Chapter 3

Deposition processes in Hot-Wire CVD

3.1 Introduction

In this chapter an overview of studies regarding the different steps in the deposition and growth of silicon thin films in Hot-Wire CVD (i.e. gas decomposition, evaporated radicals, gas phase reactions and film growth) will be given. Also, the results of X-ray photoelectron spectroscopy measurements of the silicon content on the surface of the filaments used in Hot-Wire CVD will be described.

3.2 Deposition of silicon by Hot-Wire CVD

In this section, an overview of the research that has been performed by various groups around the world on the reactions that are occurring in Hot-Wire CVD (at the filament surface, in the gas phase and at the film surface) will be reviewed.
3.2.1 Filament materials

Presently, the filament materials most used are tungsten (W) and tantalum (Ta). Besides these materials, Matsumura reported on the use of molybdenum (Mo), vanadium (V) and platinum (Pt) as filament material [45]. The main conclusions of this study, with respect to the filament material, were that the film properties were independent of the filament material, but dependent on the filament temperature. More recently, Duan et al. [46] used rhenium (Re) as filament material, mostly to study the gas phase reactions occurring and the gas species produced in Hot-Wire CVD. Finally, Morrison et al. [47] reported on the deposition of microcrystalline silicon using graphite as catalyst.

3.2.2 Decomposition at the filament surface

In 1988, Doyle et al. performed one of the first investigations on the decomposition of silane at a hot tungsten filament [48]. This investigation resulted in a linear relationship between the film growth rate ($G$) and the decomposition efficiency ($\alpha_d$). In 1991, Horbach et al. [49] found a similar relationship as Doyle, but in a higher temperature range. At a filament temperature $T_{fil} < 1800^\circ$C the logarithms of both the decomposition coefficient and the growth rate are proportional to $1/T_{fil}$). At $T_{fil} > 1800^\circ$C they both saturate. This saturation is explained by complete silane decomposition. The dissociation of silane on a hot tungsten surface has been investigated by Tonokura et al. [50]. From this study, it followed that silane dissociates to give H and Si atoms through the following successive surface dissociation reactions:

\[
\text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H} \rightarrow \text{SiH}_2 + 2\text{H} \rightarrow \text{SiH} + 3\text{H} \rightarrow \text{Si} + 4\text{H}.
\]

It was found that the activation energy for Si atom production is about 234 kJ/mol for the tungsten filament. This activation energy is much lower than the energy required for direct bond breaking in order to remove Si from the metal surface. For example, the bond dissociation energy of Si from the tungsten (100) surface is estimated to be about 535 kJ/mol [51]. This low activation energy leads to the conclusion that the process is catalytic of nature.

The decomposition probability of one SiH$_4$ molecule by one collision with the hot filament ($\alpha_d$) has been determined by Honda et al. [20]. This value is derived from both the number of silane molecules colliding with the catalyzer surface and the number of deposited silicon atoms. The number of colliding silane molecules per unit time, $\Gamma$, is described as

\[
\Gamma = \frac{1}{2} \rho v \pi D_{fil} L,
\]

(3.1)

where $\rho$, $v$, $D_{fil}$ and $L$ are the density of silane molecules, the mean thermal velocity of the molecules, the diameter of the filament and the length of the
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The number of deposited silicon atoms per unit time, $G$, is described by

$$ G = dN_A \pi D \int f(x)dx / M_{Si}. $$

(3.2)

Here, $d$, $N_A$, $D$, $f(x)$ and $M_{Si}$ are the density of a-Si:H, Avogadro’s number, the diameter of the reactor tube, the measured deposition rate and the atomic weight of silicon, respectively. The efficiency of gas use for silane, $\Lambda$, is given by

$$ \Lambda = \frac{G}{F}. $$

(3.3)

where $F$ is the number of supplied silane molecules per unit time. The number of collisions on the catalyzer surface by one molecule, $A$, is described by

$$ A = \frac{\Gamma}{F}. $$

(3.4)

It was found that a silane molecule collides 0.2 to 2 times with the catalyzer surface. The derived relation between the gas use efficiency $A$ and the silane decomposition probability $\alpha_d$ is

$$ 1 - \Lambda = 1 - \alpha_d. $$

(3.5)

The value for $\alpha_d$ at a filament temperature $T_{fil}$ of 2000°C is about 40%.

