

GAP STATES IN DOPED AMORPHOUS SELENIUM

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Using a time-of-flight technique for an evaporated a-Se film with pure Se : doped(Li ,Cl)Se : pure Se sandwich structure, gap state properties of doped Se are examined. Addition of Li increases deep hole traps, which are attractively charged. Addition of Cl increases deep electron traps. Electron life time or Schubweg of Cl doped a-Se is determined for the first time.

I. INTRODUCTION

The charged center model [1,2] has been successful in explaining most optical and transport properties of chalcogenide glasses. The distinctive feature of this model is that the inherent defects, which are positively (D^+) or negatively (D^-) charged in equilibrium, can interconvert one another by charge exchange and bond rearrangement under applied excitation field. For example, in time-of-flight measurements, electrons are captured by D^+ centers, resulting in D^0 centers. When hole excitation energy from D^0 is smaller than electron excitation energy from the same center D^0 , holes instead of electrons will be released predominantly, leaving D^- centers behind. Indeed, the fact that no electron response is observed for a- As_2Se_3 is explained by this mechanism [3].

The present study is aimed in particular at the direct observation of these processes, namely, the possible sign conversion of drifting carriers through charged centers, in doped a-Se. This may be achieved by tracing charge transit through a sample with pure Se : doped Se : pure Se sandwich structure. When electropositive elements are introduced as dopants, holes will be captured strongly by D^- with increased concentration in the doped region. Whether electron release or hole release is dominated, may be determined by the transit trace. The complementary information will be obtained by using electronegative elements as dopants.

II. SAMPLES

The sample structure is shown in Fig.(1). The first layer (thickness L_1) is made by evaporating Se onto a substrate held at room temperature. The second layer (thickness d) is made by co-evaporating Se and the dopant (Li, Cl). The third layer (thickness L_2) is made by evaporating Se onto the second layer. The first and the third layers in the structure act as drifting layers for charges to form a well-shaped Gaussian distribution.

III. RESULTS

The hole response is not observed for uniformly Li doped (0.4 at.%) specimen. On the other hand, electron transport is almost unaffected. (Electron drift mobility value of the pure Se specimen at room temperature is 5.8×10^{-3} cm²/Vs and is activated with 0.33 eV.) These results suggest that the addition of Li

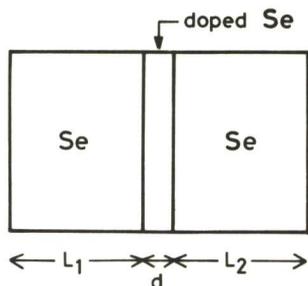


Fig.(1) Sample structure

increases hole trap (possibly D^-) concentration. In Fig.(2), hole signal (voltage) observed for a sample with sandwich structure containing the same Li concentration is shown. Layer dimensions are $L_1 = 10 \mu\text{m}$, $d = 50 \text{ nm}$, and $L_2 = 10 \mu\text{m}$, respectively. The hole signal for a pure a-Se specimen $20 \mu\text{m}$ thick is also shown in the figure. (Hole drift mobility value of the pure Se specimen is $1.6 \times 10^{-1} \text{ cm}^2/\text{Vs}$ and is activated with 0.21 eV .) Two curves show clearly that holes are captured completely at the doped region. The same result is obtained for a sample

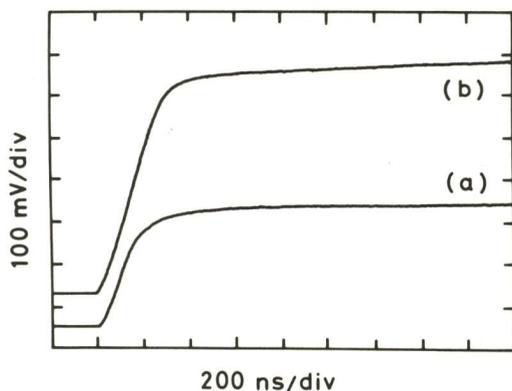


Fig.(2) Hole transit voltage signals for (a) a sandwich structure film with $L_1 = 10 \mu\text{m}$, $d = 50 \text{ nm}$, $L_2 = 10 \mu\text{m}$ and $C_{\text{Li}} = 0.4 \text{ at.}\%$, and (b) a pure Se film $20 \mu\text{m}$ thick. Bias field is $0.5 \times 10^5 \text{ V/cm}$.

