Photoinduced changes of ac transport in a-As_2Se_3 films: Role of defects and band tails

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The role of defect states and band tails in the increase of capacitance (imaginary part of ac conductivity) with illumination at 20 K is discussed for a-As_2Se_3 thin films. The time increase of capacitance with illumination has two components, fast and slow. The initial abrupt increase is attributed to the hopping of holes in the band tails. The slow increase is related to the creation of new defects and the subsequent electron hopping between them. When illumination is switched off, the contribution of hopping of holes in the tail states ceases, while the contribution of newly created defects persists. This persistent change is annealed out at room temperature. The illumination and annealing behaviors of the slow process can be related to those of the light-induced electron-spin resonance. [S0163-1829(99)00624-4]

Chalcogenide glasses when illuminated by band-gap light undergo various changes in their electrical, optical, and other properties.[1] Some of these changes can be reversed back to their original configuration by annealing below the glass transition temperature (T_g). The changes in electrical properties can be associated with the creation of charged (D^+ and D^-) and neutral (D^0) defect centers by illumination.[1]

By observing light-induced electron-spin resonance (LESR) in amorphous chalcogenides,[2] it is seen that there exist two separate components, fast and slow,[2,3] of the increase of signal with illumination. They have been classified as arising due to ''charge transfer'' and ''defect creation,'' respectively.[2] The induced LESR signals can be annealed out at room temperature. Kondo *et al.*,[4] by studying capacitance in a-Se, concluded that the annealing behavior of capacitance and LESR signals show a similar behavior. The role of defect states in the increase of capacitance, with illumination, however, is still not clear.

We have studied the illumination-induced changes on the capacitance of amorphous As_2Se_3 (a-As_2Se_3) films, which is one of the typical amorphous chalcogenides. The two distinct increases, i.e., the abrupt and the slow increases, have been found and the origin of these changes is discussed in the present study.

Thin films of a-As_2Se_3 (thickness $\sim$0.5 μm) were prepared onto indium tin oxide (ITO) (width 1 mm) coated glass substrates at room temperature in a vacuum of approximately 1×10^{-6} Torr. Gold (width 1 mm) was evaporated as the top electrode to make the sample in a sandwiched configuration. Before depositing Au, the samples were annealed at 433 K for 2 h in vacuum. The samples were illuminated, from the ITO side, by a halogen lamp (40 mW/cm^2) through an ir cutoff filter. The samples were annealed at different annealing temperatures, for 120 min, in the same cryostat without removing them. Other details are similar to those reported earlier.[4] Capacitance was measured using a LCR bridge (Hewlett-Packard 4248 A) in the capacitance mode at various frequencies. It has an accuracy of 1×10^{-14} farads and measurements in the range of 10^{-16} farads are possible. Capacitance measurement is a precise tool, as the measurements cannot be affected in the frequency range below 1 MHz by the series resistance of the contact metal and very small changes can be monitored.

The variation of capacitance during illumination (40 min), after stopping the illumination (20 min), and again during illumination (60 min) for a-As_2Se_3, at 1 KHz, is shown in Fig. 1. The capacitance increases abruptly as soon as the illumination is switched on (states A and E in Fig. 1), followed by a gradual increase in capacitance (states B and F in

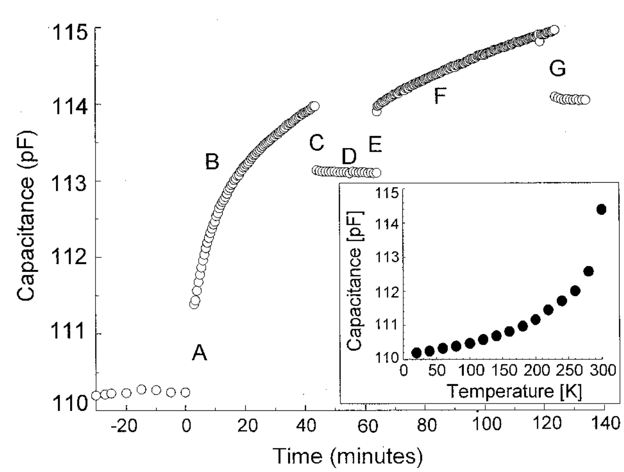

FIG. 1. Variation of capacitance with time for a-As_2Se_3 films at 20 K for the representative frequency of 1 KHz. States A through G denote the various conditions and are explained in the text. Note, the capacitance before $t=0$ min is the stabilized capacitance, before illumination, at 20 K. The inset shows the temperature dependence of capacitance in the dark conditions.

