Problem of catalyst ageing during the hot-wire chemical vapour deposition of thin silicon films

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The filament in a hot-wire chemical vapour deposition (HWCVD) reactor is an important component. When tantalum (Ta) filaments are used for the deposition of thin silicon films, strong degradation takes place: there is a large amount of silicon not only at the surface but also in the bulk of the tantalum catalyst. Ta–Si phases form on the filament surface and in the bulk, which can lead to a porous structure of the catalyst filament. Filament contamination (silicide formation and thick silicon deposits (TSDs)) is the reason for the changes in filament resistance. It also reduces filament lifetime, which is a serious concern for HWCVD deposition technology. A cleaning procedure for the filament at high-temperatures in a vacuum (about 2000 °C) can neither remove the thick silicon deposits nor fully restore the filament surface properties. In order to decrease the silicon content in the tantalum catalyst and suppress TSD formations on the filament surface, we use radio-frequency alternating current (RF, 13.5 MHz) instead of direct current (DC) to heat the filament. The skin effect of the RF current reduces the formation of TSDs on the surface and silicon diffusion into the filament. We show that it is possible to clean the filament surface of TSDs by means of a high-frequency current. Combined RF+DC filament heating allows us to increase the lifetime of the catalyst (almost twofold) and to improve HWCVD process reproducibility without any deterioration in the quality of the deposited film.

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1. Introduction

HWCVD is an alternative to plasma-enhanced chemical vapour deposition (PECVD) for depositing silicon thin films at a higher deposition rate without reducing the film quality [1]. HWCVD uses thermal energy in combination with catalytic reactions [2–4] to decompose molecules from the process gas mixture. Compared to PECVD, it involves very small amounts of ions and therefore negligible ion bombardment of the growing surface. This can be an advantage for the growth of thin silicon films because ion bombardment during deposition often leads to a reduced quality of the thin silicon film [5]. Another advantage of this method is the simple setup and the fact that it is easier to up-scale than the PECVD method [6].

While the process gas (silane) decomposes on the filament surface, solid silicides or liquid silicon can occur on the filament surface, which leads to a lower deposition rate due to screening and degradation of the catalyst [7]. For example, we can generally use a tantalum filament in pure silane for the deposition of an amorphous silicon layer with a thickness of only about 20 µm [8]. Therefore, it is clear that the rather short filament lifetime (the time of filament usage) and low reproducibility of the deposition process are the main obstacles to using this method to produce cheaper thin silicon films.

Today, W and Ta catalyst filaments are widely used [9–11]. However, despite remarkable progress during the past decade, there are only a few groups involved in producing an entire silicon thin film solar cell by HWCVD [12] because of the problem of filament ageing. There is still insufficient knowledge on filament degradation as a function of deposition conditions.

Mahan et al. [1] discovered that with increasing exposure time of the filament to silane, appreciable Si was found on the surface along the whole length of the used filament, even in non-thickened central regions. The thicker regions at the filament ends (so-called “cold ends”) appear because the filament ends are colder than the rest of the filament due to the need to fix the filament to massive and therefore colder support contacts. The Si deposited on the filament surface is not re-evaporated from these relatively cold areas. As a result, thick alloy formation and silicon deposits can be seen (Fig. 1(c, d)). The HWCVD reactor can be designed in such way that these formations do not participate in film deposition and are neutralised with the aid of a proper baffle design or by admitting H2 precisely at the regions where cracks and deposits may form [13].

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Nevertheless, the thick silicon deposits (TSDs) were observed on the filament in unpredictable places (Fig. 1e, f) at some distance from the “cold end”. Usually, TSDs grow with filament lifetime. Therefore, during filament ageing, there are two different phenomena. The first is the formation of “cold ends” and other thickenings (>50 µm) of the filament (TSDs). The second is rather thin (10–20 µm) silicide (Me–Si alloy) growth on the filament surface.

In this paper, experiments with different filament shapes (Ta wire and ribbon) are described and the results presented. The present section outlines the behaviour of the filament electrical resistance and reports on investigations of filament degradation. The results of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction studies of the catalyst after use are presented. In second part, the behaviour of filament resistance and the change in filament morphology during annealing in vacuum are considered. The third section focuses on different ways of increasing filament lifetime. Finally in the conclusion, the results are reviewed.

