a-Si:H FILMS DEPOSITED AT HIGH RATES IN A "VHF" SILANE PLASMA: POTENTIAL FOR LOW-COST SOLAR CELLS

A.Shah*, E.Sauvain*, N.Wyrsch*, H.Curtins, B.Leutz, IMT, University of Neuchâtel, Neuchâtel, Switzerland
D.S.Shen, V.Chu, S.Wagner, E.E.Dept., Princeton University, Princeton, N.J., USA
H.Schade, H.W.A.Chao, Chronar Corp., Princeton, N.J., USA
* work partly done during leave from University of Neuchâtel, at Princeton University, USA

ABSTRACT

"Very-High-Frequency" Glow Discharge (VHF-GD) is a high-rate deposition method for amorphous silicon based on the use of plasma excitation frequencies in the range 30 - 150 MHz; thereby the high-energy tail of the electron energy density function is enhanced, increasing the deposition rate R, without a corresponding increase in electric field and ion bombardment. Here, an extensive set of opto-electronic properties (σ_{dark}, E_a, σ_{ph}, CPM, PDS, TOF, SSPG, Steady-State Hecht plot) are presented for samples prepared by VHF-GD for above frequency range and R≈12-15 Å/s. Emphasized are hole transport properties. With values of $(\mu^D\tau^t)_h$ by TOF around $3x10^{-10}$, but upto $\approx 5x10^{-9}$ cm^2V^{-1}, VHF-GD is judged to be adequate for solar-cell applications.

INTRODUCTION

Economically, the film deposition rate R is a key parameter in the production of low-cost thin film solar cells. In a glow discharge system, R depends on the silane dissociation efficiency (radical formation) which in turn is related to the total electron density n_e of the plasma. Both n_e and R can, in general, easily be stepped-up by increasing the total electric power supplied to the plasma. This, however, will at the same time result in larger plasma sheath field amplitudes and therefore enhanced ion bombardment and undesired defect creation on the growing a-Si:H film surface. One of the ideas motivating the development of the photo-CVD technique was the deposition of a-Si:H films (and related alloys) in the absence of an electric field so as to reduce ion bombardment induced damages. Photo-CVD does, in fact, lead to high-quality layers. Sofar, however, high deposition rates combined with good material properties have not yet been demonstrated by this technique.

Recently, we have presented the new "Very-High-Frequency" Glow-Discharge (VHF-GD) deposition technique (1), by which high deposition rates combined with good material properties can be obtained. The basic idea behind the VHF-GD method is the use of higher plasma excitation frequencies, in order to alter the electron energy distribution function (EEDF) and also n_e. We observe a strong dependence of the EEDF and of n_e on f. An increase in f leads to a more pronounced high energy tail in the EEDF (2). This part of the EEDF controls the ionization rates and, as a consequence, also the total electron density n_e (there is a balance between generation and loss of electrons). The VHF method operates at lower plasma impedances (higher n_e) and lower sheath field amplitudes for a fixed RF power level, when compared to lower frequency plasmas (e.g. 13.56 MHz). These properties are in general beneficial for the deposition of good quality a-Si:H at high rates.

Various results concerning the properties of a-Si:H films prepared by the VHF-GD technique have already been presented in (1,3-6).

In this paper we shall present electro-optic results for films prepared at different frequencies f between 30 and 150 MHz, at a deposition rate R≈12-15 Å/s. We will focus on the minority carrier (hole) transport properties. These are of major importance in solar cell applications. The hole and electron drift mobility x deep trapping lifetime product [$(\mu^D\tau^t)_h$ and $(\mu^D\tau^t)_e$, respectively] have been determined by the Time-Of-Flight (TOF) technique, using Hecht's plot. The ambipolar diffusion length L_{amb} was determined through the Steady-State-Photograting (SSPG) method; using L_{amb} thus measured, we calculated the hole drift mobility x small signal response time product $(\mu^D\tau^s)$.

The steady-state Hecht plot was used to evaluate the hole mobility x recombination lifetime product

0160-8371/88/0000-0282 $1.00 © 1988 IEEE

$(\mu^D\tau^r)_h$ for the 70 MHz sample only.

