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ADVANCED AMORPHOUS MATERIALS FOR PHOTOVOLTAIC CONVERSION

SEMIANNUAL REPORT

OCTOBER 1, 1979 - MARCH 31, 1980

R.W. GRIFFITH, A.E. DELAHOY, M.D. HIRSCH,
F.J. KAMPAS, AND P.E. VANIER

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Table of Contents

ADVANCED AMORPHOUS MATERIALS FOR PHOTOVOLTAIC CONVERSION

	Page
List of Figures	iv
Summary	1
I. Introduction	3
II. Plasma Deposition System with Apparatus for Optical Emission Spectroscopy	4
III. Results from Optical Emission Spectroscopy	5
IV. Effects of Incorporated Atmospheric Impurities: Modifications in Optoelectronic Behavior	13
A. Majority-Carrier Transport	14
B. Minority-Carrier Transport	18
C. Expanded Discussion of Anomalous Photoconductivity	20
Table 1	26
References	27

List of Figures

	Page No.
Figure 1. Block diagram of apparatus for optical emission spectroscopy	28
Figure 2. Optical emission spectrum from 180-350 nm of silane rf glow discharge. Discharge conditions were 50 W and 100 mTorr. The 0.75 m monochromator was used with 0.5 mm slits, a scan rate of 25 nm min ⁻¹ , and a 0.1 s time constant	28
Figure 3. Spectrum from 300-450 nm. Same conditions as Fig. 2.	28
Figure 4. Spectrum from 400-670 nm. Same conditions as Fig. 2.	28
Figure 5. Intensities of the Si(288 nm) line, the SiH(414 nm) band, and the H _α (656 nm) line vs rf power at 100 mTorr	29
Figure 6. Optical emission spectrum of silane rf glow discharge (15 W, 100 mTorr) containing 1000 ppm O ₂ . The 0.75 m monochromator was used with 0.5 mm slits, a scan rate of 2.5 nm min ⁻¹ , and 1 s time constant	29
Figure 7. Emission spectra of silane rf glow discharges (50 W, 250 mTorr) showing the differences in SiCl emission for two different silane tanks. Also shown is emission from N ₂ (C ³ Π _u - B ³ Π _g) when 1000 ppm NH ₃ is added (upper spectrum) or when 1000 ppm N ₂ is added (lower spectrum). The 0.2 m monochromator was used with 0.5 mm slits, a scan rate of 25 nm min ⁻¹ , and 1 s time constant	30
Figure 8. Ratio of intensities of the N ₂ (358 nm) band to the Si(391 nm) line vs concentrations of N ₂ (50 W, 250 mTorr)	30
Figure 9. Emission spectrum of the 50 W argon discharge used to clean the substrates prior to deposition of a-Si:H alloys. Argon pressure is 100 mTorr	30
Figure 10. Dark conductivity versus reciprocal temperature for a-Si:H alloy produced under low impurity conditions, and for alloy grown with 1000 ppm N ₂ in the silane gas stream.....	30
Figure 11. Optical bandgap E ₀ deduced from plot of (αhν) ^{1/2} versus photon energy hν at room temperature	31

List of Figures (Cont'd.)

	Page No.
Figure 12. Photoconductivity versus reciprocal temperature as a function of impurity content in the silane gas stream (50 W, 250 mTorr, $T_s = 260^\circ\text{C}$). Low impurity Film a was deposited with no intentional impurities; Film b with 1000 ppm N_2 ; Film c with 1000 ppm O_2 ; and Film d with 540 ppm N_2 and 1000 ppm O_2 . Flux $f_\lambda = 10^{14} \gamma/\text{s cm}^{-2}$ at $\lambda = 550 \text{ nm}$	31
Figure 13. Dark conductivity and photoconductivity versus reciprocal temperature for n^+ -type, nitrogen-doped film produced in presence of airleak (15 W, 100 mTorr, $T_s = 370^\circ\text{C}$). Flux $f_\lambda = 10^{14} \gamma/\text{s cm}^{-2}$ at $\lambda = 600 \text{ nm}$	31
Figure 14. Photoconductivity versus reciprocal temperature for phosphorous-doped a-Si:H alloy. Flux $f_\lambda = 10^{14} \gamma/\text{s cm}^{-2}$ at $\lambda = 600 \text{ nm}$	31
Figure 15. Infrared transmission spectrum of oxygenated alloy a-Si:(H,O)	31
Figure 16. Effects of impurity incorporation on illuminated J-V characteristics for Schottky solar cell structure $\text{SiO/Pd/a-Si:(H,O,N)/n}^+\text{a-Si:H/substrate}$. Bulk alloy layer is produced: a) under low-impurity processing conditions; b) in the presence of 3000 ppm air	32
Figure 17. Anomalous peaks with thermal quenching in photoconductivity versus reciprocal temperature. Flux $f_\lambda = 10^{14} \gamma/\text{s cm}^{-2}$ at $\lambda = 550 \text{ nm}$	33
Figure 18. Supralinearity in photoconductivity as a function of illumination intensity ($\lambda = 550 \text{ nm}$). Dashed line is monomolecular (linear) growth	33
Figure 19. Simple two-level model for explaining anomalous photoconductivity (top figure): (a) supralinearity (increasing f); (b) thermal quenching (increasing T)	33

Semiannual Report

(Oct. 1, 1979 - Mar. 31, 1980)

Summary

The primary objectives of this project are twofold: i) to investigate new amorphous semiconductor (a-SC) materials, in which recombination centers are passivated, using plasma deposition techniques; and ii) to characterize the optoelectronic properties pertaining to both majority-carrier and minority-carrier transport in as-deposited films and in devices. The specific goals in FY 1980 are: i) to continue investigations of the effects of atmospheric impurities, i.e., nitrogen and oxygen, on the optoelectronic properties of a-Si:H alloys; and ii) to initiate a study of the effects of these impurities upon the photovoltaic conversion efficiencies of diagnostic devices that are fabricated using such alloys.

In the last six months the following activities were emphasized in the program: i) an expansion of plasma studies using optical emission spectroscopy in order to identify emitting reactive species due to impurities; ii) electrical and optical measurements on alloys with calibrated impurity levels by measurements of photoconductivity, photoluminescence, vibrational spectroscopy, etc.; and iii) completing the apparatus for device measurements of spectral response, dark I-V characteristics, illuminated I-V characteristics, etc. Associated with the last activity, the fabrication of solar cells was begun using low-impurity a-Si:H materials and various a-Si:(H,O,N) alloys.

1.) Optical emission spectroscopy was routinely used to monitor the plasma in order to detect impurities that can potentially affect film properties. The following impurity species were detected by this technique as a function of processing conditions: N_2 , SiO, and SiCl. The presence of N_2 and SiO in the plasma was directly correlated with altered film properties. The SiCl molecule arises from the decomposition of unintentional chlorosilane impurities

originally contained in the silane.

2.) Further documentation has been obtained of the effects of oxygen and nitrogen impurities upon film properties. Results are emerging with regard to the effects of impurities upon solar cell conversion efficiency.

