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MODIFICATIONS IN OPTOELECTRONIC BEHAVIOR OF PLASMA-DEPOSITED AMORPHOUS SEMICONDUCTOR ALLOYS VIA IMPURITY INCORPORATION *

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We discuss electronic properties of plasma-deposited a-Si:H alloys as functions of oxygen and nitrogen impurities. Over a wide range of processing conditions, features displayed by the data include: i) "anomalous" behavior in photoconductivity versus temperature for films deficient in either, or both, impurities (peaks appear that are associated with thermal-quenching processes and supralinearity); and ii) modification to "classic" behavior in photoconductivity owing to *synergistic effects of oxygen and nitrogen.* Correlations with photoluminescence are presented. *Optical emission spectroscopy* is discussed within the context of an emerging spectroscopy for the detection of emitting reactive species in the plasma. The presence of impurities, particularly N_2, can be diagnosed.

INTRODUCTION

The distribution of gap states for nominally intrinsic a-Si:H alloys may sensitively depend upon the degree of incorporation of common atmospheric impurities encountered in plasma deposition. For any glow-discharge deposition system, levels of nitrogen and oxygen impurities are correlated with: i) the quality of the vacuum (influenced by air leaks, outgassing of residual chamber air and moisture, backstreaming from pumping systems, etc.); and ii) the purity of process and carrier gases. The separate effects of each impurity have already been studied in the case of reactively sputtered a-Si:H [1,2]. In this paper, we give a preliminary account of correlations that are observed between film properties and concentrations of nitrogen and oxygen impurities introduced into the silane gas stream. A fundamental question arose during the course of this study: To what exact extent can the density-of-states distribution (and the electronic properties of films) be manipulated by the control of impurity levels in "a-Si:H" materials?

EXPERIMENTAL PROCEDURE

Predominantly monohydride a-Si:H alloys were grown in a capacitively-coupled rf glow-discharge reactor with a novel high-vacuum capability. The base vacuum was $\sim 4 \times 10^{-7}$ torr at $T_s \gtrsim 270°C$. Most films were grown on the cathode with negative biases 2-50 V. Alloys reported upon here were produced under conditions $p = 0.03$-0.25 torr and $P = 15$-50 W. "Low impurity" film standards were grown from specially distilled silane containing <5 ppm N_2. Calibrated amounts of N_2 and O_2 (e.g., diluted in Ar) were added to the silane gas stream. Using IR transmission data, the range of hydrogen content in our films was calculated by two different methods in the literature: 4-7% [3] and 33-43% [4], respectively.

Conductivity measurements were made after samples were annealed to 200°C in vacuum, and then slowly cooled. Photocurrent was measured by chopping monochromated light

*Work performed under the auspices of the U.S. Department of Energy.

at 5 Hz and detecting the signal by lock-in techniques. In photoluminescence measurements, temperature control over 4.2-300 K was achieved by use of a continuous-transfer cryogenic system. Plasma species were monitored by optical emission spectroscopy over the range λ=200-800 nm using a 0.2 m J-Y monochromator and Hamamatsu R136 photomultiplier. Further details of procedure and results will be published elsewhere [5].

RESULTS AND DISCUSSION

A. Temperature-Dependent Dark Conductivity (DCT) and Photoconductivity (PCT).

Fig. 1 illustrates transformations in DCT with impurity content of the silane gas stream. Low impurity Film *a* (<5 ppm N_2) exhibits free electron transport with single activation energy $E_\sigma=(E_C-E_F) \approx$ 1.1 eV. It is observed for all low impurity films that E_F lies below midgap. Without knowledge of any other film impurities, we can only suppose that gap states intrinsic to the a-Si:H alloy *per se* pin E_F. PCT for *a* in Fig. 2 is anomalous in appearance with low magnitude and multiple peaks. The nature of such peaks will be discussed later.

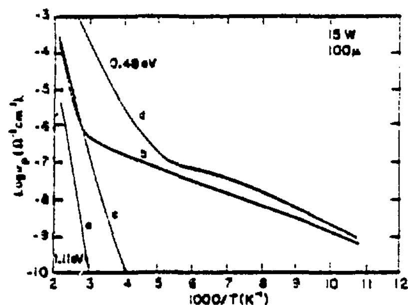


Fig. 1. DCT at 15 W, 100 μ for Different Impurity Levels.

Film *b* (600 ppm N_2) exhibits hopping transport in DCT below T≈350 K. In the absence of added O_2, we observe for all processing conditions that ~150 ppm N_2 is a threshold for defect transport in DCT. However at 50 W and 250 μ, excessive amounts of added N_2 (e.g., 10^4 ppm) changed the plasma chemistry sufficiently that defects were not introduced. The "anomalous" PCT for *b* is very pronounced, peaking at ~170 K.

