

PHOTOVOLTAIC POWER GENERATION

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ABSTRACT

Choice of materials for photovoltaic solar cells is discussed, taking into account two factors, viz. conversion efficiency and production costs. Thereby, physical considerations (band gap) and general factors (material availability and toxicity) are developed. Deposition of hydrogenated amorphous silicon (a-Si:H) for solar cells, in a silane glow discharge plasma is discussed in more detail; possibilities (e.g. amorphous alloys, tandem cells) and limitations (e.g. light induced-degradation) are mentioned. The novel "VHF" plasma deposition process introduced by the authors' laboratory is given special consideration.

KEYWORDS

Materials availability; toxicity; cost factor; amorphous silicon; plasma deposition; VHF plasma.

INTRODUCTION

With the help of photovoltaic solar cells the energy contained in sunlight can be converted directly into electrical energy. This method of energy conversion has the great advantage of being extremely simple, free from the use of any mechanical moving parts, easily applicable in the form of small, decentralized units and finally, associated with relatively few safety, pollution and waste disposal problems. At present, the use of photovoltaic power generation is steadily increasing: the world-wide annual production of photovoltaic solar cells has increased threefold in the last ten years, commercial prices have been reduced by more than a factor of 2, and the energy conversion efficiencies of commercially available solar cells of a given type are also steadily being augmented (showing an increase of about 30 % in the last ten years). Photovoltaic power plants that are in operation since 10 to 20 years give us a clear indication of the very high level of reliability that can be obtained with this power generation technology. The main medium-term potential for photovoltaics lies in tropical, subtropical (e.g. Mediterranean) and alpine regions, due to the increased regular availability of sunlight there. Furthermore, one of the main disadvantages of solar energy are the short-term fluctuations in power supply (day-night cycles, weather influences) and therefore some form of energy storage is often needed - now, energy storage is most easily implemented in the form of water storage, be it by alpine hydroelectric storage lakes or, else, by small storage tanks for photovoltaic irrigation pumps in tropical countries. We may therefore expect the use of photovoltaic power generation to grow considerably, especially in the above mentioned regions, over the next few decades.

The purpose of the present paper is to briefly present the state-of-the art of photovoltaic technology and to discuss the main research and development problems that have yet to be tackled, before a more widespread use becomes possible. It will thereby be useful to distinguish between the three main groups of semiconductor materials used for photovoltaic solar cells: (1) crystalline silicon, (2) amorphous silicon and other amorphous, tetrahedrally-bonded semiconductors and (3) compound semiconductors, like GaAs, CdTe, CuInSe₂, InP etc. mainly used in their (poly)crystalline form. Solar cells belonging to the second group of materials, i.e. to amorphous semiconductors, and, in particular, to hydrogenated amorphous silicon (a-Si:H), are generally fabricated by plasma-assisted chemical vapour deposition (plasma-CVD). We will therefore in this contribution treat the fabrication of amorphous silicon solar cells in more detail and indicate the relationship between plasma properties and resulting characteristics of a-Si:H solar cells. Finally, we will deal with a new development in plasma deposition that was initiated (Curtins *et al.*, 1987)

at our own laboratory at Neuchâtel, namely the use of higher excitation frequencies for plasma-CVD deposition. This method that has been called the Very High Frequency (VHF) - glow discharge deposition method (Shah *et al.*, 1992) has a potential for cost reduction and perhaps also for other improvements.