A. Majority-carrier transport

Alloys that are deficient in both impurities, or in either impurity, were found to exhibit anomalous behavior in photoconductivity: the phenomena of thermal quenching, supralinearity, and infrared quenching were all observed. This anomalous behavior was found for a-Si:H alloys produced under a wide range of processing conditions: $P = 15\text{--}100\text{ W}$, $p = 30\text{--}1000\text{ mTorr}$, and nominal substrate temperatures up to medium-high values, $T_s \approx 300^\circ\text{C}$. Classic behavior in photoconductivity versus reciprocal temperature is restored by the synergistic incorporation of oxygen and nitrogen impurities. These impurities can be added in calibrated concentrations to the silane gas stream, or equivalently, via calibrated airleaks directly into the deposition chamber. At very high substrate temperatures (e.g., $T_s = 370^\circ\text{C}$), extremely photoconductive films can be produced by tailoring the impurity incorporation in alloys, e.g., $\sigma_p(300\text{ K}) > 10^{-3}\ (\Omega\cdot\text{cm})^{-1}$ was obtained under AM1 illumination. Such alloys show the effects of pronounced electronic doping by nitrogen on the basis of: i) Fermi level shifts toward the conduction band edge; ii) the classic doped appearance of the photoconductivity versus reciprocal temperature; and iii) the retention of normal optical gaps $E_0 = 1.65\text{--}1.70\text{ eV}$. Highly oxygenated a-Si:(H,O) alloys exhibited very poor photoconductivity. For example, $\sigma_p(300\text{ K}) = 6 \times 10^{-11}\ (\Omega\cdot\text{cm})^{-1}$ was found at a flux of $10^{14}\ \gamma\text{'s cm}^{-2}\text{s}^{-1}$ for an alloy with ~40% incorporated oxygen.

B. Minority-carrier transport

Relative photoluminescence efficiency was measured at low temperatures as a function of impurity incorporation for several processing conditions.

As an example, the relative peak efficiency for alloys produced at $T_s = 370^\circ\text{C}$ was found to decrease by only 15% when ~ 3000 ppm air was directly admitted into the plasma deposition chamber. Measurements of dark conductivity yielded an activation energy of 0.40 eV for the alloy doped by the airleak.

As a function of impurity incorporation, preliminary correlations were made between the relative photoluminescence efficiency of alloys and the solar cell efficiency of diagnostic Schottky devices in which such alloys constitute the bulk layers. For this purpose, a typical device structure was chosen to be $\text{SiO/Pd/a-Si:(H,O,N)/n}^+\text{a-Si:H/Mo}$. It was found that solar cell efficiency (particularly J_{sc}) is a more sensitive measure of impurity incorporation than that provided by the low-temperature photoluminescence efficiency. For example, in the case of the aforementioned alloys, the solar cell efficiency decreased by 51% owing to the airleak ($\sim 100 \text{ mW cm}^{-2}$ illumination with a tungsten lamp). As will be discussed, similar results with impurity incorporation are exhibited for alloys that are produced at lower substrate temperatures and under an expanding range of processing conditions.

I. Introduction

Hydrogenated amorphous silicon alloys (a-Si:H) show considerable promise for the fabrication of thin-film solar cells.⁽¹⁾ This material exhibits high optical absorptance, can be produced relatively easily, and can be electronically doped. Solar cells with the highest efficiency have so far been fabricated from a-Si:H alloys that are deposited via the glow discharge decomposition of silane (SiH_4). However, the optoelectronic properties of these materials, and therefore the photovoltaic efficiency, are quite dependent upon preparation conditions. Such processing conditions include pressure, flow rate, substrate temperature, rf power, and impurity levels. Indeed, in the last case the effects of atmospheric impurities upon film properties have already been reported for plasma-deposited a-Si:H materials^(2,3) as well as for reactively-

sputtered materials.^(4,5) The optimization of electrical properties for a-Si:H alloys may result from an understanding of the relationship between the processing conditions and the specific chemical reactions in the plasma that lead to film growth. Therefore, we are studying correlations between the optoelectronic properties of as-deposited a-Si:H alloys, devices fashioned using these alloys, and the plasma chemistry.⁽⁶⁾ Optical emission spectroscopy^(2,3,7) is one tool for understanding the plasma chemistry that we shall report upon here.

II. Plasma Deposition System with Apparatus for Optical Emission Spectroscopy

The rf capacitively-coupled plasma deposition system was described previously.⁽³⁾ In the deposition chamber of this parallel-plate cylindrical system, silane gas flows radially-inward from a circumferential ring on the bottom electrode (25 cm diameter). The gas is exhausted through a pumping port at the center of this electrode by a mechanical-pump/roots-blower combination. Since the roots blower has a specified base pressure of 0.1 mTorr, backstreaming is minimized from the pump to the deposition chamber. Radio frequency power is applied to the bottom electrode, while the top electrode is grounded. Substrates are placed on the bottom electrode which is resistively heated. Prior to deposition, the chamber is diffusion-pumped at the desired substrate temperature into the 10^{-7} Torr range in order to reduce contamination from adsorbed gases and moisture. For cleaning the substrates, a 50 W argon discharge at 100 mTorr pressure is maintained for 30 min after the diffusion pumping. Typical power levels and chamber pressures maintained during depositions were 15-50 W and 30-250 mTorr, respectively.

Quartz windows are used on the deposition chamber so that the ultraviolet region of the spectrum (>180 nm) may be studied by optical emission spectroscopy (OES). These windows are at the ends of three-inch (7.6 cm) ports that contain metal screens which prevent film deposition upon the windows. The optical system for OES is conventional (see Fig. 1). Two different monochromators were

employed: a 0.2 m Jobin-Yvon monochromator with a R136 Hamamatsu photomultiplier tube (PMT), and a Spex 0.75 m monochromator with a R955 Hamamatsu PMT in a thermoelectrically cooled housing that reduces the dark current. The latter monochromator was used for higher resolution studies and for accurately determining the wavelength of lines to be identified. The monochromator with the smaller focal length was useful for routine monitoring of deposition conditions. Current from the PMT's was measured by a Keithley 480 picoammeter. The analog output from the picoammeter was smoothed by an op-amp RC filter and plotted on a strip-chart recorder. This low-pass filter was useful for removing noise from the emission spectrum that was due to fluctuations in the discharge (particularly at low pressures). A slit width of 0.5 mm was commonly employed with both monochromators, giving a resolution of 2 nm with the 0.2 m monochromator and 0.5 nm with the 0.75 m monochromator. A typical scan rate of the spectrum was 25 nm min^{-1} , although scan rates as low as 2.5 nm min^{-1} were occasionally used with the 0.75 m monochromator for higher resolution or higher sensitivity.

III. Results from Optical Emission Spectroscopy

We first summarize the results of optical emission spectroscopy^(2,3,7) and then proceed to a detailed survey of representative spectra.

Optical emission spectroscopy (OES) of the silane glow discharge deposition of a-Si:H reveals the presence of the species Si, SiH, H, H₂, and possibly SiH⁺. The importance of these species to the growth and electrical properties of a-Si:H alloys is not totally understood, since SiH₂ and SiH₃, which do not emit, are probably also present in significant amounts in the plasma. Therefore, in order to extract maximal information about the plasma chemistry in film deposition, OES should be regarded as a useful tool that must be complemented by additional techniques. The species N₂, SiO, and SiCl are also detected under certain circumstances. The high sensitivity of OES for N₂ is quite useful as small amounts of this impurity can affect the electrical

properties of a-Si:H films. Oxygen, however, is probably more easily detected by infrared transmission spectroscopy of the films than by the observation of SiO in the discharge emission spectrum. OES is a very sensitive method for the detection of chlorosilane impurities in silane tanks, but further studies are required to learn what effects small concentrations of these impurities have upon film properties.

An optical emission spectrum scanned over 180-670 nm using the 0.75 m monochromator is shown in Figs. 2-4 for a silane glow discharge at 50 W and 100 mTorr. Some emission intensities versus rf power are given in Fig. 5. Figure 6 illustrates part of an emission spectrum for an oxygenated deposition (1000 ppm O₂) that was scanned at high sensitivity. The species Si, SiH, SiH⁺, H₂, H, SiCl, SiO, and N₂ appear in these spectra. In this section we discuss: i) the identification of these species; ii) the circumstances under which they appear; and iii) the intensities of the emissions observed. There will also be a brief discussion of the emission spectrum of the argon cleaning discharge. A list of the stronger emission features attributed to the various species is given in Table 1.

