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HIGH-RATE DEPOSITION OF HYDROGENATED AMORPHOUS SILICON BY THE VHF-GD METHOD

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ABSTRACT

The effects of plasma excitation frequency f on the deposition of hydrogenated amorphous silicon by the silane radio frequency glow-discharge technique is investigated. f is varied over a part of the VHF (Very High Frequency) band from 25 to 150 MHz. The deposition rate has been increased by a factor of ~5 with f~70 MHz when compared to typical rates of ~3 Å/sec observed in conventional glow-discharge systems operating at 13.56 MHz under similar experimental conditions. Measurements of the optical and electrical film parameters show that this high-rate deposited material has a quality comparable to that of the material prepared at a low rate of typically ~3 Å/sec and at 13.56 MHz. Support for this statement comes also from a comparison the characteristics of Schottky-diode type solar cells prepared at high and at low deposition rates.

1. INTRODUCTION

Mass production of low-cost solar cells, photoreceptors and other hydrogenated amorphous silicon (a-Si:H) thin film devices calls for a large increase of the deposition rate R. The direct current (DC) and the radio frequency (RF) capacitively-coupled silane glow-discharge (GD) methods are the most widely applied techniques for the preparation of a-Si:H films. Their growth rates (for the obtention of good material quality), however, have sofar been limited to typically ~3 Å/sec. The target value would be around ~20 Å/sec [1,2]. As pointed out e.g. by [3], R can be increased by increasing the RF input power and/or the SiH_4 gas feed, by replacing SiH_4 by higher silanes (Si_2H_6) or by modifying other macroscopic deposition variables. Such films, however, show in general poor structural (microvoids, high hydrogen content, etc.) and opto-electronical properties due to gas phase polymerization, stronger ion bombardment damages and other undesired side-effects. Jackson and Amer [1,4] have shown that best quality films (films with a low defect density) are obtained at the lowest possible RF power levels.

Hamasaki et al. [3] have described the method of plasma confinement in a 9 MHz GD system by which an increase of the deposition rate R has been obtained. The method uses a (mechanical) mesh surrounding the two electrodes in order to limit the discharge in the space between the two electrodes and suppressing the diffusion of reactive species towards the reactor walls. By this technique, deposition rates of several tens of Å/sec have been demonstrated. The films exhibit reasonable photoconductivities, they have however relatively large hydrogen contents of ~20 at.% (calculated from the 2000 cm^{-1} Si-H streching band, [5]). Other disadvantages of the method are: on one hand a considerable increase of the sheath field amplitude (at the substrate holder electrode), which in turn increases ion bombardment damages, and on the other hand an additional source of impurities (plasma-enhanced desorption). A deterioration of the material quality may therefore be expected.

In this paper we describe another modification of the classical GD method, by which a considerable increase of the deposition rate R can be obtained without noticeable deterioration of the material quality. It is based on an optimization of the plasma excitation frequency f. The influence of this parameter has not been investigated systematically in the past, in the case of a-Si:H. The only frequencies sofar studied were almost exclusively in the DC to ~30 MHz range as well as some other isolated frequency values (e.g. the microwave frequency at 2.45 GHz, [6,7]). The reason for this has to be seen in the fact that commercial RF equipment is readily available and in the widely-spread opinion that plasma excitation frequency merely has secondary effects in plasma processing for values of f larger than the ion transit frequency (being of the order of 5 MHz, see e.g. [8-10]). Studies related to etching problems and deposition of various thin films (Si-N, etc.), however, show that plasma characteristics are strongly influenced by f [9,10]. The following discussion confirms the above statement in the case of a-Si:H deposition.

We will present experimental data related to the dependence of R and of some important a-Si:H film parameters on the plasma excitation frequency f over the range 25 to 150 MHz. According to the nomenclature in [11] this frequency range is part of the VHF (Very High Frequency, 30-300 MHz) band. The deposition method described here will therefore be referred to as the "VHF-GD" method in all that follows.

It will also be shown that the plasma-glow can very well be confined between the two electrodes through a adequate choice of f without the need of (mechanical) mesh or any other physical device; this is what one could call a plasma 'self confinement' effect.

2. EXPERIMENTAL

All a-Si:H samples discussed in the following (Table I), were prepared in a capacitively-coupled VHF-GD system described elsewhere [12]. Dow Corning 7059 glass with a utilizable surface of 64 cm^2 and a thickness of 0.8 mm were used as substrates. Immediately after pumping down the chamber to $<2x10^{-6}$ mbar, an H_2-plasma cleaning was applied to the electrodes and to the chamber walls for ~10 min.. After heating up of the substrate in an H_2 environement (0.2 mbar) during $1^1/_2$ h and right before deposition, the substrate was again H_2-plasma cleaned for ~5 min. Cooling down of the sample after deposition was done at a typical rate of ~2 °C/min. The deposition parameters are listed in Table I (T_s= substrate temperature, P= RF power density, p= total pressure, F_{SiH4}= silane gas flow).

