Industrialization of Hot Wire Chemical Vapor Deposition for thin film applications

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ABSTRACT

The consequences of implementing a Hot Wire Chemical Vapor Deposition (HWCVD) chamber into an existing in-line or roll-to-roll reactor are described. The hardware and operation of the HWCVD production reactor is compared to that of existing roll-to-roll reactors based on Plasma Enhanced Chemical Vapor Deposition. The most important consequences are the technical consequences and the economic consequences, which are both discussed. The technical consequences are adaptations needed to the hardware and to the processing sequences due to the different interaction of the HWCVD process with the substrate and already deposited layers. The economic consequences are the reduced investments in radio frequency (RF) supplies and RF components. This is partially offset by investments that have to be made in higher capacity pumping systems. The most mature applications of HWCVD are moisture barrier coatings for thin film flexible devices such as Organic Light Emitting Diodes and Organic Photovoltaics, and passivation layers for multicrystalline Si solar cells, high mobility field effect transistors, and silicon heterojunction cells (also known as heterojunction cells with intrinsic thin film layers). Another example is the use of Si in thin film photovoltaics. The cost perspective per unit of thin film photovoltaic product using HWCVD is estimated at 0.07 €/Wp for the Si thin film component.

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1. Introduction

1.1. The Hot Wire CVD technique for the deposition of thin film silicon

Hot Wire Chemical Vapor Deposition (HWCD), also called Catalytic Chemical Vapor Deposition (Cat-CVD) [1] is a deposition method in which the precursor gases, e.g. silane or silane/hydrogen in the case of thin film silicon deposition, are catalytically dissociated at resistively heated filaments [2]. The deposition regime is fundamentally different from that where plasmas are involved, such as PECVD (Plasma Enhanced Chemical Vapor Deposition). HWCVD is a relatively new deposition technology that has shown technological and scientific developments over the past 20 years, providing improved control of parameters. The technology is undergoing significant progress, similar to the developments that plasma enhanced CVD (PECVD) has gone through in the 1970s and 1980s. HWCVD is becoming increasingly mature [3] and presently yields optoelectronic devices with state-of-the-art properties, even though our understanding of gas-phase and growth reactions is far from complete.

The high efficiency of H2 dissociation at a tungsten wire has been utilized since the 1960s [4]. The first patent [5] and publication [6] on HWCVD appeared in 1979 (then called ‘thermal CVD’) in the USA. Approximately 6 years later, Matsumura and Tachibana [7] used this technique for the preparation of fluorinated amorphous silicon. The preparation of hydrogenated amorphous silicon (a-Si:H) was investigated by Doyle et al. [8] and Matsumura [9,10] in the late 1980s, showing the high deposition rate as the prominent feature. Increased interest in the deposition method came in 1991 due to Mahan et al. [2,11], who demonstrated for the first time the possibility to produce device-quality a-Si:H with a hydrogen concentration below 1 at.-%. Due to this development, many laboratories entered the field and presently, well over 30 research laboratories have HWCVD deposition facilities. The first thin film silicon solar cells were made in 1983 at the University of Kaiserslautern and at NREL, while the first TFTs were made in 1995 at Utrecht University and JAIST (Japan). Within Europe, more than 10 groups are using the technology to create novel thin films and devices. In Japan, the main (academic) players are JAIST, Osaka University, Gifu University, and Tokyo Institute of Technology. Several companies have developed commercial systems, such as CVD (Cambridge, USA), sp3 (Santa Clara, USA), Elettrovaria (Italy), Ulvac (Japan), Canon-Anelva (Japan), and first applications of HWCVD layers have been introduced in electronic products (Mitsubishi Electric, Ishikawa Seisakusho). The use of HWCVD processes in consumer products is usually not made public by the manufacturers, but in Table 1 the commercial applications of HWCVD are listed as far as they have been publically presented.

The technology has yielded silicon thin films with amorphous, proto-, micro-, and polycrystalline properties [12,13]. Doped layers,
both p-type and n-type, have been shown to be feasible. Alloys, such as SiGe:H [14], SiN:H and SiC:H have been demonstrated, both in the amorphous phase and the nanocrystalline phase. Even SiO2 layers have been made with the HWCVD technique [15,16]. Oxide layers can be more difficult to obtain because there is a risk of oxidation of the hot catalytic metal filaments with oxidizing species [17].

1.2. The Hot Wire CVD technique for the deposition passivating SiNx:H layers

Plasma-free deposition of dielectric layers has attracted much attention because of the potential to prevent ion bombardment damage [18,19]. Dielectric layers, such as silicon nitride with device quality properties, made at a high rate of 3 nm/s, have been demonstrated to be good passivation layers for multicrystalline solar cells [20]. A schematic visualization of this application is shown in Fig. 1. The high rate allows deposition of the SiNx to the right thickness for an optimal rate allows deposition of the SiNx to the right thickness for an optimal be good passivation layers for multicrystalline solar cells [20].

Using initiated CVD (i-CVD), polymer layers can be deposited conformally on many kinds of surfaces [22]. In i-CVD the reactions are initiated by the catalytic decomposition of organic precursor molecules at a heated filament and polymerization takes place at the substrate surface at temperatures close to room temperature. Fig. 2 shows a schematic representation of the i-CVD process. A large variety of polymer materials has been made, for example, PTFE (Poly-tetra-fluoro-ethylene; Teflon) [23], trimethylvinylcyclohydrinoxane (V3D3) [24], and PGMA (Poly-glycidyl-methacrylate [25,26].