In the emission spectrum of Fig. 2, the most prominent features are the strong lines in the ultraviolet due to the electronic transitions of atomic silicon. Some of the multiplets consist of a single line (such as Si UV43 at 288 nm), whereas others contain as many as six components (such as Si UV1 at 251-253 nm) owing to fine structure effects; i.e., to spin-orbit coupling. The silicon multiplets UV1 and UV3 are partially resolved in Fig. 2.

A complicated band at 413-428 nm due to SiH is the next most important feature of the emission spectrum. Several other weaker bands due to SiH are also seen. (See Fig. 3 and Table 1.) All of these bands correspond to the same electronic transition (a de-excitation to the electronic ground state), but they each comprise distinct vibronic bands (specific vibrational transitions

with unresolved rotational structure). For example, the most prominent SiH band includes the six separate vibronic bands $(\nu, \nu)_{0,1}$, with vibrational quantum numbers $\nu = 1, 2, 3$ and branch indices $i = 1, 2$. A weak band at 399 nm has been tentatively identified as SiH^+ . Other bands expected for SiH^+ have not been found, nor has it been possible to resolve the 399 nm band into components that could be compared with the known structure of this band, because of the low emission intensity. This feature does not appear at all under some sets of processing conditions, particularly at lower power. The weakness of the emission intensity for the ion SiH^+ relative to that for the neutral species SiH is to be expected. In the plasma it is more probable that electron-impact processes lead to a low-lying excited state of the neutral molecule (~ 3 eV above the ground state) than that ionization of the SiH molecule (ionization potential of 8 eV) is effected by the tail of the electron energy distribution.

Emission from atomic and molecular hydrogen is seen in the visible part of the spectrum (Figs. 3 and 4). As with SiH^+ , the intensity of the H and H_2 emission relative to Si and SiH emissions, depends greatly upon reactor conditions. For example, at 15 W and 100 mTorr, only the Balmer alpha line H_α (656 nm) and several of the molecular hydrogen lines can be seen. By contrast, at 50 W Fig. 4 shows the Balmer series H_α , H_β (486 nm) and H_γ (434 nm), as well as the open rotational structure of H_2 . The continuum background seen in Figs. 2 and 3 is due to H_2 ; its intensity also greatly depends upon rf power and pressure. The extent of the tail for the electron energy distribution can be appreciated by noting that initial energies for the emitting state in the H_2 spectra are as high as 14 eV above the ground state.

Intensity dependences as a function of power are shown in Fig. 5 for the Si (288 nm) line, the SiH (414 nm) band, and the H_α (656 nm) line at 100 mTorr. These measurements were made with the 0.2 nm monochromator. Emission lines from H_2 have intensity dependences that are similar to H in this figure.

Weak emission from the SiO molecule was observed when small amounts of oxygen were intentionally admixed with the silane. For example, Fig. 6 shows SiO emission bands detected from a silane glow-discharge in which 1000 ppm O₂ was added at low pressure (i.e., no premixing in the gas manifold occurred). The small relative emission intensity of SiO with respect to atomic Si is apparent from this figure. Each SiO peak corresponds to a distinct vibrational transition; the common electronic transition ($A^1\Pi-X^1\Sigma^+$) involves a de-excitation from an initial state ~5.3 eV above the ground state.

An emission peak at 281 nm, seen originally with the 0.2 m monochromator only when one specific silane tank was used, was tentatively assigned to SiCl (see Fig. 7). This molecule could arise by the decomposition of chlorosilane impurities originally contained in the silane. Such impurities are possible since silane is often manufactured by the reduction of SiCl₄ or of SiHCl₃. Using the 0.75 m monochromator, it was subsequently possible to resolve the SiCl peak into two components at 280.7 nm and 282.4 nm, and to detect these components when other silane tanks were used (see Fig. 2). For each of three silane tanks tested, analysis by SIMS⁽⁸⁾ showed a qualitative correlation between the concentration of chlorine incorporated in a-Si:H films and the emission intensity of SiCl observed in the plasma. In particular, a monotonic increase in emission intensity tank-by-tank corresponds to the following ordering of ranges of incorporated Cl (the ranges were defined by a variety of processing conditions): 2-60 ppm, 40-100 ppm, and 400-600 ppm.

There does not appear to be any obvious correlation between the chlorine concentration and electrical properties of a-Si:H films, although an inverse relation with photoconductive response is possible. The fact that our three tanks of silane have varying concentrations of other impurities, particularly H₂ (0.17-4.0%) and N₂ (5-600 ppm), complicated the determination of any unique effect of the chlorosilanes. Of course, the maximum concentration of Cl in an

a-Si:H film was found to be only 600 ppm. If the chlorine acts to passivate defects by participation in bonds such as $\equiv\text{SiCl}$ and $=\text{SiHCl}$ it is possible that a small concentration would not have an appreciable effect upon electrical properties.

The emission from molecular nitrogen (second positive system) that appears in Figs. 2 and 3 is due to the presence of approximately 40 ppm N_2 impurity in the silane tank used for that particular deposition. According to the manufacturer, the other two silane tanks contained approximately 5 ppm and 600 ppm impurity N_2 . Once again, the sensitivity for detection depends upon processing conditions. For the purpose of calibrating the N_2 content in the plasma, Fig. 8 shows the ratio of the intensity of the N_2 (358 nm) band to the Si(391 nm) line at 50 W, 250 mTorr. These measurements were taken with the 0.2 m monochromator. For this calibration, nitrogen diluted to 1% in ultrahigh-purity argon was added to the silane gas stream.

Emission from N_2 also appeared when the vacuum system developed a leak, when a process gas line had been insufficiently purged, or even when ammonia was added to the silane. The latter case is illustrated in Fig. 7 in which the upper spectrum (1000 ppm NH_3 added to silane gas stream) may be compared with the lower spectrum (1000 ppm N_2 added). The upper spectrum exhibits only the usual emission from the second positive system of N_2 . In this example for which NH_3 was added, the presence of molecules with N-H bonds was not detected by OES -- despite the fact that NH_3 , NH_2 , NH (and NH^+) are all potentially emitting species. Therefore, when NH_3 is introduced into the plasma in sufficiently small quantities, a possible conclusion is that reactive intermediates which arise from the decomposition of this molecule will rapidly reform to produce the rather unreactive, strongly-bonded N_2 molecule (9.8 eV dissociation energy).

An emission spectrum taken during the argon discharge cleaning prior to film deposition is shown in Fig. 9. Emission due to atomic silicon and the OH radical is seen along with the expected argon lines. The atomic silicon is presumably due to silicon sputtered from the lower electrode by Ar^+ bombardment, whereas OH arises from the decomposition of adsorbed water in the discharge. Again, OES can be used as a diagnostic tool for monitoring the presence of adsorbed moisture in the deposition chamber, possibly as a function of time during the argon cleaning.

