Electronic Processes in Thin-Film PV Materials

Final Report

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Abstract

The electronic and optical processes in an important class of thin-film PV materials, hydrogenated amorphous silicon (a-Si:H) and related alloys, have been investigated using several experimental techniques designed for thin-film geometries. The experimental techniques include various magnetic resonance and optical spectroscopies and combinations of these two spectroscopies. Two -step optical excitation processes through the manifold of silicon dangling bond states have been identified as important at low excitation energies. Local hydrogen motion has been studied using nuclear magnetic resonance techniques and found to be much more rapid than long range diffusion as measured by secondary ion mass spectroscopy. A new metastable effect has been found in a-Si:H films alloyed with sulfur. Spin-one optically excited states have been unambiguously identified using optically detected electron spin resonance. Local hydrogen bonding in micro-crystalline silicon films has been studied using NMR.

Introduction

For the past few years the principal investigator and his colleagues have employed several spectroscopic techniques, such as nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), electron spin resonance (ESR), infrared absorption, Raman scattering, photoluminescence (PL) and optically detected magnetic resonance (ODMR) to evaluate the structural and electronic properties of a-Si:H and related alloy systems. The experimental arrangements have been designed specifically for thin film geometries in order to investigate films and multiple layer structures. Facilities exist to perform both cw and time resolved experiments. The aim has been to understand the basic physical mechanisms underlying both the electronic states introduced by impurities, defects or disorder and the instabilities in these amorphous thin

films. The research group also has the capability to produce films and devices based on a-Si:H and related alloys by the PECVD technique.

Objectives

The major objectives of this subcontract are (1) to identify metastabilities caused by carrier recombination or by frozen-in departures from equilibrium, and to determine if the metastabilities that plague devices are "intrinsic" and therefore not correctable or "extrinsic" and therefore capable of being eliminated in future devices, (2) to characterize the important defects and impurities in the bulk and at surfaces and interfaces because interfaces are becoming more important with the advent of tandem cells with several heterojunctions, and (3) to measure the motion of hydrogen in a-Si:H and related alloys on a microscopic scale because the motion of hydrogen is thought to play an important role in many of the metastable effects that occur in a-Si:H and related alloys and the microscopic mechanism for this motion is not known.

Approaches

Three new approaches, that have not been employed in the past, have been emphasized: (1) below-gap spectroscopy, such as optical absorption, photoluminescence (PL), PL excitation, electron spin resonance and other spectroscopies using primarily a tunable Ti sapphire laser system to excite carriers well below the optical gap (down to ~ 1.1 eV). (2) novel nuclear magnetic resonance (NMR) techniques such as measurements of the spin-lattice relaxation in a dipolar field (T_{1D}), to probe local hydrogen motion in doped and intrinsic a-Si:H and selected alloys. (3) doping with group VI elements that introduce new metastabilities into a-Si:H and related alloys.

Results and Discussion

For the past decade the group headed by Professor Taylor has been engaged in research on electronic processes in a-Si:H and related alloys. This research has been performed primarily under this subcontract with NREL through the University Participation Program for Photovoltaic Research.

Several recent research accomplishments of the group are of particular significance. These accomplishments include:

- (1) The identification of two step optical excitation processes [1,2,3] through the manifold of silicon dangling bond defects (D^+ , D^- , D^0). These two step transitions, that require two photons in sequence, are the most important absorption mechanism at low temperatures for energies below about 1.5 eV. These processes are probably also important at higher temperatures and therefore could be an important absorption process for solar cells.
- (2) The first measurement of local hydrogen motion [4] in intrinsic, doped, and compensated a-Si:H. This local motion, which is measured using an NMR technique, correlates with the longer range hydrogen motion measured by SIMS, but the reason for this correlation

remains unknown. The local motion is slightly faster in the clustered phase of hydrogen than in the dilute phase, and the local motion increases after light soaking. Because the Staebler-Wronski effect involves *local* hydrogen motion (if hydrogen motion is involved at all), these results provide data for a microscopic picture of this hydrogen motion.