The thickness d of the samples has been evaluated from weight increase measurements taken as weight difference before and after deposition and assuming a material density of 2.2 g/cm^3. The dark conductivity σ_{dark}, the pre-exponential factor σ_0 and the activation energy E_a are deduced from the Arrhenius plot log(σ) versus the reciprocal absolute temperature T. σ_{dark} and the photoconductivity σ_{AM1} refer to values at 25 °C (samples were measured in gap arrangement with two Al electrodes at a field strength of ~300 V/cm in a vacuum better than 10^{-7} mbar). The measurements were done with temperature gradients smaller than ~1°C/min in order to obtain straight line characteristics. σ_{AM1} was determined simultaneously with σ_{dark} under 100 mW/cm^2 HLX white light illumination.

Tauc's relation $\sqrt{\alpha h\nu}$ versus $h\nu$ has been applied to calculate the optical bandgap E_{opt} (α denotes the optical absorption coefficient). The defect density N_D and the Urbach tail energy E_0 were evaluated by means of the photothermal deflection spectroscopy (PDS) method , by using the model given by Jackson and Amer [4].

3. RESULTS AND DISCUSSION

Fig.1 shows the deposition rate R as function of f for a constant set of plasma parameters.. The surprising feature in the shape of R(f) relates to the presence of a maximum at an 'optimal' frequency f_{opt}=70 MHz. Below and above this frequency R decreases rapidily. The shadowed area represents typical values of R obtained for excitation frquencies between DC and 13.56 MHz with deposition parameters yielding good material quality. A preliminary interpretation of this curve has already been given in [13,14]. Here we shall limit ourselves to a summary of the essential factors. A change of f modifies the electron energy distribution function (EEDF) of the plasma [9,10]: High frequency plasmas have a relatively larger density of high-energy electrons when compared to low frequency plasmas; i.e. the high-energy tail of the EEDF is enhanced with increasing f. As a consequence one expects more ionization processes (the density of electrons capable of ionizing increases with f; for SiH_4 the ionization thresholds are between 11 and 15 eV [1]) and a larger total electron density n_e. There is, however, another counteracting effect competing with the first one: Increasing f causes also the average electron energy of the EEDF to be reduced, which in turn leads also to a reduction of the density of electrons having an energy larger than the ionization threshold energies. As a consequence, n_e is reduced, as well. The first effect we believe to be predominant below a certain frequency f_{opt}, the second one above f_{opt}. The total electron density would accordingly have some sort of maximum at f_{opt}. It is reasonable to assume that the silane dissociation efficiency, and therefore also the deposition rate R, are correlated with n_e. From these considerations a maximum in the curve R(f) is expected at f_{opt}. In the present case one has

SAMPLE

PARAMETER	A130287/2	A210287/1	A210287/2	A100287/1	A160287/1	A200287/1	A140287/2	A230287/1	A220287/1
Deposition parameters	T_S= 270°C, P=0.09 W/cm^3, p=0.35 mbar, F_{SiH_4} = 22.0 sccm								
f [MHz]	38			70			130		
d [μm]	2.8	5.2	22.8	2.2	5.0	23.6	2.2	5.9	27.6
R [A/sec]	14.4	14.5	11.9	21.2	21.0	17.2	14.9	16.4	14.5
c_H [at.%]	~ 5 - 8								
E_{opt} [eV]	~ 1.70								
N_D [$\times 10^{15}$/cm^3]	16	8.1	4.1	15	9.3	3.1	18	11	4.1
E_0 [meV]	62	58	51	59	60	55	58	59	59
σ_{dark} [$\times 10^{-11}$/Ωcm]	26	20	12	3.2	9.5	3.5	2.5	5.2	1.0
σ_0 [1/Ωcm]	3700	2600	2900	1700	2700	2700	5800	2800	3600
E_a [eV]	0.78	0.78	0.79	0.81	0.80	0.82	0.85	0.81	0.86
σ_{AM1} [$\times 10^{-5}$/Ωcm]	1.6	(1.5)	(0.4)	1.0	(1.4)	(0.2)	1.1	(0.6)	(0.8)

Table I: Deposition parameters and properties of a-Si:H films deposited by the VHF-GD method. All films have been prepared under identical conditions for 3 plasma excitation frequencies of 38, 70 and 130 MHz. The (bonded) hydrogen content c_H has been determined from the 640 cm^{-1} IR absorption band according to the formula given in [5].