EXPERIMENTAL

All the a-Si:H films were prepared by the VHF-GD method (1-3) on Dow Corning 7059 glass substrates (64 cm^2). Half of the substrate surface was coated with chrome (Cr ≈2000 Å), serving as back contact for the Schottky diodes used in the TOF and steady-state Hecht plot measurements. The deposition parameters are: deposition temperature T_s=280 °C, total pressure p=0.3 mbar, RF power density P=20 mW/cm^3, silane flow rate ϕ_{SiH4}≈12 sscm. During the deposition of the a-Si:H layer, we observed that the deposition rate is slightly higher (≈5 %) on the Cr-coated glass than on uncoated glass. In addition, we observed also a different aesthetic appearence between the part of the film deposited on Cr and the one deposited on glass, indicative of different microstructural properties. The comparison of the TOF and steady-state Hecht plot results [Schottky diodes on Cr underlayer] with the results measured on films directly deposited on glass [Photothermal Deflection Spectroscopy (PDS), Photoconductivity, Constant Photocurrent Method (CPM), SSPG] should therefore be carried out with some caution. The problem of the deposition of a-Si:H on Cr could be reduced by the use of a n^+ layer between the Cr and the intrinsic film; this merits further investigations.

The thickness of the films (averaged over the Cr-coated and the uncoated glass deposited films) were determined gravimetrically from the weight increase of the substrate before and after deposition, assuming a constant density of 2.2 g/cm^3 for a-Si:H. All the samples, except the Schottky diodes, were annealed at 220 °C for 3 hours under vacuum, and cooled down to room tempreature with a gradient of 0.5 °C/min prior to the PDS, CPM, SSPG, σ_{ph} (AM1) and σ_{ph} (700 nm) measurements.

The dark conductivity σ_{dark} and the photoconductivity σ_{ph} are measured in a gap configuration in a vacuum chamber at pressure lower than 10^{-7} mbar, with an electric field of 300 V/cm. The activation energy of σ_{dark} is deduced from an Arrhenius plot of conductivity versus reciprocal absolute temperature; σ_{ph} (AM1) is measured under 100 mW/cm^2 white light illumination by an HLX halogen lamp (coarse approximation for AM1 spectrum, but with spectrum more similar to AM1.5); σ_{ph} (700 nm) measurements were performed at 700 nm using a 50 nm bandpass filter at a generation rate $G=10^{19}$ s^{-1} and the results were extrapolated to $G=10^{21}$ s^{-1}. The optical badgap E_{opt} is deduced from Tauc's plot. The defect density and Urbach tail energy E_0 were determined both from PDS and from CPM absorbtion curves. For the conversion of the integrated PDS and CPM subgap absorbtion values into the values for the density of deep defects, we used the Jackson and Amer factor (10) and the Smith factor (9), respectively . The TOF measurements were performed in the way previously described in (11). The Schottky barrier metal was semi-transparent Pd (dots of ø=2 mm). For electron measurements, electric fields of appropriate polarity in the range 1 to 16 kV/cm were applied; for hole measurements, the polarity was reversed and values between 10 and 80 kV/cm had to be used. $(\mu^D\tau^t)_e$ and $(\mu^D\tau^t)_h$ were obtained using the Hecht formula and fitting the total charge Q collected during the TOF experiment divided by the photogenerated charge Q_0 as a function of electric field strength E.

The description of the SSPG measurement method for the ambipolar diffusion length , as well as the theoretical basis leading to the calculated values for the product of the hole drift mobility x small signal response time $(\mu^D\tau^s)_h$ are given in (12). The ambipolar diffusion length was measured with monochromatic light (HeNe laser, 632.8 nm) at an intensity I varying from ~5 to ~60 mW/cm^2. For each of these intensities, the diffusion length was deduced from a plot of the ratio of the photoconductivites with and without grating, plotted as a function of the grating period (the latter is varied by using different angles of incidence of the split laser beam on the film). The value of L_{amb} can be extrapolated to its equivalent at 100 mW/cm^2 HeNe laser light, in the same way as in other photoconductive measurements, by using the power law dependence of L_{amb} versus intensity.

The steady-state Hecht plot was used to determine the holes mobility x recombination lifetime product $(\mu\tau^r)_h$ for the 70 MHz sample. The measurement was done on the same Schottky diode as used for the TOF measurement, in the way described in (8,16): The collection effieciency was measured with a bias light and a probe light of 700 nm, for a reverse voltage from 1 to 8 V applied on a 5 µm thick device.

The samples were deposited at Neuchâtel and the measurements were executed at Neuchâtel and Princeton Universities, except for the SSPG measurements which were performed at Chronar.