- (3) The first observation of a new metastable effect in a-Si:H alloyed with sulfur [5,6]. This metastability, which is manifested as persistent photoconductivity at high sulfur concentrations, has been interpreted as the optical activation of inefficient sulfur donors in a-Si:H. Because this effect tends to "mask" the changes produced by the usual Staebler-Wronski effect, it is possible that alloying with sulfur or selenium may produce more stable i-layers for devices.
- (4) The identification of those optically-detected ESR signals that are effectively spin one and those that are spin one-half in a-Si:H [7,8]. We have used both PL- and absorption-detected ESR to identify unambiguously the spin-one component and solve this twenty-year-old problem. This new understanding will ultimately provide a measurement of the carrier separation for photo-excited pairs in a-Si:H as a function of, for example, excitation energy.
- (5) The first measurements of light-induced degradation in amorphous silicon-sulfur alloys using photoconductivity, PL and ESR. Although the subgap optical absorption does change with optical excitation in these alloys, the changes as measured by ESR and PL are less than in a-Si:H [9]. Thus, although light-induced metastable changes are induced in the amorphous silicon-sulfur films, for reasons that are not yet known, recombination via these metastable defects does not control the magnitude of the conductivity or photoconductivity.
- (6) The first measurements of NMR and ESR in μ c-Si:H as a function of plasma excitation frequency. Although the NMR line attributed to clustered hydrogen is similar to that observed in a-Si:H, the line attributed to dilute hydrogen is narrower in the μ c-Si:H samples [10].
- (7) The first observation [11] of a second "intrinsic" ESR center in a-Si_{1-x}N_x:H. Using low temperature, high microwave power ESR measurements, we have shown that a second nitrogen-related center occurs along with the well known silicon (K) center. This observation provides a natural explanation for the theoretical prediction that the K centers have positive effective electron-electron correlation energies, because the K centers are compensated by the nitrogen centers and both are charged (not paramagnetic) in the annealed state. These observations could be important in understanding defects in wider-gap layers for future PV devices.

The first three accomplishments are the most recent and perhaps also the most significant. We therefore highlight our very recent research accomplishments by discussing these three topics in more detail.

(i) Below-Gap Excitation Processes in a-Si:H and Related Alloys

Radiative recombination in a-Si:H has been well studied with above gap excitation. In this case, the carriers are generated in the extended states. These carriers have equal probability of sampling any given site in the localized bandtail states. This ambiguity causes difficulty in distinguishing details of the different recombination mechanisms. Subband excitation, on the other hand, has the potential to excite only a particular set of states below the gap, such as bandtail states or mid gap states. For these excitation processes one may be able to neglect thermalization from the extended states and compare the excitation and recombination more directly. Several groups have studied optical recombination in a-Si:H using subband laser light. However, all of these measurements were either made at only a few discrete laser wavelengths or made at energies just slightly below the optical gap. Changing the exciting photon energy in an essentially continuous manner from above the gap to well below the gap provides a more direct probe of the recombination processes.

Figure 1 shows PL spectra collected at 80 K for various excitation energies, E_x . The absolute PL intensities are arbitrary, but the relative intensities among the spectra shown in Fig. 1 are as shown. The PL spectra are corrected for system response and representative error bars are shown at low PL intensities. Note that the data in Fig. 1, which were taken at constant absorbed photon flux, cover a dynamic range of approximately 12 orders of magnitude.

The most dramatic feature of the data in Fig. 1 is the fact that the PL spectra are very similar independent of the excitation energy and independent of whether the PL is observed below or above the excitation energy. PL data taken with E_x at 1.60 eV and below have portions where the PL energies are greater than E_x . Because it is well established that the PL is due to recombination between electrons in the conduction band tail with holes in the valence band tail, the PL must be excited by two photons, one which generates the electron and one the hole, whenever the PL energy exceeds E_x .