PHOTOVOLTAIC MATERIALS AND FABRICATION TECHNOLOGIES

In full sunlight and with a surface exactly vertical to the incident light-rays, one collects roughly 1000 W of light energy per m^2 . Out of this, some 5 to 35 % (or 50 to 350 W) can be converted, by photovoltaic cells, into electrical energy, whereas the rest will be lost (i.e. mainly converted at some point or other into heat). If one compares the values of electrical power available per m^2 of photovoltaic panel to the typical power levels required for agricultural, domestic and industrial uses of electricity, one immediately sees that photovoltaic power generation is almost always going to require considerable surfaces. One also understands immediately that the two main priorities of photovoltaic research are going to be: (1) increase of solar cell efficiencies from present (commercial) values of around 10 % to values as high as possible and (2) decrease of solar cell prices from present commercial prices of around 5 \$ per W_p to as low prices as possible [W_p stands for "peak"-Watt at standard operating conditions of 1000 W/m^2 incident sunlight and a cell temperature of 25 °C]. In fact, one would wish to reach a combination of 20 % cell efficiency at 2 \$/ W_p . Now, it is relatively easy to achieve just one of these two goals, at the detriment of the other one: Indeed, laboratory cells have been fabricated with efficiencies around and even well over 20 %, however, the fabrication procedures involved become extremely sophisticated and costly (with prices well over 100 \$/ W_p). On the other hand, amorphous silicon technology permits one to reduce fabrication costs to presently about 2 \$/ W_p , but the stable efficiency of commercial amorphous silicon cells is, at this moment, limited to about 5 %. The main thrust of future efforts has, therefore, to be towards a combination of both goals: high-efficiency and low price. Both parameters, i.e. efficiency and cost are closely linked to an appropriate choice of materials and fabrication processes.

The most important physical parameter involved in the choice of a semiconductor material for photovoltaics is the energy gap E_g of the semiconductor. The value of the energy gap E_g has to be adjusted to the average photon energies available in the sunlight spectrum. In fact, for the basic solar cell configuration, all photons with energy $h\nu < E_g$ are lost (h being Planck's constant and ν the frequency of the incident light), i.e. these photons are not usefully absorbed by the semiconductor material. On the other hand, all photons with energies $h\nu > E_g$ only contribute partly to the photovoltaic conversion process: they create by absorption in the semiconductor an electron-hole pair with a usable energy of E_g , whereas the excess energy $h\nu - E_g$ is almost immediately lost by thermalization. The efficiency of this spectral conversion process is, therefore, in the basic case of a photovoltaic configuration with a single gap E_g , never 100 %, and takes on a maximum of almost 50 % for an intermediate value of E_g near 1.2 eV.

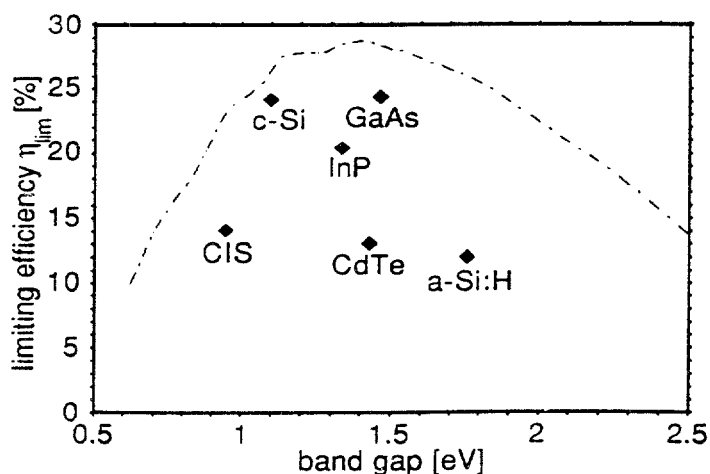


Fig. 1: Semi-empirical limiting efficiency η_{lim} as a function of energy gap E_g for the basic structure of a single-gap photovoltaic solar cell without concentration of sunlight (according to Shah and Tscharnner, 1991) and some experimental values for the efficiencies of best laboratory cells obtained to date (Kazmerski, 1989). Note that tandem cells (i.e. double junctions with two different gaps) and other sophisticated structures may have higher efficiencies than η_{lim} .

After the generation of electron-hole pairs by optical absorption, it will be necessary to separate electrons and holes (before they can recombine) and this is done by an internal electrical field, obtained by the solar cell that is structured as semiconductor diode (see also Fig. 4a). Only thanks to this separation will an external voltage appear at the solar cell output. The separation process has basically its own inherent losses: even in the very best case something like 30 to 50 % of the remaining energy is lost. The separation process is slightly more efficient for diodes with higher gaps E_g ; thus the optimum gap E_g is now shifted upwards to around 1.5 eV. Taking into account empirical relationships for the best (most favourable) current-voltage characteristics obtainable today for semiconductor diodes with different gaps E_g and using the efficiency values for the spectral conversion efficiency η_s , as described above, one can determine a semi-empirical limiting efficiency $\eta_{lim} = f(E_g)$ for a single-gap photovoltaic solar cell (Shah and Tscharnner, 1991); this curve is reproduced in Fig. 1, together with the best laboratory efficiency values obtained so far. Fig. 1 has been computed assuming "ideal" conditions, i.e. all useful photons with $h\nu > E_g$ are absorbed, and all electron-hole pairs generated thereby can be collected, if the cell is short-circuited. In fact, the cell is never thick enough to absorb all useful photons and the semiconductor material is never good enough to allow for full collection, even under short-circuit conditions.