RESULTS AND DISCUSSIONS

The deposition rate versus frequency curve R(f) with the deposition conditions used here show a less pronounced maximum than the one discussed in (1)[the latter were optimalised for a maximum R at 70 MHz (R≈20 Å/s)].This is ascribed to the fact that a lower silane flow ϕ_{SiH4} is used here and therefore depositions were done at higher silane depletion. This has the effect of reducing the deposition rate for deposition frequencies around the maximum at 70 MHz. By comparing the Si weight depostion rate with the Si gas flow, we estimate roughly that under conditions of deposition for 70 MHz, the depletion is around 30 %.

Before presenting the values of the measured parameters σ_{ph} , E_o, N_D (total deep defect density) for our a-Si:H films, let us point out that all these parameters are thickness dependent (6). Here we will present opto-electronic properties of a-Si:H layers, all having approximately the same thickness d≈ 5 µm. This thickness was choosen in order to reduce the influence of the surface/ interface defects on the measurement of total defect density.

Conductivity, CPM and PDS measurements (Fig. 1)

The photoconductivity measured for the 70 MHz sample is σ_{ph} (AM1) = 1.5 x10^{-5} $\Omega^{-1}cm^{-1}$. This value does not vary much over the range of frequencies, showing, however, a slight maximum at 2.2x10^{-5} $\Omega^{-1}cm^{-1}$ for the samples deposited at 70 to 100 MHz . On the other hand, the 'monochromatic' photoconductivity σ_{ph} (700 nm) measured with a light almost uniformly absorbed throughout the sample, shows a more pronounced trend than σ_{ph} (AM1). The values found by PDS measurement for the total defect density is N_d=1.4 x10^{16} cm^{-3} and for the measured (valence)band-tail Urbach parameter E_o=52 meV. By the CPM method, these values are N_d=1 x10^{16} cm^{-3} and E_o = 60 meV, respectively. All these values do not show substantial variations for the full set of samples, over the whole frequency domain. The CPM subgap integrated absorbtion value is correlated with the same slight frequency dependence as observed for the photoconductivity data, i.e. CPM values show a slight minimum at N_d=0.6 x10^{16} cm^{-3} for the samples from 70 to 100 MHz. The activation energy E_a of the dark conductivity shows a slightly increasing trend, from 0.73 eV at 43 MHz up to 0.8 eV at 150 MHz. The optical gap E_{opt} keeps constant around the value of 1.75 eV over the whole frequency range. Similar, but more pronounced trends in the opto-electronic properties were already observed and published for a set of samples grown over the same domain of plasma excitation frequencies, but at substantially varying R (3).