Silane, like methane, has a continuous absorption spectrum in the vacuum ultraviolet. Absorption begins at about 165 nm (photon energy $h\nu = 7.5$ eV) to produce an excited state which we will denote by SiH_4^* . The continuous nature of the absorption implies that SiH_4^* dissociates or is ionized. Since the ionization energy of silane is approximately 11.7 eV, SiH_4^* must be an unstable state. A recent study of the 147 nm photolysis of silane ($h\nu = 8.4$ eV) gives some hints concerning the decomposition of SiH_4^* .⁽⁹⁾ The products of the decomposition were H_2 , Si_2H_6 , Si_3H_8 , and a solid silicon hydride film. By measuring the concentration of the gaseous products mass spectrometrically as a function of time, the authors concluded that the primary reactions in the photolysis of silane are:

The two reactions were calculated to have quantum yields of 0.83 and 0.17, respectively. The authors indicate that the formation of Si and SiH from SiH_4^* is possible on energetic grounds, but that these primary species do not have to be invoked in order to explain their results. Unfortunately the primary products of eqns. (1) and (2), namely SiH_2 and SiH_3 , have no known emission spectra, despite considerable efforts to detect them. Thus, using OES alone,

it is not possible to study the presence of these species in the silane glow discharge. However, it seems quite likely that SiH_2 and SiH_3 are indeed present, and may, as a function of processing conditions, be important in the growth of a-Si:H alloys. The emitting species Si and SiH that are detected by OES could arise from the decomposition of SiH_4^* or via the decomposition of SiH_2 and SiH_3 .

The SiH^+ ion, tentatively identified in the emission spectrum of Fig. 3, could arise from the ionization of SiH (ionization potential of 8 eV), or from the ionization of SiH_4 . It is known that the "cracking pattern" of silane produces SiH_2^+ , SiH_3^+ , SiH^+ , and Si^+ . The cation SiH_4^+ itself is unstable, e.g., the reaction $\text{SiH}_4^+ \rightarrow \text{SiH}_2^+ + \text{H}_2$ is endothermic by only 0.2 eV. The fact that we did not detect any of the well characterized emission from Si^+ must be due to the low concentration of this species.

Turning now to hydrogen emission spectra in Figs. 2-4, the possible sources of molecular hydrogen include: i) hydrogen impurity in silane tanks; ii) molecular hydrogen produced by subsequent gas-phase reactions of the primary products of silane decomposition; and iii) reactions at the substrate which produce a-Si:H films. Naturally the last source is of the greatest interest. Unfortunately, at this stage very little can be said about surface reactions. From the study of silane photolysis in ref. 9, it was concluded that wall reactions of SiH_3 and SiH_2SiH_2 radicals led to film formation. In that case, SiH_2 from eqn. (1) is a major reactive intermediate that would react with SiH_4 before reaching the walls, and so was not involved in film formation. However, the photolysis study was done at silane partial pressures of several Torr. At lower pressures that are appropriate to the plasma deposition described here, a-Si:H alloys are more likely the result simply of polymerization of H, SiH, SiH_2 , and SiH_3 . Preliminary results with atomic absorption spectroscopy of Si indicate that the concentration of this species in the plasma is too low to account for a significant contribution to film formation.

It is difficult to draw any conclusions about the plasma chemistry from the dependences of emission intensity upon power shown in Fig. 5, since these intensities are a measure of the number of excited species that emit. The exponential increase in intensity with power that occurs for lower power reflects the increase in average electron energy with power. The larger slope for the atomic hydrogen emission is due to the higher energy of the initial state for that emission compared to the initial state energies for Si and SiH (see Table 1).

Optical emission spectroscopy appears to be the most sensitive method for the detection of small amounts of nitrogen that can affect a-Si:H film properties. By comparison, it is difficult to detect N_2 in SiH_4 by mass spectrometry since N_2^+ has approximately the same e/m value as Si^+ . The presence of N_2 in SiH_4 can, of course, be inferred by the presence of N^+ in the mass spectrum, but this approach has less sensitivity than OES. It is not surprising that OES failed to detect atomic nitrogen (N) and SiN in our relatively low-power silane glow discharges: N_2 is not very reactive and has a high dissociation energy (9.8 eV). For the same reasons, only small amounts of nitrogen were incorporated in the a-Si:H alloys. For example, gaseous concentrations of 600 ppm N_2 in silane resulted in ~100 ppm N that was incorporated in alloys produced at 50 W and 250 mTorr. The fact that small amounts of incorporated nitrogen can affect the electrical properties of a-Si:H films is presumably related to the ability of N to introduce shallow defects or to act as a donor in the amorphous network (see Sect. IV).

In a sense, the properties of oxygen in the silane glow discharge are opposite to those of nitrogen. Molecular oxygen emits very weakly, in general, and was not seen in any depositions for which O_2 was added. However, oxygen demonstrates extreme reactivity toward silicon hydrides so that, depending upon the manner in which oxygen was added, 0.1% O_2 in the discharge could result in

a-Si:(H,O) alloys with [O] ~40% (see Sect. IV). Since SiO is intrinsically a good emitter, the small intensity in Fig. 6 of the SiO emission compared to the silicon lines (and to the SiH band) implies that the observed SiO was not a reactive intermediate in the incorporation of oxygen in the film. Instead, this emitting species must be by-product of that incorporation. This situation contrasts with the case of chlorine: the small amounts of chlorine incorporated in our a-Si:H films do correspond to the weak emission that is detected from SiCl molecules in the plasma. In other words, SiCl may well be an intermediate in the incorporation of chlorine.

IV. Effects of Incorporated Atmospheric Impurities: Modifications in Optoelectronic Behavior

Many sources of common atmospheric impurities (nitrogen and oxygen) are encountered in the plasma deposition of a-Si:H alloys: ubiquitous airleaks in the system; backstreaming from the pumping system; outgassing of adsorbed chamber air and moisture; impurities in process and carrier gases, etc. It is little wonder, then, that the optoelectronic properties of films reported in the literature to date reflect in varying degree the unintentional incorporation of such impurities as nitrogen, oxygen, carbon, and other elements. Indeed, for otherwise fixed processing conditions in a given deposition system, the proverbial irreproducibility of materials properties may well be ascribed to variable sources and concentrations of impurities from one deposition run to the next.

The effects of impurities upon the photovoltaic quality of a-Si:H alloys have barely been explored. In any definitive study, the solar cell conversion efficiency, the open-circuit voltage, and the short-circuit current would all need to be correlated with calibrated concentrations of impurities contained in the alloy layers of a diagnostic device. Of course, as a function of impurity content, it may also be useful to test the hypothesis that measurements

of low-temperature photoluminescence could provide a guide to minority-carrier transport properties that relate to solar cell efficiencies. The systematic effects of nitrogen and oxygen impurities upon both solar cell efficiency and relative photoluminescence efficiency are topics of our current comparative investigation.

Accordingly, we first discuss the documented effects of atmospheric impurities upon majority-carrier transport (Sect. IV.A) and then briefly note trends that are emerging with regard to the effects of such impurities upon solar cell conversion efficiency (Sect. IV.B). In Sect. IV.C we explore in more detail the nature of anomalous photoconductivity, including the universality of such behavior.

A. Majority-carrier Transport

Rather striking modifications of dark conductivity and especially of photoconductivity are found as the result of the incorporation of nitrogen and oxygen impurities in a-Si:H alloys.^(2,3,10) The separate effects of each impurity have already been studied in the case of reactively sputtered a-Si:H alloys.^(4,5) The details of preparing materials under low impurity conditions, or with calibrated concentrations of impurities in the plasma, are discussed elsewhere.^(2,3,10) We simply note here that the phrase "low impurity" specifically pertains to minimizing sources of impurities during plasma deposition, hence the resulting alloys will be produced with a minimal level of incorporated atmospheric impurities for a given set of processing conditions. Varying the processing conditions clearly alters the film deposition rate, the relative concentrations of reactive species in the plasma due to residual impurities, etc. Therefore actual concentrations of contaminants in "low-impurity" materials vary from one processing condition to the next.

