Effect of Poly(vinylidene fluoride) Interface Layer on Charge Storage and Residual Potential in Amorphous Selenium Films

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ABSTRACT: Thermally stimulated discharge current and the potential decay behavior of amorphous selenium (a-Se) films ($\sim$ 100 μm thick) were studied as a function of the thickness of a poly(vinylidene fluoride) (PVDF) interface barrier layer in the range 2000–8000 Å. The incorporation of a PVDF layer into an a-Se film resulted in (1) a considerable reduction in its charge storage capacity, (2) a considerable increase in its initial surface potential, and (3) a considerable reduction in its residual potential and the enhancement of its X-ray sensitivity. These effects were attributed to the blocking and field-enhanced mobility role of the PVDF interface barrier layer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1962–1966, 2004

Key words: amorphous; interfaces; barrier

INTRODUCTION

Amorphous selenium (a-Se) in its pure, alloyed, doped, and active matrix/multilayer array forms finds applications[1–3] in electrophotography both as a xerography and a xeroradiography (XR) photoreceptor imaging material. However, as of today, a-Se films do not meet all the X-ray imaging requirements of XR technology. This limitation in the utility of XR is primarily due to the inadequate X-ray sensitivity (S) of a-Se films. International efforts[4–12] are in progress to understand the mechanism of S in a-Se and to find different ways to enhance it. To understand the physics of a-Se films, many fundamental investigations have already been made[4–12] to study its various important parameters, such as its defect states, mobility of charge carriers, effect of dopants, calculations of electron-hole pair generation energy, and S. In our continuing efforts[4–7] to study the thermally stimulated discharge (TSD) current behaviour of a-Se films to improve its S, we recently found some interesting results based on a new concept, that is, the incorporation of an interfacial barrier layer of a suitable polymeric material in combination with a-Se films in XR mode. We found that the incorporation of poly(vinylidene fluoride) (PVDF) interface layer considerably reduced the charge storage capacity (buildup of residual potential) in a-Se films. TSD studies were performed as a function of

PVDF film thickness ($\sim$ 2000–8000 Å) in the temperature range 295–385 K. The previously mentioned effect of the polymer interface layer on the residual potential in a-Se films was investigated in the TSD mode to see whether the polymer layer in any way effected the position of charge-carrier trapping levels in a-Se films, as we observed,[6,7] in combinational doped a-Se films. However, because we found that interface film effected only the charge storage capacity, the buildup of residual potential in PVDF-incorporated a-Se films was also investigated by a direct method with the potential decay technique. In this technique, the decay of the surface potential; that is, dark and on X-ray exposure (with the XR aspect kept in view) is studied at room temperature as a function of time. These studies also showed that the buildup of residual potential was considerably reduced in a-Se films, and its S increased on the incorporation of the PVDF interface film. These interesting results are reported in this article.

EXPERIMENTAL

Thin films ($\sim$ 2000–8000 Å) of PVDF (obtained from Polysciences, Inc.) were vacuum-deposited onto ultrasonically cleaned aluminum substrates 50 × 50 × 1 mm³ in size with a vacuum evaporation technique described earlier.[13] Subsequently, on top of these PVDF films, thick films ($\sim$ 100 μm) of a-Se were vacuum-deposited under a vacuum of about 10^{-5} torr, as described previously.[4,5] Thus, a sample configuration of Al/PVDF/a-Se was obtained. The adherence of PVDF films with aluminum substrate deteriorated
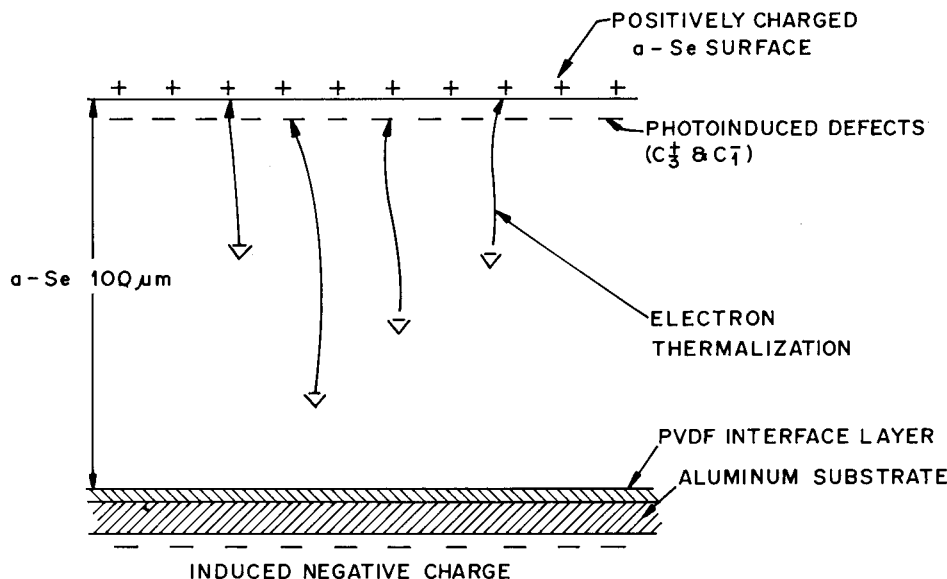
Figure 1 Mechanism of polarization in a-Se films with an interface layer of PVDF.