How thick should a solar cell be to absorb say 90 % of the useful part of sunlight? This depends upon material structure (crystalline vs. amorphous) and nature of band gap (indirect vs. direct). Crystalline semiconductors with indirect band gaps (such as silicon, germanium, etc.) have - due to restrictions by quantum mechanical selection rules - absorption coefficients that are relatively low and therefore will require typically cell thickness of around 10 μm and more, whereas in all other cases (crystalline semiconductors with direct band gaps as well as all amorphous semiconductors), absorption coefficients are generally considerably higher, allowing for solar cell thicknesses of around 1 μm . On the other hand, collection will be invariably better in the crystalline case and is strongly hampered by defects in the amorphous case. We are thus faced for widespread power generation with three basic technological options for photovoltaics: (1) use of crystalline silicon in form of wafers (100 - 300 μm) or possibly of "thick" polycrystalline films (10 - 50 μm), (2) use of amorphous silicon "thin" films (1 μm and less), (3) use of semiconductors with direct band gaps, preferably in a polycrystalline thin film form.

In the third group, the main materials studied so far for photovoltaic applications and showing any experimental success are GaAs, CdTe, CuInSe₂ and InP. These four compound semiconductors have components that are either highly toxic or very rare or both (see Tab. 1). It is therefore the authors' opinion that they cannot constitute a viable long-term option for photovoltaic power generation. Some other materials such as FeS₂ (pyrite) and even some other principles, such as photoelectrochemical cells (Grätzel, 1991) are being investigated, but have not yet led to industrially viable solar cells.

element	average amount of elements in the earth's crust g/t or ppm	limits for human exposure* mg/m ³	remarks about toxicity
Si	277200	10	mineral dust
Ga	15	-	-
As	5	0.5	toxic, carcinogenic
Cd	0.15	0.05	very toxic, carcinogenic
In	0.1	0.1	-
Se	0.09	0.1	toxic
Te	0.002	0.1	very toxic

* Threshold limit values of airborne contaminants by inhalation, ingestion, skin absorption, or contact to any material or substance.

Tab. 1: Availability/toxicity of some important photovoltaic materials.
Source: Handbook of Chemistry and Physics (1981/82)

We are thus practically left with silicon as (so far) only proven viable material for photovoltaic power generation: here, both crystalline and amorphous forms deserve to be considered. Crystalline silicon at present shows significantly higher stable efficiencies (commercially 10 to 15 %) than amorphous silicon (commercially 5 %). On the other hand, the projected cost for large-scale production of photovoltaic solar modules according to presently available technologies, are presently a factor 2 higher per W_p for crystalline silicon than for amorphous silicon (see Shah and Tscharnner, 1991). Indeed, crystalline silicon involves at present costly and delicate wafer-sawing, whereas amorphous silicon fabrication is based on the simple and basically inexpensive plasma-assisted deposition process described in the next section. Even more important than costs are, in the long run, the energy amounts invested in the materials (so-called "gray

energy") and in the fabrication processes themselves; here again, the amorphous option has an advantage of a factor 2.

AMORPHOUS SILICON DEPOSITED IN A GLOW DISCHARGE PLASMA

In the last 2 decades, plasma-assisted techniques have been found to be one of the main factors in the development of new deposition and etching processes for the fabrication of semiconductor devices. In fact, thanks to the glow discharge (GD) plasma reactor, Chittick *et al.* (1969) were able to obtain a novel material, hydrogenated amorphous silicon (a-Si:H), by the decomposition of silane (SiH_4) gas within the plasma. In contrast to thermally evaporated or sputtered amorphous silicon without hydrogen, as had been previously produced and investigated, these new hydrogenated amorphous silicon layers prepared from silane (SiH_4) by the plasma process, showed an excellent photoconductivity as well as many other useful semiconductor properties. The absorption is about 20 times higher than that for crystalline silicon. Thus, a $0.5\text{ }\mu\text{m}$ thin a-Si:H layer is thick enough to absorb the greater part of the visible light down to the energy of the "gap" of hydrogenated amorphous silicon.