Aiming for water vapor barrier films, Bakker et al. [25] and Coclite [27] demonstrated that even thin i-CVD layers of PGMA (down to only 300 nm) are good planarizing layers. Bakker showed that the rms surface roughness of the Asahi U-type TCO substrate was decreased from 42.3 nm to 14.3 nm with a 335 nm thick PGMA layer. This property is of importance to water vapor barrier multilayers as it facilitates filling the pores and cracks that may be present in earlier deposited (inorganic) layers [28].

Further, as is generally the case in HWCVD, also for polymer films high deposition rate can be obtained. In i-CVD, high rate is achieved when the amount of adsorbed monomers on the surface is high. Thus, the deposition rate increases as the ratio of monomer partial pressure (Pmon) and saturation pressure (Psat) increases. Therefore, this increases for precursors of which the monomer-saturated vapor pressure is smaller, such as for monomers with higher alkyl chains [29]. It is important to note that the choice of monomers is constrained by the need to have sufficient vapor pressure to deliver the monomer into the reactor. Another way to increase the deposition rate is by decreasing the substrate temperature, as this also decreases Psat. However, the monomer partial pressure should never exceed its saturation pressure (Pmon), as this leads to droplets and discontinuity of the film. As an example of deposition rate, 2–3 nm/s for PGMA deposition can be routinely

### Table 1: Commercial applications of HWCVD.

<table>
<thead>
<tr>
<th>Process</th>
<th>Application field</th>
<th>Manufacturer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gate side wall insulation</td>
<td>Si ULSI</td>
<td>ULVAC (equipment)</td>
<td>[33–34]</td>
</tr>
<tr>
<td>Surface passivation of III-V</td>
<td>High speed compound semiconductor devices</td>
<td>Canon-Anelva (equipment); Mitsubishi Electric Corp. (devices); Mitsuishi</td>
<td>[35]</td>
</tr>
<tr>
<td>transistors and lasers</td>
<td>PV (thin film cells and silicon heterojunction</td>
<td>ULVAC (equipment); Canon-Anelva (equipment); Nexpower Technology (devices)</td>
<td>[36–38]</td>
</tr>
<tr>
<td>a-Si:H thin film</td>
<td>passivation), TFT-LCD, photocopyer drums</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTFE</td>
<td>Low friction surfaces, protective coatings, medical implants</td>
<td>GVD Corp. (equipment)</td>
<td>[39]</td>
</tr>
<tr>
<td>Diamond-like coatings</td>
<td>Thermal conductivity substrates in CMOS; hard</td>
<td>sp3 diamond technologies (equipment); Seki Technotron Corp. (equipment);</td>
<td>[40]</td>
</tr>
<tr>
<td>H radicals</td>
<td>coating for cutting tools</td>
<td>Condias GmbH (equipment)</td>
<td></td>
</tr>
<tr>
<td>SiNx gas barrier film</td>
<td>Dry etching, photoresist removal, treatment of</td>
<td>Tokyo Ohka Kogyo Co., Ltd., Daipia Wintes, Co., Ltd.</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>ink-jet metal prints, and surface cleaning</td>
<td>Ishikawa Seisakusho (equipment); Mitsubishi Plastics (coatings); MDF (coatings)</td>
<td>[42]</td>
</tr>
<tr>
<td>Polymer/SiNx or SiOx multilayer gas barrier coating</td>
<td>OLED, PV</td>
<td>Mitsubishi Plastics</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 1. Schematic visualization of the application of HWCVD SiNx:H in multicrystalline Si solar cells.](image-url)
achieved [26]. For the production of organic/inorganic multilayers that have excellent barrier properties, the SiNx layers discussed in the previous section can be elegantly combined with the polymer layers deposited by iCVD. The SiNx deposition conditions do however need to be adjusted to avoid thermal damage to the prior deposited polymer layers which all have a low glass transition temperature. This is achieved in the laboratory by moving the substrate further away from the hot filaments [30], but in a production environment, to maintain high deposition rates, active cooling of the substrate is required. In roll-to-roll production techniques this can be achieved by running the foil over a cooled susceptor.

A water vapor transmission rate of $5 \times 10^{-6}$ g/m$^2$/day was obtained with a simple three-layer structure of two low-temperature HWCVD SiNx layers and iCVD PGMA interlayer [31]. For mass scale production, we envisage a roll-to-roll deposition system with alternating hot-wire zones for nitride and polymer deposition. The envisaged system is schematically shown in Fig. 3.

1.4. Known cases of implementation of HWCVD at the industrial level

In Table 1, commercial applications of HWCVD are listed as far as they have been publically presented.

2. Characteristics of HWCVD for inorganic layer production

2.1. Primary reactions

In the HWCVD process the feedstock gases are very efficiently cracked into atomic radicals at the surface of a hot filament (usually tungsten or tantalum) [43], which is held at a temperature higher than 1600 °C. It can be calculated that during the residence time of the silane gas, each molecule collides with the filament surface more than 10 times. This leads to very efficient radical production compared to PECVD, since in HWCVD the gas collides with a 2D surface while in PECVD the decomposition relies on electron impact with molecules in a 3D space. In HWCVD, at sufficiently large filament temperatures, the hot filament completely atomizes the colliding molecule. In contrast to the conventional PECVD technique, no significant amount of ions is created.