with thickness $d = 25 \text{ nm}$, and concentration $C_{\text{Li}} = 0.1 \text{ at.}\%$, under the highest feasible bias field $E_T^0 = 2.0 \times 10^5 \text{ V/cm}$. The hole Schubweg at $2.0 \times 10^5 \text{ V/cm}$ is $< 7 \text{ nm}$. This gives 10^{-14} cm^2 for the value of hole capture cross section given that the number of hole traps is equal to that of added Li's. Considering the obtained value is the lowest limit estimate, it may be concluded that the hole traps are attractively charged when unoccupied. This result is relevant to our anticipation that hole traps are D^- centers. However, any sign of hole release or possible electron release from the trap states is not observed up to $t \sim 0.1 \text{ ms}$.

The hole trap concentration in Li doped Se may be estimated by maximum concentration of the positive charges captured in the doped region. After the continuous illumination from the same side as the light pulse incidence, the hole signal is annihilated, suggesting that the captured positive charges induce a strong built-in field which cancels the externally applied bias field E_T^0 in the first Se layer. Field distribution in the film is measured using electron transit as a probe. Electron signals are shown under various applied bias field E_T (field direction is reversed) in Fig.(3), just after positive charges are trapped sufficiently in the doped region under initial bias field $E_T^0 = 0.8 \times 10^5 \text{ V/cm}$. Two kinks are observed in the range $E_T > E_T^0$, while only one is observed in the range $E_T < E_T^0$.

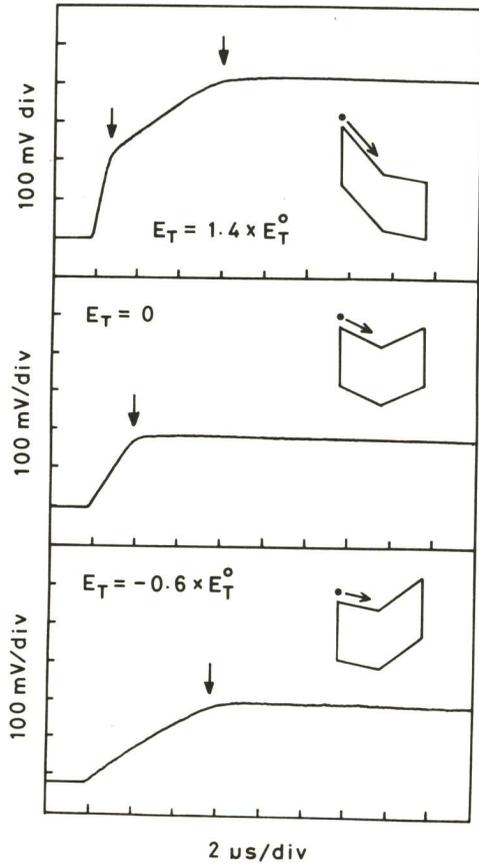


Fig.(3) Electron transit through the same Li doped sample shown in Fig.(2)(a), just after sufficient holes are accumulated in the doped region under initial bias field $E_T^0 = 0.8 \times 10^5$ V/cm: The expected electric field distributions in the film are shown in the inserts

It should be stressed that the electron signal is observed not only at $E_T = 0$, but down to $E_T \sim -E_T^0$. These results are well understood by the inserted figures showing expected field distributions under applied bias. Namely, the first kink is regarded as the time when electrons reach the doped region, and the second one (if it exists) as the time when electrons arrive at the opposite electrode. This is confirmed by estimating the inner electric field of the first (E_I) and the third Se layer (E_{III}), using the value 5.8×10^{-3} cm²/Vs for electron drift mobility of pure Se. The obtained values are close to the expected values, $E_I = E_T^0 + E_{T1}$, and $E_{III} = -E_T^0 + E_T$. These results imply that the hole trap area density is $> 5 \times 10^{11}$ /cm², or hole trap concentration is $> 10^{17}$ /cm³ for a-Se containing 0.1 at.% Li.