2. Experimental

The HWCVD multichamber system described elsewhere [14] was used for the deposition of n, p-doped and undoped silicon thin films. A W-shaped wire tantalum filament about 35 cm long and 0.5 mm in diameter and a straight ribbon geometry (65 × 3 mm, 50 µm thick) were used for deposition [15]. The W-shape was chosen to reduce the stress on the filament during heating and cooling and to minimise the sagging of the filament. The filament temperature (Tfil) was controlled by a two-colour pyrometer (Keller PZ40). The accuracy of the pyrometer in the range of 1500–2200 °C was ±15 °C. When the temperature of a filament was non-uniform along the catalyst, the temperature was determined in the central area showing maximum luminescence. It is important to note that there was no darkening of the chamber windows due to deposition. Therefore, the measuring conditions of Tfil were constant.

During the deposition procedure, the filament temperature was kept constant, whereas the filament voltage (V) and current were allowed to vary. The pressure in the deposition chambers was varied from 1 Pa to 12 Pa. The total pressure (ptotal) was measured with an MKS Baratron pressure transducer. The partial pressure of silane was determined by the formula: pSilane=(silane mole fraction)×ptotal.

The electrical power applied to the filaments, as well as the filament conductivity versus time, was carefully monitored during catalyst use (V and J at the power supply device output, accuracy ±0.05 V and ±0.05 A). It should be noted that the contacts and wires in our HWCVD reactors have a much lower resistance (about 10−3 Ω) compared to that of the hot filament and therefore any influence on our measurements can be ruled out.

After every deposition process, a standard annealing regeneration procedure was generally used: the temperature of the filament was increased in vacuum (Tfil was about 2000 °C) in order to keep the filament surface relatively clean and increase the filament lifetime (high-temperature post treatment of filament in vacuum). At the “end” of the filament life, we usually observed higher filament resistance and non-uniform distribution of filament temperature along the catalyst (deviation of more than 50 °C).

After deposition, the properties of the deposited films were characterized by Fourier transform infrared spectroscopy (FTIR), and dark- and photoconductivity measurements. The IR absorption spectrum of the sample was corrected for the absorption of the low-resistance c-Si wafer substrate that was measured as a reference.

The photoconductivity was measured under AM1.5 illumination. Voltages from 1 to 100 V were applied to the Ag contacts (1 mm gap between contacts) on the thick silicon layer (about 400 nm) surface and the current was measured, allowing the ohmic behaviour of the material to be tested. The thickness of the films was measured by a surface profilometer from Veeco Instrument Inc., type DEKTAK 3030 (accuracy of ±15 nm), and the deposition rate was calculated from the known deposition time and the film thickness.

Ta filaments in straight ribbon geometry (65 × 3 mm, 50 µm thick) were used to understand changes in the catalyst after filament ageing. The ribbon geometry allows secondary ion mass spectrometry investigations and X-ray photoelectron spectroscopy. XPS spectra were obtained by a PHI 5600 ci XPS system using monochromated Al K alpha radiation (1486.6 eV). XPS investigations (in the middle part of the filament) were carried out after the ribbon filaments had been exposed to different deposition conditions.

In order to investigate filament degradation under alternating current heating, a special design of the radio-frequency (RF) matchbox was employed, which allowed us to apply DC and RF (13.56 MHz) current to the filament and heat it using different sources separately or simultaneously. During experiments, no parasitic plasma was observed due to a low RF potential on the filament rods.

Cross sections of the filaments in different places were prepared. For the visualisation of the filament cross section, an etching procedure (50 ml dist. water + 25 ml nitric acid (65%) + 5 ml HF (40%)) was used in order to improve the microscopic view contrast [16].

