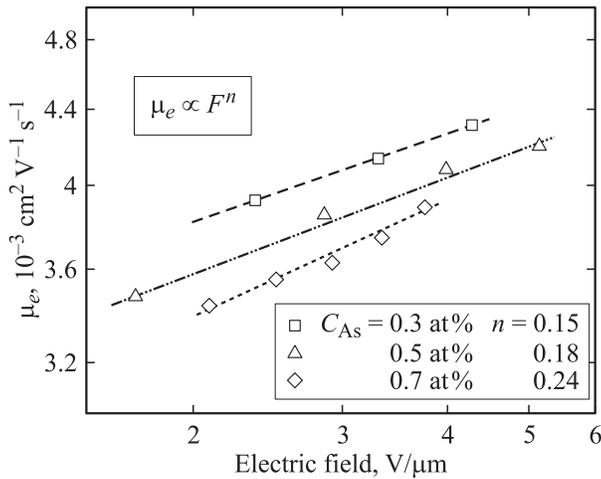


Figure 3. The dependence of electron mobility versus applied electric field F in a -Se:As:Cl (both axis are logarithmic).

from these two figures is that by appropriately choosing the relative amounts of As and Cl, we can control the hole range. There is some latitude in choosing the composition of stabilized a -Se for a given $\mu\tau$ product. For example, the hole range for 20 ppm doped a -Se:0.3%As is about the same that for 40 ppm doped of Se:0.5%As. About ~ 20 ppm Cl is needed to compensate for 0.2% As addition.

We also investigated the influence of As and Cl on the electron lifetime and drift mobility. The electron mobility μ_e in a -Se depends on the applied electric field [16]. In order to get comparable values for different samples we

measured the dependences of μ_e versus electric field, as shown in Fig. 3, and determined the values corresponding to the same electric field, which was chosen to be $4 \text{ V}/\mu\text{m}$. Fig. 4 show the effects of As and Cl on electron transport parameters. It is apparent that the electron lifetime τ_e behavior is opposite to that of holes. Increasing the concentration of As increases the electron lifetime, whereas increasing the Cl content decreases the lifetime. The electron mobility tends to decrease as the As content is increased, but the increase in the lifetime is greater and thus the electron range $\mu\tau$ increases by adding As, a distinct technological advantage. The electron mobility is not affected by Cl doping as apparent from Fig. 4.

The influence of As and Cl doping on the properties of a -Se. Double arrows are used to stress the strength of influence

	Holes			Electrons		
	τ	μ	$\mu\tau$	τ	μ	$\mu\tau$
As	\downarrow	0	\downarrow	\uparrow	\downarrow	\uparrow
Cl	$\uparrow\uparrow$	0	$\uparrow\uparrow$	$\downarrow\downarrow$	0	$\downarrow\downarrow$

The results are qualitatively summarized in the Table. It is interesting that only small amounts of Cl (typically in the ppm range) are needed to observe large changes in the properties compared with the amount of As (typically, 0.1–1%) needed for similar changes. For example, the reduction in hole lifetime induced by an increase of As concentration from 0.3 to 0.5 at % may be compensated by the addition of only 20 ppm of Cl (see Fig. 2).

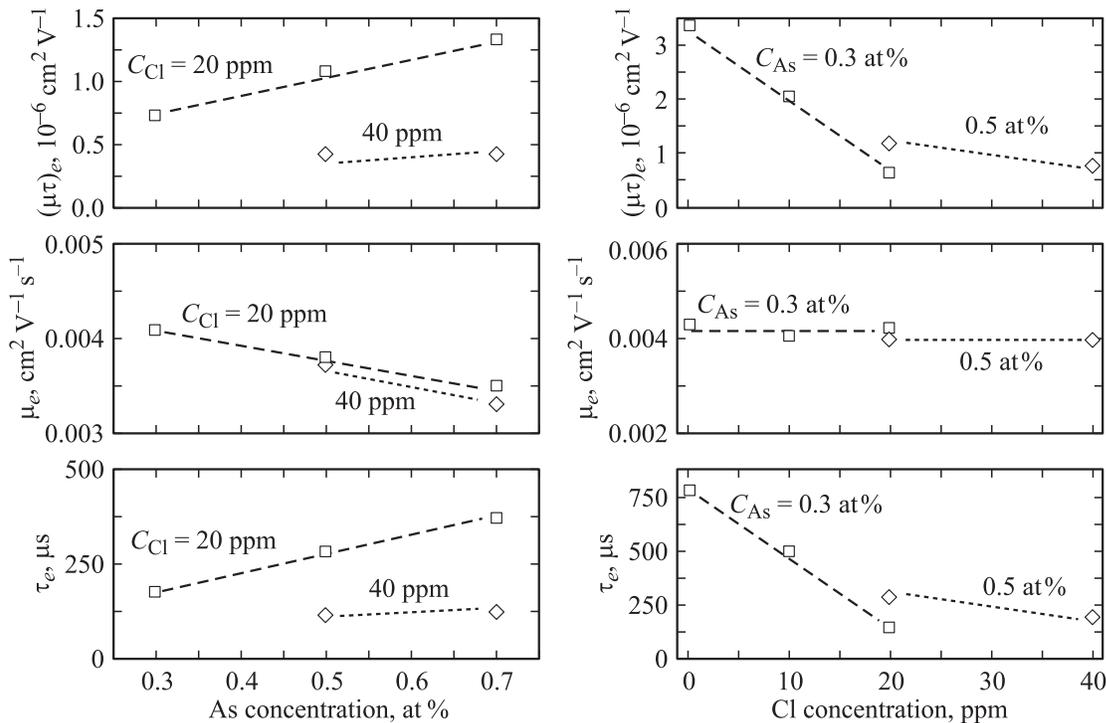
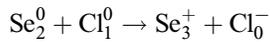


Figure 4. The influence of As and Cl doping on electron lifetime, mobility and electron range in a -Se.