The quality of the produced a-Si:H film is related to the specific deposition process used. The most commonly used deposition reactor is a capacitively-coupled radio frequency glow discharge (RF-GD) system, which is shown in Fig. 2. In this reactor chamber, SiH_4 is decomposed by the discharge formed between two parallel electrode plates, one of which is connected to the RF-generator. The substrate is usually placed on the grounded electrode. With this configuration it is possible to grow a-Si:H films with good electronic properties. This type of reactor is most widely used at present because it allows for deposition of films of large areas (1 m^2 and above). It has therefore been applied to the industrial production of a-Si:H solar cells and other a-Si:H devices (optical line scanners for Telefax, flat-panel displays, photoconductors for photocopying machines etc.).

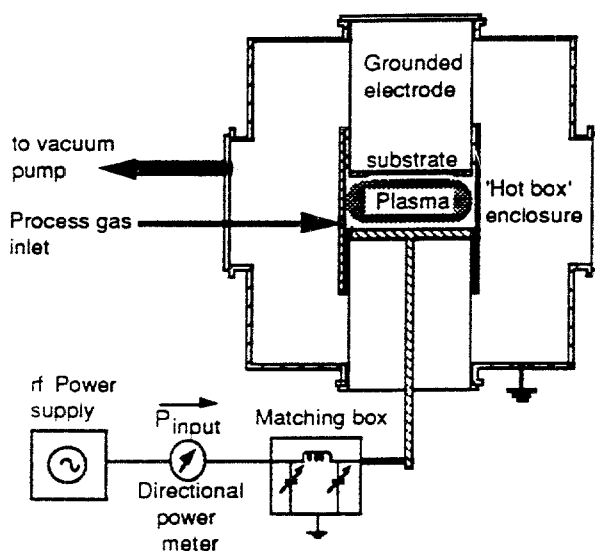


Fig. 2: Arrangement of a RF plasma-CVD glow discharge deposition reactor. Typical parameters are: $P = 0.1 - 1\text{ mbar}$, SiH_4 -gas flow = $5 - 200\text{ sccm}$, RF power $5 - 20\text{ W}$, substrate temperature $200 - 300\text{ }^\circ\text{C}$, cathode-anode distance $15 - 30\text{ mm}$.

Generally, the "amorphous" or disordered phase leads to the existence of localized states within the "forbidden" band gap (Fig. 3a). The existence of these localized gap states constitutes the major difference between an amorphous and a crystalline semiconductor. The network disorder itself results in bandtail states, which reach exponentially into the gap. In an amorphous network, there are also always a certain amount of point defects (e.g. broken bonds, or so-called "dangling bonds") and these lead to "defect states" that are located somewhere in the middle of the "forbidden" band gap. Because of their location in the centre of the band gap, these defect states (dangling bonds) act as recombination centres and are particularly detrimental to the electrical properties. Actually, instead of speaking of a "band gap" in the case of an amorphous semiconductor, it would be more correct to speak of a "mobility gap" (as indicated in Fig. 3a). This mobility gap is an energy region containing localized states (i.e. states with zero mobility) in contrast

with the bands that contain extended states, having a finite, non-zero mobility. Still, the term "band gap" is currently used, because of the analogy with crystalline semiconductors.

In the non-hydrogenated form of amorphous silicon there are about 10^{19} defect states per cm^3 , i.e. so many defect states that the material is totally unsuitable for semiconductor devices. Thanks to the introduction of hydrogen into the network by means of the silane (SiH_4) plasma process, almost all of the dangling bonds become saturated by a hydrogen atom and then no more act as defect states. Thus, in hydrogenated amorphous silicon only about 1% of the original number of defect states (i.e. $10^{16}/\text{cm}^3$ or less) remain and we obtain a semiconductor of reasonable quality that can be used to fabricate devices.

