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20. Abstract

In the tetrahedrally coordinated amorphous semiconductors the dominant defects deep in the gap are attributed to dangling bonds on the group IV atoms. These defects are commonly thought to have effective electron-electron correlation energies U_{eff} which are positive, although some tight-binding estimates suggest negative U_{eff} . Defect states near the band gap edges are invoked to account for many experimental results including the usual appearance of an Urbach absorption edge. These shallow defect states are usually attributed to strained bonds but two-fold-coordinated group IV atoms have also been suggested. The application of light of near-band-gap energies alters the density of paramagnetic dangling bonds. For large spin densities ($n_s > 10^{17} \text{ cm}^{-3}$) this increase is probably due to the creation of new defects, but it is possible that at lower densities ($n_s < 10^{16} \text{ cm}^{-3}$) the rearrangement of electronic charge in existing defects is important. Impurities also contribute to the defects observed in tetrahedral amorphous semiconductors. Particular species include trapped atomic and molecular hydrogen, trapped NO_2 molecules, singly-coordinated oxygen atoms and E' centers.

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ABSTRACT

In the tetrahedrally coordinated amorphous semiconductors the dominant defects deep in the gap are attributed to dangling bonds on the group IV atoms. These defects are commonly thought to have effective electron-electron correlation energies U_{eff} which are positive, although some tight-binding estimates suggest negative U_{eff} . Defect states near the band gap edges are invoked to account for many experimental results including the usual appearance of an Urbach absorption edge. These shallow defect states are usually attributed to strained bonds but two-fold-coordinated group IV atoms have also been suggested. The application of light of near-band-gap energies alters the density of paramagnetic dangling bonds. For large spin densities ($n_s > 10^{17} \text{ cm}^{-3}$) this increase is probably due to the creation of new defects, but it is possible that at lower densities ($n_s < 10^{16} \text{ cm}^{-3}$) the rearrangement of electronic charge in existing defects is important. Impurities also contribute to the defects observed in tetrahedral amorphous semiconductors. Particular species include trapped atomic and molecular hydrogen, trapped NO_2 molecules, singly-coordinated oxygen atoms and E' centers.

INTRODUCTION AND BACKGROUND

The successful doping of films of hydrogenated amorphous silicon ($a\text{-Si:H}$) [1,2] and the subsequent production of efficient, large area solar cells from this material has made the understanding of defects of fundamental importance. In addition, the potential use of $a\text{-Si}_x\text{Ge}_{1-x}\text{H}$ and other tetrahedrally-coordinated alloys in multilayer photovoltaic devices requires a much better understanding of the important defects in these amorphous semiconductors. Because of this interest, these amorphous films can now be grown very reproducibly and many of their properties are very well characterized. However, several important aspects of the defects in these alloys remain controversial.

The major contribution to electronic states with energies near the center of the gap comes from dangling bonds on the group IV atoms. In $a\text{-Si:H}$ there exists an electron spin resonance (ESR) response at $g = 2.0055$ which is at least 10^{15} spins cm^{-3} even in the best films. This response is attributed to an unpaired spin on a silicon dangling bond. In alloys of $a\text{-Si}_x\text{Ge}_{1-x}\text{H}$ there exist two ESR signals one attributed to a silicon dangling bond and one to a dangling bond on germanium. For $x < 0.9$ the germanium dangling bond signal is usually $> 10^{17}$ spins cm^{-3} .

The usual interpretation [3] of these ESR signals is in terms of unpaired spins which are highly localized on three-coordinated Si or Ge atoms. These spins occur at neutral sites (D^0) which have not been compensated by the addition of hydrogen to the films. The dangling bonds are commonly assumed to be neutral in the ground state as a result of the fact that the effective electron-electron correlation energy U_{eff} is a positive quantity [3]. Although it is less commonly accepted, the possibility that at least some of the Si and Ge dangling bonds form a negative U_{eff} system has also been suggested [4]. If U_{eff} is negative, then there exist both positively and negatively charged analogs of the dangling bond defect (D^+ and D^-) which form the ground state of the system. The charged defects D^+ and D^- are, of course, spinless. Either of these suggestions is consistent with the fact that the density of states deep in the gap generally exhibits only one resolved peak which occurs somewhere near the middle of the gap [3].