The positive charges accumulated in the doped layer after continuous illumination might convert D^- into D^+ . Then, the positive charges in the second region could be frozen in, since hole excitation from D^+ requires a very large activation energy of about 1.5 eV according to the charged center model. The decay rate of the trapped positive charge density can be traced by measuring electron transit under 0 bias, keeping the sample in the dark. In reality, it decreases exponentially with decay constant of about an hour at room temperature. This result, however, does not necessarily contradict with the view that the positive charges are on D^+ centers, since the charge decrease may also be caused by electron supply from the states at interfaces with electrodes.

In contrast to Li doped cases, the addition of Cl annihilates electron response, while hole transport is almost unaffected [4,5]. For example, electrons are captured completely at the second region with $d=50$ nm, $C_{Cl}=1.0$ at.%, showing that the addition of Cl increases electron trap (possibly D^+) concentration. However, any sign of electron release or possible hole release is not observed, as with Li doped cases. The electron signal observed for a sample with smaller d ($=10$ nm) and the same C_{Cl} is shown in Fig.(4), together with that observed for pure Se film $20 \mu\text{m}$ thick. Two kinks are observed clearly for the doped sample. From the relative signal height and time between kinks, it is concluded that about 60 % of initially excited electrons are captured at the doped region. Electron Schubweg at 0.5×10^5 V/cm for a-Se containing 1.0 at.% Cl is about 10 nm.

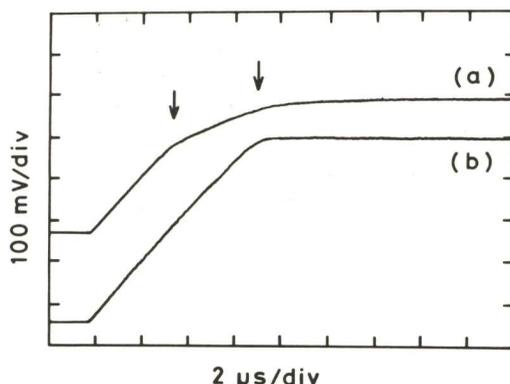


Fig.(4) Electron transient signals for (a) a sandwich structure film with $L_1=10 \mu\text{m}$, $d=50$ nm, $L_2=10 \mu\text{m}$ and $C_{Cl}=1.0$ at.%, and (b) a pure Se film $20 \mu\text{m}$ thick. Bias field is 0.5×10^5 V/cm

Electron signal disappears completely under illumination, as with Li doped specimens. However, the built-in field distribution in the film, measured by using hole transit as a probe, shows that a considerable amount of negative charges are captured in the pure Se layers, especially for samples containing small Cl quantities.

IV. DISCUSSION

In the framework of charged center model, the fact that Li doping increases negatively charged traps might be interpreted as meaning that the Li atoms, when they are embedded in a-Se, are positively ionized. This, by charge neutrality, results in the increase of D^- concentration. The effect of Cl doping on the electron transport might be interpreted by the similar argument that some of the added Cl atoms are negatively charged, increasing D^+ centers.

In both cases, expected charge release from unstable D^0 , which are either electron captured D^+ or hole captured D^- , is not observed. This result may suggest merely that the electron or hole release time is much longer than the present experimental time range. Another possible interpretation is that the dissociation of D^0 into D^+ and D^- occurs faster than the charge release process.

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