

The influence of the substrate temperature on charge transport in vacuum deposited amorphous selenium films*

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Current commercial large area flat panel direct conversion x-ray image detectors use doped amorphous selenium (a-Se) alloys as the x-ray photoconductor for the conversion of x-ray radiation to collectable charges. The simple metal/a-Se/metal structure has a large dark current that prevents its use in practical detectors. For this reason, the x-ray photoconductor is not a simple metal/a-Se/metal structure but rather a multilayer structure in which electron and hole injection blocking layers have been inserted next to the electrodes to reduce the dark current. The desirable electron and hole transport in the injection blocking layers are usually achieved by suitably alloying and doping the selenium material, which is a very difficult task. We have proposed a novel way to produce hole-injection blocking layers based on lowering the temperature of the substrates during the film deposition process. X-ray photoconductor layers containing such cold-deposited hole-injection blocking layers have been successfully tested in pilot high resolution x-ray image detectors for mammography. In this paper, we present one possible explanation for the observed changes in the electronic transport in a-Se based films produced at low substrate temperatures.

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1. Introduction

The technology for x-ray detection and imaging has advanced rapidly during the last decade, fuelled by improvements in the technology of amorphous silicon large area thin film transistor arrays and innovations in the deposition techniques for scintillators and photoconductors. Amorphous selenium (a-Se) is an x-ray photoconductor material whose properties make it suitable for both static and dynamic x-ray medical imaging. It has been shown [1] that due to advances in a-Se alloy photoconductors and low-noise application specific integrating circuits, the a-Se flat panel image detectors have superior performance in medical imaging applications, compared with the indirect conversion detectors based on using a scintillator as the detector working medium

Recently extensive research has been under way towards the development of a-Se x-ray image detectors with active pixel architectures [2] and second-generation a-Se based detectors for imaging with very high resolution [3-5]. The smallest objects of interest for mammography are various micro-calcifications in the breast, with a size of about 80 μm . Such small objects cannot be imaged with the current commercially available flat panel detectors for mammography, because their pixel size is typically 85 μm .

For a number of reasons, the smaller pixel sizes are not currently available with the traditional amorphous silicon technology, and any digital medical image detector that will have higher spatial resolution should use other image readout circuits like crystalline silicon based charge coupled devices (CCDs) that operate in a time delayed integration (TDI) mode [3]. In such a mode of operation, the pixel readout times become much shorter. For example, the pixel readout speed in traditional a-Se detectors for dynamic medical x-ray imaging are not higher than 30 s^{-1} [1], while a detector operating in scanning mode and using a TDI CCD will need to have a pixel readout speed that is in excess of 1000 s^{-1} . Such high pixel readout speeds lead to different requirements for the properties of the a-Se based photoconductor, which will be explained below.

The simple metal/a-Se/metal structure has a large dark current, which prevents its use in practical detectors [5]. For this reason, the x-ray photoconductor is not a simple metal/a-Se/metal structure, but rather a multilayer structure in which electron- and hole-injection blocking layers have been inserted next to the electrodes to reduce the dark current. In an electron-injection blocking layer, the holes can move and cross the layer but electrons become deeply trapped. In a hole-injection blocking layer, the electrons can move across the layer while the holes

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become deeply trapped. As explained in [5], the trapped charges in the blocking layers act to decrease the electric field near the metal electrodes and thus minimize the injection current and hence the total dark current in the photoconductor layer. The usual way in which the electronic transport properties in the injection blocking layers are modified is by alloying and doping the starting a-Se material. It has been shown that hole-injection blocking layers can be produced by doping the a-Se material with alkali metals, while electron injection blocking layers can be produced from As_2Se_3 or from a-Se heavily doped with chlorine [6]. However, the heavy alkali doping used to produce hole-injection blocking layers encourages crystallization [7] and to compensate for this, the material is additionally alloyed with 2-10% arsenic [6]. Such high amounts of As lead to a substantial decrease in the electron mobility, which is a distinct disadvantage when electrons are collected at the pixel electrodes and high pixel readout speeds are needed.