3. Results and discussion

3.1. Tantalum catalyst degradation during the hot-wire chemical vapour deposition of thin silicon films

Recently, it was shown that the quality of deposited thin silicon films declines with the duration of filament use [1,17] and that the deposition rate decreases when the voltage on the filament is kept constant [1,18]. A possible reason for the drop in deposition rate is a decrease in filament temperature during ageing [19]. It is important to note here that the filament temperature is an important technological
parameter (instead of the applied voltage), since the species generated on the surface of the hot filament and therefore the deposition rate and film quality are highly dependent on it [20]. Hence, to keep the temperature of a catalyst constant during use, it is necessary to readjust the $J-V$ settings when the filament conductance changes. At the end of the filament lifetime, about 60% more power must be applied in order to maintain the previous filament temperature (Fig. 2). The effect of the power enhancement could possibly be attributed to an increase in filament thickness at the “cold ends”, which results in stronger heat transfer to the supporting contacts and an increase in the filament surface due to cracks and fissures on the surface, and therefore to a stronger heat transfer to the gas.

In order to investigate filament ageing with respect to the properties of the deposited amorphous hydrogenised silicon films (a-Si:H), a series of experiments were carried out. A W-shaped wire filament was used with interruptions for filament annealing (see Section 3.2). The filament temperature ($T_{fil}$) was 1500 °C, the total gas flow rate was 10 sccm of SiH$_4$, the total gas pressure was 0.3 Pa, and the substrate heater temperature was 150 °C. The influence of filament ageing on the a-Si:H film quality was examined by repeatedly sampling film deposition on the glass substrate and Si wafers.

During the experiments, $T_{fil}$ was kept constant by varying the supplied electrical power (by readjusting the $J-V$ settings). The deposition rate of a-Si:H increased by 28% with the duration of filament use (see Fig. 3). A strong decrease in the photoconductivity to the dark conductivity ratio of the deposited a-Si:H and therefore in the film quality was already observed after 600 min of filament usage (about 7 µm of total deposited a-Si:H). It is important to note that the increase in the deposition rate correlates with the increase in supplied power (see Fig. 2). The drop in the film’s electronic properties and the
increase in the deposition rate are most likely related to differences in radical chemistry compared to the virgin wire [7,21].

The morphology of the filament changed after contact of the hot filament with the silane (see Figs. 1, 4) [22,23]. The diameter of the filament did not change strongly in the middle part, but there was an increase in the diameter at the “cold ends” (see Fig. 4). There were fissures and voids on the filament surface after use. The tantalum kernel was surrounded by different phases [23]. Additionally, the fissures and filament surface at the “cold ends” were often covered by a thick layer of pure silicon (>50 μm). We generally observed a thick, very porous phase at the outer filament surface, and thinner and denser phases close to the Ta kernel (see Fig. 4) [23]. In the direction from the bulk to the surface of the filament, the concentration of Ta decreased while the concentration of Si increased. Tantalum silicides can occupy more than 10–40% of the filament diameter (up to 100 μm thick) in the central part of the filament and up to 80% at the “cold ends” [22,23].

The increase in filament resistance correlates with the silicon concentration in the bulk of the filament [15]. The filament with the highest concentration of silicon in its bulk exhibits the highest post-preparation resistance. The results of the microstructure investigation of the filaments by X-ray diffraction are in good agreement with the secondary ion mass spectrometry (SIMS) measurements [15]. Fig. 5 shows the XRD patterns, recorded by Θ–2Θ scanning of the ribbon filaments before and after use and annealing, as well as after the application of alternating current (AC) power for filament heating (see Section 3.3). Different Ta and tantalum silicide (TaS3Si) peaks were observed after the filament ageing.

The increasing amount of silicides at the expense of tantalum led to an increase in filament resistance due to higher tantalum silicide resistance [15,24]. These silicides make the filament brittle [25]. In addition, at high-temperatures, the silicides were amorphous and crystalline, and led to filament surface corrosion due to a higher thermal expansion coefficient [26] compared to Ta.

The previously published data [15] prove that the change in filament resistance with time strongly depends on the deposition process conditions. When the silane partial pressure is “low” (<3 Pa), the resistance of the filament always increases with time. “High” silane partial pressure (>3 Pa) leads to a rapid decrease in the filament resistance with the duration of filament use [15]. The reason for this is a phenomenon that we call “thick silicon deposits” (TSDs) on the filament (Fig. 1(e, f) and Fig. 6). The TSDs can be observed by the filament temperature drop at their location. We note that the TSDs were observed on all filaments that exhibited a drop in resistance.