### 3.2.3 Evaporated radicals

At sufficiently high filament temperature, the silane is thus fully cracked into one Si and four H atoms. Only at temperatures below 1700K, SiH$_2$ and SiH$_3$ could be detected [52]. It is suggested that in this temperature regime, a Si/W alloy is formed on the filament [53]. It is presumed that this alloy affects the decomposition of silane at the filament surface. Matsumura also found that at filament temperatures above 1700K, the major species desorbed from the filament is the Si atom. The maximum production of Si atoms is observed at about 1800K. These results were obtained with W, Mo and Ta filaments. The Si atom is the only major species above $T_{fil} = 1700$K for all three filaments. The temperature dependence below $T_{fil} = 1700$K is large and different for these three filaments. Activation energies for Si atom desorption from the filament below 1700K are found to be (251±63), (96±25) and (71±20) kJ/mol for Mo, Ta and W filaments, respectively [52]. Another important observation reported by Inoue et al. [52] is the fact that the dilution of the silane gas with hydrogen does not change the signal intensities of Si, SiH$_2$ and SiH$_3$. It seems that H$_2$ has no effect on the catalytic decomposition processes of SiH$_4$. 
3.2.4 Gas phase reactions

At low pressures (< 5 \( \mu \text{bar} \)), the Si and H atoms that come from the filament thermally diffuse to the substrate [20], with minor to no gas phase reactions. Duan et al. reported on single photon ionization mass spectrometry measurements on 1.8 x 10^{-2} \( \mu \text{bar} \) at W filament temperatures of 1950°C [54]. The major silicon containing gas species detected is Si, with minor contributions of SiH\(_3\) and Si\(_2\)H\(_x\). However, these pressures are several orders lower than the pressures used during actual silicon deposition, e.g. the pressure used during the depositions described in this thesis is 0.1 mbar.

At higher pressures (> 5 \( \mu \text{bar} \)), the silicon atom is highly reactive. It can abstract an H atom from silane, resulting in SiH and SiH\(_3\), or it can insert into a Si-H bond [55]. Molenbroek described three possible insertion reactions, namely:

\[
\begin{align*}
\text{Si} + \text{SiH}_4 & \rightarrow \text{SiH} + \text{SiH}_3, \\
\text{Si} + \text{SiH}_4 & \rightarrow \text{HSiSiH}_3 \ (*) \text{ and} \\
\text{Si} + \text{SiH}_4 & \rightarrow 2\text{SiH}_2.
\end{align*}
\]

Because the first and third reactions are endothermic, they are unlikely to occur. HSiSiH\(_3\) is formed through an exothermic reaction and will thus be the most probable species to exist. The formation reaction of HSiSiH\(_3\) has been the subject of ab-initio molecular orbital calculations by Sakai et al. [56]. According to these calculations, triplet Si atoms as well as singlet Si atoms react with SiH\(_4\) to yield HSiSiH\(_3\). Since Si atoms produced at the hot filament should be triplets, the formation reaction is spin forbidden if HSiSiH\(_3\) is in singlet manifold. There are two possibilities: (i) singlet HSiSiH\(_3\) is produced by the non-adiabatic reaction pathway from Si(\(^3\)P) + SiH\(_4\) triplet surface, or (ii) triplet HSiSiH\(_3\) is generated but it is relaxed to singlet manifold by collisions with a third body. It follows, that HSiSiH\(_3\) is unstable and that it will react with SiH\(_4\) in the gas phase. There are three possible reactions, namely [52]:

\[
\begin{align*}
\text{HSiSiH}_3 + \text{SiH}_4 (+M) & \rightarrow \text{Si}_3\text{H}_8 (+M) \quad (3.9) \\
\text{HSiSiH}_3 (+M) & \rightarrow \text{H}_2\text{SiSiH}_2 (+M) \quad (3.10) \\
\text{HSiSiH}_3 + \text{SiH}_4 & \rightarrow \text{SiH}_2 + \text{Si}_2\text{H}_6 \quad (3.11)
\end{align*}
\]