In HWCVD, the catalytic filament does not reach a sufficient temperature to enable large amounts of free electrons to leave the metal surface by thermionic emission. The emitted current is strongly dependent on the temperature. For clean and pure W, the threshold for emission is $T > 2300$ °C, well above the commonly used wire temperatures. According to Qi Wang [44], based on Richardson’s law in vacuum, thermionic...
emission of electrons can occur resulting in a flux of up to $10^{17}$ electrons/cm$^2$·s for a W wire that is at 1930 °C. Only if the wire is at a negative voltage with respect to the substrate, the electrons may accelerate in the electric field between the wire and the grounded substrate. However, normally the voltage applied to the wire to heat it is only around 10 V. The trajectory of the thermal electrons may also be altered due to the magnetic field around the wire. Further, the geometrical path of electrons in a gas may limit their kinetic energy. Therefore the electron energy is roughly estimated to be ~5 eV, which is insufficient for electron impact ionization of the gas. It should be born in mind though, that higher negative wire voltage may lead to ions, but on the other hand, positive wire voltages can be used to completely eliminate any electron acceleration toward the grounded substrate.

The reactive species are subsequently transported to the substrate in a low pressure ambient (typically only 2 Pa for amorphous silicon). This enables a high deposition rate without gas-phase particle formation. It has been shown that ultrahigh deposition rates can be achieved (more than 100 times that of PECVD [45]). These rates are achieved in a laboratory reactor with only two tungsten filaments located at 3.2 cm from the substrate. The saturated defect density of the a-Si:H is low, at a value of $2 \times 10^{16}$ cm$^{-3}$ as measured by the constant photoconductivity method (CPM) [46]. Even for high deposition rate samples, it is typically $(2-4) \times 10^{16}$ cm$^{-3}$ and independent of the deposition rate, up to 13 nm/s, though the void density increases by a factor of 100 [47]. The low defect density means that these voids will essentially be passivated with hydrogen bonds. Early solar cells (in 2001) made on stainless steel (SS) with these films up to a deposition rate of 50 Å/s have initial and stabilized efficiencies similar to cells made at low rate, of 5.7 and 4.8%, respectively [45].

2.2. Catalytic filament materials

The most frequently used filament materials are tungsten (W) and tantalum (Ta). Matsumura [10] reported on molybdenum (Mo), vanadium (V) and platinum (Pt) as filament materials. Duan et al. [48] and Van Veenendaal et al. [49] used rhenium (Re) as the filament material. Van Veenendaal et al. [49] showed that, except for the highest filament temperature $T_{fil}$ used (1950 °C), polycrystalline silicon can be deposited with crystal orientation exclusively in the (220) direction. Morrison and Madan [50] reported on the deposition of microcrystalline silicon using graphite (C) as the catalyst. Brühne et al. [51] also reported on the use of graphite for the deposition of microcrystalline silicon with (220) orientation only. The deposited layers did, however, contain a considerable amount of carbon. Iridium (Ir) appears to be the most suitable filament for SiO$_2$ deposition [3] as it is highly resistant to oxidation.

2.3. Required filament temperatures

Using tungsten filaments at sufficiently high filament temperature, silane is fully cracked into one Si and four H atoms. Only at temperatures below 1430 °C, SiH$_4$ and SiH$_2$ could be detected [52]. It is suggested that in this temperature regime, a Si/W alloy is formed on the filament [53]. From further experiments, we deduced that this alloy affects the decomposition of silane at the filament surface and virtually blocks the decomposition of H$_2$ [54]. Matsumura [55] also found that at filament temperatures above 1430 °C, for W, Mo, and Ta filaments, the major species desorbed from the filament is the Si atom. The maximum production of Si atoms with W filaments is observed at approximately 1530 °C [52]. The temperature dependence of Si production below $T_{fil} = 1430 °C$ is large and different for these three filaments. Activation energies for Si atom desorption from the filament are found to be $(251 \pm 63)$, $(96 \pm 25)$ and $(71 \pm 20)$ kJ/mol for Mo, Ta, and W filaments, respectively [52]. The energy needed for Si atom production is much lower than 4 times the Si–H bond dissociation energy of 300 kJ/mol. Both the large differences for the different filaments and the small values of the activation energies indicate that the decomposition of SiH$_4$ on the hot filament is caused by catalytic reactions at the filament surface.

2.4. More conformal deposition

To assure homogeneous deposition thicknesses in PECVD, the substrate onto which the films are deposited should form an equipotential plane. This means that the potential at any point of the substrate should be the same. This is less critical in HWCVD. Further, due to acceleration of ions that are present in the plasma towards the substrate, the deposition rate is (partially) anisotropic. This means that the local deposition rate is dependent on the slope of the local surface and not entirely surface limited. Therefore it is difficult to conformally coat features with high aspect ratios unless it is done at low deposition rate. In HWCVD, the substrate and substrate holder are not part of the electrical dissociation enhancement method and thus do not act as an electrode. This also implies that more conformal deposition on any type of surface shape (nano- to macroscale) is possible without risking anomalous field strengths leading to locally strong discharges. Excellent step coverage of HWCVD-SiN$_x$ was demonstrated [56,57]. A recent example of conformal coverage of a-Si:H n-i-p layers of a thin film solar cell is shown in Fig. 4. The Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) cross section is shown of completed nanorod-type cells with ~100 nm thick a-Si:H i-layer. The cells are deposited over nanorod-type ZnO/Ag structures [58]. The difference in conformality of HWCVD layers and PECVD layers is clearly seen.