The experiments revealed that the reaction mechanism on the filament surface, which generates Si containing radicals, must be considered as a complicated, multiple-step process that not only includes reactions such as silane adsorption, silane dissociation into adsorbed Si and H, Si diffusion on the filament surface, and H and Si desorption, but also the indiffusion of silicon atoms into the filament, the production of a SiMe alloy, the formation of TSD on a filament surface, and therefore catalyst degradation [23].

The observed dependence of the aged filament resistance on the ageing time is the result of competition between two processes: an increase in resistance due to TaS3Si alloying by Ta expense and a drop in resistance due to the growth of TSDs.

3.2 High temperature post treatment of filament in vacuum. Annealing effect

Recently, it was demonstrated that operating the filament at high Tfil (about 2000 °C) in a vacuum leads to a decrease in silicon on the filament surface [1,7,15]. Therefore, in order to increase the filament lifetime and to obtain a more reproducible catalytic process, we attempted to evaporate the silicon from the filament surface by the annealing procedure.

It is important to note that during the annealing procedure, we observed a sudden increase in the filament temperature (Fig. 7), while the electrical power delivered to the catalyst decreased due to a decrease in current through the filament when the voltage was constant (so-called annealing effect) [24]. The filament resistance after annealing was about 10% higher. The time between setting the temperature and the change in temperature to higher values increases as the filament ages (see ref. [24] for more details). The “older” the wire, the longer the waiting time and the higher the required starting temperature.
Due to the fact that the resistance of molten silicon is a metal-like value [19,27], silicon evaporation could be a reason for the increase in filament resistance after annealing. The morphology of the filament surface most probably also plays an important role. It is likely, that the evaporation from the porous surface takes longer in the case of aged filaments. While the liquid silicon is electrically shunting on the filament surface, it is possible that after silicon has been evaporated from the filament surface, the resistance of the catalyst increases and more electrical power is applied to the Ta kernel and silicides. This, in turn could lead to an increase in the filament temperature during annealing. It appears that the annealing procedure has a complicated nature combining several processes: silicon evaporation, recrystallisation of Ta, and further progress of silicidation [23,24].

Recently [15], it was shown that after annealing (about 5 min), the concentration of silicon at the surface and near the surface (<3 µm) is greatly reduced. However, this hardly ever affects the Si concentration in the bulk of the catalyst. The estimation of the silicon–tantalum atomic ratio ($\rho_{Si}/\rho_{Ta}$) at the surface by XPS measurements (quantification in accordance with [28]) yielded $\rho_{Si}/\rho_{Ta}$=0.07 and 3.5 with and without annealing, respectively. Properties similar to those of an annealed surface were observed after a “pure hydrogen” ($T_{H2}$=1600 °C, p=1 Pa) process ($\rho_{Si}/\rho_{Ta}$=0.1).

The results of XRD measurements support the previous observations that filament ageing in silane-containing atmosphere involves the formation of various silicides [23]. A comparison of the patterns of the used filaments with and without annealing (Fig. 5b, c) revealed that annealing does not considerably decrease the amount of detected tantalum silicide. The intensity of the Ta peaks decreases after filament use, indicating a change in the filament from pure metallic Ta to a mixture of Ta and tantalum silicides.

The amount of Si on the filament surface depends on the conditions of the HWCVD process. Above all, these conditions are filament temperature [1] and silane partial pressure [15]. Fig. 8 presents the results of an experiment in which the deposition procedure was stopped every hour in order to anneal the ribbon filament in the vacuum. The annealing of the filament after every deposition in vacuum led to an increase in the filament resistance (Fig. 8, grey arrow). The resistance dropped again after 1 h of use in pure silane (pressure of 1 Pa) (dashed grey arrow). Nevertheless, it becomes clear that annealing does not prevent the overall variation in filament resistance during, because the behaviour is rather similar to that of continuous deposition without annealing breaks (black line, ref. [15]). The filament resistance rose gradually until the formation of TSDs (6 h old filament) independently on annealing procedure. A decrease in silicon concentration on the filament surface after annealing was observed, but no detectable difference was observed in the filament bulk [15].