Figure 10 shows the effects upon the dark conductivity of adding 1000 ppm N₂ to the silane gas stream at P = 50 W, p = 250 mTorr, and T_s = 260°C. As

illustrated in Figs. 2, 3, 7, and 8, the N_2 impurity in the plasma can easily be detected by optical emission spectroscopy. In Fig. 10 the dark conductivity for the low-impurity material is (approximately) singly-activated with slope $E_G = 1.02$ eV. From an extrapolation of the quantity $(\alpha h\nu)^{\frac{1}{2}}$, the optical gap for the same material is found to be $E_G \approx 1.65$ eV. See Fig. 11. Hence, E_F lies below midgap for this low-impurity alloy produced at medium-high substrate temperature. By contrast, the film with the nitrogen impurity exhibits phonon-assisted hopping transport below about $T \approx 360$ K. Depending upon the processing conditions, as little as several hundred ppm N_2 can introduce shallow defects that engender hopping in dark transport. The relevance of this observation is, of course, that N_2 is a ubiquitous impurity encountered in plasma deposition. In fact, despite manufacturers' specifications, such levels of N_2 contamination are occasionally found in silane tanks.

Figure 12 illustrates modifications in photoconductivity versus reciprocal temperature owing to the incorporation of oxygen and nitrogen impurities in a-Si:H alloys. Alloys that are deficient in both impurities, or in either impurity, exhibit anomalous behavior in photoconductivity. In particular, the phenomenon of thermal quenching (peaks near room temperature or below) is apparent for Film a (low impurity conditions), and for Films b (1000 ppm N_2) and c (1000 ppm O_2). Anomalous photoconductivity in these alloys is actually characterized by as many as three phenomena: i) the thermal quenching; ii) supralinear dependence upon illumination intensity; and iii) infrared quenching.⁽¹¹⁾ By contrast, synergistic effects of oxygen and nitrogen impurities restore classic behavior in photoconductivity as illustrated for Film d (540 ppm N_2 and 1000 ppm O_2). Analyses by SIMS⁽⁸⁾ show that the transformation $a \rightarrow d$ in Fig. 12 is effected by a twentyfold increase in the incorporated impurity content: from 0.2% O and 20 ppm N to 4% O and 400 ppm N.

The anomalous thermal quenching phenomenon occurs in regions of temperature for which the excess majority carriers far out-number the dark carriers. (See Fig. 12.) On the other hand, the thermal quenching behavior at high temperature in the classic photoconductivity of Film *d* is easily understood by noting that at this flux, the number of dark carriers now exceeds the excess carrier density. Under these circumstances, the density of hole-occupied recombination centers for free-carrier electrons is nearly the same as in thermal equilibrium: the quasi-Fermi levels are not displaced far from the dark Fermi level. Consequently, raising the temperature has the effect of: i) thermally exciting additional holes into the centers; ii) increasing the recombination rate of majority-carrier electrons; and thereby iii) quenching the electron photoconductivity as observed. As a function of illumination intensity, monomolecular recombination $\sigma_p \sim f_\lambda$ is consistently found in this region of temperature.

It is interesting that the introduction of calibrated airleaks directly into the plasma deposition chamber exactly confirms the aforementioned modifications of film properties for medium-high substrate temperature, e.g., $T_s \approx 270^\circ\text{C}$. At rather higher substrate temperatures, alloys produced in this manner exhibit more pronounced effects of electronic doping by nitrogen. For example, Fig. 13 shows the photoconductivity and dark conductivity of an alloy deposited at $T_s \approx 370^\circ\text{C}$ in the presence of ~ 3000 ppm air. The high-temperature activation energy is only $E_g \approx 0.4$ eV, whereas an optical gap of the normal size, namely $E_0 = 1.7$ eV, was found from extrapolation of the quantity $(\alpha h\nu)^{\frac{1}{2}}$. Consistent with the doping of this material, unusually high photoconductivity was also attained: $\sigma_p(300\text{ K}) = 4 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$ at a flux of $10^{14} \gamma/\text{s cm}^{-2}$. The shape of the photoconductivity in Fig. 13 is very similar to the classic behavior in photoconductivity exhibited in Fig. 14 by a film that was intentionally doped with PH_3 under the indicated processing conditions. (For this particular film, doped by 600 ppm PH_3 in the plasma, the room-temperature photoconductivity

increased from $\sigma_p = 1.8 \times 10^{-8} (\Omega \cdot \text{cm})^{-1}$ for the undoped material to $\sigma_p = 4.8 \times 10^{-6} (\Omega \cdot \text{cm})^{-1}$ at a flux of $10^{14} \text{ } \gamma\text{'s cm}^{-2}\text{s}^{-1}$.) Thus, depending upon the processing conditions, nitrogen has the ability to introduce shallow defects (Fig. 10), or to act as a fourfold-coordinated substitutional donor in the amorphous network (Fig. 13).

Even in the absence of an airleak, high substrate temperatures $T_s \approx 325\text{--}375^\circ\text{C}$ may be expected to promote impurity incorporation in materials by at least two mechanisms. Firstly, high T_s significantly increases the outgassing rate of atmospheric (and other) impurities from chamber surfaces into the plasma where active species are created. Of course, this partial chamber "bakeout" prior to deposition may actually decrease certain residual impurity levels, notably water vapor that is one source for oxygen. Secondly, the effect of high T_s is to heal the amorphous network (provided that sufficient hydrogen is incorporated), thereby decreasing the gap state density and permitting more efficient substitutional doping by impurity nitrogen in particular. Both mechanisms will be enhanced for materials grown at low deposition rates. These mechanisms appear to be illustrated by the case of an alloy that was plasma-deposited at a low deposition rate under conditions similar to those shown in Fig. 13, but with no intentional airleak. Depending upon illumination intensity, this material exhibited classic behavior in photoconductivity versus reciprocal temperature. The dark activation energy for this alloy, $E_g \approx 0.77 \text{ eV}$, and the photoconductivity, $\sigma_p(300 \text{ K}) \sim 10^{-6} (\Omega \cdot \text{cm})^{-1}$ at $10^{14} \text{ } \gamma\text{'s cm}^{-2}\text{s}^{-1}$, are more representative of values found in the literature. Of course at high T_s , both impurity incorporation and altered intrinsic Si-H bonding may be responsible for this behavior.

In order to illustrate an extreme example of impurity incorporation, 1000 ppm O_2 was added to the silane glow discharge at low pressure, i.e., no premixing

of oxygen and silane occurred in the gas manifold. Whereas only weak emission was observed from molecular SiO in the plasma (Fig. 6), the resulting film was a true alloy with oxygen, a-Si:(H,O). As shown in the infrared transmission data of Fig. 15, the effects of the oxygen impurity upon the chemical bonding of this alloy are manifested by two features: i) the Si-O-Si asymmetric stretch mode at $\tilde{\nu} \sim 1000 \text{ cm}^{-1}$ (4); and ii) the "induction effect" in which the monohydride $\equiv\text{SiH}$ stretch mode at 2000 cm^{-1} has been displaced to $\sim 2100 \text{ cm}^{-1}$ owing to the backbonding of oxygen in the configuration $\equiv\text{SiHO}$.⁽¹²⁾ (Films produced at 15 W, 100 mTorr contain nearly 100% monohydride bonding.) Using the integrated absorption of the Si-O-Si stretch mode alone, it was estimated that the a-Si:(H,O) alloy contained $\sim 15\%$ oxygen, whereas calibration with analyses by SIMS indicates $\sim 37\%$ incorporated oxygen. Optical and electrical parameters for this highly oxygenated alloy were typical of a dielectric, e.g., the wider optical gap $E_0 = 2.0 \text{ eV}$ and excessively low photoconductivity $\sigma_p(300 \text{ K}) = 6 \times 10^{-11} (\Omega \cdot \text{cm})^{-1}$ at a flux of $10^{14} \text{ } \gamma\text{'s cm}^{-2} \text{ s}^{-1}$. For smaller concentrations of incorporated oxygen, the presence of the Si-O-Si bridging configuration suggests that oxygen may passivate various defects, such as weak molecular bonds. Indeed, several hundred ppm O_2 added to the silane gas stream removes the hopping transport depicted in Fig. 10 and results in dark conductivity identical with the low impurity alloy in that figure.