At first sight the lack of any dependence of the PL lineshape on whether the excitation energy is above or below the PL energy is very surprising because these two excitation mechanisms should be very different, at least over some energy range. At high excitation energies, as for example $E_x \geq 2$ eV, the PL must be excited by a single photon. On the other hand at low excitation energies, as for example $E_x \leq 1.5$ eV, the PL above E_x is excited by a two-step process (involving two successive photons) through the manifold of silicon dangling bond states. One possibility for such a two-step process is that the first photon excites an electron into a D° state creating a filled D^- state, and then the second photon of identical energy excites the electron from the D^- level into the conduction band before it can recombine. The net result is a hole in the valence band, an electron in the conduction band and a neutral silicon dangling bond (D°). Note that for $E_x \leq 1.2$ eV, where essentially the entire PL lineshape is generated by two-step excitations, the PL lineshape is very similar, at least on a log scale, to the PL generated entirely by one-photon excitation. This similarity may suggest that the PL decay at 80 K is geminate (involves an electron and hole created by the same photon or through the same D° defect) for all values of E_x . In any case, the two-step excitation processes are very efficient in generating excited carriers even at energies as high as 1.6 eV. This statement remains correct at least up to

Fig. 1. PL intensities (logarithmic scale) at 80 K as functions of energy for different values of excitation energy, E_x , as labeled on the figure. Selected error bars are shown at low signal levels. Breaks in the data occur near E_x because of the influence of the strong laser exciting light on the measurement of the much weaker PL signals. Data below about 1.5 eV were taken using a Ge detector and those above about 1.5 eV with a GaAs detector. See the text for details.

temperatures as high as 200 K. [2,3] Whether or not this absorption process is important at temperatures above 300 K in PV devices is not yet clear.

(ii) Local Motion of Bonded Hydrogen in a-Si:H

Previous studies of hydrogenated amorphous silicon have revealed that there are two distinct hydrogen environments that are spatially isolated from each other. In NMR measurements these two environments are manifested in a narrow [full width half maximum (FWHM) of ~ 4 kHz] Lorentzian line superimposed on a broad Gaussian (~ 25 kHz FWHM) line. The narrow line can be explained as due to the contribution of protons that are either randomly distributed or slightly clustered (dilute component) in the bulk of the material, and the broad line can be attributed to protons that are strongly clustered (clustered component), perhaps distributed on the internal surfaces of microvoids. We have recently completed a detailed study of the

Fig. 2. The macroscopic diffusion constant as measured at 500 K by SIMS¹ in various samples of undoped, doped, and compensated a-Si:H plotted as a function of the rate of local motion $(T_{1D})^{-1}$ as measured at 297 K by the ¹H NMR dipolar echo technique [4]. Because of the different temperatures at which the two measurements were made and the lack of a clearly defined activation energy for the dipolar echo data, the functional form (power law exponent) exhibited by this plot carries no obvious physical significance. The doping levels in the a-Si:H samples are as follows: ■ 10^{-4} B-doped; ▲ 3×10^{-5} B-doped; ◆ 10^{-5} B-doped; □ 10^{-3} P-doped; ● 10^{-3} P/B-compensated; ○ undoped.

microscopic motion of the clustered and dilute hydrogen in intrinsic, doped (B or P), and compensated (B and P together) a-Si:H.

By studying the temperature dependence of the dipolar spin-lattice relaxation time, T_{1D} , we can probe the motion of hydrogen in amorphous silicon on a microscopic scale (up to a few tens of angstroms). We studied the temperature dependence of T_{1D} in all samples. If one assumes that the variation of T_{1D} with temperature is thermally activated, then an estimate of this activation energy yields a value of ≤ 0.2 eV in all cases. The heavily-doped samples exhibit the smallest activation energies and the intrinsic and compensated samples the largest. In all cases these values are much smaller than the activation energies for macroscopic diffusion (as measured by SIMS) which are between 1.2 eV and 1.4 eV.

It is tempting to compare these microscopic results with the previously measured values for the macroscopic diffusion constant. This procedure is, of course, dangerous in an inhomogeneous material, but will allow us to place a bound on the degree to which the local "diffusion" (local jump frequency actually) is faster than the measured macroscopic diffusion constant. Figure 2 shows the relationship between the diffusion constant D_H from SIMS and the local jump frequency from the NMR. There appears to be a direct relationship between these two quantities.