Recently, we have developed and investigated a new method for the production of hole-injection blocking layers [9, 2-4]. We have shown that films produced from stabilized a-Se (Se alloyed with 0.2-0.5% As and little or no Cl) on substrates kept at sufficiently low temperatures have very poor hole transport and good electron transport. In such films, the mobility-lifetime product for the electrons ($\mu_e \tau_e$) is much larger than that for holes ($\mu_h \tau_h$) and the films can act as efficient hole-injection blocking layers in many practical detectors that collect electrons at the pixel electrodes and require fast pixel readout times [2-4]. The layer that has $(\mu_e \tau_e) \gg (\mu_h \tau_h)$ is called an “n-like layer”, in as much as electrons are much more mobile than holes; but the term should not be confused with the usual definition of an n-type crystalline semiconductor. We have demonstrated that the decrease of $\mu_h \tau_h$ with decreasing substrate temperature during the film deposition process is mainly due to the decrease in the hole lifetime (τ_h) [9]; however the observed dependence of the hole transport on the substrate temperature has not been hitherto explained. In this paper, we present one possible explanation for the observed changes in the electronic transport properties of a-Se films related to deposition onto cold substrates.

2. Experimental

The stabilized a-Se thick films were prepared by thermal evaporation and deposition techniques using a conventional stainless steel vacuum coater at a pressure of $\sim 1.33 \times 10^{-4}$ Pa. The film evaporation procedure is described in detail in [9]. The films were produced on Al or glass (Corning 7059) substrates. In the case of glass substrates, Al was pre-deposited to act as the bottom electrode. A semi-transparent Au or Pt top electrode was finally sputtered on top of the a-Se layer to complete a metal/a-Se/metal sandwich structure for time-of-flight (TOF) transient photoconductivity measurements. We have produced photoconductive films from stabilized a-Se (Se:0.2-0.5%As:0-10ppmCl) as well as films from pure

(99.999%) Se materials. For each material, a set of samples was produced at different substrate temperatures in the range 2-80 °C. The boat temperature was kept constant at about 250 °C. The films produced at substrate temperatures below the glass transition temperature (T_g) of the starting material are referred to as *cold deposited* films. The cold deposited films were annealed at a temperature of ~ 50 °C ($T_{\text{annealing}} \sim T_g$), directly in the vacuum system. The duration of the annealing was usually about one hour. However, some of the films were annealed for a period of 2-3 hours. The thickness of the deposited films was in the range 40-200 μm , as measured by a precision micrometer (0.1 μm sensitivity and ± 1.5 μm precision).

The carrier drift mobility μ was measured by conventional time-of-flight (TOF) experiments, and the lifetime (deep trapping time) τ was measured by an interrupted-field-time-of-flight (IFTOF) technique [10]. To avoid the build up of trapped charge within the a-Se film, a TOF measurement consisted of a single light pulse (a single shot experiment) rather than repetitive pulses. The samples were rested for at least 24 hours in the dark prior to measurement, and were kept short circuited and in the dark between measurements. All the measurements were conducted on “relaxed” (aged) samples, that is 2-3 days after the film was produced.

A differential scanning calorimeter DSC2910 was used to investigate the thermal properties (glass transition temperature, crystallization temperature, etc.) of the starting materials and of the produced films, as well as to estimate the stability of the produced layers towards crystallization.

3. Results

We have found that good quality a-Se films can be produced on substrates kept at temperatures that are much lower than the T_g of the starting Se material. The film production process in this case involves two steps: first the deposition of the film and second, a mild annealing of the film at a temperature around the glass transition temperature of the Se material, for a duration of about one hour. Careful examination of the surface of such cold deposited samples after the annealing, under low magnification microscopy, has shown that there are no appreciable visual differences between the surface of cold deposited and annealed samples, and the surface of the samples deposited under conventional conditions ($T_{\text{substrate}} > T_g$). Further evidence that the cold deposited and post annealed samples should have similar crystallization resistances to those prepared using the traditional substrate temperature range ($T_{\text{substrate}} > T_g$) comes from the results of differential scanning calorimetry (DSC) studies on films prepared by both methods. As shown in Fig. 1, we have recorded the thermograms for the starting material, for hot deposited films ($T_{\text{substrate}} = 65$ °C) and for cold deposited films ($T_{\text{substrate}} = 8$ °C, annealed at 50 °C for one hour). All other deposition parameters were kept the same. Remarkably, the difference between T_g and

as the sample ages over time, the shorter chains will tend to organize into longer ones. The average distance between the chains will also tend to decrease. This should lead to an observable increase in the hole lifetime. Furthermore, according to the valence alternation pair (VAP) theory [12], the chain ends (Se_1^0) are unstable defects in a-Se, and they gradually will be transformed into pairs of Se_1^- and Se_3^+ which will lead to changes in both the hole and electron lifetimes. In contrast, our observations are that, as a result of annealing or ageing, the hole lifetime stays the same or gets worse, while the electron lifetime stays the same or increases.