B. Minority-carrier Transport

As a function of impurity incorporation, preliminary correlations were made between the relative photoluminescence efficiency of alloys and the solar cell efficiency of diagnostic Schottky devices in which such alloys constitute the bulk layers. For this purpose, a typical device structure was chosen to be

$$\text{SiO/Pd/a-Si:(H,O,N)/n}^+\text{a-Si:H/Mo}$$

in which the bulk layer is either an a-Si(H,O,N) alloy or a-Si:H material produced under low-impurity conditions. No attempt was initially made to optimize the efficiency of this structure since the relative conversion efficiency was of interest for various alloys.

Relative photoluminescence efficiency was measured at low temperatures for alloys deposited at several processing conditions. Excitation of photoluminescence was accomplished using a low-power He-Ne laser with a diffuse beam (2 mW, $h\nu = 1.96$ eV). As one example, emission spectra were compared at 50 K for alloys produced under low-impurity conditions versus controlled impurity conditions at $P = 15$ W, $p = 100$ mTorr, and $T_s = 370^\circ\text{C}$. The highest photoluminescence efficiency was attained for the material deposited under low-impurity conditions. The relative peak photoluminescence efficiency was found to decrease by only 15% for an alloy prepared by admitting 3000 ppm air directly into the plasma deposition chamber. In addition to the lack of significant spectral quenching, no low-energy spectral component was observed at 50 K despite the evidence of fairly pronounced impurity doping by the airleak as illustrated in Fig. 13.

By contrast, the solar cell efficiency dramatically decreased owing to the same airleak rate during the growth of the bulk alloy layer. In particular, the efficiency was reduced by 51% at 100 mW cm^{-2} illumination (tungsten lamp) relative to the solar cell fabricated with the alloy produced under low-impurity conditions. This decrease is mainly attributed to a reduction in the short-circuit current J_{sc} . Therefore, solar cell efficiency (and particularly J_{sc}) is a more sensitive measure of impurity incorporation than that provided by the low-temperature photoluminescence efficiency. Now according to Fig. 13, very high photoconductivity was exhibited by the alloy produced in the presence of the airleak. In fact, $\sigma_p(300\text{ K}) \sim 10^{-3} (\Omega\cdot\text{cm})^{-1}$ for AM1 sunlight implies a small bulk series resistance, perhaps $R_s = 0.1\text{--}1\ \Omega\cdot\text{cm}^2$. This improvement is

probably masked, however, by other series resistances. Evidently, minority-carrier recombination is increased owing to impurity incorporation so that better majority-carrier transport is not a guarantee of improved solar cell efficiency.

The illuminated J-V characteristics of Fig. 16 confirm these trends at a lower substrate temperature, namely at $T_s = 270^\circ\text{C}$. Again, the performance of two Schottky devices is compared as a function of impurity incorporation in the bulk alloy layer. For Fig. 16a, the alloy was produced under low-impurity processing conditions. For Fig. 16b, the a-Si:(H,O,N) alloy was deposited in the presence of 3000 ppm air. The indicated efficiency for each characteristic is an external efficiency for the active area. It was measured with a tungsten lamp for which the spectral distribution is shifted to the red compared to AM1 sunlight. In true sunlight (100 mW cm^{-2}), the current J_{sc} and the efficiency are roughly doubled. Figure 16 shows that the solar cell efficiency decreased by 43% as a consequence of increased impurity incorporation in the bulk alloy layer. It is also of interest that the more efficient solar cell was fabricated with an alloy that exhibits an anomalous peak in photoconductivity at low temperature ($T \approx 160 \text{ K}$) because of the low-impurity processing conditions. Further studies with diagnostic devices are being carried out.

C. Expanded Discussion of Anomalous Photoconductivity

In order to explore the nature of anomalous photoconductivity further, we proceed to examine the illumination dependence of the anomalous peaks. Figure 17 shows two anomalous peaks in photoconductivity versus reciprocal temperature for an alloy produced at 50 W, 250 mTorr, and $T_s = 270^\circ\text{C}$. This particular data was obtained at the flux $f_\lambda = 10^{14} \text{ } \gamma/\text{s cm}^{-2} \text{ s}^{-1}$ for wavelength $\lambda = 550 \text{ nm}$ ($h\nu = 2.25 \text{ eV}$). For the thermal quenching side of the T_A peak (high-temperature side), Fig. 18 now illustrates the novel phenomenon of supralinearity in photoconductivity as a function of illumination intensity. For reference,

the dashed line in this figure denotes exact monomolecular behavior, i.e., the linear growth $\sigma_p \sim f$. Figure 18 therefore shows that there is a region of illumination intensity for which $\sigma_p \sim f^\nu$ where the power ν exceeds unity. Supralinear behavior with a power as large as $\nu \approx 1.6$ is attained for the thermal quenching side of the T_A peak. A similar plot for the T_B peak reveals more moderate supralinear behavior with $\nu \approx 1.2$. With increasing monochromatic intensity f_λ , this peak shifts to higher temperature. Infrared quenching of photoconductivity is also exhibited in the region of the T_B peak, i.e., this peak is reduced when a broad spectrum of sub-bandgap radiation is simultaneously imposed.⁽¹¹⁾ The recombination kinetics tends toward bimolecularity with $\nu \approx 0.5$ for phototransport on the low-temperature side of this anomalous peak (Fig. 17).

Anomalous behavior in photoconductivity is observed over a wide range of processing conditions (under appropriate impurity controls, as discussed): $p = 30\text{--}500$ mTorr, $P = 15\text{--}100$ W, and a range of substrate temperatures up to at least $T_s \approx 300^\circ\text{C}$. Moreover, this behavior is independent of: i) the type of substrate (7059 glass, quartz, or sapphire); ii) contacts on top, or underneath, the film in a gap cell geometry; iii) the nature of the Ohmic contact (e.g., Mo versus Ag); and iv) film thickness over the range $0.1\text{--}10\ \mu\text{m}$ (true bulk effect). The anomalous peaks are also observed to persist under the following conditions: i) broadband illumination (450–650 nm); ii) dc measurement (no chopping of illumination); and iii) heating versus cooling cycles for the measurement (implying no thermally-stimulated currents).

It is interesting to note that anomalous photoconductivity is observed in a wide variety of materials. The phenomena of thermal quenching, supralinearity, and infrared quenching have been observed for both amorphous and crystalline semiconductors, as well as for certain insulators. For example, thermal quenching of photoconductivity (and in some cases, supralinearity) is

exhibited by materials as diverse as: c-CdSe:I:Cu,⁽¹³⁾ c-Ge:Mn,⁽¹⁴⁾ a-ZnSe,⁽¹⁵⁾ a-Se,⁽¹⁶⁾ and the single-crystal insulator β -AgI.⁽¹⁷⁾ Together with related results for a-Si:H alloys, this universality of behavior does not, of course, suggest precisely the same chemical and physical origins for states that are responsible for the phenomena. For example in the case of c-Ge (or c-Si), substitutional double-acceptor transition metals such as Mn, Co, Ni, Fe, and Zn have been indicted as sources of recombination centers in the crystal bandgap that give rise to anomalous photoconductivity.