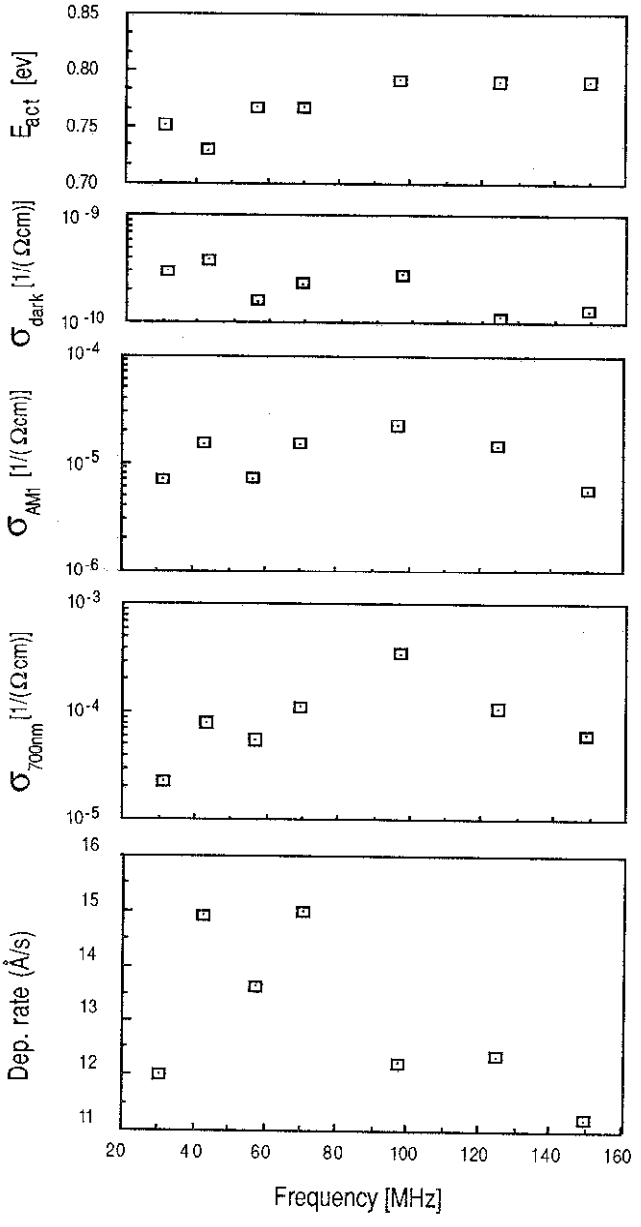

Figure 1 : Activation energy E_a, dark conductivity σ_{dark}, AM1 photoconductivity σ_{AM1}, photoconductivity at 700 nm (uniformly absorbed light; G = 10^{21} cm^{-3}) σ_{700nm} and deposition rate as a function of plasma excitation frequency.

Time of Flight (TOF): electron and hole transport (Fig. 2)

The value of $(\mu^D\tau^t)_{e,h}$ is obtained by fitting the time-integrated photocurrent versus the applied electric field.The function used to make the fit for the electrons is the modified Hecht equation, which takes into account the internal electric field due to the Schottky barrier (13) . $(\mu^D\tau^t)_e$ is nearly constant for the set of samples, and its average value is 1.5 x10^{-8} cm^2V^{-1}. This value is in the range of values previously published for intrinsic a-Si:H (11,15-17). $(\mu^D\tau^t)_h$ is of particular interest for solar cell applications, because holes are the minority carriers and therefore they limit the transport properties in a solar cell. . The value $(\mu^D\tau^t)_h$ for the 57 MHz sample is unexpectedly high at 4.3 x10^{-9} cm^2V^{-1} (Fig.2). A new sample at this frequency should yet be prepared, in order to confirm this surprising value. The average $(\mu^D\tau^t)_h$ value measured on our samples (except on the 57 MHz sample) is 2 x10^{-10} cm^2V^{-1}. This value is in the range of published values for solar-cell quality a-Si:H (11,15-17). The results presented in Fig. 2 show the scattering of the values, which were measured on different Schottky diodes, made on the same film. Even if the measured values, for both $(\mu^D\tau^t)_{e,h}$, do not show significant variations over the frequency range, the electronic signals during the measurement were much better (i.e. less noisy) for the 70-100 MHz samples. One of the conditions to fullfil in order to compare $(\mu^D\tau^t)_{e,h}$ for different samples is to have the same photogeneration ($\mu^D\tau^t$ is influenced by the magnitude of the photogenerated charge and one should work at the lowest possible light intensity to measure an accurate value). Due to differences between the signal/noise ratio of the signals for the different samples, this condition was not easy to fullfil. The thickness of our samples (≈5 μm) also affects the scattering of the measured values: the thicker the sample, the smaller and noisier is the time-integrated current. The problem was especially acute for hole neasurements, i.e. for $(\mu^D\tau^t)_h$.

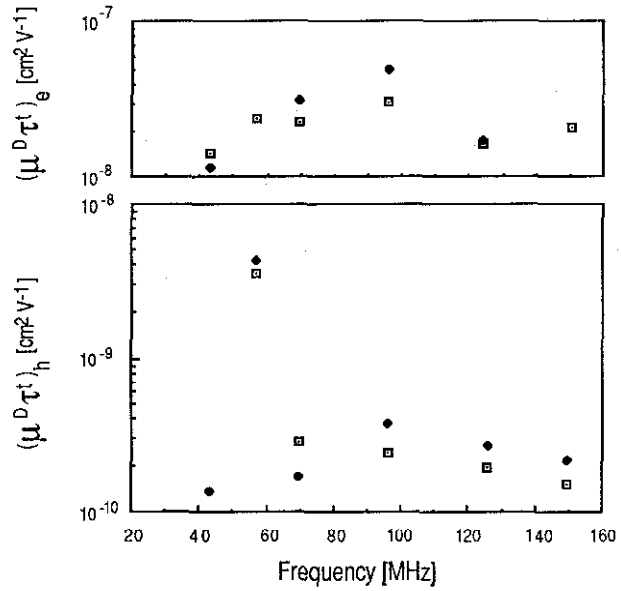

Figure 2 : Drift mobility x deep trapping lifetime products for electrons $(\mu^D\tau^t)_e$ and hole $(\mu^D\tau^t)_h$ as a function of plasma excitation frequency for two different sets of Schottky diodes.