The tantalum silicides represent a strong diffusion barrier for Si atoms [29]. In the case of tungsten, the rate of Si evaporation from the surface was 3–5 orders of magnitude higher than the indiffusion rate [21]. The balance between these two processes should not differ much for Ta. Therefore, after the appearance of the silicides on the filament surface, there was a strong diffusion barrier against the diffusion of Si atoms into the filament body. Nevertheless, the microscopic images show that corrosion of a filament could bring about dramatic changes, especially at the “cold ends” (see Fig. 4). The most probable reason for this is the different mechanical properties of silicides and pure tantalum (different thermal expansion coefficients, durability, and strength). The cracks at the filament surface and grain boundaries are most likely the main sources of the breakthrough of silicides and further diffusion of Si into the filament during deposition and annealing (see Fig. 4).

Due to the very low diffusion rate of Si in the silicides, the subsequent annealing of the filaments in vacuum did not completely rectify the catalyst surface because outdiffusion of the silicon should not take less time than indiffusion during the deposition process, because deposition time is much longer than annealing time.

A comparison of the filament behaviour and compounds with and without annealing showed that annealing did not decrease the risk of TSDs. The appearance and intensive growth of the silicon-covered regions occurred at a rather high silane partial pressure and rather low filament temperature with and without annealing breaks (after 300 min: 6 h old filament, see Fig. 8). In such cases, there could be enough thermal power locally for silane decomposition, but not enough power to evaporate the generated silicon atoms completely. It is very likely that the filament covered locally by a thick (>50 µm) silicon layer caused the redistribution of the electrical field and therefore led to non-uniform temperature distribution along the filament [24].

If a decrease in filament resistance is observed, the catalyst must be replaced because it is impossible to remove the TSDs by a conventional, direct current, annealing procedure [24]. Filaments that are not covered by thick silicon can be used again after a regeneration/annealing procedure which cleans the filament surface. However, the filaments become more and more brittle due to growth of silicides.

### 3.3. AC heating as a possible way of increasing filament lifetime

Obviously, the main source of filament contamination during HWCVD of thin silicon films is silicon. Therefore, filament lifetime could be extended if the filament is in contact with a decreased...
amount of silicon and the silicon only remains on the filament surface for a short time. The easiest way of achieving this is by increasing the filament temperature and/or decreasing the silane partial pressure. In practice, we observed a long filament lifetime (over 4500 min) when low partial pressure of silane was used (0.33 Pa), while the average time of a W-shaped wire filament was about 2000 min ($p_{\text{SiH}_4} = 1$ Pa, $T_{\text{fil}} = 1600^\circ$ C). A high filament temperature (about 2000°C) led to the evaporation of silicon and/or silicon-rich silicides from the filament surface [28,30]. Therefore, a filament that is exposed to a low partial silane pressure and a high-temperature (more than 1900°C) should have a longer lifetime. Unfortunately, these requirements contrast with the fact that the best quality amorphous and microcrystalline thin films were deposited at much lower temperatures of the filament (1450–1550°C) [31,32]. An increasing filament temperature led to the growth of porous and defect-rich material. On the other hand, rather high $p_{\text{SiH}_4}$ partial pressure is necessary for a high deposition rate of the thin silicon films. These facts contradict the idea of increasing filament lifetime by increasing $T_{\text{fil}}$ and decreasing silane partial pressure.

We also have to take into account the fact that the design of the HWCVD reactor and especially the shape of the filament influence the filament lifetime (for example, sagging of the filament due to gravity). The mechanical vibration caused, for example, by opening or closing the gate valve can destroy the filament [18].

We propose four other possible ways of increasing the filament lifetime:

1. post-deposition chemical cleaning procedure (for example, by annealing/exposure of hot filament to F-containing gases);
2. special construction of HWCVD chamber, avoiding undesirable contact of silane and filament (for example, remote process using only H-dissociation);
3. formation of a special catalyst surface, which could function as a barrier against Si indiffusion allowing a catalyst to stay clean at process temperatures;
4. use of AC heating current.