3. Consequences of implementing a HW chamber in a roll-to-roll reactor

Table 2 gives an overview of the main differences between the conventional RF-PECVD and the Hot Wire Chemical Vapor Chamber.
(HWCVD) process. A preliminary study of in-line continuous HWCVD for thin film solar cell manufacturing was done at Utrecht University [60]. It was demonstrated for a system with moving, upward-facing substrates that the film thickness was homogeneous over an area of 20 cm × 20 cm in a chamber with 30 cm × 40 cm dimensions. Fig. 5 gives a schematic lay out of the wire-substrate configuration. Amorphous (protocrystalline) as well as nanocrystalline silicon thin films with device-quality properties were achieved. The local deposition rate (with only two wires) was 1 nm/s, and a linear speed up to 30 cm/min (multiple passes) was used to produce device-quality i-layers with protocrystalline nature. The doped layers were obtained from another chamber by conventional PECVD. The deposited p-i-n solar cells had an initial efficiency of 8.3%. This was reached despite air breaks after the p layer and before the n layer. It was proposed that a tenfold increase of the number of filaments (to 20 filaments) would allow a linear speed of 15 cm/min for p-i-n deposition in a single pass. In order to reach 1 m/min web speed, 125 filaments would suffice. It was envisaged that this would fit in a chamber of only 150 cm length by placing them closer to each other (by which the local deposition rate is doubled). It should be noted that such a “short” chamber and foils running at 1 m/s is an extreme case just to illustrate the strong reduction of vacuum deposition volume with respect to a conventional RF-PECVD reactor. Careful design will be needed to arrive at the right dimensions of the heating and cooling regions and to limit the temperature gradients. The design of a complete production line is beyond the scope of this article.

One of the pilot systems in existence is located at the Fraunhofer Institute for Surface Engineering and Thin Films (IST) in Braunschweig, Germany [61]. This system is an in-line Hot-Wire CVD system with two load lock chambers, three HWCVD chambers, and two intermediate chambers with a heater and a plasma etcher. It is suitable for deposition areas of 40 cm × 40 cm. The thickness deviations within this area are less than ± 5%. To achieve this, the hot-wire assembly is made somewhat larger; it is 50 cm × 60 cm. Wire arrays have been used with 10 or 17 wires. The system has been used to evaluate the HWCVD technology for the solar industry. It is tested by investigating the passivation quality of HWCVD Si layers on c-Si wafers (to be used in Si heterojunction solar cells or so-called HIT cells). Also n- and p-type a-Si:H films have successfully been made by HWCVD, using PH₃ and B₂H₆, respectively. Complete HIT cells have been made with the passivating i-layer deposited by HWCVD, showing energy conversion efficiencies of 17%. The authors conclude that inline HWCVD has high potential for cost-effective heterojunction (HIT) solar cell fabrication [61]. The p-layers deposited by HWCVD appeared to require more elaborate optimization.

### 4. Technical consequences of implementing HWCVD in a roll to roll reactor

Below we discuss the technical steps of introducing Hot Wire CVD in a thin film silicon PV product line. Since Hot Wire CVD lends itself particularly well for roll-to-roll or continuous in-line processing due to the nature of the filaments as linear sources, we limit ourselves to the implementation of these types of reactors for deposition on foil or rigid continuously moving substrates. Implementation in an in-line deposition reactor (e.g., on moving glass sub- or superstrates) would to a large extent require the same modifications as implementation in a roll-to-roll line. However, an advantage of in-line deposition reactors is that the orientation of substrates can more easily be chosen facing down or vertical (or tilted). The process of Hot Wire CVD has been reported for all of these orientations. An existing method for vertical substrates and vertical filaments was developed by ULVAC [62]. It is also possible to implement HWCVD in stationary (batch-type) reactors (such as the AKT systems in so called Sunfabs, and TEL Solar systems), which would be using principles similar to those used by ANELVA [63], but this will not be discussed in large detail in this article. We will concentrate on roll-to-roll/in-line deposition in the following.

#### 4.1. Removal of RF power supplies, RF matching networks, and introduction of DC or 50-Hz line power

When introducing HWCVD, the RF power supplies and RF matching networks as used in PECVD of VHF PECVD are no longer needed. The RF circuitry can be removed completely. The substrate grounding is no longer a stringent requirement. The substrate and substrate holder are not part of the electrical dissociation enhancement method and thus they do not act as an electrode. This also implies that deposition on any type of surface shape (nanoscale to macroscale) is possible without risking anomalously high field strengths leading to locally strong discharges. Grounding is still advised but the electrical grounding does not need to support RF frequencies (let alone high currents at these frequencies), which greatly simplifies the electrical connection for moving substrates or foil.