Because the macroscopic diffusion constants D_H are time dependent according to the function t^β where $\beta \approx 0.2$, one must be certain that this time dependence does not account for the measured differences between the microscopic and macroscopic results. The macroscopic measurements are typically made on the scale of tens to hundreds of hours while the T_{1D} measurements are on the scale of 1 ms. However, even when D_H is adjusted for this vast difference in measurement times, the macroscopic value is over 20 orders of magnitude greater than the microscopic measurement would indicate.

Whether or not the local motion can be described as a diffusion mechanism, or is perhaps more appropriately described as a non-diffusive process such as a local tunneling mechanism, is still unclear. The trend shown in Fig. 2 would suggest that the two diffusion processes are related, but any detailed model suggested to date has difficulty with such rapid local motion for essentially all of the hydrogen in the sample. Clearly, an accurate model description of these results will have strong implications for the role of local hydrogen motion in the metastabilities observed in a-Si:H, including perhaps an understanding of the Stabler-Wronski effect.

(iii) Optical Activation of Inefficient Sulfur Donors in a-Si:H

Alloying a-Si:H with varying amounts of sulfur (a-SiS_x:H alloys) produces an increase in the n-type conductivity and a decrease in the conductivity activation energy with increasing sulfur concentration up to approximately $x = 0.01$. In films made by the PECVD technique, the H concentration remains approximately 10 at. % independent of x in this alloy system. At $x = 0.01$ the room temperature conductivity, σ , is approximately $2 \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ and the activation energy, ΔE , is about 0.6 eV. Therefore, compared to n-type doping with phosphorus or arsenic, the sulfur doping is very inefficient. [5,6] By analogy with the situation in crystalline silicon, one can understand at least qualitatively the doping in a-SiS_x:H. In crystalline silicon both S and Se are efficient (usually substitutional) double donors. It is easy to understand why sulfur is such an inefficient dopant in a-SiS_x:H because most of the time it goes into the amorphous network two-fold coordinated, just as it does in SiS₂ glass.

Perhaps the most compelling evidence for the n-type doping behavior of some of the sulfur in a-SiS_x:H is the effect that this element has on compensating p-type samples. For essentially all sulfur concentrations ($x < 0.1$), the addition of boron is much less effective in producing p-type conductivity than it is in a-Si:H. For example, for $x \approx 10^{-3}$, the addition of about 10^{-3} boron produces a dark conductivity that is more than an order of magnitude less than that observed in a-Si:H at the same boron doping level. At larger sulfur concentrations the effect of compensation can be even larger.

In addition to the doping, there are metastabilities introduced by alloying with sulfur that are different from those that commonly occur in a-Si:H. This fact is most easily seen at high sulfur concentrations, $x > 0.01$, where one is dealing with silicon-sulfur alloys. For these materials there exists a metastable, photo-induced increase in the dark conductivity similar to that which has been observed in compensated samples of a-Si:H, in doping modulated samples, and in some multilayer heterostructures of a-Si:H and other amorphous alloys. This metastable increase has often been called persistent photoconductivity (PPC). The PPC effect has the opposite effect

on both the dark and photo-conductivities from that of the well-known Staebler-Wronski effect. The PPC effect also exhibits slightly different annealing behavior.

At lower sulfur concentrations ($x < 0.01$), the PPC effect becomes relatively less important, and there exists a competition between the ordinary Staebler-Wronski and the PPC effects. This situation is shown for the dark and photoconductivities in Fig. 3. From this figure it is apparent that at a sulfur concentration of about $x = 6 \times 10^{-3}$, the dark conductivity actually increases slightly after prolonged light soaking and the photoconductivity decreases much less than in a-Si:H. At these concentrations we have suggested [5,6] that the PPC effect is simply the optical activation of sulfur-related donors that have been de-activated, or passivated, by nearby hydrogen during growth. A similar effect occurs in hydrogenated crystalline silicon doped with sulfur or selenium. This optical activation is reversible since annealing at elevated temperatures will return the dark and photo-conductivities to their original values. As a result of the optical activation, the dark conductivity increases, the activation energy decreases, and the Fermi level moves toward the conduction band. These changes are reversed upon annealing.