Ambipolar diffusion length by SSPG (Fig. 3)

The SSPG measurements were done with an applied electric field of 65 V/cm, choosen low enough to rule out any drift pheneomena (14), and the diffusion length was measured at different light intensities, from 2 to 60 mW/cm^2. The thus determined L_{amb} varies with the light intensity of the

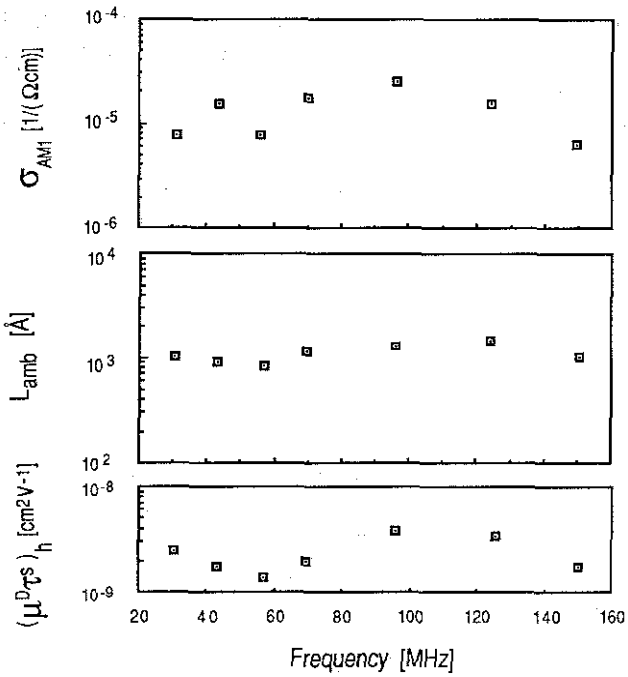

Figure 3 : AM1 photoconductivity σ_{AM1}, ambipolar diffusion length L_{amb} and holes drift mobility x small signal response product $(\mu^D\tau^s)_h$ as a function of plasma excitation frequency.

measurement: $L_{amb} \sim I^{\alpha}$. For our samples, we found α to vary from 0.9 to 0.95. Using this power law, one can extrapolate the diffusion length for an illumination of 100 mW/cm^2 of He-Ne laser light. The values for the extrapolated diffusion length vary from 790 Å for the 57 MHz sample up to 1220 Å for the 125 MHz sample. These values are smaller than the value of 1400 Å published in (12) for a 3 µm sample. In contrast to what is observed in (12), we observe that the variation of L_{amb} with the deposition frequency follows the variation of σ_{ph} (AM1). The SSPG- $(\mu^D\tau^s)_h$ can be calculated from L_{amb}, assuming the Einstein relation between drift mobility and diffusivity, and using the following equation:

$$L_{amb}=\sqrt{\frac{kT}{q}\frac{2b}{b+1}(\mu^D\tau^s)_h}$$

where kT/q is the thermal voltage, $b= \mu^D_e/\mu^D_h$ is the ratio of the drift mobilities , and τ^s is the small signal response time (14). From the comparison of the measured σ_{ph} (AM1) and L_{amb}, Ritter et al. in (14) found b=1.6. For our samples, we find $b \approx 7$. But we need futher investigations before understanding the possible source of this difference in b. For a given measured value of L_{amb}, $(\mu^D\tau^s)_h$ will be modified by the ratio b, but not very sensitively: if b is increased from 1.6 to 7, the resulting calculated value for $(\mu^D\tau^s)_h$ will be multiplied by a factor of 0.7.Here, we have calculated $(\mu^D\tau^s)_h$ assuming b=7 (Fig.3). Its value varies between 1.4 x10^{-9} and 3.3 x10^{-9} cm^{2}V^{-1}. As the SSPG technique has sofar not been extensively used, the published values still need to be compared with further measurements before drawing any further conclusions.

Steady-state µt -product of holes

The evaluation of the steady-state Hecht plot for the typical 70 MHz sample, leads to $(\mu\tau)_h$ of the order of 5 x10^{-8} cm^{2}V^{-1}. Assuming an electric field of 10^4 V/cm in the solar cell, the holes' collection length is then 5 µm (undegraded), which is certainly larger than the thickness of the usual a-Si:H thin film solar cells.

