The Recombination Process in Hydrogenated Amorphous Silicon Germanium Alloys

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In this work we use spin dependent photo-conductivity (SDPC) to study the recombination process of photo-excitccl carriers in hydrogenated amorphous silicon germanium alloy (a-$Si_x Ge_{1-x} H$). Tlie incorporation of Ge in these alloys is marked by a sudden change in the SDPC signal ($-\Delta\sigma/\sigma$) from (a-Si:H)-like to (a-Ge:H)-like. These results, combined with g-factor and lineshape analysis of tlie spectra, indicate that the Ge incorporation creates new states in tlie conduction band that doininate the transport and recombination of the photo created free carriers. The origin of the spin dependent recombination in a-$Si_x Ge_{1-x} H$ is also discussed

I. Introduction

Today, hydrogenated amorphous silicon (a-Si:H) is an electronic semiconductor of controllable quality. On tlie basis of the present knowledge of tlie physics and chemistry of a-Si:H films, remarkable progress has been made in manufacturing devices, such as high efficiency p-i-n solar cells, thin film transistors, and imaging devices. Nowadays, tlie industrial applications of amorphous semiconductors film represent a market of around one billion dollars. Tlie commercial perspectives of solar electricity generation are still brighter. The need of efficient, cheap, and stable materials for the photovoltaic conversion of sunlight led many research groups to investigate new compound amorphous semiconductors. Variable band-gap amorphous alloys of electronic quality are essential in the manufacturing of efficient multiple junction (or tandem) solar cells. The electric output of tandem solar cells can be notably increased by a proper choice of tlie opto-electronic properties of tlie layers composing the structure.[1,2] Even for single gap solar cells, the properties of tlie active layer has to be matched to tlie spectral distribution of sunlight in order to get an optimized electric power output. Most of tlie research efforts on semiconductor alloys havc bccn

directed towards the understanding, and eventual mastering, of tlie properties of silicon-germanium alloys (a-$Si_x Ge_{1-x} H$). Until now the success has been rather limited. It has been found that the optical band-gap can be easily tailored in the (1.1 - 1.8) eV energy range. However, tlie electronic properties of the films deteriorate enormously on alloying, in terms of midgap density of states (DOS) and mobility-lifetime product ($\mu\tau$) of electrons and holes.[3-8] In addition, deposition conditions leading to high quality a-Si:H films produce very defective a-Ge:H material. It is already known that deposition of Ge atoms with good local surroundings requires quite different plasma conditions, and also quite different plasma-surface interactions, than that for the deposition of Si.

Hence, the degradation of the electronic properties of tlie alloys may originate either from non-optimized deposition conditions, or froin a process having a more fundamental nature. Electron time-of-flight, post-transit spectroscopy, and photoconductivity data show that tlie incorporation of Ge in the a-Si:H network substantially broaden the cb-tail region in the neighborhood of the mobility edge and increase the density of deeper tail states in the gap.[6-8] These results are supportcd by clcctron spin resonance (ESR), light-induced

ESR (LESR), and optically detected magnetic resonance (ODMR) measurements, which also indicate a considerable increase of tlic density of dangling bonds (db) with Ge incorporation.[3] The vb-tail is almost not affected with Ge incorporation.[3,4,6−8] The alloying effects oii the cb-tail DOS are convincingly supported by photoemission spectroscopy measurements[9], as well as by theoretical considerations[10] based on tight-binding calculations, which estimate the consequences of bond length, bond angle, and dihedral angle fluctuations, on the electronic DOS of crystalline Si and Ge. It is theoretically found that the Si vb-cclge is affected exclusively by diliedral angle fluctuations whereas in Ge variations of bond lengths aiid bond angles affect, in addition, tl-e ciectronic DOS at the cb-edge.