In reactions (3.9) and (3.10), M stands for a third body (e.g. an atom or molecule). Up to now, no Si\(_3\)H\(_8\) has been detected. Therefore, Inoue et al. suggest that reaction (3.9) can be neglected. However, Molenbroek suggests that abstracting H\(_2\) from the Si\(_3\)H\(_8\) molecule forms Si\(_2\)H\(_6\) [55]. The reaction product of reaction (3.10), H\(_2\)SiSiH\(_2\), is a rather stable closed shell molecule and it has been expected to be an important precursor species for the film growth. In
the experiments described by Inoue et al. [52], the most prominent species detected is Si$_3$H$_6$. They suggested that SiH$_2$, produced via reaction (3.11), further reacts with SiH$_4$, according to

$$\text{SiH}_2 + \text{SiH}_4 (+\text{M}) \rightarrow \text{Si}_2\text{H}_6 (+\text{M}).$$

(3.12)

The presence of atomic hydrogen in the reactor, results in the occurrence of the following reaction:

$$\text{H} + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}_2.$$  \hspace{1cm} (3.13)

The SiH$_3$ species does not react with SiH$_4$ and the only gas phase reaction of SiH$_3$ is self-recombination.

Gallagher also proposed a gas phase growth reaction, in which Si atoms react with silane [57]:

$$\text{Si} + \text{SiH}_4 \rightarrow \text{Si}_2\text{H}_4^* \rightarrow 2\text{SiH}_2^*, \text{SiH} + \text{SiH}_3^*, \text{Si}_2\text{H}_2 + \text{H}_2, \text{Si}_2\text{H}_4^*,$$

(3.14)

where Si$_2$H$_4^*$ is an unstable intermediate. Some of the reaction products will react with silane to produce more stable silanes, such as Si$_3$H$_6$ and Si$_4$H$_8$.

From a theoretical point of view, the main gas phase reaction species are thus: SiH$_3$, Si$_2$H$_6$, Si$_3$H$_6$ and H$_2$SiSiH$_2$. It is expected that the detection of the actual gas phase reaction species will take place in the near future.

### 3.2.5 Film growth

Although Matsumura concluded that the deposition process in Hot-Wire CVD is very different from that in both the conventional thermal CVD as well as in PECVD [45], Gallagher is convinced that the models used in PECVD as well as in HWCVD should be about the same [57]. The film surface will be mostly H covered, with approximately the same ratio $R$ between the amount of dangling (Si-) and hydrogen passivated bonds (Si-H) as in the vapor. There, this ratio is $n_{\text{radical}}/n_{\text{silane}}$. This follows from the fact that the most frequent gas-surface collisions are with SiH$_4$, since silane is the most abundant gas in the reactor.

This dynamic equilibrium reaction is given by:

<table>
<thead>
<tr>
<th>Species</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF-PECVD</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1 [58]</td>
</tr>
<tr>
<td>SiH</td>
<td>1 [58]</td>
</tr>
<tr>
<td>SiH$_2$</td>
<td>0.6±0.2 [59]</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>0.1-0.4 [60-62]</td>
</tr>
<tr>
<td>Hot-Wire CVD</td>
<td>0.29-0.54 [63]</td>
</tr>
</tbody>
</table>
\[ \text{Si} - \text{H}\text{H}_4 \leftrightarrow \text{Si} - \text{H} + \text{SiH}_3 \]  
(3.15)