In the laboratory, the filaments are usually powered by DC electric power sources. Calculations of the required electric power in HWCVD assuming a scaled up wire assembly that would give the same overall deposition rate as listed in Table 3 as key deposition parameter show that 10–20 kW of input power per m² of substrate area is used.
This calculation is based on inter-filament distance of 40 mm, filament temperature 1700–1800 °C at filament diameter 0.5 mm (this would require 10.5–11.5 A). This is roughly the same as the input power in RF PECVD systems, which is also determined by electrical losses due to reflected power in capacitively coupled RF systems. Like RF feedthroughs, the DC feedthroughs will have to carry large currents (10–50 A) and will need to be rated as such. DC power supplies as used in R&D of the HWCVD technique can be costly but typical prices per kW are lower for DC than for RF supplies. Typical prices for DC power supplies used in HWVCVD are in the range of 3000–6000 €/10 kW. Prices for RF power supplies are in the range of 20,000–25,000 €/10 kW, so roughly 5 times as expensive. In addition, the deposition rate in HWCVD is a factor 4–5 higher than the cost of ownership (CoO) related to power supplies is reduced by a factor of 20 to 25×.

As an alternative to DC power, also line-power 50-Hz or 60-Hz frequencies can be used to power the filament. This considerably brings down the cost of the power supplies and simplifies the system as a whole. However, apart from a handful of papers [64], showing the principles, and thesis work at University of Barcelona [65], the use of regular power line frequencies has not thoroughly been investigated for silicon thin film deposition so far. However, in HWCVD for diamond like coatings, which is done industrially, it is much more common to use 50-Hz or 60-Hz line frequencies.

4.2. Transportation of the web

It is expected that no changes in the web transport mechanism are needed, except that the web has to be able to move 4–5 times faster in the existing machine to collect the same thickness of film. Further, as mentioned above, the grounding requirements can be relaxed or even ignored. In some cases (plastic foils with low glass transition temperature) substrate cooling might be required. In roll-to-roll deposition, this can be accomplished by moving the foil over a susceptor that is temperature (1700 °C at 5 higher so that the cost of ownership (CoO) related to the substrate, originating from the H atoms of SiH4. The atomic H density in HWCVD is one order of magnitude higher than in PECVD. H. Umemoto et al. [67] have determined the atomic H density present in HWCVD at 10 cm from the filament for pure H2 conditions and H2/SiH4 mixtures. In pure H2 they measure 1.5 × 1014 cm−2. This density is two orders of magnitude higher than in typical RF glow discharge reactors (1012 cm−2 in pure H2). Upon addition of 0.2 sccm SiH4, they find a lower H density of 7 × 1012 cm−2 (see Fig. 6). Upon greater additions, equivalent to a pressure of 0.1 Pa of SiH4 (3 sccm) (2% SiH4/H2), Umemoto et al. [68] still find a H density of 7 × 1012 cm−3 in HWCVD. Similar reduction in H density upon addition of SiH4 is also observed in PECVD [69]. These authors found a H density of 2 × 1011 cm−3 upon 0.4 Pa SiH4 addition to pure H2 (1% SiH4/H2). The remaining H density in HWCVD thus is still more than an order of magnitude higher than in a typical SiH4/H2 PECVD case [70]. Typical deposition conditions are listed in Table 3.

The roughly 10–100 times lower processing pressures at equal gas flow rates require a pumping system with larger capacity. This might require replacing the pumps and lead to an add-on investment in the production line. On the other hand, industrial production lines commonly already handle large flows, e.g., using multi-stage rootsblower pumps, which may readily be able to handle the required flow/pressure combination in HWCVD.

4.4. Substrate temperature

The optimum substrate temperatures for good quality a-Si:H and μc-Si:H are the same in HWCVD and PECVD. The substrate heats up during deposition due to radiation from the filaments and reaches an equilibrium temperature. The time needed to reach equilibrium depends on the heat capacitance and conductances in the system, so in a continuous system a preheat stage would be required. This is

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Poly-Si:H</th>
<th>μc-Si:H (poly-approach)</th>
<th>μc-Si:H (amorphous-approach)</th>
<th>a-Si:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire material</td>
<td>W</td>
<td>W (2-wire)</td>
<td>Ta (2-wire)</td>
<td>Ta (2-wire)</td>
</tr>
<tr>
<td>d_substrate-wire (mm)</td>
<td>40</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>T_substrate (°C)</td>
<td>1800</td>
<td>1820</td>
<td>1750</td>
<td>1700</td>
</tr>
<tr>
<td>T_gas (°C)</td>
<td>500</td>
<td>510</td>
<td>250</td>
<td>250</td>
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<tr>
<td>Dilution ratio</td>
<td>15</td>
<td>25</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>H2/SiH4</td>
<td>Pressure (Pa)</td>
<td>10</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Deposition rate (Å/s)</td>
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<td>14</td>
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<td>Activation energy (eV)</td>
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<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Photo-/dark conductivity ratio</td>
<td>10²</td>
<td>2.4 × 10²</td>
<td>10³</td>
<td>10⁶</td>
</tr>
</tbody>
</table>

![Fig. 6. H atom density in the absence and in the presence of 0.2 sccm flow of SiH4. The flow rate and the pressure of H2 were fixed at 150 sccm and 5.6 Pa, respectively. The catalyster temperature was 2200 K. In region (a), only H2 was introduced. The H atom density was 1.5 × 10¹⁶ cm⁻². In region (b) 0.2 sccm of SiH4 was added. The H atom density decreased gradually. It took about 5 min to level off. The steady state density was 7 × 10¹⁶ cm⁻². In region (c), the SiH4 flow was stopped and only H2 was supplied. The H atom signal increased gradually again (reprinted from H. Umemoto et al., Effects of atomic hydrogen in gas phase on a-Si:H and poly-Si growth by catalytic CVD Journal of Non-Crystalline Solids 299–302 (2002) 9–13 with permission from Elsevier [67]).](image-url)
normally already present in industrial systems. The equilibrium temperature during deposition is at its optimum value (~200 °C) without any heater elements other than the hot filaments at deposition rates of ~1–2 nm/s for a-Si:H and ~1 nm/s for μc-Si:H. As mentioned above, if higher deposition rates are desired, more filaments should be installed and artificial substrate cooling may be required.