This section of the paper is concerned with the application of AC current for catalyst heating to suppress TSD formation and reduce the amount of silicon remaining on the filament surface.

As is well known, an AC flow in a conductor is not uniformly distributed. It is concentrated near the surface (skin effect) [33,34]. In a wire of circular cross section, the radial distribution of the current density is a Bessel function of an argument proportional to the square root of the frequency (depth-penetration skin effect). The distribution of the alternating current density in a flat conductor (ribbon) is more complicated [34]. We chose the RF current ($13.56$ MHz) in order to obtain a small thickness of the “hot skin” layer. For Ta and Si (at 1400°C, resistance of molten silicon is a metal-like value [27]), $d_{\text{skin}}$ (13.56 MHz) was about 10 μm. Due to the skin effect, the current density was mainly concentrated on the conductor surface and therefore on the silicon deposits (if any) or the silicide coverage. High current and therefore a high concentration of electrical power on the surface region could lead to evaporation of silicon from the surface.

In the case of DC heating, the current density is uniformly distributed across a conductor. Therefore, when silicides or TSDs appear on the filament surface, the density of the current is redistributed between the Ta kernel and the silicon/silicides on the surface and drops at the TSD location due to the increasing filament diameter there. The decrease in current density should lead to a drop in the filament temperature and, in turn, the temperature decrease should lead to further growth of silicon on the surface. Experiments recently conducted confirmed the supposition that TSD formation is a self-accelerating process [24].

In order to test this idea of using AC heating, a series of experiments was performed using a combination of RF and DC power. We checked the ribbon filament resistance by reading out the voltage and current through the filament with DC power supply. When 50% of the power (about 70 W) was applied by RF current (in addition to 50% DC power), the resistance of the ribbon filament increased less during the deposition process than in the standard, pure DC power heating process [15]. After filaments were used for 400 min without annealing, the concentration of silicon in the bulk of this catalyst was much smaller (1%) compared to a filament heated by pure DC (8% at DC operation) [15]. The XRD analysis of RF-heated filaments also revealed a much smaller peak intensity for tantalum silicides compared to DC-heated filaments (see Fig. 5. d). The XPS analysis showed that the concentration of silicon at the surface was also smaller for RF+DC operation without subsequent annealing: $\rho_{\text{B}1}/\rho_{\text{DC}1}$ (RF+DC) was 1.5 (3.5 for DC heating). There is no significant difference in the SIMS and XPS spectra between 50% DC+50% RF heating and pure RF heating of the filament (no DC power). Fig. 9 shows optical microscope images of a cross section of the ribbon filaments after different heating methods under the same deposition conditions (identical $T_{\text{fil}}$, $p_{\text{SiH}_4}$ deposition time). The photos clearly show that in the case of (RF+DC) heating, the filament surface contains less silicides than for DC heating. No TSDs were observed on the surface of the ribbon when the catalyst was operated with RF heating in pure silane atmosphere. Even the increase in pressure from 1 Pa to 12 Pa did not lead to any TSD formation when the filament was heated by RF.

In order to investigate the possibility of cleaning filaments already contaminated with TSDs, the next experiment was performed. We kept the filament under “high silane pressure” conditions throughout the initial part of experiment (12 Pa, silane). At first, we used only DC heating power. We observed the TSDs on the filament surface after 100 min of use (Fig. 10 (left)). When we applied RF power (DC power was decreased to keep $T_{\text{fil}}$ constant), the deposits disappeared from the filament surface (Fig. 10 (right)). A piece of silicon deposit remained on the filament, because it had only one contact point and,
reason for the increase in formation of tantalum silicides alloys on the surface of the catalyst is a heating. This fact and evidence of the low post treatment resistance of geometry of the catalyst\cite{15}. Recently \cite{15}, it was shown that the described above for the (DC)). The deposition conditions were the same as in the experiment carried out for 37 h.

RF heating was also applied in addition to DC heating for W-shaped wire filament heating in our multichamber system (25% (RF)+75% (DC)). The deposition conditions were the same as in the experiment described above for the ribbon filament.

