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Reversible photoinduced changes of electronic transport in narrow-gap amorphous Sb_2Se_3

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Decreases in both dark conductivity and photoconductivity after intense and prolonged photoirradiation have been observed in the narrow-band-gap amorphous Sb_2Se_3; they are similar to those observed in hydrogenated amorphous silicon (a-Si:H) (the Staebler-Wronski effect). The ac conductivity, on the other hand, decreases after illumination, which is in contrast to that observed in a-Si:H. Unlike a-Si:H, these photoinduced changes are not interpreted in terms of light-induced defect creation. The broadening of energy levels of preexisting thermal-equilibrium defects by illumination could produce all of these photoinduced changes in the present system. [S0163-1829(99)14203-6]

Prolonged band-gap illumination induces degradation in most amorphous semiconductors and insulators.[1] In particular, reversible photodegradation of photoconductivity and dark conductivity was found in hydrogenated amorphous silicon (a-Si:H) and is usually called the Staebler-Wronski (SW) effect.[2] A similar reversible photodegradation has been observed for the photocurrent but not for the dark current in amorphous chalcogenide semiconductors with optical band gaps almost the same as or greater than that of a-Si:H.[3] The origin of this photodegradation is now commonly accepted to involve light-induced metastable defects (LIMD). However, details of the mechanism are still not clear, although a number of models for LIMD creation have been proposed.[1] Interestingly, no significant photodegradation has been observed in either device-quality hydrogenated amorphous germanium[4] (a-Ge:H) or in amorphous arsenic tritelluride (a-As_2Te_3) with air mass 1-like illumination.[5] Both of them are narrow-band-gap semiconductors; one is a tetrahedrally coordinated semiconductor with a Tauc gap of 1.05 eV and the other an amorphous chalcogenide with a gap of 0.84 eV. A direct correlation between the band gap and the photoinduced defect density has been reported in amorphous silicon alloys, with the induced defect density increasing by three orders of magnitude as the band gap increases from 1.5 to 2.6 eV.[6] Thus materials with a band gap around 1.5 eV must mark the limit of those which show photodegradation under usual photoirradiation conditions.

In this work we have verified photodegradation in a-Sb_2Se_3, an amorphous chalcogenide whose Tauc gap is 1.24 eV at room temperature, which is larger than that of a-Ge:H but smaller than that of a-Si:H (1.8 eV). Thin films of a-Sb_2Se_3 with thicknesses of $\sim$0.7 μm were deposited at room temperature on Corning 7059 substrates for measurements of transport and fundamental optical absorption, and on indium-tin-oxide (ITO) glass for photocapacitance measurements, by a conventional evaporation technique. Note that the actual composition of the films might be different from the source composition of Sb_2Se_3. The exact stoichiometry of the films is, however, not an important concern for the present study. Optical transmission and reflectance measurements were performed on a sample of Corning 7059 substrate using a Cary 2390 spectrometer. The optical gap determined by employing the Tauc formula increased from 1.21 to 1.29 eV as the sample was cooled from 373 to 100 K. Metallic electrodes of Au, Al, and In were examined to ascertain which gave a good Ohmic contact with a-Sb_2Sb_3; Au and Al were found to give Ohmic contacts up to an electric field strength of $1.6\times10^4\ \mathrm{V\,cm^{-1}}$. On the other hand, In, having a small work function, made non-Ohmic and more resistive contacts to a-Sb_2Se_3, suggesting p-type conduction; this was also confirmed by the sign of the thermoelectric power. Before the evaporation of a-Sb_2Sb_3, coplanar electrodes of Au with a gap spacing of 50 μm and a gap width of 5 mm were fabricated on the substrates for the transport measurements in order to avoid thermal crystallization. All samples were annealed at 392 K before light irradiation. A halogen lamp was used with a heat-absorbing filter to illuminate the films with an intensity of 300 $\mathrm{mW\,cm^{-2}}$. A personal computer controlled a shutter to regulate the illumination time, and a Keithley 617 electrometer was used to measure time-dependent photoconductivity and dark conductivity automatically.