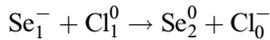
The accepted density of states distribution for *a*-Se shows clearly defined shallow traps and deep traps [5,17] for both types of carriers. Within the shallow trap controlled transport model, the measured carrier range $\mu\tau$ is given by

$$\mu\tau = \mu_0\tau_0 = \frac{\mu_0}{C_t N_t},$$

where μ_0 is the microscopic mobility (in the transport band), τ_0 is the intrinsic deep trapping time in the absence of shallow traps, C_t is the capture coefficient, and N_t is the concentration of deep traps. Thus, the improvement in the hole $\mu\tau$ product with small additions of Cl as in Fig. 2, *a* and *b* implies that the hole deep trap population, N_t is reduced with Cl addition; we make the reasonable assumption that there is no substantial change in the microscopic mobility and C_t . It is generally believed that the deep localized states are connected with under- or overcoordinated defects, that is, the deep traps in *a*-Se are Se_3^+ and Se_1^- charged overcoordinated and undercoordinated defects [5]. One possible interpretation for the observed effect is that since Cl is highly electronegative it will tend to capture an electron within the structure when it interacts with a Se chain or with charged defects so we may expect

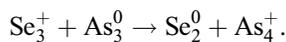


and



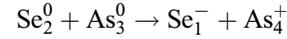
in which the number of primary bonds is conserved. In the first reaction, Cl generates Se_3^+ defects, and there is an increase in the electron trap concentration. In the second reaction, Cl eliminates Se_1^- defects and thus decreases the hole trap concentration. We assume that Cl_0^- centers do not act deep hole traps. Unlike As, Cl does not seem to affect the electron and hole drift mobilities in *a*-Se:As which implies that Cl does not modify the shallow trap concentrations in the presence of As in *a*-Se. In stabilized *a*-Se, the Cl doping effect is limited only to the deep trapping time. (It should be remarked that Cl doping of pure *a*-Se, on the other hand, has been reported to reduce the drift mobility [18] i.e. affect the shallow hole traps).

It is more difficult to explain the effects of As in terms of simple defect forming reactions. Experiments indicate that the As addition reduces the hole lifetime but increases the electron lifetime. The hole mobility remains the same but the electron mobility is decreased. As has only a very small electronegativity difference from Se which implies the formation of both As_2^- and As_4^+ type charged defects. Normally bonded As_3^0 atoms can react with Se_3^+ defects to create a As_4^+ by the structural reaction



This process can explain the electron transport results because it reduces the Se_3^+ (electron trap) concentration, which means longer electron lifetimes. The resulting As_4^+ defects act as shallow traps thereby reducing the electron

drift mobility only. The decrease in the hole lifetime can be interpreted by the structural reaction,



which increases the Se_1^- (hole trap) concentration, and As_4^+ act as shallow electron traps as postulated above. One would expect that As_2^- type centers will also be formed within the *a*-Se:As structure. Such centers can also trap holes. Thus, it is difficult to unambiguously explain the role of As. The formation of As_4^+ should intuitively need somewhat more energy than As_2^- because As_4^+ needs to spatially connect to four neighbours (more lattice distortion will be needed to find four neighbours) whereas As_2^- simply fits into a chain. Although we do not yet have a complete model for the compensation effects of As and Cl in the *a*-Se structure, we do nonetheless speculate that under and overcoordinated charged defects play an important role. There have been other discussions in the literature on the compensation mechanism between As and Cl in stabilized *a*-Se [19] though, to date, there is no accepted final model that can explain all the observations.

4. Conclusions

The electronic properties of *a*-Se as a function of the source (boat) temperature and as a function of As (up to 0.7%) and Cl (up to 40 wt.ppm) concentrations have been experimentally studied by carrying out conventional and interrupted field time-of-flight (IFTOF) transient photoconductivity measurements that provide accurate determinations of the drift mobility and the deep trapping time (lifetime). No variation in electron and hole lifetimes and mobilities for pure *a*-Se was observed with the source temperature, that is, no dependence was observed on the deposition rate as well as the vapor composition. The composition of the vapor in terms of different relative amounts of various Se molecular species does not influence the electronic properties of the resulting *a*-Se films deposited at a substrate temperature above the glass transition temperature. The addition of As reduces the hole lifetime but does not change the hole mobility. Arsenic addition increases the electron lifetime while reducing the electron mobility. The electron range $\mu\tau$ however increases with the As content which is a technologically desirable result for X-ray photoconductors that have the radiation receiving electrode biased negatively. The increase in the electron $\mu\tau$ with the As content means that the overall concentration of deep electron traps must be substantially reduced by the addition of As. Arsenic is less effective in increasing the electron lifetime when the structure has more Cl present. Cl addition in the ppm range increases the hole lifetime but reduces the electron lifetime. The drift mobility of both carriers remains the same. Cl is less effective in decreasing the electron lifetime when there is more As present in the structure. We interpret the results in terms of potential under and overcoordinated charged defects that can exist in the structure.

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