Spin dependent measurements are a convenient method of studying recombination centers.[11,12] Ill particular spin-dependent photoconductivity (SDPC) has been used with success to elucidate several processes involved in the recombination of excess carriers ill a-Si:H[13−19]. The great advantage of this technique, is that: 1) the measurements can be done at device operation temperatures (arouncl room temperature); 2) the technique is short range and chemically selective, so that for sufficiently localized electronic states tlie SDPC spectra can provide quite detailed information about the spin-wave function as well as tlie chemical nature of tlie localized ceiiter involved in recombination. Iii this work we extend SDPC measurements to a-Si$_x$Ge$_{1-x}$II alloys.

II. Experimental

The samples of a-Si$_x$Ge$_{1-x}$H have been prepared either by a conventional parallel plate capacitively-coupled glow discharge (GD) reactor or by co-sputtering policrystalline targets of silicon aiid germanium. The samples with higlier germanium content were deposited by rf sputtering. The glow discharge system was powered by a DC electric field. Alloying of silicoii with germanium mas obtained froin different SiH$_4$/GeH$_4$ gas mixtures. Tlie total gas flow [SiH$_4$+GeH$_4$] was kept constant at 10 sccin. Additional dilution of the process gases with H$_2$ was found to improve tlie film quality. Gas pressure (0.3 mbar) and substrate terperature (200°C) mas held constant for all

deposition runs. Further information on GD deposition conditions and sample properties are given in Ref.[5,8]. The sputtered samples were grown in an argon plus hydrogen atmosphere and the substrate temperature was 200°C. The deposition conditions were those giving high quality a-Ge:H films.[20]

Standard techniques have been used in order to characterize the specimens. Optical transmission measurements between 500 and 2000 nm was used for the determination of the film thickness, the optical bandgap and tlie refractive index. The composition of the films was determined via the optical gap, and in some cases by electron microprobe analysis.

Tlie SDPC technique detects spin resonance by changes in the steady-state photoconductivity.[11−19] For the SDPC experiments, the a-Si$_x$Ge$_{1-x}$H thin films grown oiito Corning 7059 glass, and equipped with Al electrodes, are placed in an X-band ESR cavity. The sample is illuminated with a tungsten lamp ($\approx$ 60 mW/cm^2), and kept at a constant temperature in tlie 100-300 K range, by cooling it with dry nitrogen. Tlie spin-dependent change of the photoconductivity is specinlly sinall for these a-Si$_x$Ge$_{1-x}$H alloys (typically $\Delta\sigma/\sigma \leq 10^{-5}$), but can be mésured with a gcod signal-to-noise ratio, by modulating the static magnetic field aiid detecting the photo current (Iph) with a lock-in technique.

III. Results and discussion

SDPC has been particularly useful for the understanding of recombination processes in a-Si:H.[14−19] In the case of a-Si$_x$Ge$_{1-x}$:H, and alloys in general, the recombination process is more complex in nature than in elemental amorplious seiniconductors turning the interpretation of SDPC spectra in these materials particularly difficult. Before treating the more intricate problem of the alloys let us discuss the a-Ge:H case. Although similar in some respects, a-Ge:H and a-Si:H differ appreciably in what concerns the spin system. Of particular concern to the problem being addressed here (SDPC), it has to be mentioned that due to a larger spin orbit coupling constant ($\lambda_{Si} = 0.019$eV, $\lambda_{Ge} = 0.138$eV), the spin orbit relaxation time T_1 is approximately two orders of magnitude shorter in a-Ge:H than in a-Si:H ($T_1 \propto \lambda^{-2}$). As a consequence of the
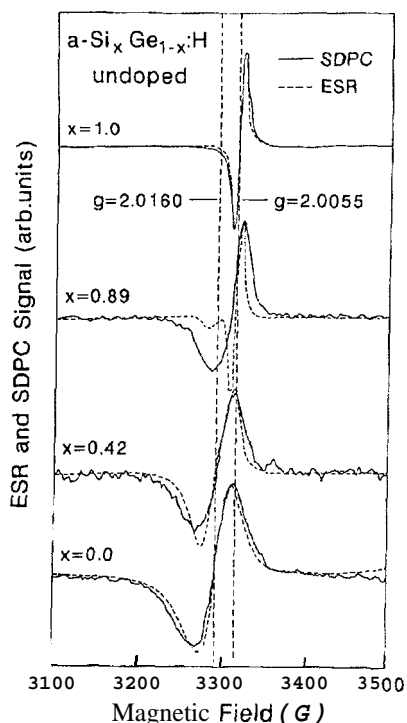
Figure 1: ESR (dashed line) aiid SDPC (full line) signal as a function of the external magnetic field, for alloys with differeiit compositions. Tlie characteristic g-values of a-Si:H (2.0055) and a-Ge:H (2.01G) SDPC signal are shown as vertical liiies.