If one accepts the above hypothesis, then the PPC effect is simply the optical activation of inefficient sulfur donors in a-SiS_x:H alloys. This effect occurs even at low sulfur concentrations where it is partially masked by the ordinary Staebler-Wronski effect. We have suggested that this additional metastability may be used to produce more stable intrinsic layers for PV devices [6] based on a-Si:H, but the suggestion has yet to be tested carefully.

Fig. 3. Dark conductivities (open symbols) and photoconductivities (solid symbols) at 300 K for $a\text{-SiS}_x\text{:H}$ alloys as functions of irradiation time with 100 mW/cm^2 of white light. The sulfur concentrations are 5.6×10^{-3} , 4.0×10^{-5} and $< 10^{-6}$ for the circles, squares and triangles, respectively. Note that the photoconductivity data for the "intrinsic" sample (filled triangles) have been divided by a factor of 10 for clarity. The "intrinsic" sample was made to have the same activation energy for dark conductivity as the sample containing 5.6×10^{-3} sulfur ($\Delta E \sim 0.77 \text{ eV}$). Arrows indicate the dark conductivities in the annealed state.

References

1. "Excitation Spectroscopy of Thin-Film Disordered Semiconductors" S.Q. Gu, P. C. Taylor, J.T. McKinley, A. Ueda, X. Wang and N.H. Tolk, SPIE Conf. Proc. 1854, 77 (1993).
2. "Photoluminescence Above the Excitation Energy in a-Si:H" X. Yin, J.M. Viner, S.Q. Gu, M.E. Raikh, and P. C. Taylor, Phys. Rev. B 49, 5073 (1994).
3. "Below-Gap Excitation of Photoluminescence in a-Si:H," X. Yin, M.E. Raikh, and P. C. Taylor, MRS Symp. Proc. 377, 167 (1995).
4. "Hydrogen Motion in Hydrogenated Amorphous Silicon (a-Si:H)" P. Hari, P. C. Taylor, and R.A. Street, J. Non-Cryst. Solids 198-200, 52 (1996).
5. "Optical Activation of Inefficient Sulfur Dopants in Hydrogenated Amorphous Silicon: A New Metastable Effect" S.L. Wang and P. C. Taylor, Solid State Commun. 95, 361 (1994).
6. "The Potential of Hydrogenated Amorphous Silicon-sulfur Alloys for Absorber Materials in Photovoltaic Devices" S.L. Wang and P. C. Taylor, MRS Symp. Proc. 420, 873 (1996).
7. "Optically Detected ESR Studies of Recombination Processes in a-Si:H D. Mao and P. C. Taylor, J. Non-Cryst. Solids 190, 48 (1995).
8. "Spin Dependence of Photoinduced Excitations in a-Si:H" N. Schultz, Z.V. Vardeny, and P. C. Taylor, MRS Symp. Proc. 467, (1997), in press.
9. "Light-Induced Effects in Hydrogenated Amorphous Silicon Films: Study of Stability" Jong-Hwan Yoon, B. Yan, P. C. Taylor, and Czang-Hol Lee, MRS Symp. Proc. 467, (1997), in press.
10. "¹H NMR in μ c-Si:H Deposited with Different Plasma Excitation Frequencies and Silane Concentrations" P. Hari, P. C. Taylor, and F. Finger, MRS Symp. Proc. 420, 491 (1996).
11. "On the Nature of the Paramagnetic Defects in Hydrogenated Amorphous Silicon Nitride" (D. Q. Chen, J. M. Viner and P. C. Taylor), Solid State Commun. 98, 745 (1996).

Papers Published under Subcontract XAD-3-121142

Since 1993 under this NREL subcontract we have published forty three papers on the electronic and structural properties of a-Si:H and related alloys.