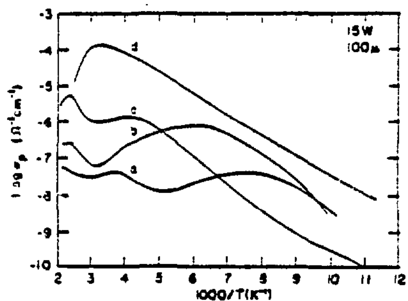


Fig. 2. Corresponding PCT. Flux F_λ = = 10^{14} γ's $cm^{-2}s^{-1}$ at λ = 550 nm.

As typified by Film *c* (1200 ppm N_2, 700 ppm O_2) in Fig. 1, the addition of oxygen removes the nitrogen-related defects in DCT. Under these conditions, only ~100 ppm O_2 removes hopping in DCT, but does not strongly modify the peak of *b* in Fig. 2. This result implies that recombination centers responsible for thermal quenching in PCT are not the same states that give rise to hopping in the dark. PCT for *c* importantly exhibits modification toward "classic" photoconductivity [6] with increasing O_2. (The vestigial valley at ~330 K in Fig. 2 for *c* would "fill up" with increasing incorporated O). The data therefore indicate that N and O play a *synergistic role* in effecting the transformation from low impurity, anomalous PCT into "classic" PCT.

Finally, Film d was produced in the presence of an air leak that raised the base vacuum to 2.4×10^{-6} torr. Consistent with PC and photoluminescence excitation spectra that show no change in optical gap, d in Fig. 1 shows evidence of electronic doping by N that shifted E_F from below midgap toward E_C: $E_\sigma = 0.48$ eV. PCT for d exhibits classic (doped) behavior with $\eta\mu\tau \gtrsim 10^{-4}$ cm^2V^{-1} at $f_\lambda = 10^{14}$ γ's $cm^{-2}s^{-1}$. The "anti-activation" energy, −0.54 eV, implies recombination centers located at $(E_C - E_r) \approx$ 1.02 eV (plus a possible trap depth ΔE). Below ~300 K, the activation energy (≈ 0.09 eV) is either $\Delta E/2$, with the recombination path directly between free electrons and states "r", or it describes hopping amongst states below E_C.

Fig. 3 illustrates the preceding trends at conditions 50 W, 250 μ: a (low impurity); b (1000 ppm N_2); c (1000 ppm O_2); and d (540 ppm N_2, 1000 ppm O_2). Note c shows that 1000 ppm O_2 dampens peaks, but does not eliminate them[1]. Again, the synergistic effects of O and N are demonstrated: PCT for a is modified to the classic behavior d.

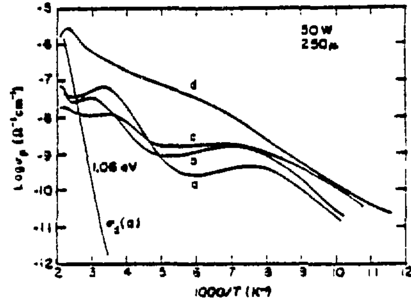


Fig. 3. PCT and DCT at 50 W, 250 μ. $f_\lambda = 10^{14}$ γ's $cm^{-2}s^{-1}$ at $\lambda = 550$ nm.

Fig. 4 illustrates PCT and DCT for a film (600 ppm N_2, 100 ppm O_2) at low power and very low pressure. As little as 100 ppm O_2 removed hopping in DCT. The anomalous peak became less prominent after an anneal at 350°C for ~13 h. This may indicate partial removal of centers that induce thermal quenching.

Intensity dependances of a peak in PCT are shown in Fig. 5. (Gas impurity is 600 ppm N_2). With increasing intensity f, the peak shifts to higher T. $\sigma_p \sim f^\nu$ is slightly supralinear ($\nu \approx 1.2$) in a region of the thermal quenching (high-T side of peak), and tends toward bimolecularity ($\nu = 0.5$) on the low-T side. "Anomalous" peaks in PCT persist[2] under the following conditions: i) broadband illumination (450-650 nm); ii) dc measurement (no chopping); and iii) either heating or cooling (implying no thermally-stimulated currents).