The research of Montrimas et al. [13, 14] suggests that deep carrier traps of totally different origin probably exist in a-Se. According to the transmission electron microscope studies published in these works, each a-Se film has been found to contain numerous nanocrystalline inclusions. Some of them have the structure of trigonal selenium, while the others have the structure of monoclinic Se. It has been suggested [13] that trapping at the interface between the crystalline inclusions and the amorphous phase can have a significant impact on charge transport in a-Se films. These authors have shown that the interface surrounding the crystalline inclusions of trigonal allotrope modification of Se can deeply trap holes, while the interface around the inclusions of monoclinic Se allotrope deeply traps electrons. Furthermore, the concentration of the nanocrystalline inclusions has been measured as a function of the substrate temperature, and the reported dependence [13] is reproduced in Fig.2. The results of Montrimas and Petr tis (Fig.2), clearly show that the concentration of crystalline inclusions changes by about 4 orders of magnitude as the substrate temperature is decreased from 60-70 °C to about 8 °C. It is worth noting that the substrate temperature, according to their results, also has an effect on the size and the

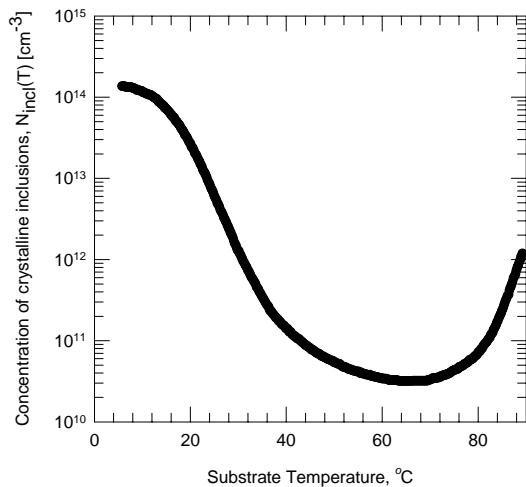


Fig. 2. Concentration of nano-crystalline inclusions in a-Se films produced from pure Se as a function of substrate temperature. Data were extracted from [13].

morphological structure of the crystalline inclusions. The authors have found that the average size of the crystalline inclusions produced at $T_{\text{substrate}} = 8-30$ °C is about 50 nm, while the inclusions in the films produced at higher substrate temperatures are bigger in size, reaching 200 nm for $T_{\text{substrate}} = 80-90$ °C. Crystalline inclusions of a trigonal type are predominant in layers produced at substrate temperatures above 50 °C, while both monoclinic (mainly β) and trigonal inclusions exist in the layers produced at substrate temperatures lower than 30 °C. The authors have also pointed out that the existence of the nano-crystals in the a-Se films is not the only reason for the existence of deep charge carrier traps in them. They have argued that intrinsic deep traps with concentrations below 10^{13} cm^{-3} can form in the a-Se films, due to structural fluctuations in the amorphous phase.

The results reported in [13] and reproduced in Fig. 2 are somewhat counter intuitive. Indeed one would expect lower crystallinity in films produced on colder substrates, because the cold substrate favours the disorder in the growing film. However, when Se is evaporated onto a cold substrate, the vapour species ("chains", or molecules, consisting of less than 5-6 atoms) impinging on the film freeze immediately on the film surface, eventually resulting in a condensed film structure that has high disorder, short Se chains, higher distances between the chains, and a huge number of metastable structural defects, which are most likely to be coordination defects. The above structure of the films deposited on cold substrates ($T_{\text{substrate}} < T_g$) favours the process of agglomeration of metastable defects and short range atomic migration, which encourages the formation of numerous irreversible structural defects, that is, crystalline inclusions, of monoclinic and trigonal type. In the case of high substrate temperatures ($T_{\text{substrate}} > T_g$), the short Se chains arriving at the surface of the film can migrate and polymerize together to form long Se chains in the film. Thus, the number of metastable coordination defects that will be formed will be lower, and many of them will be annealed out during the film growth process. For such reasons, the number of formed stable crystalline inclusions will be much lower for Se films produced on hot substrates ($T_{\text{substrate}} > T_g$). Such concepts can explain the behaviour presented in Fig.2, and have been used by the authors of [15] to explain new results related to light induced crystallization in a-Se.