1. "Photoluminescence in Hydrogenated Amorphous Silicon" (P.C. Taylor), *Brazilian J. Phys.* **23**, 132 (1993).
2. "Doping Efficiency of n-Type a-Si:H Doped with a Liquid Organic Source" (K. Gaughan, Zhaohui Lin, J.M. Viner, P.C. Mathur and P.C. Taylor), in *Amorphous Silicon Technology - 1993*, edited by E.A. Shiff, M.J. Thompson, A. Madan, K. Tanaka and P.G. LeComber (Materials Research Society, Pittsburgh, 1993), Vol. 297, p. 503.
3. "Electronic and Optical Properties of n-Type a-Si:H" (K. Gaughan, Z. Lin, J.M. Viner, P.C. Taylor, P.C. Mathur and R.M. Mehra), *J. Non-Cryst. Solids* **164-166**, 343 (1993).
4. "Persistent Photoconductivity in a-Si_{1-x}S_x:H at Low Sulfur Concentration" (S.L. Wang, J.M. Viner, M. Anani and P.C. Taylor), *J. Non-Cryst. Solids* (1993).
5. "Excitation Spectroscopy of Thin-Film Disordered Semiconductors" (S.Q. Gu, P.C. Taylor, J.T. McKinley, A. Ueda, X. Wang and N.H. Tolk), *SPIE Conf. Proc.* **1854**, 77 (1993).
6. "ODESR Studies of a-Si:H with Subgap Excitation" (D. Mao, S.Q. Gu and P.C. Taylor), in *Amorphous Silicon Technology - 1993*, edited by E.A. Shiff, M.J. Thompson, A. Madan, K. Tanaka and P.G. LeComber (Materials Research Society, Pittsburgh, 1993), Vol. 297, p. 333.
7. "Optically Detected ESR Studies of a-Si:H" (D. Mao and P.C. Taylor), *J. Non-Cryst. Solids* **164-166**, 367 (1993).
8. "Photoluminescence Above the Excitation Energy in a-Si:H" (X. Yin, J.M. Viner, S.Q. Gu, M.E. Raikh and P.C. Taylor), *Phys. Rev. B* **49**, 5073 (1994).
9. "Doping Dependence of Local Hydrogen Motion in Hydrogenated Amorphous Silicon" (P. Hari, P.C. Taylor and R.A. Street), in *Amorphous Silicon Technology - 1993*, edited by E.A. Shiff, M.J. Thompson, A. Madan, K. Tanaka and P.G. LeComber (Materials Research Society, Pittsburgh, 1993), Vol. 297, p. 297.
10. "Microscopic Motion of Hydrogen in the Dilute and Clustered Phases of Hydrogenated Amorphous Silicon" (P. Hari, P.C. Taylor and R.A. Street), *J. Non-Cryst. Solids* **164-166**, 313 (1993).

