SCOPE OF VHF PLASMA DEPOSITION FOR THIN-FILM SILICON SOLAR CELLS

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ABSTRACT

The world-wide attempts in obtaining thin-film crystalline silicon are reviewed. Based on literature published sofar, it appears that high-temperature manufacturing steps seem to be unavoidable for obtaining high conversion efficiencies of crystalline silicon based solar cells. High process temperatures are in contradiction for the use of low-cost substrates like e.g. glass or aluminium. Such substrates, however, are essential for obtaining low module manufacturing costs. The Very High Frequency Glow Discharge Process (VHF-GD) could have the potential to overcome the temperature - efficiency contradiction.

INTRODUCTION

Solar cells based on crystalline silicon wafers show high efficiencies, however, their cost reduction potential is already almost fully exploited using conventional techniques. Thin-film solar cell concepts, like amorphous silicon (a-Si:H), copper indium diselenide (CIS) and CdTe have still a good cost reduction potential due to large-area, low-temperature manufacturing. These technologies contain, however, at least one striking disadvantage, mainly due to too low efficiencies or problems with the reproducibility at the pilot production level. Furthermore, new aspects like short pay-back time in energy, in costs and in environmental investments for future cell manufacturing have to be seriously taken into account.

THIN-FILM SILICON

It makes sense to combine the advantages of the well-established wafer-based silicon technology and thin-film technology in order to obtain thin-film crystalline silicon solar cells. The demands on this "magic" thin film silicon, looking at low-cost high efficiency solar cell manufacturing, can be expressed by the following catalogue:

1 Thin-film silicon must be *condensed* from the gas-, liquid- or the plasma-phase on a (foreign) substrate.
2 The substrate should be a *(cheap) non-silicon material* as e.g. glass, plastic or metal.
3 There should be *no* special requirements on the *preorientation* from the substrate to the growing film.
4 The process for deposition of thin-film silicon should be a *low-temperature process* (T< 400°C).
5 The *deposition rate* of thin-film silicon must be *high;* hence *total process time should be low.*
6 The thickness of the films (including light-trapping) should be *sufficient for absorbing* the whole sun spectrum, whereas,
7 the *diffusion / drift length* of thin-film silicon must be larger than the thickness of the cell.
8 It should have the potential for *large-area* module manufacturing.

REVIEW OF THIN-FILM SILICON PROCESSES

Such an ideal thin-film silicon which fulfills simultaneously all previous points is sofar only a vision. No technological process is sofar at hand to produce such a material. Note that the points 6 and 7 include the demand for a high efficiency, whereas all other points refer to the demand for cost reduction.

Within the last years, several laboratories in the world have picked up the challenge to deposit thin-film silicon. Tab. 1 gives an overview of the most important contributions. A detailed analyse of Tab. 1 shows the following features:

- cell efficiencies significantly higher than 10% seem sofar exclusively be reserved for processes higher than 900°C;
- a preorientation from the substrate is required or a wafer-type, self supporting substrate has to be applied;
- the a-Si:H/a-SiGe:H technology comes quite close to the ideal case (8 points). However, it is questionable whether much higher efficiencies can be obtained in future. It is the only non-crystalline silicon cell included for comparison;
- the process time for all cells is very long except the wafer-type based ribbon silicon cell or the hot wire process (still no cells presented sofar);
- the Micromorph cell contains a stable microcrystalline cell with still a promising potential for obtaining higher efficiencies at low process temperature.

The Micromorph tandem cell is the first thin-film silicon cell that consists of an amorphous silicon cell and an entirely microcrystalline p-i-n cell. It can thus be considered as the desired combination of the advantages of amorphous and crystalline silicon at low temperatures.. Looking at the status of Micromorph cell in Tab. 1, one must concede, however, that the comparison to other thin-film silicon cell approaches that are not tandem cells, might not be fair. All tandem concepts containing cells with two different gap energies can make better use of

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Requirements catalogue Approach [Ref]	1 conden- sation	2 low-cost substrate	3 pre- orientation	4 temperature [°C]	5 process -time	6 total absorption	7 diffusion -length	8 large -area	efficiency (stabilized)
Chem. Vap. Dep. MPI Stuttgart [1]	+	-	-	1000 (-)	-	+	+-	-	17.3%
Liquid Phase Epitaxy Uni. Canberra [2]	+	0	-	960 (-)	-	+	+	-	18 %
Silicon on Oxide Mitsubishi El Corp. [3]	+	?	+	> 1000 (-)	?	0	+	-	14.42
String- Ribbon Evergreen [4]	-	+	+	875 (-)	+	+	+	-	14.5%
Adv. Silicon-Films Astro Power [5]	+	?	?	?	?	+	+	+	12.2 %
Solid Phase Cryst. Sanyo El. Co [6]	+	+	+	600 (-)	-	+	0	+	9.2 %
Excimer cryst. Kaneka Corp. [7]	+	+	+	550 (0)	-	+	0	+	8.6 %
Hot Wire Ec. Poly. Palais. [8]	+	+	+	500 (0)	+	+	?	-	no cell
Closed Chamb. CVD HMI/TU Munich [9]	+	+	+	300 (+)	-	+	?	?	no cell
Micromorph cell IMT Neuchâtel [10]	+	+	+	200 (+)	-	+	?	+	>10 %*
a-Si /a-Ge USSC [11]	+	+	+	220 (+)	0	+	+	+	10.9 %