considerably for thicknesses greater than 8000 Å. In fact, beyond this thickness, the samples had a tendency to peel off prior to measurement. Therefore, the measurements in these investigations were restricted up to only 8000 Å. The Al/PVDF/a-Se samples so obtained were rested in the dark for 3 months and were then used for TSD measurements. We made TSD measurements by putting a pressure electrode on top of a polarized sample and heating at a rate of 5 K/min. The current so released was measured by a Keithley 610C electrometer to plot the TSD spectra. Next, the potential decay measurements were made by the corona charging of these samples and the measurement of the potential in the dark and on X-ray exposure (50 kvp, 10 mAs) with a calibrated probe coupled with the Keithley 610C electrometer. The rate of exposure was measured with a Keithley dosimeter, and it was about 26×10^{-3} R/s.

To study the TSD behavior of the Al/PVDF/a-Se films, we polarized the films by a mechanism reported earlier[6,7] and shown again in Figure 1 for the sake of the convenience of understanding the results and discussion of this article. In this mechanism, the samples were first irradiated with white light from a 100-W tungsten filament for about 30 min. A water filter was used to cut off the IR radiation. The intensity of illumination was about 1000 lux. The irradiation produced reversible photostructural defects of type.[14-16] C_3^+ and C_1^- on the surface of the a-Se film up to a depth of a few micrometers. After exposure, the films were charged positively under corona discharge. This resulted in the buildup of a field across the a-Se film. The magnitude of this field depended[17] on the amount of dark current flowing through the film during charging. This dark current is known[17] to originate from the

transportation of electrons toward the positively charged top surface under the existing field. The dominant process for the availability of these electrons inside the selenium film is known[17] to be their injection from the aluminum substrate into the selenium film by the surmounting of the interfacial barrier existing at the aluminum–selenium interface. In this case, the barrier was due to the PVDF interface layer. During the transportation of electrons, a part of them gets retrapped in photo-induced electron trap states existing at different energy levels in the film, and part of them reach the top and gets neutralized with the top positive surface charge. So this trapped charge (due to retrapping) appeared as a net stored charge (residual potential) in a-Se films and was responsible for various peaks detectable in the TSD spectra. These charged samples were then dark-rested for about 2 h for the complete neutralization of the top surface charge and for polarization to take place. In negatively charged a-Se films, polarization could also be achieved in a similar way as discussed previously; the only difference in this case is that the holes would be the trapped charge carriers.

RESULTS AND DISCUSSION

Figure 2 shows the TSD spectra of irradiated and positively charged a-Se films with and without the incorporation of a PVDF interface layer. Curve A corresponds to only selenium, that is, without an interface layer, whereas curves B, C, and D correspond to a-Se films incorporated with interface layers of PVDF 2000, 5000, and 8000 Å thick respectively. As shown in these curves, each case showed two relaxation peaks positioned around 310 and 374 K and designated as
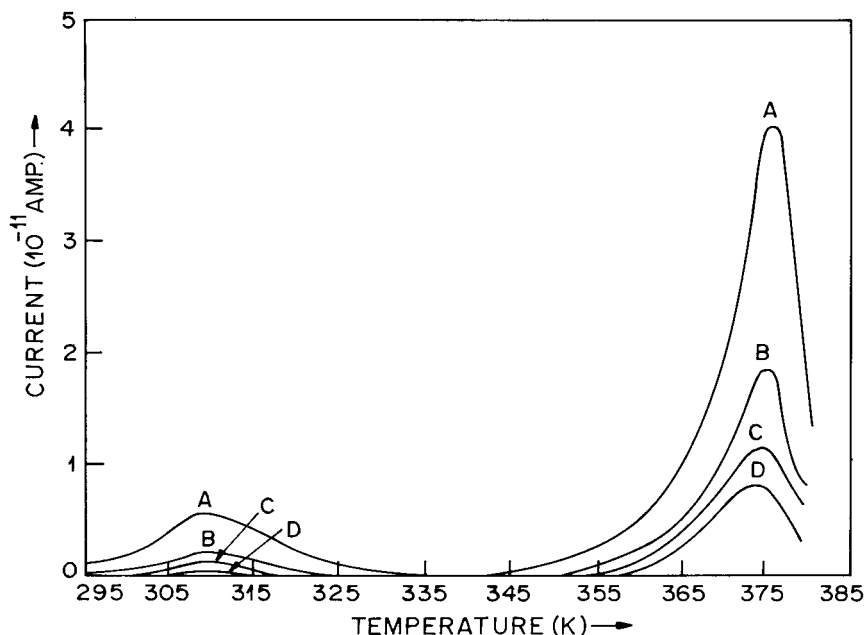
Figure 2 TSD spectra of irradiated and positively charged a-Se films ($\sim$ 100 μm thick) with and without a PVDF interface layer. Curve A corresponds to films without an interface layer, and curves B, C, and D correspond to films with PVDF interface layers 2000, 5000, and 8000 Åthick respectively.