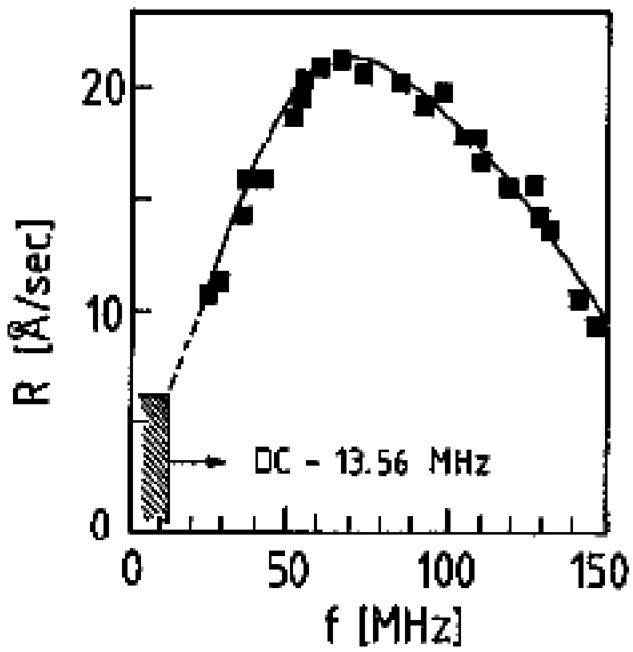

Fig.1 Deposition rate R as function of plasma excitation frequency f. The shadowed area represents typical values of R between DC and 13.56 MHz for good quality a-Si:H films, as given in the literature. The deposition parameters are: T_s=280 °C, P=0.1 W/cm³, p=0.28 mbar and F_{SiH4}=20 sccm

$f_{opt.}$=70 MHz (see Fig.1). Another important experimental observation, of an effect that possibly accentuates this maximum, has been made: Around $f_{opt.}$~70 MHz the plasma glow is extremely well confined to the space between the two electrodes. This effect of so-called 'plasma self-confinement' is considerably reduced below and above ~70 MHz.

Next, let us turn our attention to the quality of this VHF-GD samples deposited at a high rate. Table I summarizes (for comparison purposes) the deposition rate and the optical and electrical properties for three sets of samples, prepared at 38, 70 and 130 MHz, respectively. Each set contains three different sample thicknesses of approximately ~2 , ~5 and ~20 µm. From the behaviour of properties for different sample thicknesses, one can independently deduce bulk and surface/interface properties of the a-Si:H films.

Fig.2 summarizes the (total) PDS defect density N_D=N_s/d+N_b as function of the reciprocal thickness d. Here, N_s denotes the surface/interface defect density, N_b the defect density of the bulk. Additional parameters for the samples in Fig.2 are listed in Table I. The slope of the curve in Fig.2 is equivalent to N_s, the intersection point with the ordinate corresponds to N_b.

From this data one can draw a significant conclusion: N_s and N_b are independent of f over the range 38 to 130 MHz (although the deposition rate varies alomst by a factor of two). This would indicate either that all samples have similar properties or otherwise that PDS is not very sensitive to changes occuring in the material over the frequency range and the range of deposition rates considered. To obtain an additional information about the influence of R on N_D, 3 additional samples (not listed in Table I, denoted by the symbol x in Fig.2) of different thicknesses were deposited at 70 MHz. The RF power level was thereby reduced by a factor of more than 2 (compared with the other samples A100287/1, A160287/1 and A200287/1 deposited at 70 MHz and listed in Table I) such as to obtain a deposition rate of ~10 Å/sec. As can be seen from Fig.2, all 3 values of N_D for these additional samples are on the same curve as the ones listed in Table I. One can therefore conclude that N_D is practically insensitive to variations of R (at least for values of R up to ~ 20 Å/sec). In addition, one can assume that ion bombardment damages are practically negligible (ion bombardment energy is reduced with decreasing RF input power level). An interesting observation relates to the fact that the deposition rate is slightly thickness dependent (see Table I). This can probably be ascribed to a progressively thicker coverage degree of the RF electrode by a-Si:H.

σ_{dark} decreases with increasing frequency, while the activation energy E_a increases over the same frequency interval. As has already been discussed in [14] this phenomenon is attributed to internal film stress: The use of higher plasma excitation frequencies seems to lower internal film stress. This property may turn out to be beneficial in overcoming the crucial problem of degradation in a-Si:H cells. Practically no changes are observed in σ_{AM1} between 38 and 130 MHz.