11. "Photoluminescence in B-Doped $\mu\text{-Si:H}$ " (S. Q. Gu, J. M. Viner, P.C. Taylor M. J. Williams, W.A. Turner and G. Lucovsky) , in *Microcrystalline Semiconductors - Materials Science and Devices*, Y. Aoyagi, L.T. Canham, P.M. Fauchet, I. Shimizu and C. C. Tsai, eds. (MRS, Pittsburgh, 1993), Vol. 283.
12. "Nuclear Magnetic Resonance Studies on Hydrogenated Amorphous Silicon Prepared by Very High Frequency Glow Discharge" (Q. Li, P.C. Taylor and F. Finger), *Phil. Mag. B* **69**, 169 (1993).
13. "Electronic and Optical Properties of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ Films Produced From Admixtures of Silane and Ditertiarybutylsilane" (K. Gaughan, J.M. Viner and P. C. Taylor), in Amorphous Silicon Technology - 1994, edited by E. A. Shiff, M. Hack, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1994), Vol. 336, p. 553.
14. "Electronic and Optical Properties of a-Si:H Films Alloyed with Sulfur" (S.L. Wang, Z. H. Lin , J.M. Viner and P. C. Taylor), in Amorphous Silicon Technology - 1994, edited by E. A. Shiff, M. Hack, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1994), Vol. 336, p. 559.
15. "Optical Activation of Inefficient Sulfur Dopants in Hydrogenated Amorphous Silicon: A New Metastable Effect" (S.L. Wang and P. C. Taylor), *Solid State Commun.* **95**, 361 (1994).
16. "Light Induced Metastable Changes in $\text{a-SiS}_x\text{:H}$," (S.L. Wang and P. C. Taylor), in Amorphous Silicon Technology - 1995, edited by M. Hack, E. A. Shiff, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1995), Vol. 377, 307.
17. "Below-Gap Excitation of Photoluminescence in a-Si:H ," (X. Yin, M.E. Raikh and P. C. Taylor) , in Amorphous Silicon Technology - 1995, edited by M. Hack, E. A. Shiff, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1995), Vol. 377, p. 167.
18. "Photoluminescence Above the Excitation Energy in a-Si:H " (X. Yin, J.M. Viner, S. Q. Gu, M.E. Raikh and P. C. Taylor), *Phys. Rev. B* **49**, 5073 (1994).
19. "Effect of Light Soaking on the Local Motion of Hydrogen in Hydrogenated Amorphous Silicon" (P. Hari, P. C. Taylor and R. A. Street), in Amorphous Silicon Technology - 1994, edited by E. A. Shiff, M. Hack, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1994), Vol. 336, p. 329.
20. "Local and Long-Range Hydrogen Motion in a-Si:H ," (P. Hari, P. C. Taylor and R. A. Street), in Amorphous Silicon Technology - 1995, edited by M. Hack, E. A. Shiff, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1995), Vol. 377, 185.

21. "Temperature Dependence of the Electron Spin Resonance in Nitrogen-rich Amorphous Silicon Nitride" (D. Chen, J.M. Viner, P. C. Taylor and J. Kanicki), Phys. Rev. B **49**, 13420 (1994).
22. "Photobleaching of PL and Temperature Dependence of ESR in Nitrogen-Rich Amorphous Silicon Nitride Films" (D. Chen, J.M. Viner, P. C. Taylor and J. Z. Kanicki), in Amorphous Silicon Technology - 1994, edited by E. A. Shiff, M. Hack, A. Madan, M. Powell and A. Matsuda (Materials Research Society, Pittsburgh, 1994), Vol. 336, p. 619.
23. "Photoluminescence and Electron Spin Resonance in Nitrogen-rich Amorphous Silicon Nitride" (D. Chen, J.M. Viner, P. C. Taylor and J. Kanicki), J. Non-Cryst. Solids **182**, 103 (1995).
24. "Optically Detected ESR Studies of Recombination Processes in a-Si:H (D. Mao and P. C. Taylor), J. Non-Cryst. Solids **190**, 48 (1995).
25. M. S. Bennett, J. L. Newton and K. Rajan, Proc. of 7th European PV Conf., edited by A. Goetzberger, W. Palz and G. Willeke (D. Reidel, Dordrecht, The Netherlands, 1986), p. 544.
26. "Sulfur Doping in a-Si_x:H" (S.L. Wang, J. M. Viner and P. C. Taylor), J. Non-Cryst. Solids **198-200**, 94 (1996).
27. "Inefficient Sulfur Doping in Hydrogenated Amorphous Silicon" (S.L. Wang and P. C. Taylor), AIP Conf. Proc. **353**, 487 (1995).
28. "Thermal Stability of Hydrogen and Sulfur Atoms in a-Si_x:H Films" (T. Itoh, S. Nitta, S. L. Wang and P. C. Taylor), J. Appl. Phys. **80**, 6028 (1996).
29. "¹H NMR in μc-Si:H Deposited with Different Plasma Excitation Frequencies and Silane Concentrations" (P. Hari, F. Finger and P. C. Taylor) MRS Symp. Proc. **420**, 491 (1996).
30. "Photoluminescence in Hydrogenated Amorphous Silicon with Sulfur" (S. Chen, S. L. Wang, J. M. Viner and P. C. Taylor) MRS Symp. Proc. **420**, 605 (1996).
31. "Hydrogen Motion in Hydrogenated Amorphous Silicon (a-Si:H)" (P. Hari, P. C. Taylor and R. A. Street) J. Non-Cryst. Solids **198-200**, 52 (1996).
32. "New Nitrogen-Related Defects in Nitrogen-Rich a-Si_xN_{1-x}:H" (D. Q. Chen, J.M. Viner and P. C. Taylor), J. Non-Cryst. Solids **198-200**, 334 (1996).
33. "On the Nature of the Paramagnetic Defects in Hydrogenated Amorphous Silicon Nitride" (D. Q. Chen, J. M. Viner and P. C. Taylor), Solid State Commun. **98**, 745 (1996).