### 4.5. Filament replacement

The lifetime of the filaments is influenced by silicidation and/or carburization reactions, their temperature cycle and the way they are mounted. Depending on the way they are handled (discussed in the next section), the lifetime can range from 1 h to 1000 h. It has been claimed that graphite rods, rather than metallic wire, warrant a long lifetime of the “hot wire” and that 500 μm of film can be deposited with the same wire without any noticeable deterioration of the wire source [59]. This thickness is far more than the maximally allowable thickness that is accumulated before chamber cleaning is required. For metallic wires, consistent photoresponse of amorphous silicon i-layers has been reported over ~50 μm of film deposition with the same wires [71]. It is not known yet what is the maximum filament life with consistent deposited materials, but it is clearly long enough to survive the period between two scheduled chamber cleaning steps. Further industrial testing will however be necessary.

Nevertheless, sooner or later the filaments need to be replaced. Several procedures for replacement have been proposed.

1. **Continuous filament replacement by feeding “fresh” wire from a roll supply** [72] (Fig. 7). This mechanism requires a motor drive with tension control to straighten the wire and sliding electrical contacts that should be in a compartment where no depositing species are present. This idea has not been fully developed yet for production tools. One of the issues is the difficulty to bend the catalytic transition metal wires; for tungsten this is more difficult than for tantalum because it has higher hardness and brittleness. Tantalum is therefore preferred, but even in that case, thin wires need to be used, thus sacrificing deposition rate. In reference [72], tests have been performed with tungsten wires of 0.175 mm diameter.

2. **Periodic replacement of a wire assembly through a dedicated load lock chamber.** It is attractive to replace wire assemblies without breaking vacuum by transporting the assembly via a sliding system into an electrical contact slot while removing the used assembly through an exit load lock. Such a replacement system has been installed at JAIST institute, Kanazawa, Japan, in a multichamber cluster tool for Hot Wire CVD.

(iii) **The least disruptive wire replacement method is to replace the wire assemblies simultaneously with periodically scheduled shut downs for maintenance and reactor cleaning.** Cleaning of the reactor walls will be needed at regular intervals. If no plasma etching is installed, this will require that the system is vented and that crucial shields, liners, and enclosures are replaced by clean ones. The lifetime of the filaments can be lengthened to match the period for these maintenance shut downs or even to match a multiple of maintenance cycles. As a positive side effect of HWCVD, in case this method of reactor cleaning is used, the mounting of shields and enclosures does not need to be as accurate as in RF PECVD because there are no RF fields in HWCVD. Therefore the replacement of these components can be fast.

Another positive effect of HWCVD is that the silicon coatings on shields and liners have very low compressive stress (as all deposited films in HWCVD) and therefore the maintenance interval can be chosen longer than in PECVD as the films do not have the tendency to peel.

#### 4.5.1. Methods to lengthen the lifetime of the filament

The most important approach to extending the lifetime of the filament is to prevent silicidation. In contrast to general belief that progressive silicidation is taking place at the wire, the amount of silicides saturates at an equilibrium value (at least for Ta) as long as the surface temperature is >1800 °C [53]. At these temperatures, the thermal desorption rate of Si from the metal surface is higher than the reaction rate of Si with the metal. Therefore, operational lifetime of the filament can be increased by using a sufficiently high filament temperature and by not switching off the power supply to the filament in the presence of silane gas (even better is to avoid any thermal cycling, as this prevents repeated shrinking and expansion of the wire and the thus induced brittleness). Secondly, at the electrical clamps of the wire, there is an unavoidable colder region of the wire where silicidation will take place. Various methods have been proposed to prevent silane gas from interacting with the colder ends of the wire. These methods vary from flushing the ends with H₂ gas or inert gas and covering the ends with...
caps [73] to simply keeping the wire mounts at a large enough distance (>5 cm) from the silane injection area (sometimes combined with limitation of the heat transfer between mounts and filament itself) [74].

There have been a number of studies on the lifetime of filaments, however, these have not all been published as these were performed by industrial laboratories who have been developing proprietary techniques. With proper pre-treatment of the filaments, lifetime issues can be overcome [75–77]. In particular, we have presented a conditioning treatment as well as a regeneration treatment for Ta wires of 0.5 mm diameter [78]. The filament conditioning treatment consists of a 30-min vacuum annealing at $T_{\text{fil}} = 2050 \, ^\circ\text{C}$ after each deposition run and the regeneration treatment consists of a vacuum annealing state of 4 h at $T_{\text{fil}} = 2100–2200 \, ^\circ\text{C}$ when the filaments are aged (see Fig. 8). The conditioning treatment is needed in case the filament is cooled down between two runs. In a roll-to-roll system, the “runs” (i.e., the time between the switching ON and switching OFF of the wires) will be considerably longer, which will greatly reduce the number of the conditioning treatments as well as regeneration treatments. This clearly implies that HWCVD is very suitable for in-line and roll-to-roll systems with continuous deposition rather than in batch-type systems.