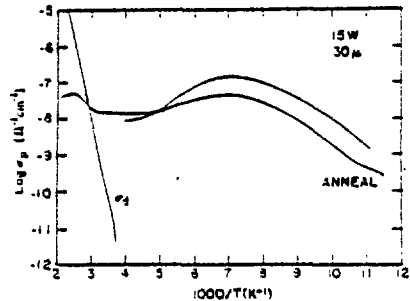


Fig. 4. Anomalous PCT at 15 W, 30 μ Before and After Long-Term Anneal.

The phenomena of thermal quenching and supralinearity were previously observed in a variety of materials: CdSe:I:Cu [7], Ga:Mn [8], and possibly in a-ZnSe [9]. The essence of such anomalous behavior[3] is contained in the following simple model [10]. Suppose there exist two levels of recombination centers located at $E_2 > E_F > E_1$ with rather *different* electron capture cross sections $\sigma_{2n} \gg \sigma_{1n}$. Here $\Delta n = f/(\omega_1+\omega_2)$, where $\omega_i \equiv \tau_i^{-1} \equiv v\sigma_{in}p_{ri}$ $(i=1,2)$. Now in a (restricted) region for which $\omega_2 \gg \omega_1$, but where the quasi-Fermi level for trapped electrons $\phi_{n2}(f,T) > E_2$, $\omega_2 \sim 1/f^\alpha$ for

increasing f, and so supralinearity results: $\Delta n \sim f/\omega_2 \sim f^{1+\alpha}$. Thermal quenching occurs for increasing T since $\phi_{n2} \rightarrow E_2$ implies increasing ω_2 relative to ω_1. Thus $\Delta n \rightarrow f/\omega_2 \ll f/\omega_1$. Activation on the low-T side of the peak occurs because the recombination path to dominant states "1" proceeds through electron traps (geminate-pair processes can also be involved). Evidently, the synergism of O and N suppresses centers (states "2") that cause thermal quenching, as illustrated by transformations $a\rightarrow c$ and $a\rightarrow d$ in Figs. 2 and 3, respectively. If phototransport is bipolar at low T, then an exactly symmetrical argument holds for holes[4].

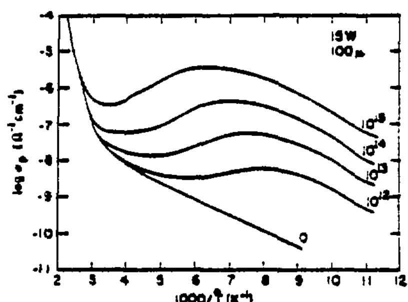


Fig. 5. Intensity Dependences of Anomalous Peak (f_λ in units γ's $cm^{-2}s^{-1}$; λ=550 nm).

3. Spectral and Temperature-Dependent Photoluminescence (PLT)

PL emission spectra at 50 K are illustrated in Fig. 6 for some films of Figs. 1 and 2. Except for the doped film *d*, all spectra are dominated by the canonical peak at ~1.3 eV [11,12]. This peak also dominates in films with: i) N impurity alone ($\lesssim 10^4$ ppm N_2); ii) O alone ($\lesssim 1000$ ppm O_2); and iii) both impurities, in the absence of pronounced shifts of E_F (as for c). Oxygenated films show no hint of the strongly thermally-quenched peak near 1.1 eV associated with charged defects of nonbridging oxygen [13]. Conceivably, higher levels of O_2 in the gas stream could create such defects, after saturating all bridging sites Si-O-Si[1].

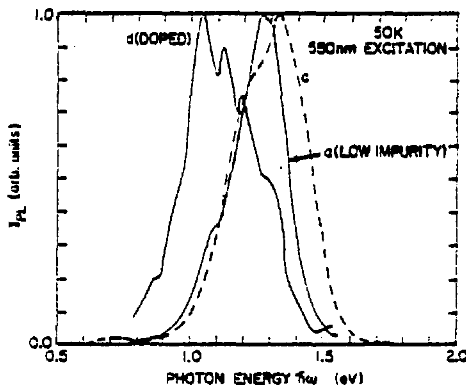
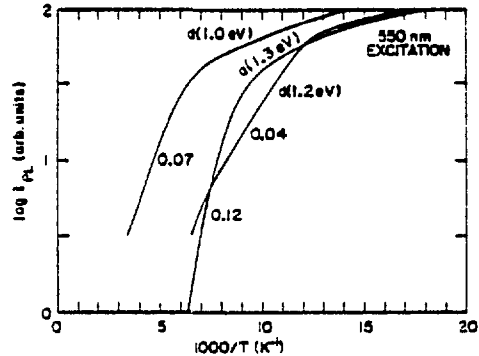


Fig. 6. Spectral PL for Different Impurity Levels (Fringes due to Interference Effects).