Figure 1 shows the time dependence of the photocurrent $I_p(t)$ with an illumination intensity of 300 $\mathrm{mW\,cm^{-2}}$ measured at 243 K at which $I_p(t)$ is easy to measure due to the decreased dark conductivity. In order to observe the time dependence of the dark current $I_d(t)$ as well, the sample was intermittently illuminated; first it was illuminated for 10 sec, kept in the dark for 1 h to obtain a steady-state value of $I_d(t)$, followed by the next illumination, and the illumination time was increased exponentially, amounting to $\sim$44 h in total. $I_p(t)$ was measured at the end of each illumination

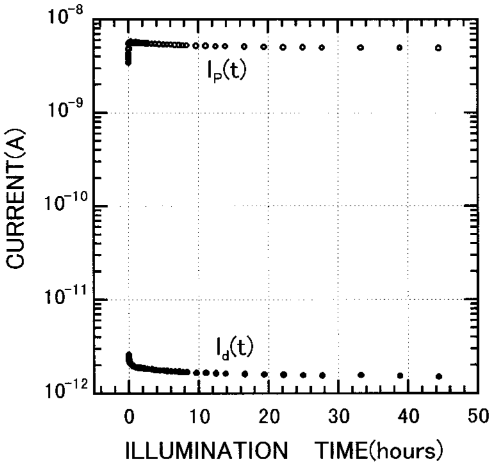

FIG. 1. Decrease of photocurrent $I_p(t)$ (○) and dark current $I_d(t)$ (●) measured with intermittent illumination of 300 mW cm^{-2} at 243 K for a-Sb$_2$Se$_3$. Each $I_d(t)$ was measured after an interval of 1 h cessation of illumination (not shown).

time and the steady-state value of $I_d(t)$ was measured at the end of each 1 h cessation of illumination. All the intervals of 1 h for the cessation of illumination are omitted in Fig. 1. A slow decrease of photocurrent from 5.7 to 4.9 nA and a rapid decrease of dark current from 2.6 to 1.5 pA are noticed for the total time of ~44 h irradiation. The decrease of the dark current (~42%) is larger than that of the photocurrent (~14%). This is similar to the SW effect in a-Si:H, except that the changes of both the photocurrent and dark current can exceed an order of magnitude for a-Si:H.[7] These changes can be attributed to LIMD creation.[1] Note, however, that a decrease of the dark current was not predicted and has not been observed in amorphous chalcogenides.[1]

Both the decreased photoconductivity and dark conductivity were restored to their original values by subsequent annealing at room temperature. These phenomena were observed for the samples with non-Ohmic contacts of In as well, thus indicating that they are bulk effects. Figure 2 shows isochronal annealing, with an annealing time of 20 min at different temperatures, of photocurrent and dark current of a-Sb$_2$Se$_3$ degraded at 220 K by continuous illumination of 300 mW cm^{-2} for ~40 h. Note that decreases in both the dark current and photocurrent after illumination are different from those presented in Fig. 1; this is due to the difference in the light exposure temperature, i.e., 243 K in Fig. 1 and 220 K in Fig. 2. The dark current begins to be restored to the initial state at around 250 K, while the annealing of the photocurrent begins above 280 K, being less pronounced, suggesting that these photoinduced changes are annealed out by particular annealing temperatures.

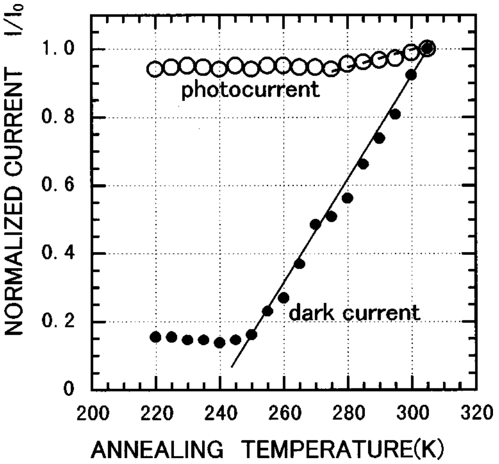

FIG. 2. Isochronal annealing of degraded photocurrent (○) and dark current (●) of a-Sb$_2$Se$_3$, with an annealing time of 20 min. Each photocurrent and dark current (I) is normalized by its respective original value (I_0) before continuous light exposure of 300 mW cm^{-2} for ~40 h at 220 K.

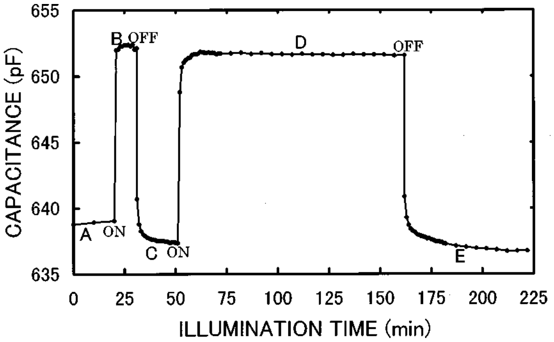

FIG. 3. Change of capacitance of a-Sb$_2$Se$_3$ measured with 150 mW cm^{-2} illumination at 20 K.