Near the band edges there are thought to be shallow defects which contribute to the exponential or Urbach tail which is always observed in the absorption edge of tetrahedrally-coordinated amorphous semiconductors. Once again, the most commonly accepted interpretation of these states is in terms of strained bonds in the amorphous network [6], but specific defects have also been suggested [4,7]. In particular, it has been speculated that neutral two-fold coordinated Si and Ge atoms (T_2^0) may be responsible for these shallow electronic states [7].

Thus there are two essentially opposite points of view with regard to the fundamental, "intrinsic" defects in a-Si:H and related alloys. The first, and most commonly accepted, view is that the dominant deep defects are neutral dangling bonds with positive U_{eff} and the dominant shallow defects are the result of strained bonds. The second view is that at least some of the deep defects are spinless dangling bonds with a negative U_{eff} and the shallow states are specific two-fold-coordinated defects (T_2^0).

When light of roughly band gap energies is incident on a-Si:H there exist in general three transient, optically-induced ESR signals. These three signals, which have g-values of 2.004, 2.013 and 2.0055, are attributed to electrons trapped in localized electronic states below the conduction band edge, to holes trapped in localized states below the valence band edge and to silicon dangling bonds, respectively. The dependence of these three signals on doping [6-11] has suggested that the resonances at 2.004 and 2.013 are due to electrons and holes, respectively, trapped at strained or weak bonds near the band edge [12,13]. In a second interpretation [7] these two signals are suggested to be due to electrons and holes which are trapped at T_2^0 defects yielding T_2^- and T_2^+ charge states, respectively.

The optically-induced ESR response at $g = 2.0055$, which is attributed to Si dangling bonds, has also been interpreted within the framework of more than one model. Whether or not this defect constitutes a negative U_{eff} system remains a controversial point.

Impurities also play important roles in determining the important defects in films of tetrahedrally-coordinated amorphous semiconductors. It is known from nuclear magnetic resonance (NMR) and ESR studies, respectively, that molecular hydrogen (H_2) and atomic hydrogen can be trapped in these films under the appropriate conditions. Molecular hydrogen, in particular, is a nearby ubiquitous impurity in a-Si:H and a-Si_xGe_{1-x}:H films.

In addition to defects associated with hydrogen, other impurity species can create observable levels of defects when present in sufficient quantities. Such defects include trapped NO_2^- radicals, singly-coordinated oxygen atoms and triply-coordinated silicon atoms which are bonded to three oxygen atoms (E' centers). The presence of the E' centers in oxygen-doped a-Si:H indicates that these materials are highly inhomogeneous with the presence of SiO_x-rich regions.

METASTABLE ELECTRONIC STATES

Optically-induced metastable changes in many transport and optical properties of a-Si:H are well known. The first observation of such an effect was a decrease in the photoconductivity after optical excitation reported by Staebler and Wronski [14]. Dersch et al. [15] first observed a metastable increase in the ESR intensity of the Si dangling bond signal after irradiation with white light at 300K. An increase is also observed after x-irradiation [16], and these increases can be annealed by cycling to temperatures of ~ 500K [15,17].

Several experiments have probed the kinetics of this metastable increase in the ESR [18-21]. At high intensities of the exciting light the ESR intensity as a function of time $n_s(t)$ exhibits a region whose $n_s(t) = t^{1/3}$. This behavior has been interpreted [19,21] as the optically-induced creation of dangling bonds where the production of new dangling bonds is limited by

the presence of the existing density of dangling bonds. This limitation occurs because the dangling bonds themselves are assumed to provide a parallel non-radiative process which competes with transitions which can generate new defects.

An example of the approximate $t^{1/3}$ dependence of the spin density with time at high exciting light intensities is given in Fig. 1. The spin densities plotted in this figure are actually only the optically-induced portion with the original "dark" spin densities subtracted. In these samples the initial spin densities are primarily due to bulk states and not surface states. The magnitudes of the dark spin densities are $\sim 3 \times 10^{15}$ spins cm^{-3} .

It is apparent from Fig. 1 that the growth rate decreases with decreasing intensity of the incident light. At times longer than those shown in Fig. 1 and at low incident intensities ($< 100 \text{ mW cm}^{-2}$) the slope decreases continuously with time such that no unique power law can be defined in this regime. This decrease in slope for an approximate power law behavior occurs in films where the dark spin density is low ($< 5 \times 10^{15}$ spin cm^{-3}). It has been suggested [18] that there may be a second process contributing to the metastable ESR at low intensities of inducing light.