The most frequently used catalytic filament metals, Ta and W, are both relatively abundant materials (similar to Sn, Zn, and Ni) and are not expected to be a bottleneck once GWp-scale solar cell production is taking place by HWCVD. If needed, alloyed Si can be separated from the metal (driven out by diffusion) and the metal can be re-used.

4.6. Interior chamber cleaning

The walls of the deposition zone must be cleaned periodically to prevent excessive dust formation and flaking due to silicon deposits over time. Basically, the walls consist of shields, liners, or enclosures that restrict the volume where deposition takes place. The shields can be cleaned ex situ by bead blasting and/or chemical cleaning or in situ by plasma etching with NF$_3$ or SF$_6$ or a CF$_4$/O$_2$ mixture. The ex situ method is in use in some production environments and has an advantage in that it also limits the exhaust of greenhouse gases. This method can be used both in HWCVD and PECVD systems. As mentioned above, in HWCVD the ex situ method is expected to be more straightforward, faster, and less frequently needed than in PECVD.

The in situ method in PECVD systems often uses the same RF electrode assembly as that used for silicon deposition to induce a discharge in the etch gas. The etching radicals reach the same places as the regular silicon deposition plasma and thus the entire surface onto which silicon deposition has taken place is cleaned by the etch gas. This is convenient but also leads to down time. An in situ method in HWCVD would require a filament temperature of 2400 $^\circ\text{C}$ to decompose NF$_3$ gas without damaging the catalytic filament [79]. This would require a larger capacity power supply than that needed for regular deposition, but it is feasible. An alternative method that does not require in situ RF plasmas (which is preferred in order to keep the hot-wire chamber simple) and that does not require opening of the reactor is to supply etch radicals to the deposition region via a remote toroidal high efficiency RF, inductively coupled RF, or microwave plasma source. Such systems are industrially available and also commonly in use, even in systems that are already equipped with RF for the deposition chamber (such as the AKT cluster tool for displays, Applied Materials, Inc.). These external plasma sources could be used for in situ cleaning of a HWCVD chamber. Moreover, today’s remote sources can be used with F$_2$, thus preventing greenhouse gas emissions.

4.7. Large area and industrial application

For ultra-large-scale-integrated (ULSI) circuits process, ULVAC Corp. is selling its Cat-CVD machine, ULVAC Cat9000, for 12 in. size Si wafers [79]. The technology for large area deposition, even in excess of 1.5 m wide (> Gen5 size), has been demonstrated also by ULVAC [62]. A photograph of the machine is shown in Fig. 9 as an example of industrial implementation. In this machine, the catalyzer as well as two substrates are placed vertically, one substrate at each side of the catalyzer. This effectively doubles the throughput with respect to single substrate deposition, increases the gas utilization ration and reduces the area of the walls to be cleaned. It is confirmed that the quality of films deposited on both substrates is equivalent. The effective (stationary) deposition area is 150 cm × 85 cm.

ANELVA introduced a HWCVD deposition system for large-area deposition, using multiple filaments arranged in a grid pattern, in 2003 [63]. With a special design for a hot-wire assembly with a showerhead [73], Anelva demonstrated a thickness uniformity of ±7.5% over 96 cm × 40 cm substrate area, and has thus overcome two main difficulties, the sagging of the filaments and the silicidation of the cold ends of the catalyst.

5. Economic consequences of implementing HWCVD in a roll to roll reactor

5.1. Smaller vacuum processing chambers and throughput

The footprint of an in-line or roll-to-roll system can be reduced with respect to PECVD. In [60] it is projected that a system with a 150-cm
A collection of noteworthy thin film solar cells using HWCVD [80]. The layers that are deposited by HWCVD are in italics.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Structure of the cell</th>
<th>Remarks</th>
<th>( \eta ) init. (%)</th>
<th>( \eta ) stab. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U. Kaiserslautern</td>
<td>Glass/Asahi U/p-i-(a-Si)-n/Ag</td>
<td>Superstrate amorphous single</td>
<td>10.2</td>
<td>7.0</td>
</tr>
<tr>
<td>NREL/SSSC</td>
<td>SS/Ag/ZnO/n-i-(a-Si)-p/iTO/grid</td>
<td>Substrate amorphous single</td>
<td>9.9</td>
<td>7.8</td>
</tr>
<tr>
<td>Utrecht Univ.</td>
<td>Plain SS/n-i-(proto-Si)-p/iTO</td>
<td>Substrate amorphous single junction</td>
<td>7.2</td>
<td>( \Delta \eta \sim 10% )</td>
</tr>
<tr>
<td>Ecole Polytechnique</td>
<td>Glass/text.TCO/n-i-(µc-Si)-p/Ag</td>
<td>Superstrate inverted microcyrst. single</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>FZ Jülich</td>
<td>glass/text.TCO/p-(µc-Si)-n/ZnO/Ag</td>
<td>Superstrate microcryst. single</td>
<td>9.4</td>
<td>( \Delta \eta \sim 10% )</td>
</tr>
<tr>
<td>FZ Jülich</td>
<td>glass/text.TCO/p-(µc-Si)-n/ZnO/Ag</td>
<td>superstrate microcryst. tandem</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Utrecht Univ.</td>
<td>SS/text. Ag/TCD/n-i-(µc-Si)-p/iTO</td>
<td>Substrate microcryst. single</td>
<td>8.6</td>
<td>8.5%</td>
</tr>
<tr>
<td>Utrecht Univ.</td>
<td>SS/text. Ag/TCD/n-i-(µc-Si)-p/i-(a-SiGe)-p/n-i-(a-Si)-p/iTO</td>
<td>Substrate microcryst. triple junction</td>
<td>10.5</td>
<td>( \Delta \eta \sim 3% )</td>
</tr>
</tbody>
</table>

Estimate a decrease of thin film silicon overall production costs by 50–75%.