The above results may suggest that LIMD creation accompanies a shift of the Fermi level towards the conduction band by prolonged illumination and returns to the original state on annealing. These behaviors are similar to those observed in p-type a-Si:H, while the change itself is small.[8] Note, however, that the Fermi level is believed to be pinned between the energies of the D^+ and D^- charged defects in chalcogenides.[9] A change in the number of defects itself could not change the Fermi level. It is hence suggested that the shift of the Fermi level is caused by a change in the energy distribution of charged defects. As deeper localized states, in principle, act as recombination centers rather than trapping centers,[10,11] localized states shifted to deeper levels for some reason will decrease the photoconductivity without increasing the number of defects. Unlike a-Si:H, the lack of a big change in photoconductivity with a small decrease in dc conductivity after prolonged illumination for a-Sb$_2$Se$_3$ is thus explained by a broadening of energy levels of charged defects instead of an increase in the number of defects. This is confirmed by the following capacitance measurements.

As the ac conductivity is sensitive to such an energy distribution,[12,13] we discuss the change in capacitance (imaginary part of the ac conductivity) obtained at 1 kHz as shown in Fig. 3. The illumination (150 mW cm^{-2}) and measurements were done at 20 K. Almost uniform photoexcitation throughout the films of a-Sb$_2$Se$_3$ can be expected, as we used films of thickness ~0.7 μm and nonmonochromatic illumination containing near-infrared light with wavelengths up to ~900 nm at which the absorption coefficient is ~7 $\times 10^3$ cm^{-1}, as obtained by the optical absorption measurements. Before illumination [state (A)] two-electron (bipolaron) hopping may dominate the capacitance.[1] A large increase of capacitance is observed during illumination of 10 min (B). After stopping illumination (C), the capacitance decreases to a smaller value than that for the initial value of state (A), which is in contrast with the behavior observed in wide-band-gap amorphous chalcogenides of Se (a-Se).[14] In a-Se, the capacitance increases after illumination, which can be attributed to an increase in the number of defects.[13] Illumination and cessation of illumination again produce an increase (D) and decrease (E) in capacitance, respectively. Note that the value after prolonged illumination [state (E)] is smaller than that after short-time illumination [state (C)]. Similar behavior has been observed in a-Si:H, except that in a-Si:H the value after stopping illumination [(C) or (E)] returns to the initial annealed state (A) under the condition of very weak illumination.[15] The increase in capacitance during illumination was suggested to be due to hopping of electrons in conduction-band tails in a-Si:H.[15] One may, then, attribute the increase in capacitance during illumination here to hopping of holes in valence-band tails, but space charges near the interface between metal electrodes and a-Sb_2Se_3 may also contribute to the increase in capacitance; hence it is not easy to discuss which mechanism is more dominant. As the present interest is, however, the decrease in capacitance after illumination and its connection with the decrease in dark current, an increase in capacitance during illumination is not discussed here in detail.

Let us discuss why the capacitance decreases after illumination. Bipolaron hopping motion (two-electron hopping between D^+ and D^-) dominates the low-temperature ac conductivity under dark conditions.[1,12] As already suggested, illumination also causes a broadening of the energy levels of charged defects, which may be the origin of the decrease of the capacitance from the initial state after stopping illumination, because the ac transport, and hence the capacitance C, is governed by the following equation.[12,13]

$$C \propto N^2 \frac{2kT}{\Delta} \tanh\left(\frac{\Delta}{2kT}\right),$$

where N and Δ are the number of defects and the extent of energy broadening of defect levels, respectively. At low temperatures, C is proportional to $2kTN^2/\Delta$, since $\tanh(\Delta/2kT)$ becomes unity. This predicts that, if either Δ increases or N decreases with illumination, then C decreases. Since the decrease in N with illumination is irrelevant, an increase in Δ must decrease C. The broadening of Δ after photoirradiation has also been suggested from time-of-flight measurements in amorphous chalcogenides.[16] Note that this decrease of capacitance is recovered completely by annealing at 160 K; this annealing temperature is low compared with that of the photodegraded dark current (~250 K) in the transport measurements, which is due to the difference in temperature at which the illumination was made (20 K for capacitance measurement and 220 K for photocurrent measurement).

In summary, we have observed photodegradation in photoconductivity and dark conductivity in amorphous chalcogenide of Sb_2Se_3. A decrease of the bulk capacitance after illumination has also been observed. These changes are returned to the original states by annealing. All of these metastable changes are interpreted by a broadening of energy states of preexisting charged defects. Unlike a-Si:H, changes are not attributed to metastable defect creation in the present narrow-band-gap material a-Sb_2Se_3. It is, however, not clear how and why the energy broadening occurs in this amorphous chalcogenide. Photoexcitation and successive recombination may rearrange the flexible structural network during illumination, which leads to a more disordered structure, resulting in the energy broadening of defect states.

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