and leads to \( R \approx \frac{n_{\text{radical}}}{n_{\text{silane}}} \). Typical values for \( n_{\text{radical}}/n_{\text{silane}} \) are \( 10^{-4} - 10^{-3} \), so a similar value is expected for \( R \). This leads to dangling bonds at an average spacing of 30-100 surface sites, or 5-15 nm. In order to grow a compact film it is necessary to overcome the tendency for the incident radicals to strike film-surface peaks more frequently than valleys. This requires not only radical diffusion over distances in excess of dangling bond separations, but also an increased affinity for settling onto valleys. Following radical-film Si-Si bonding, H2 evolution occurs from the reaction

\[ \text{Si-H} + \text{Si-H} \rightarrow \text{Si-Si} + \text{H}_2, \]  
(3.16)

within the top few atomic layers of the film.

One very fundamental difference between radio frequent (RF) PECVD and Hot-Wire CVD was however disregarded by Gallagher, namely the absence of ions in Hot-Wire CVD. These ions are very important in RF-PECVD. They are essential in creating a dense \( \alpha \)-Si:H network [64], have a significant contribution to the growth rate [64] and determine the properties of thin film silicon to a large extent [65,66]. A way to compare the two deposition techniques is to study the surface reaction probability, \( \beta \). A number of groups have reported on values of \( \beta \) for different species and these values are listed in Table 3.1. In the Hot-Wire CVD case, the lower value was determined for the deposition of \( \alpha \)-Si:H, while the higher value was found for \( \mu \)-Si:H deposition. The difference in \( \beta \) between RF-PECVD and Hot-Wire CVD can have two causes [63]: (i) a different radical responsible for the growth or (ii) a changing reactivity of the surface. The first effect follows from the abundance of atomic H present in the reactor, leading to stripping of SiHx. Furthermore, the pressure in PE-CVD is higher, resulting in more gas phase reactions. The latter effect is related to the presence of a physisorbed hydrogen layer at the surface of the growing silicon layer, as suggested by Matsuda et al. [61]. Radicals arriving at the surface will recombine with the physisorbed hydrogen, resulting in a high

Table 3.2. Reactions of Si, H and SiH3 on the surface. Subscript (s) refers to a radical bonded to Si in the film. Abbreviation d.b. stands for dangling bond.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si} + \text{SiH}_3 ) ( (s) ) \rightarrow \text{SiSiH}_3 ( (s) ) \rightarrow \text{SiH}_3 ( (s) ) + 2d.b.</td>
<td>(3.17a)</td>
</tr>
<tr>
<td>( \text{H} + \text{SiH}_3 ) ( (s) ) \rightarrow \text{H}_2 + d.b.</td>
<td>(3.17b)</td>
</tr>
<tr>
<td>( \text{SiH}_3 ) ( d.b. ) \rightarrow \text{SiH}_3 ( (s) )</td>
<td>(3.18a)</td>
</tr>
<tr>
<td>( \text{Si} + d.b. ) \rightarrow \text{Si} ( (s) ) + 3d.b.</td>
<td>(3.18b)</td>
</tr>
<tr>
<td>( \text{H} + d.b. ) \rightarrow \text{SiH}_3 ( (s) )</td>
<td>(3.18c)</td>
</tr>
</tbody>
</table>
surface reaction probability. The large contributions of ions in RF-PECVD [63] will remove this layer, resulting in a lower $\beta$. Because there are no ions present in the gas phase during Hot-Wire CVD, it is likely that such a physisorbed hydrogen layer exists. This layer will then be responsible for the high surface reaction probability in Hot-Wire CVD.

Molenbroek investigated the reactions that can occur at the surface [55]. These reactions are listed in Table 3.2. Reaction (3.17a) and (3.17b) involve the reactions of Si and H with a hydrogen passivated surface, while reactions (3.18a) and (3.18b) deal with the direct reaction of SiH$_3$, Si and H with a dangling bond.