In the case of a-Si:H alloys, there are several open possibilities for such recombination centers, including: i) certain intrinsic states of the silicon-hydrogen alloy, and ii) centers due to extrinsic trace elements that are somehow incorporated during plasma deposition. With regard to concentrations of transition metals that could conceivably contribute to the second possibility, analyses of our alloys by SIMS reveal the presence of several ppm Cu and several tens ppb Cr. But the elements Fe, Ni, and Zn are all essentially undetectable in the bulk of the films. Whatever the nature of the centers, a synergism of incorporated nitrogen and oxygen effects the transformation to classic behavior in photoconductivity, e.g., the transformation $a \rightarrow d$ at $T_g = 260^\circ\text{C}$ in Fig. 12. Such transformations at medium-high T_g may be caused by a chemical modification of the centers per se, and/or by displacements (however slight) of the Fermi level from the vicinity in the gap of the sensitizing energy levels. The absence of anomalous photoconductivity at very high T_g may not, at this stage, be taken as unambiguous evidence for intrinsic centers due to silicon-hydrogen (or even silicon-silicon) bonding. As we discussed in Sect. IV.A., even though the effect of high T_g is to reduce the overall density of gap states, chamber impurities (except, perhaps, H_2O) are less controlled in this case. These questions are currently being addressed.

Despite the fact that the specific chemical bonds responsible for anomalous photoconductivity have not yet been identified, the essence of such behavior can be understood on the basis of an adaptation^(2,6) of a simple two-level model.⁽¹⁸⁾ As illustrated in Fig. 19, it is assumed on the model that there exist two levels of recombination centers, levels "1" and "2", located at $E_2 > E_F > E_1$ with respect to the dark Fermi level. (Presumably these centers help to pin E_F .) For the case of majority-carrier electron phototransport, it is then essential that these levels have widely disparate kinetic-capture cross sections for electrons:

$$\sigma_{2n} \gg \sigma_{1n} .$$

Let us denote the excess carrier density for electrons by $\Delta n = f/(\omega_1 + \omega_2)$, where $\omega_i \equiv \tau_i^{-1} \equiv v \sigma_{in} p_{ri}$ ($i = 1, 2$) is the recombination rate per electron by the hole-occupied recombination center of density p_{ri} . For specificity we shall also consider an anomalous peak at low temperature, such as peak T_B of Fig. 17 that lies at $T_B \sim 130$ K. Then, as appropriate for low-temperature photoconductivity $\sigma_p = e \Delta n \mu$, the density Δn pertains to low-mobility electrons that carry the photocurrent by phonon-assisted hopping. Hence mobility μ is thermally activated.

We shall firstly explain the phenomenon of supralinearity with reference to Fig. 19. At a given level of illumination, initially consider a value of σ_p on the thermal quenching side of the anomalous peak (high-temperature side). Recombination in this region is dominated by states 2 with the larger capture cross section for electrons. If we now imagine that the flux f is increased at fixed temperature, then, as depicted in Fig. 19a, the quasi-Fermi level for trapped electrons $\phi_{n2}(f, T)$ and the quasi-Fermi level for trapped holes $\phi_{p1}(f, T)$ depart more and more from their thermal equilibrium position E_F . In this configuration for which $\phi_{n2}(f, T) \gtrsim E_F$, level 2 is being depopulated of holes. Inversely, level 1 is acquiring additional holes. Now in a restricted region of

the flux f , $\omega_2 \gg \omega_1$ is still satisfied precisely because of the relatively large capture cross section σ_{2n} . That is, the recombination rate for photo-carriers is still determined by states 2 so that $\Delta n \approx f/\omega_2$. But the recombination rate decreases for increasing f , following the rate of decrease in the number of holes $p_{r2} \approx (\omega_2/v\sigma_{2n})$. Hence, $\omega_2 \sim 1/f^\alpha$, where α is some power. Therefore in that region of flux (and temperature) we have $\Delta n \approx f/\omega_2 \sim f^{1+\alpha}$, i.e., supralinear behavior $\sigma_p = e\Delta n\mu \sim f^{1+\alpha}$ is obtained.

For a large enough increase in flux, a point is attained on the low-temperature side of the anomalous peak (see Fig. 19). The capture kinetics on this side proceeds via bimolecular recombination. If this transition to bimolecularity were taken as evidence for a change in dominant recombination path, then the recombination rate by states 1 would finally exceed that by states 2, i.e., $\omega_1 > \omega_2$ and $\Delta n \approx f/\omega_1$. On this scenario, accurately bi-molecular recombination is consistent with $\Delta n \sim p_{r1} \sim (f/v\sigma_{1n})^{1/2}$. Hence, the activation energy of σ_p at sufficiently low temperatures is equal to the thermal activation energy of the mobility μ . Depending upon the exact relative sizes of σ_{2n} and σ_{1n} , and of the densities for states 2 and 1, it is conceivable instead that states 2 could dominate recombination over the entire temperature range of an anomalous peak. (Of course, at high enough flux and low enough temperatures, states 1 would finally have to dominate.) As in the case of c-Si, however, this situation would probably require a different (more positive) charge state for hole-occupied states 2 versus states 1 so that $\sigma_{2n}/\sigma_{1n} \sim 10^6$. This condition would not be met if, for example: i) hole-occupied states 1 were identified with numerous self-trapped holes below E_F , and ii) hole-occupied states 2 were identified with some positive, hole-occupied donor defects lying above E_F . (It can be argued that hole polarons have a smaller capture cross section for electrons than positive, hole-occupied donors, but a larger capture

cross section than neutral centers.) Subject to further experimental tests, we shall merely assume for definiteness (and consistency) that states 1 do indeed dominate recombination on the low-T side of the peak.

Proceeding now to an explanation of the thermal quenching phenomenon, we note that an increase in the temperature T at fixed illumination intensity acts to restore thermal equilibrium: i) the quasi-Fermi levels for trapped carriers, $\phi_{n2}(f,T)$ and $\phi_{p1}(f,T)$, retreat toward E_F , and ii) the Fermi-Dirac distributions become more extended. (See Fig. 19b). The net effect is to increase the population of holes in level 2, and inversely to decrease the population of holes in level 1. For a large enough increase in temperature, $\omega_2 > \omega_1$ is restored and recombination is again dominated by states 2 that thermally quench the photoconductivity as depicted in Fig. 19. The shift in the maximum of the anomalous peak to higher temperature with increasing flux is implicit in our discussion. Namely, the interplay of flux and temperature influences the relative populations of hole-occupied states 1 and 2. An increase in the flux shifts holes away from states 2, tilting the balance in favor of states 1 (low-T side of peak). A subsequent increase in the temperature repopulates states 2 with holes at the expense of states 1, restoring the thermal quenching. As a consequence, the maximum in the peak moves to higher temperature for a higher flux. It should be noted that if phototransport were bipolar at low temperatures, then anomalous photoconductivity can be explained by an exactly symmetrical argument for hole-carrier recombination in which $\sigma_{1p} \gg \sigma_{2p}$ is now assumed to be valid.

