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# The influence of filament material on radical production in hot wire chemical vapor deposition of a-Si:H

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**Abstract**

The choice of filament material has an influence on the decomposition of silane during the hot wire chemical vapor deposition of amorphous and microcrystalline silicon films. In this paper, the Si radicals produced from W, Re, Mo and Ta filament materials are probed by laser-based single photon ionization as a function of hot wire temperature. The apparent activation energy of the Si radical production in the surface reaction regime from Ta (140–180 kcal/mol) and Mo (120–160 kcal/mol) are found to be close to the corresponding Si thermal desorption energies from these surfaces, suggesting that the Si production is controlled by the desorption process from the bare metal. On the other hand, the Si activation energies from W and Re (60 kcal/mol) are lower than the related desorption energies, suggesting silicon desorption from a silicon layer formed on the surfaces. Kinetic modeling supports this desorption mechanism. In addition to the Si radical study, the corresponding film deposition is detected in situ by multiple internal reflection infrared spectroscopy, from which growth rates are estimated. The results show similar activation energies for both the growth rate and Si formation from the various filaments, implying that Si radical production and subsequent film growth are dominated by the same elementary reactions at low pressure.


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## 1. Introduction

Hot wire chemical vapor deposition (HWCVD) of amorphous hydrogenated silicon (a-Si:H) and related materials has been under extensive research for the past 15 years, from the growth mechanisms and material properties to applications largely in the area of solar cells and thin film transistors [1–3].

This work was motivated primarily by an important engineering issue in the a-Si:H HWCVD process—the problem of filament aging and filament lifetime [1]. It has been found that a tungsten filament—which is the most commonly used material for the hot wire—can break during the deposition process [4]. The breakage usually happens at the cooler ends (100–200 °C lower temperature than the middle) of the filament where it is connected to the cold support rods. It was also found that the electronic properties of the deposited a-Si:H film degrade when the filament has been used for a certain period of time. The length of time that the filament can be used before being replaced varies from hours to months, depending on the filament temperature and the pressure and composition of the gas precursor. In general, the lower the filament temperature, the higher the silane pressure, or the lower the hydrogen feed ratio, the easier the filament breaks or ages [1].

So far there have been several ways to eliminate or improve the filament aging problem, including changing the filament design, annealing with or without hydrogen to clean the filament, or simply using other filament materials.

One material that has been found to improve the aging problem compared to tungsten is tantalum. It is known that tantalum has a relatively long filament lifetime. It also

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deposits materials (mainly polycrystalline silicon films) with different properties than does a tungsten filament under the same conditions [5,6]. A systematic *X-ray photoelectron spectroscopy* (*XPS*) study was done by van Veenendaal et al. to probe the near surface region of both a used tungsten and a used tantalum filament as a function of position along the filaments and deposition time [5]. The study revealed that, although silicon built up on both filaments, silicon content at both ends of the tungsten filament (where breakage usually occurs) was much greater than that in the middle of the filament, while silicon content on the middle and ends of the tantalum filament did not show much difference. In addition, the time-dependent study showed that silicon content increased linearly on tungsten while it saturated on tantalum. It was therefore concluded that the percentage of the silicon buildup on tungsten was enough to lead to a liquid phase silicon–tungsten alloy formation according to the W–Si phase diagram and that this serves the reason for the filament breakage [5]. On the other hand, there is no such liquid phase formation on tantalum. Two assumptions were further proposed by the authors to explain the different behaviors of tungsten and tantalum filaments: Either the dissociation of silane or the silicide formation process on these two filaments is different. Both of the two assumptions are related to the chemical reactions between silane and the filament [5].

Due to the lower silicon buildup at the same temperature compared to tungsten, tantalum is generally preferred when depositing polycrystalline or nanocrystalline silicon where lower filament temperatures are needed [3]. It was shown recently that a tantalum filament was able to deposit dense nanocrystalline silicon and thus reduce the oxidation of the material in air at a lower substrate temperature, which is desired when substrates of low melting points are necessary [6]. However, the high density only occurs at relatively low filament temperature (around 1550 °C). The film becomes more porous when the filament temperature is raised above 1700 °C. The difference between the material structures is attributed to the different radical production at different Ta filament temperatures.

Another material that improves the filament aging problem is graphite. This material, which was first tested at the beginning of the development of the HWCVD technique, was re-explored only recently and found to significantly prolong the filament lifetime [7]. In addition, graphite was also able to deposit materials (nanocrystalline silicon) at a favored lower substrate temperature, just like tantalum [8].

These results raise interesting questions as to the mechanism by which different filament materials generate the reactive radicals for film growth. In this paper, we use radical detection and kinetic modeling to study the reaction and dissociation of silane on filament surfaces as a function of filament temperature. Besides tungsten and tantalum, molybdenum and rhenium are also included in the study because of either their previous or possible future application in HWCVD [9,10]. To explain the data, we will propose that on tungsten and rhenium some silicon buildup, and not silicon alloy formation, is occurring on the filament surface and that this is not the case for Ta and Mo. In addition to radical detection, the structure and growth rate of the resultant films deposited on the substrate during the experiments were monitored in situ by multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy. It was found that, just like for tungsten [11], the growth rate from Re, Mo and Ta all followed the corresponding Si radical profile.

## 2. Experimental details

The Si radical profiles from W, Re, Mo, and Ta are detected using the *vacuum ultraviolet single photon ionization* (*SPI*) technique discussed in detail previously [12]. The radical study is carried out in a 4-in.-diameter stainless steel chamber, with a base pressure in the range of $10^{-8}$–$10^{-7}$ torr and a processing pressure below $10^{-5}$ torr. Two filaments, each made of a different material, are installed in the chamber at one time. The diameter of the filaments ranges from 0.25 to 0.5 mm. Each filament is about 23 cm in total length and wired into 10 coils. The distance between the filament and the laser focal point is approximately 3 cm. The Si radicals are produced by heating the filament to high temperature using a direct current power supply in a constant flow of silane. The temperature of each filament is determined both by optical pyrometry and by monitoring of the filament current. The accuracy of the temperature measurement is estimated to be within 50 °C.

The silane pressure is kept constant for all the measurements. Therefore, the detection of Si radicals is done under near-steady-state conditions where the silane flow rate, the production of Si at the filament, the annihilation of Si on the chamber walls (assumed to be constant) and the pumping speed are balanced with each other. A possible disturbance for the Si radical measurement could come from the desorption of previously deposited Si on the filament. To exclude this unwanted effect, the filament is annealed before each measurement until no Si desorption can be seen prior to introducing silane for the detection.

The infrared (*IR*) study of the a-Si:H film growth is performed in a separate chamber designed for *chemical vapor deposition* (*CVD*) and plasma processing [13]. A Ge(100) crystal at room temperature is used as the substrate for the film deposition. The infrared beam from an IR spectrometer is focused into the beveled edge of the substrate and undergoes total internal reflection multiple times within the crystal before being directed into a HgCdTe detector. In this way, the vibrational spectrum of Si–H bonds formed during the film growth is monitored. In addition, the growth rate is estimated by integration of the IR absorbance over the Si–H stretching region. The largest rise of the substrate temperature during the growth process