CONCLUSIONS

"Very-High-Frequency" Glow-Discharge (VHF-GD) is a method recently introduced for the high-rate deposition of a-Si:H. An extensive set of optical, electro-optical and transport properties have been determined on intrinsic a-Si:H films produced by the VHF-GD method. This set has here been extended to include a characterization of minority carrier (hole) transport. We have noticed that the samples prepared at plasma excitation frequencies from 70 to 100 MHz gave slightly better results (even if the variations of most of the measured parameters are small compared to the experimental errors). Further investigations would be necessary to find out the cause of these small variations (e.g. inhomogeneities in the film, structural changes related to different plasma excitation frequencies). Further measurements with the SSPG technique should be done to confirm the relatively high value of $b= \mu^D_e/\mu^D_h$ obtained here, and its meaning in the sense of Density of States (DOS). The value of the transport parameters measured by TOF, SSPG, steady-state Hecht plot are of the same order of magnitude as published values measured for samples grown at 13.65 MHz, at a three to five times lower deposition rate.

On the other hand, Metal / Insulator / Semiconductor (MIS) structures have already been succesfully produced with a-Si:H deposited by the VHF-GD technique as semiconductor layer. These structures have relatively high values of V_{oc} (7). All measurements done so far confirm that the VHF-GD technique is well suited for the production of low-cost a-Si:H solar cells with good efficiencies.

Finally, VHF-GD material shows a relatively low Staebler-Wronski Effect (SWE) (18), and so satisfies one of the most critical requirement for solar-cell applications.

ACKNOWLEDGMENT

The authors acknowledge financial support from the Electric Power Institute (EPRI) and from theSwiss Federal Government Renewable Energy Program (OFEN-REN)

REFERENCES

(1) H.Curtins, N.Wyrsch and A.V.Shah, Electronics Lett. **23** (1987) 228.
(2) M.R. Wertheimer, J. Vac. Technol. **A 3** (1985) 2643.
(3) H. Curtins, N. Wyrsch, M. Favre and A.V.Shah, Plasma Chem. and Plasma Proc. **7** (1987) 267.
(4) H. Curtins, N. Wyrsch, M. Favre, K. Prasad, M. Brêchet and A.V. Shah, Mat. Res. Soc. Proc. **95** (1987) 249.
(5) M. Favre, H. Curtins and A.V. Shah, J. of Non-Cryst. Sol. **97&98** (1987) 731.

(6) H. Curtins and M. Favre,to be published as a chapter in "Advances in Amorphous Semiconductors" by H. Fritsche, 1988.
(7) J. Meier et al., Appl. Phys. (A) **46** (1988) 31.
(8) V. Chu,J.P. Conde, D.S. Shen and S. Wagner, to be published in MRS Symp. Proc., Volume 118.
(9) Z E. Smith, V. Chu, K. Shepard, S. Aljishi, D. Slobodin, J. Kolodzey, S. Wagner andT.L.Chu, Appl. Phys. Lett. **50** (1987) 1521.
(10) W.B. Jackson, N.M. Amer, Phys.Rev. **B25** (1982) 5559.
(11) D.S. Shen, S. Aljishi, Z E. Smith, J.P. Conde, V. Chu and S. Wagner, SPIE Proc., Los Angeles, 763 (1987) 17.
(12) D. Ritter, K. Wieser, and E. Zeldov, J. Appl. Phys. **62** (1987) 4563.
(13) F. Karg, W. Kruhler, and M. Möller, K.v. Kitzling, J. Appl. Phys. **60** (1986) 2016.
(14) D. Ritter, E. Zeldov, and K. Weiser, J. of Non-Cryst. Sol. **97&98** (1987) 619.
(15) R.A. Street, Appl. Phys. Lett. **41** (1982) 1060.
(16) C.R. Wronski , Z E. Smith, S. Aljishi, V. Chu, K. Shepard, D.-S. Shen, R. Schwartz, D. Slobodin, and S. Wagner, AIP Conference Proc. 157 (1987) 70.
(17) D.S. Shen, S. Aljishi, Z Smith, J.P. Conde, V. Chu, and S. Wagner, MRS Symp. Proc., **95** (1987) .
(18) H. Curtins, M. Favre, Y. Ziegler, N. Wyrsch and A. V. Shah, to be published in MRS Symp. Proc., Volume 118.