Due to lower mechanical stress in deposited layers, the time between reactor cleaning runs can be extended. In case of deposition on two facing substrates, minimal chamber cleaning will be required.

With deposition on two facing substrates, throughput is doubled with respect to single substrate deposition. This will further decrease thin film silicon production costs.

### 5.2. Absence of RF power supplies and matching networks

The deposition mechanism does not require RF power supplies or related components, such as RF matching networks, RF (showerhead) electrodes, feedthroughs, and RF dark space shields. DC power can be used, providing ease of handling, or line power at 50 Hz or 60 Hz frequencies. The estimated fraction of CO\(_2\) reduction of CVD machines due to this is 30%. The cost of catalyzers (Ta) is estimated at 1 Euro per m\(^2\) of solar module product.

The use of electricity is reduced with hot wires connected to line power as there are no losses in electric power conversion or RF power coupling. The use of electricity is further reduced because waste heat (radiative heat) from the filaments is used to heat the substrates to the optimum deposition temperature. No additional heating is required apart from preheat stages before deposition.

### 5.3. Higher gas utilization

Gas utilization has been increased to 80% for silane gas. This should be compared to the 10–20% gas utilization achieved in PECVD. Cost of silane is reduced by factor 2 (assuming PECVD has a high value (40%) of utilization). Note that this yields a minor reduction in MWp/y cost (0.5%) as gaseous Si feedstock materials are not the cost limiting factor in thin film Si PV.

Smaller amounts of unreacted gas in the exhaust leads to smaller cost incurred in gas abatement and smaller environmental impact.

### 5.4. Expected efficiencies and cost/Wp

The cell efficiencies expected for solar cells made with HWCVD are equal to those of PECVD [80]. Table 4 shows demonstrated cell efficiencies. HWCVD cells have not been fully developed yet as there are only few laboratories worldwide contributing to the device performance optimization. It is therefore believed that initial cell efficiencies can be equal to state-of-the-art efficiencies for PECVD cells with the potential of enhanced yield (better uniformity and less shunting). The stabilized efficiency may be slightly higher due to the more stable nature of the amorphous silicon layers as obtained by HWCVD.

Table 5 shows the estimated relative cost change with implementation of HWCVD instead of PECVD in a commercial production plant for thin film Si (a-Si/µc-Si tandem) modules. Note that this Table assumes implementation in a new plant. It does not estimate the cost advantage...
of replacing an existing PECVD method by the HWCVD method. This cannot be summarized in a simple table as the advantage depends on how much the existing PECVD is already depreciated. The overall relative decrease in Si deposition costs is estimated at 50–55%. In the FP7 FAST TRACK project the module cost has been evaluated for a commercial production plant with an annual production of 500 MWp/year. It was shown that the cost of Si deposition (for a tandem cell) is the most expensive process step in the entire production chain of glass-to-module modules. The cost of Si deposition using PECVD is 0.15 €/Wp (Fig. 10), and this constitutes 0.15/0.53 = 28% of the total module cost. Methods to decrease the Si deposition costs are to decrease the fixed costs (through the investment costs of the CVD equipment), the operational costs (through increase of the uptime and throughput) and the materials cost (through improved utilization of process gases). HWCVD, as an alternative to PECVD, can provide cost savings in all three cost categories. The absolute decrease in Si deposition costs using HWCVD is 0.08 €/Wp. Therefore, we estimate that the module cost can be decreased to 0.45 €/Wp. The implementation of HWCVD can reduce the Si deposition costs by 50–55% and therefore the module costs by 15%.

6. Conclusion

The most important consequences of implementing HWCVD into an existing PECVD in-line or roll-to-roll reactor for thin film silicon module manufacturing are the technical consequences and the economic consequences, which have both been presented. The technical consequences are adaptations needed to the hardware and the different processing sequences due to the different interaction of the HWCVD process with the substrate and already deposited layers. The economic consequences are the reduced investments in RF supplies and RF components needed. This is partially offset by investments that have to be made in higher capacity pumping systems. Implementation of the HWCVD technology in a thin film silicon PV production plant with an in-line or roll-to-roll production process can reduce the cost of the Si deposition part of the production by 50–55% or 0.08 €/Wp. The use of HWCVD can help to achieve the overall goal of cost reduction of thin film modules to below 0.40 €/Wp.

Whether or not HWCVD is already used in a production environment is only known for a few isolated examples. There is, however, 20 years of experience in the R&D laboratories worldwide, which is documented in many scientific publications. On large area systems production systems a number of publications are available by authors from ANELVA and ULVAC. The findings in the present paper are based on experiments on intermediate-size samples, on the huge literature base, and on projections into future development.

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