Based on the findings of Montrimas and Petr tis [13], we can explain quite consistently the results from charge transport measurements on films produced at different substrate temperatures. Films produced at substrate temperatures of 50-70 °C have very low concentrations of nanocrystalline inclusions. In these films, the deep traps due to structural fluctuations (these very well might be the over- and under-coordinated charged defects) in the amorphous phase dominate the lifetimes and ranges of the carriers. A decrease in the substrate temperature $T_{\text{substrate}}$ leads to a very pronounced increase in the concentration of nanocrystalline inclusions in the films (Fig.2). In films

produced at lower substrate temperatures, the amorphous phase itself has two different components and, upon crystallization, it produces crystallites of both trigonal and monoclinic type [13]. At very low temperatures, the concentration of crystalline inclusions is very high (see Fig. 2) and the deep traps that exist due to the presence of these nanocrystals dominate the hole lifetimes and ranges. However, the majority of these nanocrystals are of trigonal type (and thus act to introduce hole traps), which explains why the hole transport is much more sensitive to the substrate temperature during the growth of the film than the electron one. During post annealing and ageing of the samples, several processes take place. Firstly, some of the inclusions that are very small will disappear, forming an amorphous phase. Secondly, some new crystal inclusions of trigonal and monoclinic type are formed. Thirdly, the crystal inclusions that have sizes bigger than a certain critical radius grow at the expense of the amorphous phase or of the smaller crystals around them. Fourthly, the inclusions of a monoclinic type are transformed into crystal inclusions of trigonal type, which is the more stable crystal form of Se. Fifthly, the amorphous part of the film homogenizes, because the phase that tends to crystallize in a monoclinic form gradually transforms into the phase that crystallizes in the trigonal Se crystal form. As a result of all these processes, depending on the exact conditions (substrate temperature, annealing temperature, annealing time, ageing time, starting material, etc.) the concentration of trigonal nano-crystals is not likely to be reduced, while the concentration of the monoclinic crystalline inclusions is not likely to be increased. Such trends qualitatively explain the experimental fact that in the cold deposited films, the hole lifetimes and ranges tend to decrease or do not change with annealing and ageing, while the electron lifetimes and ranges tend to slightly improve with annealing and ageing.

The exact substrate temperature which will force the Se molecules arriving at the substrate to freeze immediately, and thus result in an amorphous phase that will efficiently form numerous crystalline inclusions, depends on the starting Se material and on additives and dopants such as arsenic and chlorine. It is well known that Cl tends to make Se chains shorter and the a-Se network structure more flexible [16, 17], while As tends to link several Se chains together and has exactly the opposite effect on the structure of the film. For this reason, the exact substrate temperatures at which the charge transport in the film will switch from *p*- to *n*-like type and the hole transport will become deep trap limited depend on the composition of the starting Se material. In the light of the above discussion, Cl containing material will switch to *n*-like transport at a lower substrate temperature than the material containing only As, and that is exactly what is observed.

Furthermore, we can check whether the experimentally obtained results in this work are consistent with the data in [13], which are presented in Fig. 2 as a function $N_{\text{incl}}(T_{\text{substrate}})$ describing the concentration of crystalline inclusions in a-Se layers vs. substrate temperature. Assuming that almost all inclusions after the annealing of the samples are of a trigonal crystal modification of Se, we can use the function $N_{\text{incl}}(T_{\text{substrate}})$ to calculate the hole lifetime in the a-Se films, using the following relation

$$\frac{1}{\tau_h(T_{\text{substrate}})} = C_1 N_{\text{incl}}(T_{\text{substrate}}) + \frac{1}{\tau_{ho}}. \quad (1)$$

Here, C_1 is a constant that, multiplied by the concentration of crystalline inclusions, gives the deep hole trapping rate that is due to deep trapping related to the crystalline inclusions alone. The other constant τ_{ho} is a deep hole trapping time that is due to the intrinsic hole traps present in the material in the absence of any crystalline inclusions. The $N_{\text{incl}}(T_{\text{substrate}})$ is the functional dependence of the concentration of nanocrystalline inclusions from Fig. 2, which needs to be shifted on the temperature axis by T_0 degrees to account for the effects of Cl doping and As alloying, as discussed above.

The above equation can be fitted to the hole lifetime data vs. substrate temperature that we have published in [8,9]. The result is shown in Fig. 3. The latter figure clearly demonstrates that the shape of the curve describing the concentration of nanocrystalline inclusions vs. substrate temperature presented in Fig. 2 is indeed compatible with our own experimental data on the hole lifetime, measured as a function of the substrate temperature.