Fig. 1). When the illumination is switched off after 40 min, the capacitance decreases rapidly by around 30% (state *C* in Fig. 1), and then remains nearly constant for the whole time during which the illumination is turned off (state *D* in Fig. 1). When the illumination is switched on again after 20 min, we observe an abrupt increase in capacitance initially, which then changes to a slow increase of capacitance, which is similar to that observed by the illumination before the pause in illumination. The capacitance is found to keep on increasing, at a relatively slower rate. When the illumination is switched off after 60 min, the capacitance decreases sharply and then remains nearly constant. Note, a similar behavior is observed for the changes in capacitance at all the measured frequencies, but Fig. 1 shows the data for the representative frequency of 1 KHz.

We discuss these two distinct behaviors of the increase in capacitance separately. First, we will discuss the abrupt increase of capacitance when the illumination is switched on. The abrupt increase of capacitance is attributed to hopping of holes in the valence-band tails, since hole transport is more dominant in amorphous chalcogenides. In fact, band-tail hopping of holes, which gives rise to a temperature-independent photoconductivity at low temperatures, has been suggested in amorphous chalcogenides.[5] A similar abrupt increase of capacitance with illumination has also been observed in hydrogenated amorphous silicon (a-Si:H).[6] However, it is observed that in a-Si-H, the value of capacitance, after putting off the illumination, returns to the initial annealed state. The increase in capacitance during illumination for a-Si:H is suggested to be due to hopping of electrons in conduction-band tails.[6] After stopping the illumination, the holes in the valence-band tails recombine with electrons, which attributes to the rapid decrease of capacitance after stopping illumination (states *C* and *G* in Fig. 1). When the illumination is again put on after the pause in illumination, the initial abrupt increase can be attributed to the same mechanism. Through a detailed study of these abrupt changes of capacitance with illumination (e.g., frequency and temperature dependence of the abrupt increase), information about the dynamics of carrier diffusion, and thus tail states hopping, can be discussed in detail. These will be discussed in a future publication.

Next, we discuss the gradual increase of capacitance that follows the initial abrupt increase. As shown in Fig. 2(a), illumination may create new intimate pairs (IP's) of defect states (conjugate pairs of charged defects, for example P_2^+-C_1^-, where P and C, respectively, refer to pnictogen and chalcogen centers, and the subscripts and superscripts denote the coordination and charge of the defects, respectively), which may be stable at low temperatures but unstable at around room temperature.[1] It is known that the hopping of charge carriers between P_2^+ and C_1^- contributes to ac transport properties of amorphous chalcogenides.[7–10] On the other hand, some other defects, e.g., P_4^+-C_1^- pairs, may also be created. Their number, however, is expected to be small and hence contribution of these defects to ac conductivity may be ignored.[1] In a-As_2Se_3 films, the changes induced by illumination of the real part of ac conductivity have been studied in detail.[11,12] The changes introduced by low-temperature illumination (90 K) are annealed out at around 200 K, while the changes by room temperature (RT) (300 K) illumination are removed by annealing near T_g. This behavior suggested that different mechanisms are responsible for the induced changes, depending on the temperature at which illumination is performed.

Since the illumination was done at 20 K in the present work, we expect that the slow increase following the initial abrupt increase is due to the hopping of electrons and holes between these newly created defects. The bipolaron (hopping of two electrons) between two charged defect centers and/or the single polaron hopping (hoping of a single electron or hole) between a charged and a neutral defect state can contribute to the increase of capacitance. We will then discuss which mechanism (or both) dominates the gradual increase in capacitance.