34. "Optically Detected Magnetic Resonance Studies of Undoped a-Si:H" (N. Schultz, Z. V. Vardeny and P. C. Taylor) MRS Symp. Proc. **420**, 593 (1996).
35. "The Potential of Hydrogenated Amorphous Silicon-Sulfur Alloys for Absorber Materials in Photovoltaic Devices" MRS Symp. Proc. **420**, 873 (1996).
36. "The Potential of Hydrogenated Amorphous Silicon-Chalcogen Alloys for Photovoltaic Applications: The Role of Persistent Photoconductivity" (S.L. Wang, J.M. Viner, P.C. Taylor, T. Itoh and S. Nitta), *NREL/SNL Photovoltaics Program Review*, edited by C.E. Witt, A. Al-Jassim and J.M. Gee (AIP Press, New York, 1997), Vol 394, p. 557.
37. "Spin Dependence of Photoinduced Absorption in a-Si:H" (N. Schultz, Z.V. Vardeny and P.C. Taylor), in *Amorphous and Microcrystalline Silicon Technology - 1997*, edited by S. Wagner, M. Hack, E.A. Schiff, R. Schropp and I. Shimizu (Materials Research Society, Pittsburgh, 1997), Vol. 467, p. 179.
38. "Role of SiH₂ in ¹H NMR of μ c-Si:H Deposited with Different Plasma Excitation Frequencies and Silane Concentrations" (P. Hari, P.C. Taylor and F. Finger), in *Advances in Microcrystalline and Nanocrystalline Semiconductors-1996*, edited by P.M. Fauchet, R.W. Collins, J.-C. Vial, I. Shimizu, P.A. Alivisatos and T. Shimada (Materials Research Society, Pittsburgh, 1997), Vol. 452.
39. "Light-Induced Effects in a-Si:H Films Alloyed with Sulfur" (Jong-Hwan Yoon, P.C. Taylor, B. Yan, and Czang-Ho Lee), in *Amorphous and Microcrystalline Silicon Technology - 1997*, edited by S. Wagner, M. Hack, E.A. Schiff, R. Schropp and I. Shimizu (Materials Research Society, Pittsburgh, 1997), Vol. 467, p. 97.
40. "Electron Spin Resonance of Hydrogenated Amorphous Silicon Alloyed with Sulfur" (B. Yan and P.C. Taylor), in *Amorphous and Microcrystalline Silicon Technology - 1997*, edited by S. Wagner, M. Hack, E.A. Schiff, R. Schropp and I. Shimizu (Materials Research Society, Pittsburgh, 1997), Vol. 467, p. 103.
41. "Relaxation to Hopping Conductivity in Sulfur-Doped Hydrogenated Amorphous Silicon" (J.-H. Yoon and P.C. Taylor), J. Non-Cryst. Solids (1998), in press.
42. "Light-Induced Recombination Centers in Hydrogenated Amorphous Silicon-Sulfur Alloys" (J.-H. Yoon, P.C. Taylor and Czang-Ho Lee), J. Non-Cryst. Solids (1998), in press.
43. "Defect Structure in Nitrogen-Rich Amorphous Silicon Nitride Films" (B. Yan, J. H. Dias da Silva and P.C. Taylor), J. Non-Cryst. Solids (1998), in press.

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Appendix A

Excitation Spectroscopy of Thin-Film Disordered Semiconductors

S.Q. Gu, P.C. Taylor, J.T. McKinley, A. Ueda, X. Yang and N.H. Tolk, SPIE Conf. Proc. 1854, 77 (1993).

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