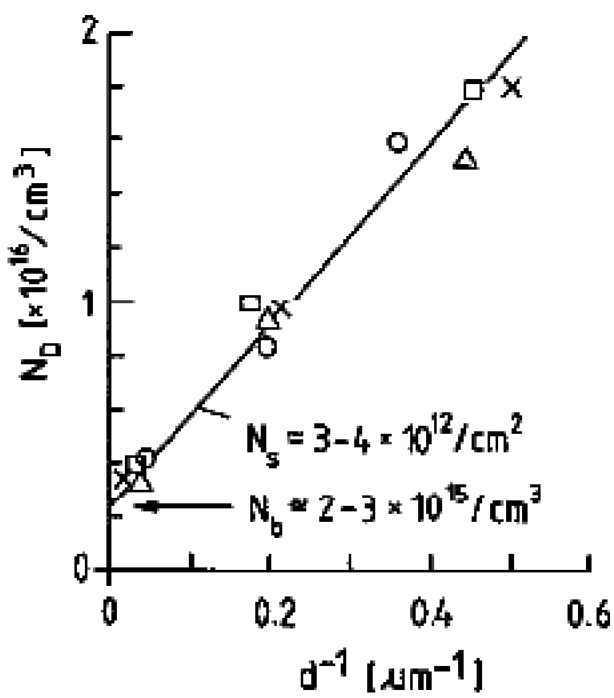

Fig.2 Defect density N_D calculated from photothermal deflection spectroscopy (PDS) data as function of the reciprocal film thickness d. N_b and N_s denote the bulk and surface/interface defect density, respectively.

(o) : f=38 MHz, (△): f=70 MHz and (□): f=130 MHz (deposition parameters for these samples are listed in Table I).

(x) : f=70 MHz, however with P=0.04 W/cm³ (all other deposition parameters are the same as for △)

How does this VHF-GD material behave in a solar-cell type of structure? In order to get some comparison values for low- and high-rate deposited a-Si:H, two Schottky-type solar cells with a Cr/n^+-type a-Si:H/intrinsic a-Si:H/Au structure were fabricated at 70 MHz. Diode Nr.1 was prepared with 5 Å/sec (intrinsic film) and has properties comparable with those of conventional RF-GD material prepared at 13.56 MHz for use in solar cells. Diode Nr.2 was fabricated at 15.7 Å/sec. Table II summarizes the measured characteristics.

DIODE	R(Å/sec)	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF	η [%]
Nr.1	5.0	551	1.25	0.50	3.4
Nr.2	15.6	531	1.17	0.51	3.1

Table II : Comparison of characteristics for two Cr/n^+-a-Si:H/intrinsic a-Si:H/Au Schottky diodes deposited at low rate (Nr.1) and at high rate (Nr.2), respectively. The measurements were done with 20 mW/cm^2 ELH white light illumination. η is the efficiency with respect to the fraction of light (=10 mW/cm^2) that is transmitted through the Au film (~50 % transmission). Both diodes are prepared by the VHF-GD method and have an active area of 16 mm^2.

Although the open circuit voltage V_{oc} and the short circuit current J_{sc} are slightly lower for diode Nr.2, the characteristics may be considered as comparable (Note: FF=Fill Factor, η=conversion efficiency). These findings are encouraging and open interesting perspectives for the application of this VHF-GD material in solar cells and other devices.

4.CONCLUSIONS

With a novel VHF-GD method, a considerable increase of the deposition rate has been achieved. This method consists of using a plasma excitation frequency f in the VHF range 30 to 300 MHz.Our preliminary results indicate: a-Si:H films prepared at ~70 MHz, at a rate between 15 and 20 Å/sec ,show similar properties as films prepared at a typical rate of ~3 Å/sec by the conventional 13.56 MHz GD technique. Support for this statement has also been obtained from a comparison of Schottky-type solar cells prepared at a high (15.7 Å/sec) and at a low rate (5.0 Å/sec), all at a fixed plasma excitation frequency of ~70 MHz.

Apparantely less internal film stress is present in VHF-GD deposited films when compared with a-Si:H films prepared at 13.56 MHz. This property may turn out to be beneficial in overcoming the problem of degradation (Staebler-Wronski effect) in a-Si:H solar cells.

Further study is however necessary for a better understanding of the influence of the plasma excitation frequency on structural, compositional and opto-electronic properties of this high-rate deposited material.

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