Whereas the unhydrogenated form of amorphous silicon cannot be usefully doped to produce p- and n-type layers (the Fermi level E_F is "pinned" near mid-gap due to the large amount of defect states), hydrogenated amorphous silicon can be doped by adding either phosphine (PH_3) or diborane (B_2H_6) to silane (SiH_4) as additional process gas input. This was systematically investigated and published by Spear and LeComber (1976). Typical doping results for glow discharge a-Si:H are given in Fig. 3b. Doping is not nearly as effective in a-Si:H as in c-Si. One sees in Fig. 3b that when the Fermi level E_F is in a range of about ± 0.5 eV midgap, it then becomes virtually impossible to move into the uppermost or lowermost 25 % of the "mobility gap". This is partly due to the existence of many band tail states in these regions. It is also due to the fact that the incorporation of dopant atoms strongly increases the density of unsaturated defect (dangling bond) states. Strongly doped a-Si:H layers have defect densities around $10^{18}/\text{cm}^3$ or even higher and thus again approach the defect density values of unhydrogenated a-Si. Doped a-Si:H layers can only be used as very thin layers to constitute semiconductor barriers. The main part of the work in a-Si:H devices has to be done by the intrinsic (i) layers, as only these layers have a reasonable quality.

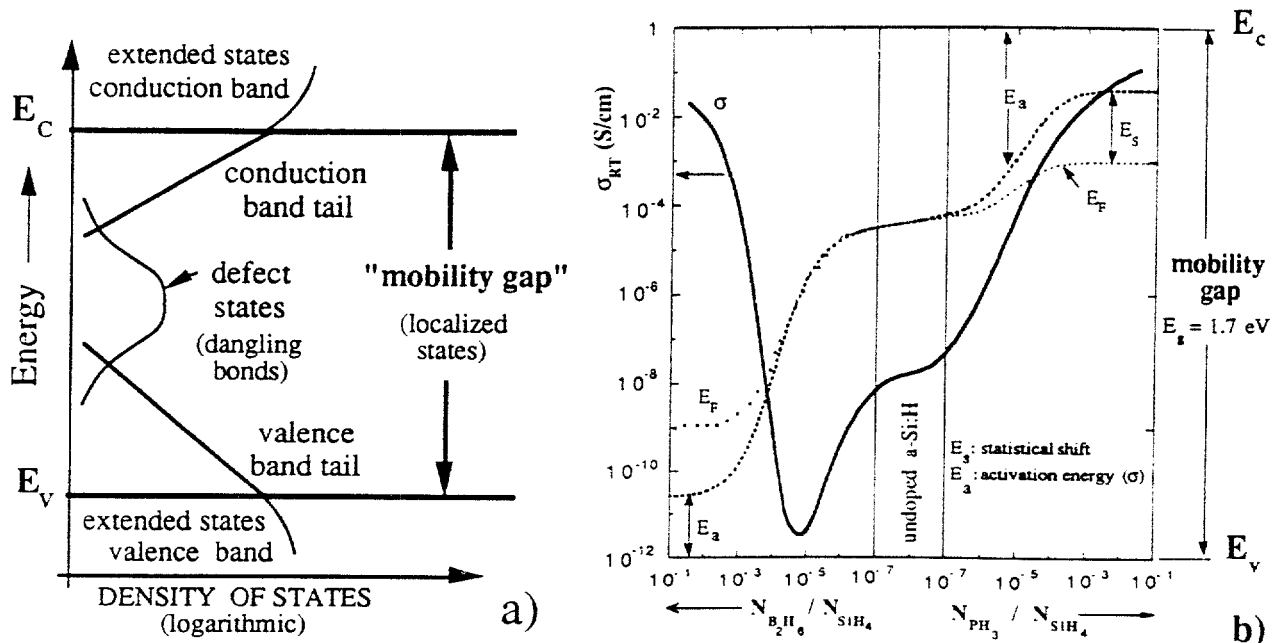


Fig. 3: a) profile of density of states as a function of energy in a-Si:H. b) dark conductivity at room temperature (σ_{RT}), activation energy (E_a) and position of the Fermi-energy (E_F) in the "mobility gap" as a function of the gas dopant concentration. σ_{RT} and E_a are results from Spear and LeComber (1984) and Okamoto (1980), while E_F was deduced by the theoretical model of Overhof and Thomas (1989) for n-doped a-Si:H and extrapolated by the author for p-doped material.