peak I and peak II, respectively. The activation energies associated with these peaks were found[4,5] to be about 0.99 and 1.6 eV, respectively. Further, the mechanism of origin of these peaks in a positively charged case was attributed[4,5] to the trapping of charge carriers (electrons) at relatively shallow and deep trapping levels, respectively. As also shown Figure 2 (curves B, C, and D), the incorporation of a PVDF interface barrier layer resulted in the reduction of charge storage capacity (the area under the TSD spectra) in a-Se films. In fact, the reduction in charge storage increased with increasing the thickness of the interface layer. Further, the effect of the interface layer was more predominant on relaxation peak I, as it became considerably reduced at an interface layer thicknesses of 8000 Å. This reduction in charge storage under the TSD spectra indirectly indicated that the buildup of residual potential in a-Se films decreased with the incorporation of the PVDF interface film. The TSD spectra of a-Se films in the negatively charged case was also found[5] to be similar to the one in the positively charged case except for the reversal in the polarity of the released current. Therefore, only one case, the positive charging results, are presented in this article.

To understand in a direct way the buildup of residual potential in a-Se films, the measurement of its surface potential as a function of the PVDF barrier layer thickness was studied with a potential decay technique, as explained before. Figure 3 shows the decay of the potential in the dark and on X-ray exposure of a-Se films with and without the incorporation of the PVDF interface layer. Curve A corresponding to

pure a-Se, that is, without an interface layer, and curves B, C, and D correspond to a-Se films incorporated with interface layers of PVDF 2000, 5000, and 8000 Å thick, respectively. As shown in the curve, the built-in surface potential just after corona charging (acceptance potential in dark) increased from 1350 to 2200 V, and the potential left after X-ray exposure (residual potential) decreased from 1040 to 920 V for a corresponding increase in PVDF layer thickness from 0 to 8000 Å. With this experimental data and Boag's[18] expression for S as given in eq. (1), we calculated the values of S both for pure and polymer-incorporated a-Se films:

$$S = \frac{1}{0.693E} (\log V_I - \log V_R) \qquad (1)$$

where V_I is the initial existing potential at the time of exposure, V_R is the residual potential after X-ray exposure and E is the measured exposure rate of about 26×10^{-3} R/s, respectively. Although the dark decay in each case shown in Figure 3 remained practically constant with the stabilized value of the initial potential at the time of X-ray exposure considered the X-ray exposure was made after 10 in each case, as shown in Figure 3.

With the values of various parameters put into eq. (1), the values of S for the various cases mentioned previously were obtained, and the electrical data so obtained is given in Table I. As shown in Table I, S of a-Se films increased due to the incorporation of the
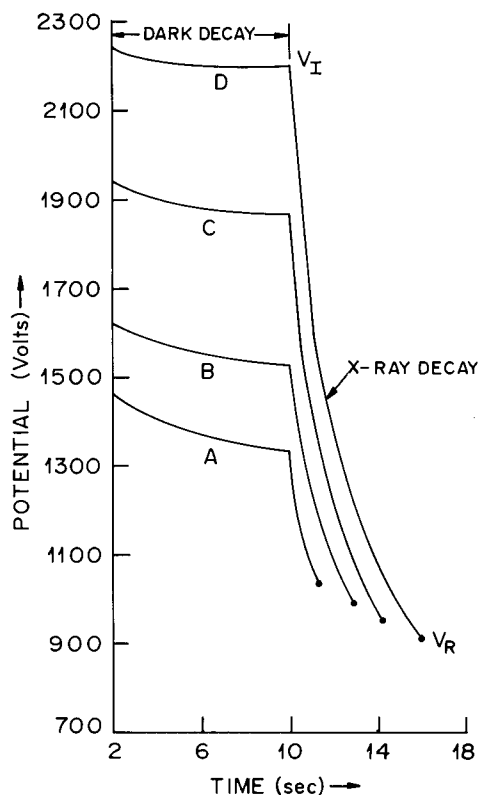
Figure 3 Potential decay characteristics of a-Se films (~ 100 μm thick) with and without PVDF interface layer. Curve A corresponds to films without an interface layer, and curves B, C, and D correspond to films with PVDF interface layers 2000, 5000, and 8000 Åthick, respectively.