From an experimental point of view, the study attempted in reference [13] is quite challenging. The transmission electron microscopy requires very thin samples and the use of microtome to prepare them from the evaporated thick films. Thus, the sample preparation process has a significant mechanical impact on the samples, and such a process can lead to crystallization in the samples. Furthermore, the electron beam causes some heating of the samples and, because the glass transition temperature of a-Se is relatively low, the microscopic examination itself can lead to the formation of new crystals or to the growth of the existing ones. In other words, the actual concentration of the nanocrystalline inclusions in the films, as well as their average size, can be significantly smaller than those values reported in [13]. Our experimental data can still be explained, assuming that the shape of the curve describing the changes in the concentration of nanocrystalline inclusions vs. substrate temperature is similar to the reported one (Fig. 2). The

required change in the concentration of nanocrystals, as the substrate temperature decreases over the studied ranges, is only 2-2.5 orders of magnitude (not 4 orders as shown in Fig. 2).

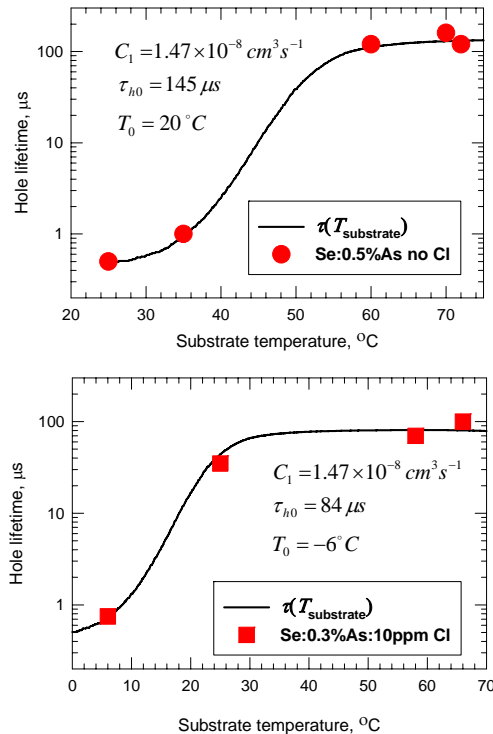


Fig. 3. Comparison between experimentally measured hole lifetimes in a-Se films produced at different substrate temperatures in our laboratory with lifetimes calculated from Equation (1) based on the experimentally measured concentration of nanocrystalline inclusions $N_{\text{incl}}(T_{\text{substrate}})$ in a-Se films produced at different substrate temperatures taken from [13].

We can try to estimate the fraction of the crystalline phase in films produced at different substrate temperatures. The concentration of nanocrystals in a-Se films produced at substrate temperatures of 60-70 °C is about $4 \times 10^{10} \text{ cm}^{-3}$, as shown in Fig. 2. If the average size of the nanocrystals does not exceed 50 nm, the relative fraction of the crystalline phase in the film will be less than $5 \times 10^{-4} \%$. In the cold deposited films, the concentration of the nanocrystalline inclusions should be 2-2.5 orders of magnitude higher, or about 0.05-0.16%, in order to be consistent with the observed decrease in the hole lifetime. Such a small crystalline fraction can not be detected with the DSC measurements and does not seem to affect appreciably the resistivity to crystallization of the produced thick Se films at room temperature.

The arguments presented in this subsection indirectly suggest that nanocrystalline inclusions may really exist in vacuum deposited a-Se films. Such crystalline inclusions may remain unnoticed by researchers, due to their small size ($\leq 50 \text{ nm}$) and because they do not appreciably affect

many of the properties of the a-Se films, as well as to their stability to crystallization. However, as shown above, such nanocrystalline inclusions may play a very important role in controlling the deep carrier trap concentrations, and thus determining the charge transport properties of a-Se films produced on cold substrates ($T_{\text{substrate}} < T_g$).

5. Conclusions

The substrate temperature has a huge impact on hole transport in a-Se films. The hole range decreases by about two or more orders of magnitude as the substrate temperature decreases, while the electron transport remains relatively unaffected. Films produced at low substrate temperatures demonstrate clearly *n*-like type transport ($\mu_h \tau_h < \mu_e \tau_e$), and if the substrate temperature is sufficiently low the hole transport becomes deep trap limited. The changes in the transport related to the deposition on cold substrates can be quite consistently explained, if we assume that nanocrystalline (typical dimensions of 50 nm or less) inclusions with different concentrations are formed in the a-Se matrix during the deposition, as described in [13]. The concentration of such inclusions is several orders of magnitude higher in films produced at lower substrate temperatures, and the trapping at the interface between the crystalline and the amorphous phases modifies the charge transport in the films. Furthermore, a simple model based on over- and under-coordinated charged defects, Se_1^- and Se_3^+ , alone cannot explain the observed dependences of the hole and electron lifetimes on the substrate temperature.

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