Reactions (3.17a) and (3.18b) result in the creation of two new dangling bonds. This means that whether Si reacts with a dangling bond or a Si-H bond, two new dangling are created in the process. If there are enough dangling bonds formed, it is possible for them to react with each other to form Si-Si bonds. Hydrogen atoms will either abstract a H to create a dangling bond (3.17b), or passivate a dangling bond (3.18c). A dangling bond can also be passivated by SiH$_3$ (3.18a).

Nozaki et al. [67] performed laser induced fluorescence (LIF) measurements and found that Si is the film growth precursor at low pressures ($10^{-2}$ µbar). At higher pressures, gas phase reactions lead to a different growth precursor. Two of the proposed candidates are disilene (Si$_2$H$_4$) and SiH$_3$.

In summary, the most likely growth precursors are Si, SiH$_3$ and Si$_2$H$_4$, depending on the pressure and filament temperature.

3.3 XPS studies on the filament surface

As was already mentioned earlier, one of the possible issues in Hot-Wire CVD is the aging of the filament, which can lead to filament failure. This aging is attributed to the decomposition of silicon on the filament or the formation of a silicide-like alloy on the filament surface. In this section, the results of the XPS studies performed on different filament surfaces will be described and discussed. These measurements have been performed in order to study the silicon content on the filaments used during deposition.
3.3.1 Filament temperature

Figure 3.1 shows the filament temperature \( T_{fil} \) as function of the current through the filament \( I_{fil} \) [68], as measured in vacuum in chamber 4 of the PASTA system for filaments with a diameter of 0.5 mm. From this figure, it follows that there is a linear correlation between the filament temperature and the filament current for all three materials used namely tungsten (W), tantalum (Ta) and rhenium (Re). These correlations are also shown in Figure 3.1.

3.3.2 XPS measurements on filament surface

To study the influence of the catalytic properties of the filament material on the growth of polycrystalline silicon thin films, different wire materials have been used, namely tungsten (W) and tantalum (Ta). X-ray Photoelectron Spectroscopy (XPS) was performed on used filaments to determine the difference in the silicon coverage of the filaments. Also, Scanning Electron Microscopy (SEM) has been performed on end-of-lifetime filaments.

![Figure 3.1. Filament temperature \( T_{fil} \) as function of filament current \( I_{fil} \) (measured by C.M.H. van der Werf)](image-url)
Table 3.2. Deposition parameters

(1 sccm = 0.0017 Pa m³/s = 4.48 x 10¹⁷ gas particles/s [69])

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΦSiH₄</td>
<td>10 sccm</td>
</tr>
<tr>
<td>ΦH₂</td>
<td>150 sccm</td>
</tr>
<tr>
<td>Tfil</td>
<td>1900°C</td>
</tr>
<tr>
<td>P</td>
<td>100µbar</td>
</tr>
</tbody>
</table>

The tungsten filaments were used for 10, 75, 90 and 180 minutes, while the tantalum filaments were used for 90 and 180 minutes. Each deposition started with a pristine wire, i.e. a wire that has been annealed in vacuum during 3 hours. The deposition parameters used (silane flow $\Phi$SiH₄, hydrogen flow $\Phi$H₂, filament temperature $T_{fil}$ and pressure $P$) are listed in Table 3.2.

The measurements were performed either position or deposition time dependent. The results will be described below.

3.3.2.1 Position dependent measurements

To study the position dependence of the silicon content in the near-surface region of the filament, measurements have been performed on the center part and the outer ends of the filament.

The deposition time was 90 minutes and the deposition started with a pristine wire. From the measured XPS spectra, the areas of the Si(2p)-, W(4f)- and Ta(4f)-peaks were determined. Using equation (2.3), the atomic ratios in the near surface region were calculated. These calculated values are given in Table 3.3.