Other experiments suggest that more than one center may be involved in the optically-induced metastabilities observed in a-Si:H films [22-24]. For example, Han and Fritzsche [23] have found that at least two states are necessary to explain the inducing and annealing behavior of optically-induced charges in photoconductivity, and Guha et al. [24] have shown that the annealing behavior of the photoconductivity depends on the temperature at which the samples are originally exposed to light. Similar conclusions can be inferred from optical absorption, optically detected magnetic resonance and time resolved photoconductivity measurements.

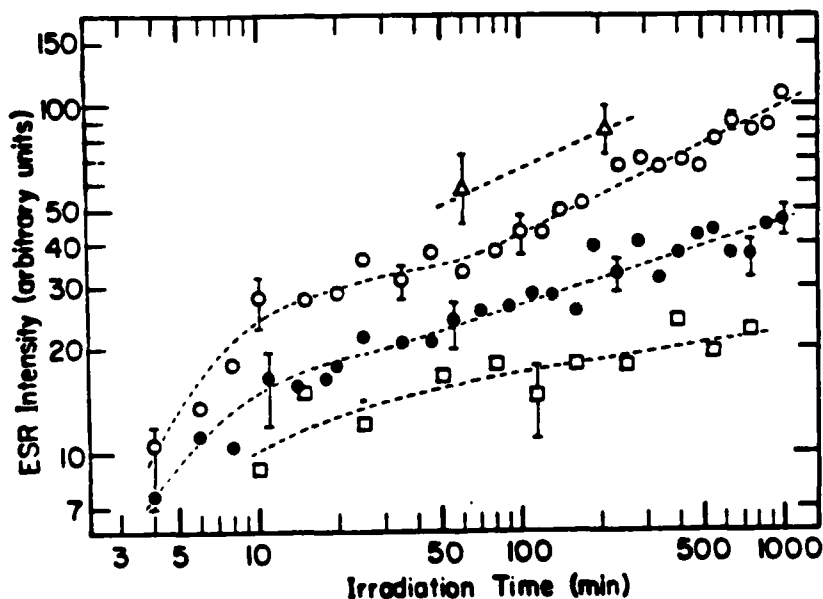


Fig. 1. Metastable, optically-induced ESR intensity in a-Si:H as a function of irradiation time at 300K (3 μm film). Open circles, closed circles and open squares represent data taken with 1.3, 0.4 and 0.1 W cm^{-2} from a tungsten source, respectively. Open triangles are data taken at 6471 Å and 700 mW cm^{-2} . The spin density at 500 min for 0.1 W cm^{-2} irradiation density (open squares) is approximately 10^{16} cm^{-3} . (After ref. 18.)

ELECTRONIC STATES AND THE URBACH EDGE

Urbach [25] first observed a tail on the band edge absorption in ionic crystals. This tail depends exponentially on the energy with a slope (on a semi-log plot) which is inversely proportional to the temperature. Although the tetrahedrally coordinated amorphous semiconductors do not, in general, exhibit this temperature dependence, they do show an exponential energy dependence.

There are several explanations of the Urbach edge in a-Si:H and related alloys. As mentioned above the most commonly accepted explanation is that this absorption results from strained bonds [6,26]. Several specific models have been proposed to calculate this effect [27,28], but the details are not yet certain. An alternative explanation suggests that the Urbach edge may involve transitions between various charge states of two-fold-coordinated silicon atoms [7].

THE ROLES OF SELECTED IMPURITIES

Impurities can sometimes play important roles in determining the important defects in tetrahedrally coordinated amorphous semiconductors. Often the most important "impurity" species is hydrogen which is added intentionally to reduce the density of states near the middle of the gap. In the process some of the hydrogen can be trapped as molecular hydrogen (H_2) in the films.

Some of the H_2 molecules trapped in films of a-Si:H or a-Si_xGe_{1-x}:H can be probed by examining the spin lattice relaxation of the bonded hydrogen atoms [29]. There exists a characteristic minimum in the temperature dependence of the spin lattice relaxation time T_1 which occurs near 40K. It is now well established [30,31] that this characteristic minimum results from a relaxation of the bonded hydrogen via H_2 molecules which are somehow trapped in the amorphous matrix.