TABLE 1

Species	Emission Wavelength λ (nm)	Transition	Energy of Emitting State (eV) above Ground State
Si	198-199	UV7	6.3
Si	206	UV52	6.8
Si	212	UV48	6.6
Si	221-222	UV3	5.6
Si	229-230	UV46	6.2
Si	244	UV45	5.9
Si	251-253	UV1	4.9
Si	263	UV83	6.6
Si	288	UV43	5.1
Si	299	1	5.0
Si	391	3	5.1
SiH	386-388	$A^2\Delta-X^2\Pi$	3.0
SiH	394-396	"	"
SiH	413-428	"	"
SiH ⁺	399	$A^1\Pi-X^1\Sigma$	3.1
H	434	H _{γ}	13.0
H	486	H _{β}	12.7
H	656	H _{α}	12.0
H ₂	continuum 160-500	$2s^3\Sigma-2p^3\Sigma$	11.9
H ₂	many lines 368-835	$3d^1\Sigma-2p^1\Sigma$ $3d^1\Pi-2p^1\Sigma$ $3p^3\Pi-2s^3\Sigma$ etc.	14.0 " "
N ₂	316	second positive system, $C^3\Pi_u-B^3\Pi_g$	11.1
N ₂	337	"	"
N ₂	358	"	"
SiCl	281-282	$B^2\Delta-X^2\Pi$	4.4
SiO	224	$A^1\Pi-X^1\Sigma^+$	5.3
SiO	230	"	"
SiO	234	"	"
SiO	237	"	"
SiO	239	"	"
SiO	241	"	"
SiO	249	"	"
SiO	259	"	"
SiO	267	"	"
SiO	269	"	"
OH	306.4	$A^2\Sigma^+-X^2\Pi$	4.05

References

1. Carlson, D. E. and Wronski, C. R., Appl. Phys. Lett. 28 (1976) 671.
2. Griffith, R. W., Kampas, F. J., Vanier, P. E., and Hirsch, M. D., 8th Intern. Conf. on Amorphous and Liquid Semicond., Cambridge, MA, 1979, J. of Non-Crys. Sol. 35/36, Part I (1980) 391.
3. Griffith, R. W., Kampas, F. J., Vanier, P. E., and Hirsch, M. D., Annual Report to DOE, BNL 51145, UC-63e (1980).
4. Paesler, M. A., Anderson, D. A., Freeman, E. C., Moddel, G., and Paul, W., Phys. Rev. Lett. 41 (1978) 1492.
5. Baixeras, J., Mencaraglia, D., and Andro, P., Phil. Mag. B37 (1978) 403.
6. Griffith, R. W., in: Murr, L. E. (ed.), Solar Materials Science (Academic Press, New York, 1980).
7. Kampas, F. J. and Griffith, R. W., J. Solar Cells (to be published).
8. SIMS analyses performed by Charles Evans and Associates.
9. Perkins, G. G. A., Austin, E. R., and Lampe, F. W., J. Amer. Chem. Soc. 101 (1979) 1109.
10. Brookhaven Group, to be published.
11. Vanier, P. E. and Griffith, R. W., Bull. Amer. Phys. Soc. 25 (1980) 330; and to be published.
12. Lucovsky, G., Sol. Sta. Comm. 29 (1979) 571.
13. Bube, R. H., J. Phys. Chem. Solids 1 (1957) 234.
14. Newman, R. Woodbury, H. H., and Tyler, W. W., Phys. Rev. 102 (1956) 613.
15. Brodie, D. E., in "Amorphous and Liquid Semiconductors" (W. E. Spear, ed.), p. 472. U. of Edinburgh, Edinburgh, (1977).
16. Viger, C., Lefrancois, G., and Fleury, G., J. Non-Crys. Solids 33 (1979) 267.
17. Govindacharyulu, P. A. and Bose, D. N., Phys. Rev. B19 (1979) 6532.
18. Rose, A., Phys. Rev. 97 (1955) 322.

Figure 1. Block diagram of apparatus for optical emission spectroscopy.

Figure 3. Spectrum from 300-450 nm. Same conditions as Figure 2.

Figure 2. Optical emission spectrum from 180-350 nm of silane rf glow discharge. Discharge conditions were 50 W and 100 mTorr. The 0.75 m monochromator was used with 0.5 mm slits, a scan rate of 25 nm min⁻¹, and a 0.1 s time constant.

Figure 4. Spectrum from 400-670 nm. Same conditions as Figure 2.

Figure 5. Intensities of the Si(288 nm) line, the SiH (414 nm) band, and the H α (656 nm) line vs rf power at 100 mTorr.

Figure 6. Optical emission spectrum of silane rf glow discharge (15 W, 100 mTorr) containing 1000 ppm O $_2$. The 0.75 m monochromator was used with 0.5 mm slits, a scan rate of 2.5 nm min $^{-1}$, and 1 s time constant.

Figure 7. Emission spectra of silane rf glow discharges (50 W, 250 mTorr) showing the differences in SiCl emission for two different silane tanks. Also shown is emission from N₂ ($C^3\Pi_u - B^3\Pi_g$) when 1000 ppm NH₃ is added (upper spectrum) or when 1000 ppm N₂ is added (lower spectrum). The 0.2 m monochromator was used with 0.5 mm slits, a scan rate of 25 nm min⁻¹, and 1 s time constant.

Figure 9. Emission spectrum of the 50 W argon discharge used to clean the substrates prior to deposition of a-Si:H alloys. Argon pressure is 100 mTorr.

Figure 8. Ratio of intensities of the N₂ (358 nm) band to the Si(391 nm) line vs concentrations of N₂ (50 W, 250 mTorr)

Figure 10. Dark conductivity versus reciprocal temperature for a-Si:H alloy produced under low impurity conditions, and for alloy grown with 1000 ppm N₂ in the silane gas stream.

Figure 11. Optical bandgap E_0 deduced from plot of $(ah\nu)^{1/2}$ versus photon energy $h\nu$ at room temperature.

Figure 13. Dark conductivity and photoconductivity versus reciprocal temperature for n^+ -type, nitrogen-doped film produced in presence of airleak (15W, 100 mTorr, $T_s = 370^\circ\text{C}$). Flux $f_\lambda = 10^{14} \gamma's \text{ cm}^{-2}\text{s}^{-1}$ at $\lambda = 600 \text{ nm}$.

Figure 15. Infrared transmission spectrum of oxygenated alloy $a\text{-Si}:(\text{H},\text{O})$

Figure 12. Photoconductivity versus reciprocal temperature as a function of impurity content in the silane gas stream (50 W, 250 mTorr, $T_s = 260^\circ$). Low impurity Film a was deposited with no intentional impurities; Film b with 1000 ppm N_2 ; Film c with 1000 ppm O_2 ; and Film d with 540 ppm N_2 and 1000 ppm O_2 . Flux $f_\lambda = 10^{14} \gamma's \text{ cm}^{-2}\text{s}^{-1}$ at $\lambda = 550 \text{ nm}$.

Figure 14. Photoconductivity versus reciprocal temperature for phosphorous-doped $a\text{-Si:H}$ alloy. Flux $f_\lambda = 10^{14} \gamma's \text{ cm}^{-2}\text{s}^{-1}$ at $\lambda = 600 \text{ nm}$.

Figure 16. Effects of impurity incorporation on illuminated J-V characteristics for Schottky solar cell structure SiO/Pd/a-Si: (H,O,N) /n⁺a-Si:H/substrate. Bulk alloy layer is produced: a) under low-impurity processing conditions; b) in the presence of 3000 ppm air.

Figure 17. Anomalous peaks with thermal quenching in photoconductivity versus reciprocal temperature. Flux $f_\lambda = 10^{14}$ γ 's $\text{cm}^{-2}\text{s}^{-1}$ at $\lambda = 550$ nm.

Figure 18. Supralinearity in photoconductivity as a function of illumination intensity ($\lambda = 550$ nm). Dashed line is monomolecular (linear) growth.

Figure 19. Simple two-level model for explaining anomalous photoconductivity (top figure): (a) supralinearity (increasing f); (b) thermal quenching (increasing T).