From the values of $\rho_{Si}/\rho_{M}$ given in Table 3.3, it follows that the difference between the middle and the edge of the tungsten filament is much larger than in the case of a tantalum filament. The lower filament temperature at the edges causes the higher silicon content at the edge of the tungsten wire, compared to the middle. At filament temperatures below 1500°C, there is an

<table>
<thead>
<tr>
<th>M</th>
<th>Position</th>
<th>$\rho_{Si}/\rho_{M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>Center</td>
<td>1.43 [70]</td>
</tr>
<tr>
<td>Ta</td>
<td>Outer ends</td>
<td>1.61 [70]</td>
</tr>
<tr>
<td>W</td>
<td>Center</td>
<td>2.08 [71]</td>
</tr>
<tr>
<td>W</td>
<td>Outer ends</td>
<td>4.47 [71]</td>
</tr>
</tbody>
</table>
increased silicide formation, leading to changes in resistance and degradation of the wire [72,73]. The much smaller difference in silicon content between the middle and edges of the tantalum filament implies that the formation of a silicide-like compound is less temperature dependent than in the case of tungsten.

3.3.2.2 Deposition time dependent measurements

In order to study the deposition time dependence of the silicon content in the near-surface region of the filaments, a deposition series was made in which the deposition times ranged from 0 to 180 minutes at standard polycrystalline silicon deposition conditions, using both tantalum and tungsten as filament material. Every filament used has been pre-annealed in vacuum for 3 hours. This pre-annealed filament was used as a reference, to see if silicon is present on the filaments prior to deposition. The XPS measurements have been performed on the center part of the filament. The values for the silicon content in the near-surface region of the filaments ($\rho_{Si}/\rho_M$), calculated from the measured XPS spectra, as a function of the deposition time and for different filament materials, are given in Table 3.4 and Figure 3.2. From Table 3.4 and Figure 3.2, it can be concluded that the silicon content in the near surface region

![Figure 3.2. Silicon content in the near-surface region of the filament ($\rho_{Si}/\rho_M$) as a function of deposition time ($t_{dep}$), for different filament materials ($M$). The lines are guides to the eye.](image)

<table>
<thead>
<tr>
<th>$M$</th>
<th>$t_{dep}$ (min.)</th>
<th>$\rho_{Si}/\rho_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ta</td>
<td>90</td>
<td>1.43</td>
</tr>
<tr>
<td>Ta</td>
<td>180</td>
<td>1.12</td>
</tr>
<tr>
<td>W</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>10</td>
<td>0.60</td>
</tr>
<tr>
<td>W</td>
<td>75</td>
<td>1.24</td>
</tr>
<tr>
<td>W</td>
<td>90</td>
<td>2.08</td>
</tr>
<tr>
<td>W</td>
<td>180</td>
<td>4.15</td>
</tr>
</tbody>
</table>
of the tungsten filament increases linearly with time and does not saturate in this time frame, while this value on the tantalum filament saturates rather quickly.

3.3.2.3 Comparison of Ta- and W-filaments

From the results shown in Figure 3.2 and Table 3.4, it is clear that the silicon content in the near-surface region of the filament is larger in the case of a tungsten filament as compared to a tantalum filament. Two processes can be suggested: (1) the time scales for the catalytic dissociation of the reactant gases is different at a tantalum surface, compared to a tungsten one, and (2) the formation of a silicide-like alloy is inhibited more on the surface of the tantalum filament than on a tungsten filament. However, the reactions taking place at the filament described earlier in this chapter lead to the conclusion that the dissociation reactions at the filament is largely filament temperature dependent, but not depending on the filament material. The second suggested process is therefore the most likely. This is also confirmed by Duan et al. [74]. Scanning electron microscopy performed on tantalum and tungsten filaments supports this. The resulting micrographs are shown in Figure 3.3.

The most striking feature in Figure 3.3 is the presence of a different morphology at the surface of the tungsten filament. Such a layer is not present on the surface of the tantalum wire. The phase present in the surface layer, resulting in a different morphology at the surface compared to the core, is most probable resulting from the reactions taking place at the filament surface. Figure 3.3 also shows the difference in filament morphology between the tungsten and tantalum. The tungsten filament is dense, while the tantalum one is porous. It is likely that this difference in filament morphology has influence on the reactions taking place at the filament.