Typical curves of T_1 as a function of temperature in films of a-Si:H are shown in Fig. 2. The magnitude of the minimum in T_1 is inversely proportional to the number of H_2 molecules which contribute to the relaxation process [30]. One can thus count the trapped H_2 molecules by monitoring the T_1 minimum. Recent experiments [32] indicate that the T_1 measurements see only a subset of the total trapped H_2 .

There are differences between the amount of H_2 trapped in freshly prepared films on substrates and in films removed from the substrates by selective etching. Results for a-Si:H are shown in Fig. 3 where the two samples were prepared at the same time [33]. It can be seen from the data of Fig. 3 that approximately 40% of the trapped H_2 in the film on the substrate is lost when the substrate is dissolved away. The trapped H_2 constitutes about 0.1 at. % in typical samples of a-Si:H. Recent experiments indicate that the extra H_2 in the freshly prepared films on substrates diffuses out of the films on a time scale of several months [34] after which time the film has the same amount of trapped H_2 as the powder which has been removed from the substrate. The mechanism for this loss of H_2 is probably the releasing of internal strains as the film ages.

In addition to molecular hydrogen, one can also trap atomic hydrogen in a-Si:H albeit under much more restrictive conditions. In films which contain substantial oxygen impurities atomic hydrogen can be produced [16] by x-irradiation at low temperatures ($T < 100K$). The atomic hydrogen is stabilized by the oxygen at temperatures below $\sim 300K$, but combines to form H_2 above this temperature.

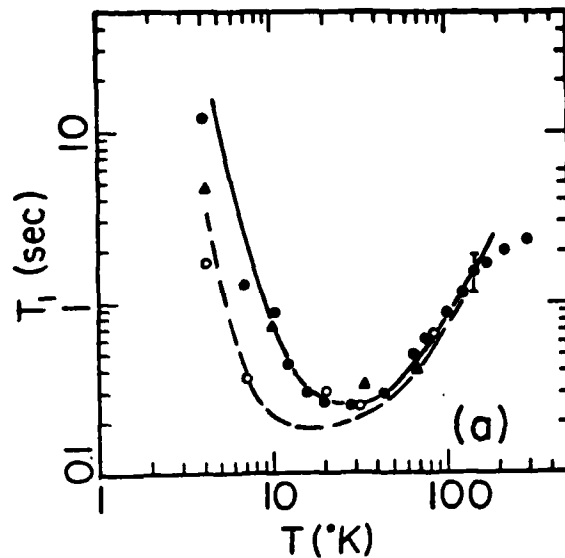


Fig. 2. T_1 as a function of temperature in two representative samples of a-Si:H of low defect density. Solid data points are taken at 42.3 MHz and open data points at 12.3 MHz. The lines are fits obtained from the model of Conradi and Norberg [30]. (After ref. 29.)

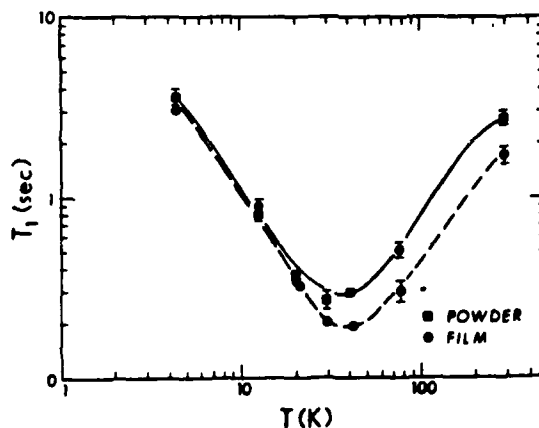


Fig. 3. T_1 as a function of temperature in flakes (solid squares) and thin-films (solid circles) of a-Si:H. The solid and dashed lines are aids to the eye. (After ref. 33.)

ESR spectra of films of a-Si:H doped with oxygen also show other defects associated with impurities. A typical ESR spectrum is shown in Fig. 4. The broad line in this figure is attributed to a hole trapped at a singly-coordinated oxygen atom while the narrower line is the Si dangling bond resonance which has been distorted for technical reasons [16]. The narrowest feature at $g = 2.0023$ is attributed to an unpaired electron on a silicon atom which is bonded to three oxygen atoms (E' center). Even for samples purposely doped with oxygen the presence of this center requires that there is clustering of the oxygen into SiO_x -rich regions in the films. This fact is but one example of the inhomogeneous nature of a-Si:H films.