larger spin orbit coupling (smaller spin lattice relaxation times) the SDPC signal of a-Ge:H, when compared to a-Si:H has the following characteristics[21]:

1) a. stroiiger dependence ori incident microwave power, $-\Delta\sigma/\sigma(Ge) \propto I$, against $-\Delta\sigma/\sigma(Ge) \propto P^{1/2}$. Tlic two behaviors follows the fact that the spin system of a-Si:H is under saturation regime, while in a-Ge:H it is not.

2) a smaller absorption amplitude $[(-\Delta\sigma/\sigma(Si)) \geq 100x(-\Delta\sigma/\sigma(Ge))]$, and ri strong temperature dependente $-\Delta\sigma/\sigma \propto T^{-4}$. This two effccts are understood using Movaghar et al.[22] SDPC model. A-Ge:H has a normally spin dependent recombination process, while in a-Si:H, the recombination is anomalously spin dependent.

In Fig. 1 we summarize typical SDPC spectra of the alloys, as a function of composition (full lines). Ill the same figure the correspondent spectra of conventional ESR on similar samples, are presented (dashed lines). It is clear from the figure that the two techniques give quite differeiit lineshapes, specially in the Si-rich alloys. Let us remember the different origin of the SDPC aiid ESR signals. In these materials ESR basically measure

the Si and tlie Ge-db.[3,4] This is clear in the x = 0.89 case on Fig. 1, where the signal coming from the Si and Ge db are easily deconvoluted. The SDPC signal is more complex in nature because it derives from a recombination process, so the SDPC signal is not just sensitive to the number and the nature of the db, the cb (or vb) states (Si-like or Ge-like) but also reflects the main process of recombination. Tlie deconvolution of all this contributions to the SDPC signal is a rather involved problem. In what follows, and in order to simplify tlie problem, we are going to use the ESR results in tlie interpretation of the SDPC lineshapes. Let us start from tlie extremes. Tlie elemental semiconductors (a-Si:H and a-Ge:H) give similar lineshapes for SDPC and ESR spectra, although the SDPC signal is wider, and has a g-factor value between the ESR g-factor values of a. spin in a db and cb state. For example, in undoped a-Ge:H tlie g-value found in SDPC is $\approx$ 2.016, between 2.018 (Ge-db) and 2.012 (Ge cb). The g-factor found indicate that tlie SDPC signal in a-Ge:H, as in a-Si:H[14,16,17], comes from the recnmbination of an electron in the cb and a hole in the db (this supposition is supported by transport measurements, where it is found that the electrons are the majority carriers in the whole alloy range[6-8,23]). As soon as Ce is incorporated the tmo spectra appear remarkably different. Note that for x = 0.89, the SDPC signal is strongly Ge-like. This is a clear evidence of a strong participation of Ge in the recombination process. Not just tlie lineshape is Ge-like, but also the amplitude of the signal. In Fig. 2 the SDPC signal against the incident microwave power is shown for various alloy compositions. Again, as soon as Ge is incorporated (x= 0.89), the SDPC signal characteristics are very similar to that found in a-Ge:H.