![Figure 3.3. Scanning electron micrographs of W (left) and Ta (right) filament](image)

Figure 3.3. Scanning electron micrographs of W (left) and Ta (right) filament
3.3.2.4 Filament failure

A major disadvantage of using tungsten as filament material is the fact that these filaments have a rather short lifetime. Under standard polycrystalline deposition conditions, the filaments have to be cleaned at high temperature after about one hour of deposition, in order to remove the silicon/silicide that is present on the filament. Combining the results of the XPS measurements performed on the filaments with the phase diagrams of Si-Ta and Si-W (Figure 3.4), an indication for the failure mechanism of W filaments can be made. In order to compare the XPS results with the phase diagram, the values for $\rho_{Si}/\rho_{M}$ have to be converted to ratios of mass. This is achieved by multiplying the calculated value of $\rho_{Si}/\rho_{M}$ by the ratio of the atomic masses of silicon and tantalum, or silicon and tungsten. With this method, it is assumed that the silicon content in the near-surface region of the filament is homogenous.

The largest measured values of $\rho_{Si}/\rho_{W}$ and $\rho_{Si}/\rho_{Ta}$ are 4.2 and 1.6, respectively. Converting these values to mass percentage results in silicon mass percentages on the surface of the Ta and W filaments of 20% and 40%, respectively. From Figure 3.4, it follows that if a tungsten filament is kept at a temperature of 1900°C, and the filament has a silicon mass percentage of 40%, a liquid phase can occur. Ruihua et al. [75] has also suggested the occurrence of this liquid phase. The presence of a liquid phase will increase the tension in the filament, due to a decrease in surface area. It is also possible that the liquid phase corrodes the filament. In the tantalum case, this is less likely.

Figure 3.4 Phase diagrams of Si-Ta and Si-W [76]
3.4 Conclusions

In this chapter an overview of studies regarding the different steps in the deposition and growth of silicon thin films in Hot-Wire CVD has been given. Studies on the decomposition of silane on the filament indeed showed that the process is catalytic of nature. Also, it was shown that the growth rate is proportional to the decomposition probability. This decomposition probability is ~40% at a filament temperature of 2000°C. At filament temperature above 1800°C, silane is decomposed into Si and 4H. At lower filament temperatures, also SiH₂ and SiH₃ have been detected as decomposition products. The dominant gas phase reactions are the reaction of Si and H with silane, resulting in SiH₃, Si₂H₆, Si₃H₆ and H₂SiSiH₂. The precursors dominating the film growth are Si, SiH₃ and Si₂H₄, depending on pressure and filament temperature. Numerous groups around the world are expanding their research activities in this field.

Furthermore, XPS measurements have been performed on tantalum and tungsten filaments used during the deposition of thin film poly-Si:H. Measurements at various positions along the length of the filament show larger silicon contents at the ends of the tungsten filament, as compared to the middle. The lower filament temperature causes this. In contrast, the difference in silicon content between the middle and edge of the tantalum filament is insignificant. Deposition time dependent measurements show an increase in silicon content of the tungsten filament with time, while the silicon content on the tantalum filament saturates rather quickly. Two processes are suggested as an explanation for these significant differences between W and Ta: (1) the catalytic dissociation of the reactant gases at a tantalum surface is different from that at a tungsten surface, and (2) the formation of a silicide-like alloy is inhibited more on the surface of the tantalum filament than on a tungsten filament. From the W-Si and Ta-Si phase diagrams follows that silicide-like alloys can occur with melting temperatures as low as 1400°C. However, these low-melting phases occur at very high Si percentages. After combining the XPS measurements with the Ta-Si and W-Si phase diagrams, it can be concluded that the presence of a liquid phase is more likely to occur in the case of a tungsten filament. Whether or not this liquid phase is present is unclear.