* value for amorphous / microcrystalline tandem gradity: + good 0 fair - unsatisfactory

Tab. 1. Different approaches for obtaining thin-film silicon. The approaches are judged looking at the eight point catalogue presented above. The process temperature classification was considered to be positive if glass substrates can be used.

the solar spectrum. In fact, the μc-Si:H bottom cell has an energy gap of about 1 eV, whereas the gap of amorphous top cell is about 1.7 eV. The Micromorph cell in Tab. 1 must be more seen under the aspect of combining amorphous silicon and crystalline silicon processing at low temperature. The a-Si:H technology contributes thereby the feasibility of serial connections where the transparent glass substrate is simultaneously one part of the encapsulation.

LOW-TEMPERATURE GROWTH MODEL OF SILICON

The following model is proposed understand the growth mechanism of crystalline silicon at low temperatures. The model is based on two necessary conditions for Si-radicals to contribute to epitaxial growth:

(i) The surface mobility must be high enough so that the radicals can first move that stick at a crystal site.

(ii) The energy impinging particles on the growth zone must not exceed the threshold energy for defect formation.

The model is briefly sketched out in Fig. 1. It was shown experimentally by Torres et al. [11] that epitaxial growth of highly boron doped monocrystalline silicon at temperatures as low as 170°C is possible.

If no orientation from the substrate is given, as sketched in Fig. 2, it is claimed that under the conditions (i) and (ii) high quality μc-Si:H can be obtained at low temperatures. As a particularity of this material, columnar growth with a high crystalline fraction is observed [10].

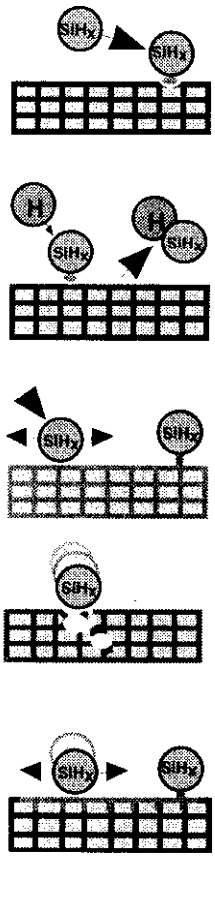
Condition (i) is guaranteed for high substrate temperatures that are used in conventional CVD processes, but high temperature is unwanted. Plasma processes, in general, offer the possibility of low temperature dissociation but condition (ii) is generally not fulfilled using standard conditions of DC PECVD or at a plasma excitation frequency of 13.56 MHz

Plasma processes have the advantage that dissociation of silane occurs at low substrate temperatures due to electron impact. However, because of the sheath potential ions are accelerated between the plasma edge and the substrate. In general lattice damage due to ion impact is caused. Neutrals furthermore undergo the charge exchange reaction (1); they can hence also cause lattice defects:

ion (fast) + atom (slow) -> atom (fast) + ion (slow) (1)

Veprek et al. [13] found that the threshold energy E_{th} for defect formation in a c-Si lattice due to hydrogen impact is 117 eV, for silicon it is about 16 eV, whereas Dutta et al. [14] estimated the peak ion energy in function of the plasma excitation frequency (Fig. 3).

Model for low-temperature Epitaxy on c-Si:H



Low substrate temperature:
A radical reacts immediately at any place, i.e. a non-crystal site.
No epitaxial growth occurs.

Atomic hydrogen etching can remove a radical from a non-crystal site.
The "error" in crystal growth can be **corrected.**

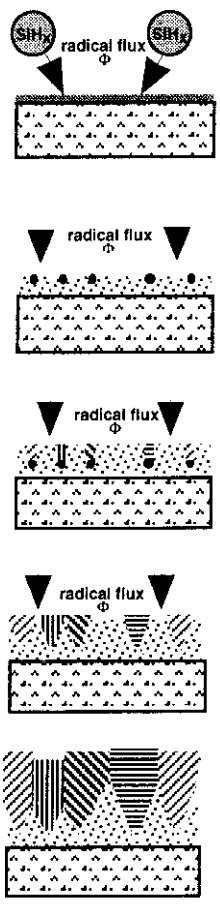
At high substrate temperature (>800°C) surface diffusion of radicals is activated.
They react at a crystal site.
CVD case
Epitaxyial growth occurs.

Too high kinetic energy of the radical cause lattice defects. The information for epitaxial growth is lost. General case for PECDV for DC or 13.56 MHz:
No epitaxy.

The energy of the radicals is high but not sufficient for defect formation, "virtual surface heating" happens. Surface diffusion is activated.
PECVD at VHF-GD conditions.
Epitaxial growth occurs.