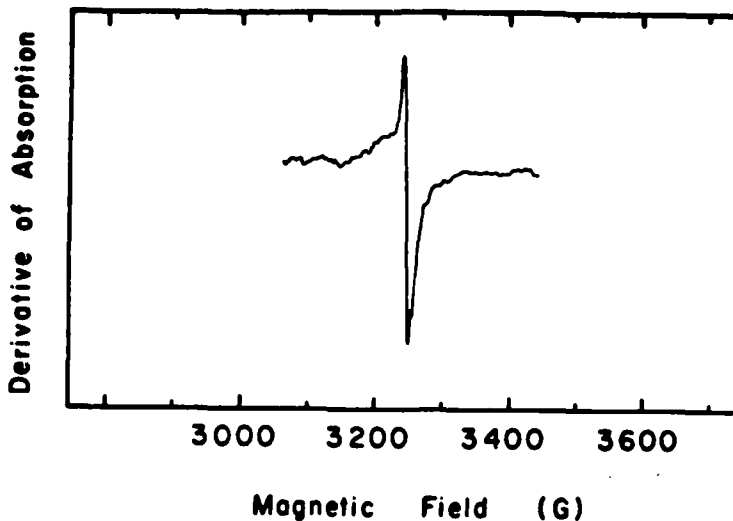


Fig. 4. Central portion of the ESR response in O-doped a-Si:H after x-irradiation at 77K. The strong central line is the Si dangling bond signal. The broad features in the spectrum correspond to an oxygen-related defect (hole center) as described in the text. The very narrow (~ 2 G) feature near $g = 2.002$ corresponds to silicon E' centers (see text). (After ref. 16.)

A final impurity species which one can sometimes trap in films of a-Si:H is the NO_2 radical. At low temperatures ($T < 80\text{K}$) these radicals can be paramagnetic (NO_2 molecules) through either optical or x-ray excitation. A typical spectrum is shown at the top of Fig. 5. The bottom trace is a computer simulated spectrum based on the known parameters for NO_2 molecules. The departure of the experimental curve from the computer simulation in the region of $g = 2.0055$ is due to the presence of the silicon dangling bond resonance in the experimental trace.

SUMMARY

Evidence is mounting that there are a number of defects in addition to the silicon dangling bond which can be important in films of a-Si:H. Some important defects may be related to impurity species. The dangling bonds are usually associated with positive effective electron-electron correlation energies U_{eff} although negative U_{eff} has been suggested for at least some of these states.

Shallow defect states near the band edge are usually attributed to strained bonds, but two-fold-coordinated silicon atoms have also been suggested. Both the dangling bonds and the shallow defect states may play important roles in determining the metastable changes which occur upon application of light. These metastable, optically-induced changes probably involve the creation of new defects, but some changes may also arise from the rearrangement of charge in existing defects.

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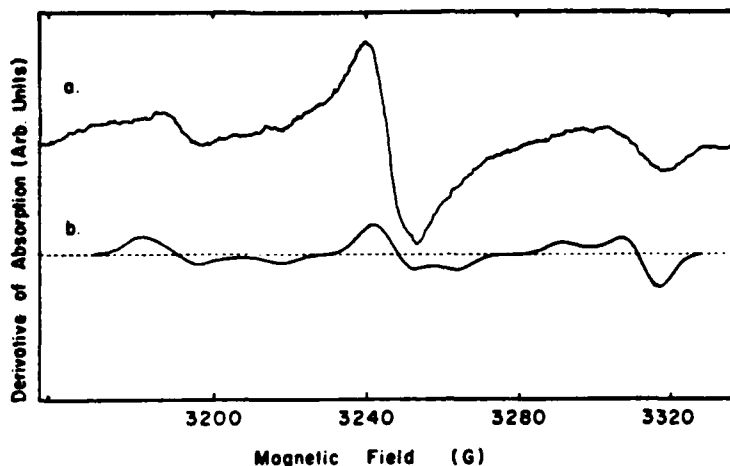


Fig. 5. Experimental (top trace) and computer-simulated (bottom trace) ESR derivative spectra of NO₂ radicals in a-Si:H after x-irradiation at 77K. The additional feature near 3240 G in the experimental trace is due to the Si dangling bond signal as described in the text. (After ref. 16.)

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