It is for this reason that a-Si:H solar cells have the **p-i-n** structure shown in Fig. 4 a): i.e. they consist of a relatively "thick" i-layer (where all the useful photogeneration of the electric carriers is done) and very thin p- and n-doped layers. The front doped layer (i.e. the p-doped layer in the structure of Fig. 4 a) should be very thin and also alloyed with carbon (a-SiC:H), so as to avoid absorption losses (photons absorbed in this doped layer will not contribute usefully to the photogeneration current). On the other hand, a-Si:H produced by the plasma process, can indeed be easily alloyed with other tetraedric semiconductors, like carbon (C) or germanium (Ge), by adding e.g. either methane (CH_4) or germane (GeH_4) as additional process gas input into the plasma reactor. These a-SiC:H or a-SiGe:H alloys have either a higher or a lower band gap, respectively, and permit the fabrication of double-junction tandem cells (as shown schematically

in Fig. 4 b). It should be mentioned that these alloyed layers (at least so far) do not have the same quality as "pure" a-Si:H layers. The density of defect states, for example, is significantly increased by alloying. It appears that one may at least partly be able to improve on these alloyed layers, if one is able to match the process parameters of the plasma process to the specific requirements of a given alloy.

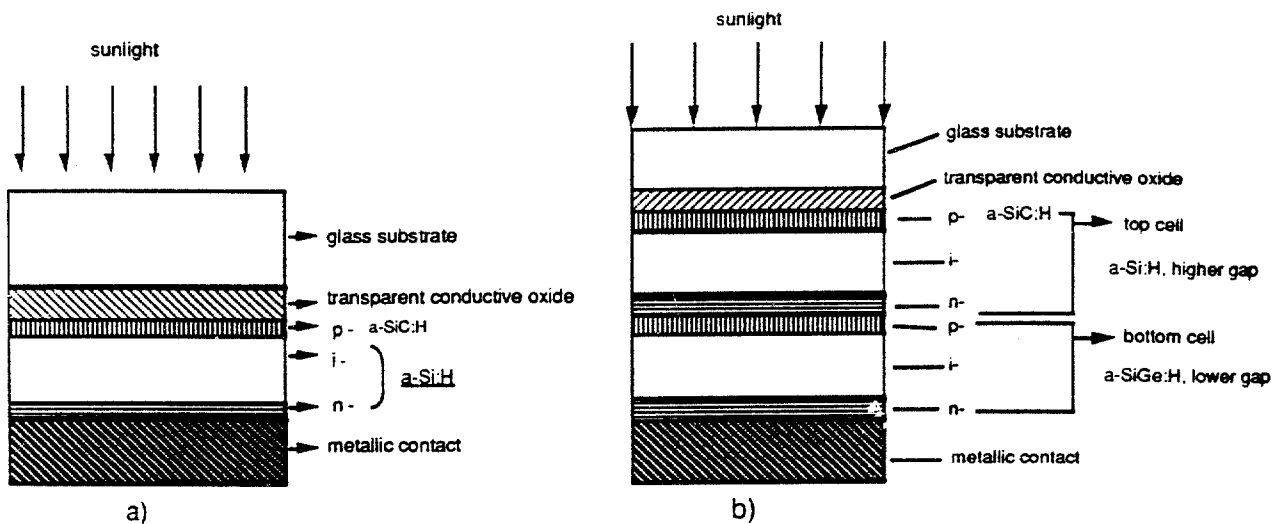


Fig. 4: Structure of a-Si:H solar cells: a) single junction pin- and b) double junction tandem.

Today (1992), the best single-junction laboratory a-Si:H cells (Fig. 4 a) have (initial) efficiencies of between 12 and 13 %; the best laboratory tandem cells (double-junctions according to Fig. 4 b) and triple-junctions) have slightly higher (initial) efficiencies (between 13 and 14 %). Large-area industrially fabricated a-Si:H solar cells are, so far, only of the single-junction type and have (initial) efficiencies between 5 and 7 %. All these efficiencies are still rather low, but there is scope for further improvement.

However, the most important limitation of amorphous silicon solar cells is, at present, the so-called Staebler-Wronski effect (SWE) or light-induced degradation effect: After the first few hundred hours of operation of an a-Si:H solar cell, roughly a third of the initial efficiency is lost. This effect is reversible; a moderate increase of temperature causes the efficiency to increase again. Thus, the exact value of the stabilized (or rather "equilibrium") efficiency depends on the temperature of operation and the intensity and pattern (timing) of the light received. For explicable and well-known reasons, tandem cells show less degradation (only about 10 %) than single-junction cells. This is one avenue of development to increase the stabilized (or "equilibrium") efficiency of a-Si:H solar cells.