Let us recall how the recombination of excess carriers occurs in order to understand the Ge-like behavior of tlie SDPC signal. It is generally accepted that at sufficiently high temperatures (above 150K), the electrons are moving somewhere above tlie mobility edge. These electrons frequently fall into band-tail localized traps. At low excitation intensities, tlie photo-conductivity is due to electrons being re-emitted from the localized traps to the conducting states. The process is limited by the competing recombination process. In this picture, tlie recoinbination is between an electron in a localized state near the cb mobility edge and a hole in a
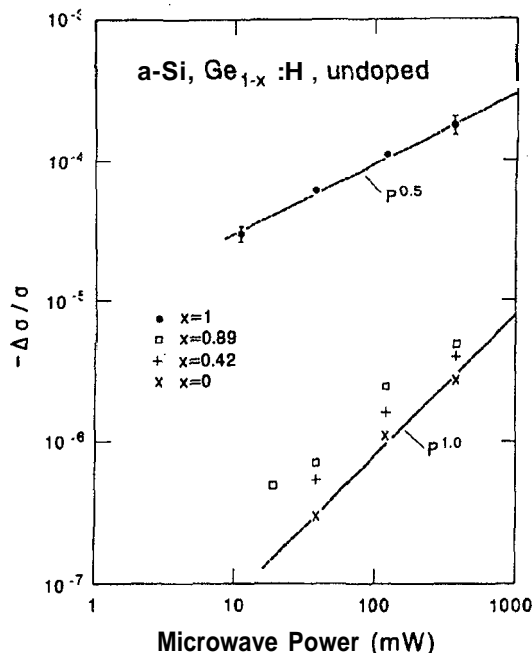
Figure 2: SDPC signal $(-\Delta\sigma/\sigma)$ as a function of incident microwave power in mW, as a function of composition. Note that even for the Si rich alloys the SDPC signal is very similar to that in a-Ge:H.

db.

The origin of this stronger Ge-like behavior can be either a strong modification of the cb tail due to alloying, or a higher density and/or capture cross section of Ge-db. The first assumption for the Ge-like behavior in the Si-rich alloys, comes from the evidence that the incorporation of germanium in the a-Si$_x$Ge$_{1-x}$:H has a very strong effect on the distribution of shallow localized states, below the cb mobility edge. The mechanism by which these new states in the cb influence the SDPC signal is the following. Assuming that the cb-tail states are Ge-like, a decrease in the spin relaxation time of the electrons occupying this states is expected. This imply in a transition from anomalously to normally spin dependent recombination, as observed in Fig. 2. Further corroboration of this model comes from g-factor analysis where it is found that the cb-tail contribution to the effective g-factor is basically Ge-like.[21]

The second possibility is that the Ge db are the dominant pass for recombination. To show that this possibility can be ruled out let us treat the x=0.89 case as an example. We assume for this alloy, that the density of Ge and Si db's are the same and equal to 1017 cm^{-3}. Since in the material the two species are randomly mixed[24], the average distance between db's is 200 Å. With this separation it may be assumed that db's wave functions do not overlap. A recombination between an electron in a Si-like cb state and a Si db will be anomalously spin dependent, while those recombining in a Ge db will be normally spin dependent, as discussed previously. Thus the recombination ill Si-db would give a SDPC absorption signal at least 100 times greater than through a Ge-db. In this case to explain the Ge-like behavior, we would have to assume that the Ge-db capture cross section is 1000 times or more higher than that of a Si db. This higher capture cross section of the Ge-db is in contradiction with TOF results[25], which show that the capture cross sections of Si-db and Ge-db are basically equal, independent of the alloy composition.

V. Coiiclusions

SDPC results on a-Si$_x$Ge$_{1-x}$:H indicate that the incorporation of Ge creates states in the cb-tail that dominate the transport and recombination of the photoexcited carriers in the whole alloy range covered in this study ($0.1 < x < 0.89$).

Acknowledgements

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