PVDF interface layer. In fact, it increased from 6.29 R^{-1} for pure a-Se films to 21.01 R^{-1} for a-Se films incorporated with a PVDF layer of about 8000 Å.

The previously explained effects of the PVDF interface layer on the TSD behavior and surface potential decay (enhancement in S) of a-Se films may now be understood as follows. It is clear, as we explained previously while discussing the polarization mechanism (Fig. 1), that the charge stored under the TSD peaks (Fig. 2) in a-Se films was primarily controlled by dark current, which in turn, was controlled by the charge carriers injected at the aluminum–selenium interface. This is because if the number of charge carriers injected at the interface is fewer then the dark current, will be less the field existing across the film, will be higher the mobility of the charge carriers will be higher their transportation will be faster the probability of retrapping and recombination would be less, and hence, the buildup of residual potential/charge stored in the a-Se film will be less. The previous discussion, therefore, shows that the barrier existing at the interface is very vital in governing the electrical properties of a-Se films; that is, the higher the barrier/blocking at the interface is the less will be the injected carrier density, and ultimately, the lower the stored charge will be, as explained previously.

In fact, in the present case of PVDF–Se combination, it was precisely this previously explained role of blocking and field enhanced mobility effect that was played by the PVDF interface film, as shown in Figure 1. However, the effective blocking of the PVDF layer for the injection of charge carriers from the aluminum substrate to the a-Se films was attributed to combined effect of two factors. First, it provided a direct barrier for charge injection due to its insulating polymeric nature. Second, it has been found[13] that the PVDF encourages significant charge trapping both at shallow and deep trapping levels in its vacuum-evaporated film form. Therefore, these injected and subsequently trapped carriers in the PVDF layer provided an internal space charge field, which resisted further injection and transportation of the electrons across the interface barrier layer. Such an effective blocking resulted in a considerable reduction in charge storage capacity/buildup of residual potential. Thus reduction in the buildup of residual potential and enhancement in S of a-Se films was attributed to the previously mentioned mechanism of blocking and the field-enhanced mobility role of the PVDF interface barrier layer. This indeed was observed, as shown by the charge stored under the two relaxation peaks (Fig. 2) and the values of V_I and V_R, as shown in Figure 3. Further, as regards the predominant role of the PVDF interfacial/blocking layer on peak I, it may now be easily understood that faster sweeping/enhanced mobility effects due to the polymer film were felt more at the shallower traps (as compared to the relatively deep traps) to which this peak has been attributed, and hence, the probability of retrapping charge carriers would be less at shallow traps as compared to the corresponding probability of their retrapping at relatively deeper levels. This is exactly what happened (Fig. 2) because there was a relatively greater reduction in the charge stored under peak I as compared to that of peak II due to the incorporation of the PVDF interfacial/blocking layer. Thus, it is clear from these investigations that S of a-Se films increased with the incorporation of a PVDF interface barrier layer. This is an important finding and may result in the development of new and more sensitive imaging materials for XR photoreceptors, especially in a multilayer configuration incorporating the interface barrier layer of various suitable polymeric materials.

TABLE I
S Parameters in a-Se films (~ 100 μm thick) Incorporated with an Interface Barrier Layer of PVDF

	Thickness of PVDF film (Å)	V_I (V)	V_R (V)	S (R^{-1})
1	0	1350	1040	6.29
2	2000	1540	990	10.65
3	5000	1870	950	16.32
4	8000	2200	920	21.01

CONCLUSIONS

The incorporation of an interfacial/blocking barrier layer of PVDF with a-Se films resulted in an overall reduction in its charge storage capacity, a buildup of residual potential, and the enhancement of its S. This was attributed to the blocking and field-enhanced mobility role of the PVDF interface layer film.

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