The other avenue of development on which many researchers are attempting to work, is to reduce the Staebler-Wronski effect (SWE) itself. It is currently known that the SWE is due to an increase of the dangling bond states from around $10^{15}..10^{16}/\text{cm}^3$ in as-deposited intrinsic layers to over $10^{17}/\text{cm}^3$ in degraded layers. Furthermore, this increase is intricately linked to the microstructure of the material. All a-Si:H layers deposited, up until now, have a large number of microvoids, which, in a good-quality layer, are relatively small (10-100 Å). Form, size and density of microvoids have been shown to decisively influence the SWE. Thus, it is hoped that a more profound knowledge of the link between plasma process parameters, deposition growth kinetics and microstructure will enable us to significantly reduce the SWE and thus help to produce remarkably better a-Si:H solar cells. So far, the attempts have been by trial and error and the results obtained are not negligible, but remain far from being convincing.

EXAMPLE OF A SPECIFIC PLASMA PROCESS DEVELOPMENT: VERY HIGH FREQUENCY (VHF) GLOW DISCHARGE (GD) PROCESS - THE NEUCHÂTEL APPROACH

There are many avenues for modifying the standard RF glow discharge process used for the deposition of aSi:H layers. At our Institute in Neuchâtel, we have varied the frequency of the RF excitation within the so-called VHF range (preferably around 70 MHz) instead of using the standard industrial frequency of 13.56 MHz. A change in the plasma excitation frequency, in fact, profoundly modifies the behaviour of a glow discharge plasma (especially of the glow discharge sheaths).

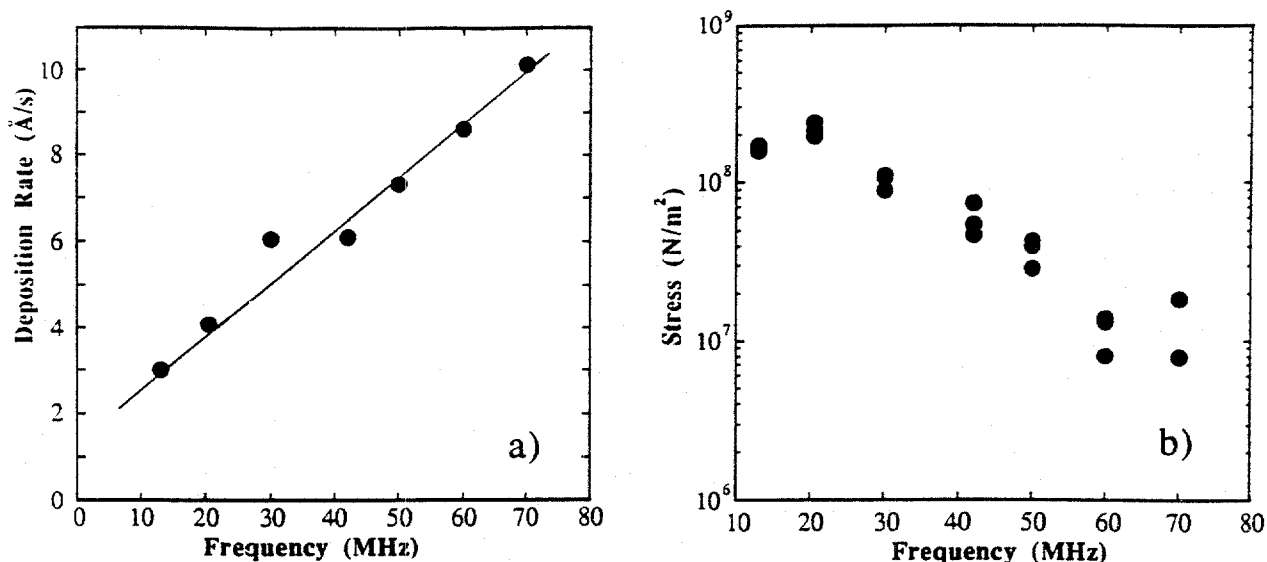


Fig. 5: Characteristic properties of VHF glow discharge deposition:
a) deposition rate as a function of the plasma excitation frequency at constant plasma power ($P_{\text{plasma}} = 5 \text{ W}$) (Howling *et al.*, 1992).
b) variation of intrinsic mechanical stress in a-Si:H films with respect to different plasma frequencies prepared under otherwise similar conditions (Shah *et al.*, 1992).