Surprisingly, we were able to use this filament for silane decomposition under such conditions for 37 h while pure DC heating was used only for 20 h (see Fig. 11). It can be seen that the increase in filament resistance under RF + DC heating is much smaller than under DC heating. The same effect has been shown before for the ribbon geometry of the catalyst \cite{15}. Recently \cite{15}, it was shown that the filament contained less Si after RF + DC heating than filaments after DC heating. This fact and evidence of the low post treatment resistance of filaments support the supposition that the indiffusion of Si and the formation of tantalum silicides alloys on the surface of the catalyst is a reason for the increase in filament resistance during use.

Fig. 11. Dependence of relative resistance on duration of filament use for DC (see Fig. 3) and DC + RF filament heating. For a better readability, error bars are only given for one curve. Lines are drawn as a visual aid.

Fig. 12 provides an optical microscopic view of the filament cross sections. A filament after DC heating (20 h depositions) is compared to a filament that was used for 37 h under the same deposition conditions but with RF + DC power heating. The figure clearly shows that after heating the filament by RF + DC, the depth of silicide at the filament surface is about the same, although the operation took almost twice as long. The filament after DC heating has very porous, needle-like silicides at the surface. This could be the reason for a difference in the aged filament resistance (see Fig. 11). It should be noted here that the skin effect on the wire filament should be less prominent than on the ribbon-shaped filaments due to the absence of the lateral skin effect \cite{34}. Therefore, the possibilities of keeping the wire filament surface relatively clean by applying RF power could be less significant than for the flat catalyst.

It is important to note that when we use DC + RF power for wire filament heating, there is no strong degradation of the deposited film properties during filament ageing compared to results obtained previously for DC heating (see Fig. 3). No decrease was observed in the ratio of photoconductivity to dark conductivity of the deposited a-Si:H or in the deposition rate (see Fig. 13). Fourier transform infrared spectra of a-Si:H films deposited after 30, 1000 and 2000 min of filament use also showed no difference. Nevertheless, we observed monotonous growth of the deposition rate and the ratio of photoconductivity:dark conductivity for the first 500 min followed by stabilization. The reason for this phenomenon is not yet clear.

4. Conclusions

After operation of a tantalum catalyst in a silane-containing process gas atmosphere, a high silicon contamination on the surface and also in the bulk of the tantalum catalyst was observed. We conclude that the annealing of the filament by direct current in vacuum (temperature of filament >2000 °C) strongly reduces the concentration of silicon in the surface area (by three orders of magnitude), but the silicon concentration in the bulk remains rather high, most probably due to a very low rate of Si diffusion through the tantalum silicides. Used filaments have complicated structures. The fissures and cracks most probably appear on the filament surface due to temperature changes and the different coefficients of thermal expansion for tantalum and silicides.

When DC heating is used, the filament resistance continuously increases with the duration of filament usage (lifetime) up to finally 125% of the initial value. We have to apply 60% more heating power in order to obtain the same filament temperature at the end of the filament lifetime. The quality of the deposited amorphous hydrogenated film decreases with filament ageing. The filament resistance behaviour reflects different processes that take place on the filament surface: silicon indiffusion and the creation of Si–Ta alloys, the storing.
of silicon in thick silicon deposits and fissures. The formation of tantalum silicides leads to increasing filament resistance, while the thick solid silicon deposits function as additional current channels and lead to a decrease in filament resistance. Both TSDs and silicides lead to catalyst degradation due to the redistribution of electrical field and temperature, and the corresponding corrosion of the catalyst. The observed dependence of the aged filament resistance on ageing time is a result of competition between these two processes.

In order to decrease the silicon contamination of the tantalum catalyst, we applied alternating current (13.5 MHz) to heat the catalyst. Due to the skin effect of the high-frequency current, the silicon indiffusion is suppressed and the formation of thick silicon deposits on the surface can be prevented. RF heating at 13.56 MHz also enables a cleaning procedure of the TSD-polluted filament surface. The application of RF power allows the filament lifetime to be significantly increased without compromising the quality of the deposited films.

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