Fig. 1: Schematical sketch of low-temperature epitaxial growth on c-Si by means of the VHF-GD process. TEM picture from previous work proves epitaxy at 170°C [12]

Model for μc-Si:H growth on glass



Due to the lack of forces that lead to oriented growth an amorphous silicon layer is formed.

Under favourable conditions, by chance, some tiny crystalline seeds are formed.

If the ion energy is too large, crystal growth and crystal damage-formation are balanced: only small crystals embedded in an amorphous matrix are formed.

If the substrate temperature is high enough, surface diffusion within the crystal area favours crystalline growth.

Under VHF-GD conditions the surface mobility of radicals is high and the defect formation rate is reduced. **Columnar growth** with a high **crystalline volume** fraction occurs [10].

Fig. 2: Schematical sketch of the columnar growth of solar-grade μc-Si:H by means of the VHF-GD process.

Using a Very High Frequency Glow-Discharge plasma at an excitation frequency of 70 MHz or higher, peak ion energies as low as 14 eV can be estimated, i.e. lower than the threshold energy E_{th} for the Si impact. At lower excitation frequencies, e.g. 13.56 MHz, however, values as high as 45 eV are typically observed.

Ions that are accelerated in the sheath by the sheath potential can loose energy due to collision with other particles (thermalization). The efficiency of thermalization of a particle of the mass M that strikes a particle of the mass m is given by the energy transfer function (2):

$$T = \frac{M \cdot m}{(M+m)^2}, \quad T = T_{max} \text{ if } M = m \qquad (2)$$

According to Somekh [14] the total number of collisions is a measure of thermalization. In the case of μc-Si:H deposition conditions, a strongly hydrogen diluted SiH_4 plasma (2% SiH_4 in H_2) is applied. In this case, only the collision of silicon radicals with similar radicals contribute to thermalization: if a fast Si-ion strikes a H-atom, only 6% of the energy is transferred, hence no thermalization occurs. For hydrogen ions is, on one hand, the threshold energy for defect formation very high, on the other hand perfect thermalization within the sheath can be assumed. Hence defect-formation due to hydrogen impact is assumed to be negligible.

Tab. 2 compares the mean free path l_H and l_{Si} with the sheath thickness d; the number of collisions n_{Si} within the sheath can be seen as a measure for the degree of thermalization of Si radicals.

For hydrogen diluted silane 13.56 MHz plasmas it can be concluded from Tab. 2 that ion energies higher than the threshold energy for defect formation are found. Furthermore, no thermalization in the sheath occurs. For a 70 MHz plasma, e.g. no thermalization occurs as well, but the energy of the Si ions is less than the threshold energy for defect formation. The VHF-GD process at 70 MHz excitation frequency (and higher) fulfills hence the

condition (ii); it plays by that, à priori, an imprtant role in low defect (crystalline) semiconductor manifacturing.

The condition (i) is also fulfilled; Heintze et al. [17] showed experimentally that at higher excitation frequencies the ion flux to the electrodes is increased. The latter one gives rise to an enhanced surface diffusion, even at low substrate temperature.

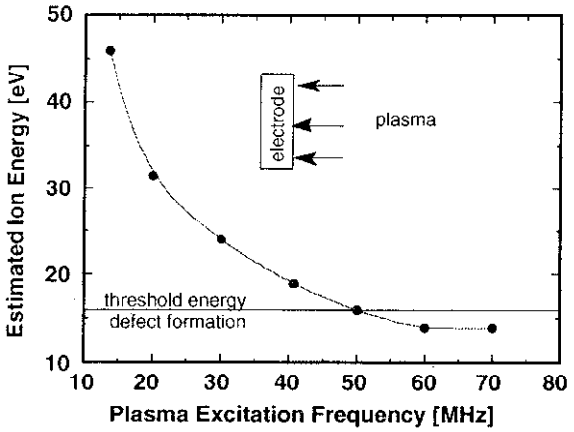


Fig. 3. Estimated peak ion energies in function of the frequency for SiH_4 plasmas. According to Dutta et al. [14].

f MHz	E* eV	d** mm	l_H mm	l_{Si} mm	n_H	n_{Si}	rem.
13.5	45	4.4	0.6	30	7.3	0	$E(Si)>E_{th}$
70	14	1.4	0.6	30	2.3	0	$E(Si)<E_{th}$

* taken from Fig. 3, **estimated from Kroll et al. [16]

Tab. 2: Effect of thermalization in a hydrogen diluted SiH_4 plasma used for the deposition of microcrystalline silicon.

CONCLUSIONS

We assume that in a strongly hydrogen diluted silane VHF plasma, as used for µc-Si:H deposition, silicon ion impact can not cause lattice damage. The increased ion flux gives rise to an enhanced surface diffusion of radicals in a more pronounced way as for a 13.56 MHz plasma. These two conditions (i) and (ii) formulated by our model are the requirements for the growth of crystals from localized seeds. The ensemble of all crystals together have by that the possibility to form high quality columnar µc-Si:H, as implemented in the micromorph cell.

It is expected that further progress in low-temperature thin-film silicon solar cell technology can be achieved that fulfills the eight requirements presented above. Further improvements of the deposition rate and of the cell performance are still needed.

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