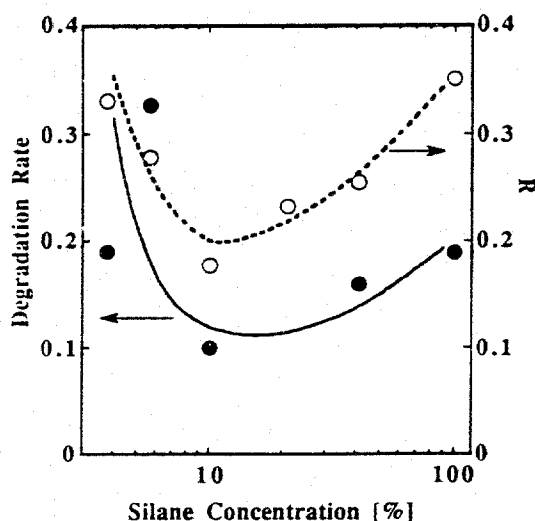


Fig. 6: a-Si:H layers produced by Ar-dilution in a VHF glow discharge: Degradation rate (slope of the photoconductivity decay during light soaking, (●) and microstructure parameter R (○) vs. silane concentration in Ar atmosphere (Kroll *et al.*, 1992); R is a measure of H-clusters and Si-H bonds on internal surfaces from IR-transmission.

Some of the results obtained so far, are summarized in Fig. 5 and 6. The deposition rate (which is indeed an economically important limitation in the industrial production of a-Si:H solar cells) can be increased by about a factor of 3 (Fig. 5 a). Internal mechanical stress (this is linked with the microstructure) at a constant substrate temperature of 200 °C, is strongly decreased (Fig. 5 b). This is due to a modification in the microstructure, caused by a variation in the ion bombardment originating in the sheath region of the glow discharge; it might have a certain potential importance in decreasing SWE, because external mechanical stress is known to influence the SWE. Finally, Fig. 6 shows the influence of argon dilution (instead of pure silane we use silane diluted by argon) on the light-induced degradation rate (●) and on the microstructure parameter R (○) for the VHF-GD process. Interestingly, for VHF conditions, a dilution of

SiH₄ of one part in ten parts of argon, leads to a slight, but distinct improvement in both degradation rate and microstructure. This and other work done at various laboratories are the first signs of some hope in the battle for reducing the SWE and thus arriving at amorphous silicon solar cells with significantly increased stable (or "equilibrium") efficiency.

CONCLUSIONS

Photovoltaic power generation is indeed a practical and convenient way of catering to energy requirements, especially in tropical, subtropical and alpine regions. Incident sunlight power is, at a maximum, around 1 kW/m². Incident sunlight energy, integrated over a full year is between 1000 kWh/m² and 2000 kWh/m², in the above-mentioned regions. On the other hand, practical photovoltaic conversion efficiencies are limited, for the foreseeable future, to the range of 10 to 20 %. This means that we will obtain something in the order of 200 kWh/m² or 200 GWh/km² of usable electric energy from such photovoltaic power plants (whether they be small decentralized units of rooftops, or larger centralized plants in remote desert regions). Thereby, the energy storage problem has yet to be solved in a suitable way (in a first phase, e.g. by hydroelectric storage lakes, and later by hydrogen storage). Within such a scenario, photovoltaic power generation should become a significant contributor to the World's total electric energy needs, in the next few decades. For this to happen, photovoltaic solar cells will have to be based on a semiconductor with a suitable "band gap", that is also abundantly available and non-toxic. Here, silicon is by far the most likely candidate. On the other hand, we will need a fabrication process that can turn out, in a low-cost fashion, and with low process energy requirements, many square kilometers of photovoltaic solar cells. At the present moment, the deposition process of hydrogenated amorphous silicon in a silane glow discharge plasma is one of the most promising candidates for achieving this goal. However, quality and stability of present amorphous silicon layers are not yet sufficient to achieve even 10 % stabilized conversion efficiencies. There is a distinct hope of improving the stability by changing the microstructure of the plasma-deposited amorphous layers. To achieve this goal of improving and controlling the growth kinetics of the glow discharge deposition process, a close collaboration between plasma physicists and semiconductor device engineers is called for.

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