Figure 3 shows the time-dependent change in the slow component of capacitance in an experiment with no interrup-

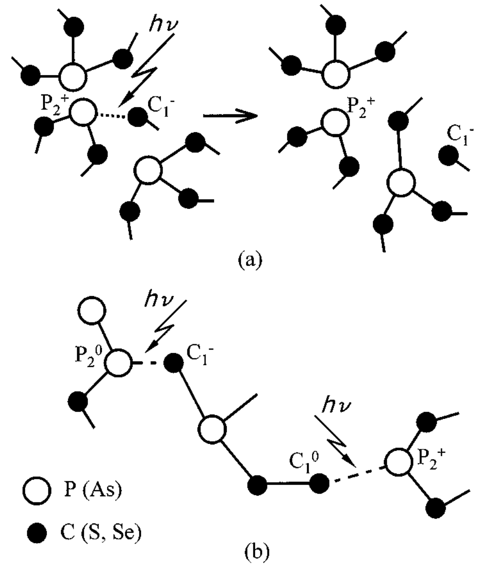

FIG. 2. Possible configurations of photoinduced defects in amorphous $As_2S(Se)_3$. (a) and (b) show the unstable (annealed out at low temperatures) and stable (annealed out at high temperatures) configurations, respectively (Ref. 15). Other details are explained in the text.

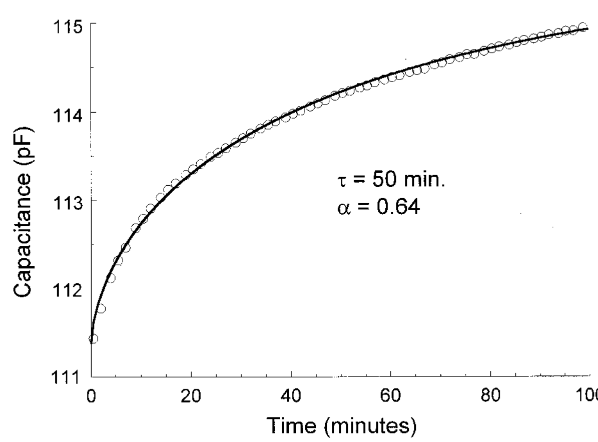

FIG. 3. Fitting of the empirical equation to the experimental data during illumination. The effective relaxation time and dispersion parameter, estimated from the fitting, are also listed.

tion of illumination. Note that the abrupt increase due to the contribution of holes hopping in the tail states has been ignored for this discussion. The time evolution of the slow component can be fitted to the following empirical equation:

$$\Delta C = \Delta C_s \left\{ 1 - \exp\left[-\left(\frac{t}{\tau} \right)^{\alpha} \right] \right\}, \qquad (1)$$

where ΔC is the induced capacitance change, ΔC_s is the saturated capacitance in the present illumination conditions, α is the dispersion parameter, and τ is the effective relaxation time. The fitting is shown by the solid line in Fig. 3. From the fitting, the values of α and τ were estimated to be 0.64 and 50 min, respectively. The fitting of the experimental data to Eq. (1) may suggest that a single process (either bipolaron or single-polaron hopping) dominates the gradual increase of capacitance, since the changes are replicated well by a single line. The dependence of the parameters α and τ on the film thickness is not clear from the present work, as we have done the measurements on the films having approximately the same thickness.