By contrast, the PL spectrum for Film *d* exhibits a peak near 1.0 eV that strongly dominates the canonical component at all T ≳ 4.2 K (see Fig. 7). Since this low-energy component is *not* rapidly quenched with T it cannot be confused with PL involving an oxygen-related charged defect. Instead, it probably involves an intrinsic defect in a-Si:H that is introduced by *nitrogen doping*. Indeed, a low-energy component in PL (0.8-0.9 eV) that persists to high T was first noted in the case of phosphorus doping [14], and may even be related to defects in c-Si introduced by ion implantation [15].

Fig. 7. PLT for Emission Components of Doped Film *d*. Comparison with Canonical Component of Low Impurity Film *a*. (Arb. Normalization).



C. Optical Emission Spectroscopy (OES)

OES is a non-perturbative technique used to detect emitting reactive species in the plasma. Complemented by other techniques, OES may lead to an understanding of the relationships among the plasma chemistry, the surface reactions that promote film growth, and the electronic (and microstructural) properties of films.

The threshold for decomposition of SiH_4 is 7.5 eV (in photolysis), producing primary neutral species SiH_2, SiH_3, and H that act as major reactive intermediates [16]. Populations of primary reactive ions such as Si^+, SiH^+, SiH_2^+, and SiH_3^+ will in general be many orders of magnitude below the neutrals, since electron energies >11.7 eV are required for ionization. Fig. 8 is part of a representative spectrum taken during film deposition with 600 ppm added N_2. The following major species were identified: Si(288 nm, 391 nm); SiH(414 nm); H_2(450-630 nm); Balmer series H_β(486 nm) and H_α(656 nm); N_2 ($C^3\pi_u \rightarrow B^3\pi_g$); and more tentatively SiH^+(399 nm) and SiCl(281 nm). N_2 is, no doubt, a ubiquitous impurity of the usual plasma deposition system. The detection level here was ~50 ppm N_2. SiCl was only present in silane that was specially distilled to eliminate N_2 (<5 ppm). Some film property dependences upon silane tanks may be attributable to this trace impurity; its detection demonstrates the sensitivity of OES. A weakness of OES is that potentially important species, such as SiH_2, absorb but do not emit between

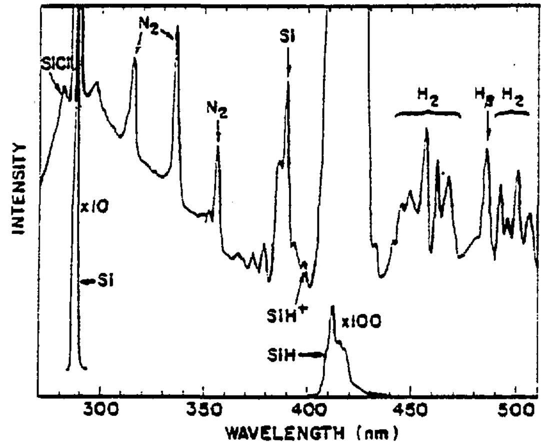


Fig. 8. OES of Plasma with 600 ppm Added N_2. (50 W, 250 μ).

200–800 nm.

Fig. 9 depicts increasing emission intensity with power, and hence with electron temperature and changing energy distribution. This Figure illustrates the sensitive dependence of the plasma chemistry upon the processing conditions, the subject of a continuing study.

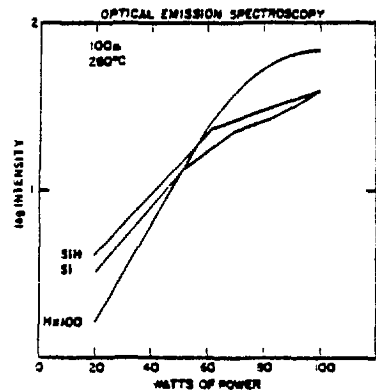


Fig. 9. OES Intensity versus Power for SiH(414 nm), Si(288 nm), and H_α(656 nm).

ACKNOWLEDGMENTS

We wish to thank A. E. Delahoy for useful discussions, and R. Gremme for technical assistance.

FOOTNOTES

1. 1000 ppm O_2 in the gas stream corresponds to ~1% bonded O in the bridging configuration Si-O-Si as estimated from the antisymmetric stretch mode at $\tilde{\nu}$ = 980 cm^{-1}.
2. We thank M. Brodsky and T. Tiedje for proposing some of these tests.
3. Detailed computer-generated fits to data will be published elsewhere.
4. In the case of electron phototransport, states "1" may perhaps be related to Spear's E_y states.

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