If the abrupt increase and decrease (contributions due to holes hopping in the tail states) is subtracted from the total increase of capacitance with illumination, we observe that the capacitance shows almost no change after the illumination is turned off. In other words, we can say that the increase of capacitance due to the electron hopping between defect states remains unaffected when the illumination is turned off. A similar behavior is observed for the case of the LESR signal,[13] where almost no change is observed after switching off the light and the signal persists. This persistent capacitance of the LESR signal is not annealed out at low temperatures but is annealed out at room temperature. It is suggested, therefore, that the gradual increase of capacitance cannot be attributed to the unstable photoinduced IP's, (i.e., P_2^+ and C_1^-). There exist two types of defect centers contributing to the LESR signals in As_xS_{1-x} films when measured at low temperatures:[14] One type of LESR signal (type I) is relatively unstable and is annealed out at around 200 K, while the other type of signal (type II) is annealed out at around 300 K. The type-I defect states have been identified with electrons and holes trapped at the As_2^+ or S_1^- center [Fig. 2(a)].[1,14] The type-II LESR signals are identified as P_2^0 or C_1^0 centers, which are shown in Fig. 2(b).[1,15] Note, the presence of many wrong bonds, e.g., $P—P$ and $C—C$ in amorphous chalcogenide films, is suggested as the origin of the LESR II signal by Elliott and Shimakawa.[15] These close pairs of defect configurations are considered to be stable against annihilative reconstruction as long as extra electrons are liberated into the conduction band. This makes these defects stable and can be annealed out only at higher temperatures. We postulate here that the situation in the a-As-S system is basically the same as that in the a-As-Se system. In fact, there are two types of photoluminescence centers both for a-As_2S_3 and As_2Se_3.[1] The tunneling or overbarrier hopping of electrons between C_1^0 and P_2^0 is possible and this may contribute to the gradual increase in capacitance [see Fig. 2(b)]. The configuration shown in Fig. 2(b) still exists after putting off the illumination and is annealed out at around room temperature, to the ground states of P_3^0 or C_2^0. The recovery of capacitance with annealing at various temperatures for a-As_2Se_3 is shown in Fig. 4. The recovery of capacitance is defined as the ratio of the recovery of the increased capacitance by illumination to its original state (capacitance before illumination). Note that the capacitance is always measured at 20 K, after respective annealings. The capacitance returns to the original state after annealing at 300 K, indicating that the changes induced by illumination have fully been annealed out.

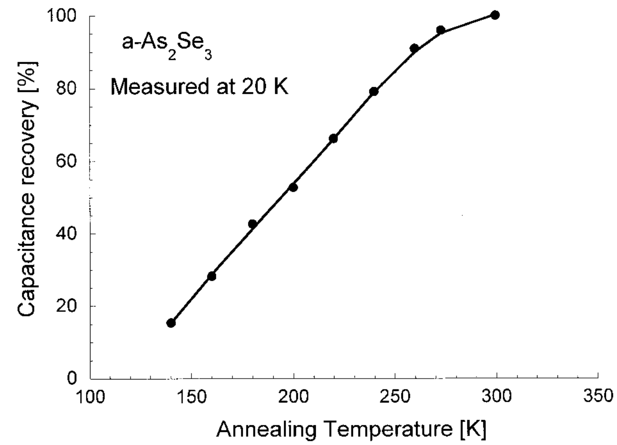

FIG. 4. Recovery of capacitance with annealing. The recovery of capacitance is defined as the ratio of the recovery of the increased capacitance to its original value. The annealing was done for 120 min at each temperature. The capacitance was measured at 20 K. The solid line is a guide to the eye.

It should be noted that a similar increase of about 15% in the capacitance has been observed for a-As-Se films by illumination and these changes can be annealed out at 170 °C.[16] These changes in capacitance can be related to unstable configurations as shown in Fig. 2(a). The different annealing behaviors from the present results can be attributed to different illumination conditions. In our earlier work,[4] we have reported the increase of the capacitance of a-Se illuminated at 20 K. These changes were annealed out at 160 K, which coincides with the annealing temperatures of the LESR signal for a-Se.

Let us discuss the other possibilities that may contribute to the increase of capacitance with illumination and why we have ruled them out to explain the increase in the present cases. One such possibility can be the change in junction capacitance with illumination that will effect the measured capacitance. We have observed that the application of both positive and negative dc bias voltage does not affect the capacitance changes during illumination, which led us to rule out this contribution.

We also dismiss the involvement of a thermal effect for the abrupt changes of the capacitance as the magnitude of the abrupt increase of capacitance corresponds to a temperature increase of nearly 200 K (see the inset of Fig. 1 for the temperature dependence of dark capacitance), which is unreasonably high for the present experimental conditions.

In summary, the effects of illumination on the capacitance of a-As_2Se_3 films have been studied at 20 K. The initial abrupt increase in the capacitance is attributed to the hopping of holes in the band-tail states and the following slow increase is due to single electron hopping between the newly created pairs of defects. When the illumination is turned off, the contribution of holes in the tail states ceases abruptly and then the capacitance remains nearly constant. This persistent photoinduced capacitance is attributed to the presence of metastable neutral centers contributing to LESR signals, which are annealed out at 300 K. The time evolution of the slow component of capacitance is expressed by a single stretched exponential function.

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