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Extension of the lifetime of tantalum filaments in the hot-wire (Cat) Chemical Vapor Deposition process

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Abstract

One of the prime components of a hot-wire (Cat) Chemical Vapor Deposition system is the filament used to pyro-catalytically crack the gases like silane. Burnt out tantalum filaments were studied to determine the possible improvement of lifetime for these filaments. The structure and chemical distribution in the filament were investigated, using electron microscopy and elemental analysis. It was found that at the high temperature centre section of a filament a thin surface silicide layer develops around a central metal core. At the filament ends a surface layer of metal silicide develops, that eventually consume the metal completely, causing breakages. Changes in the pre- and post-treatments of gas type and pressure were tested to improve the filament lifetime, arriving at a very simple procedure that increases the lifetime of the filament to several months. By annealing the hot filament both before and after a deposition run in a low pressure hydrogen ambient, a surface layer of pure silicon developed at the lower temperature ends, essentially protecting the metal from further silicidation.
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Keywords: Chemical Vapor Deposition; Filament; Tantalum; Lifetime; Silicide; Electron microscopy; Hydrogen; Energy Dispersive Spectroscopy

1. Introduction

In the hot-wire Chemical Vapor Deposition (HW-CVD) process a heated filament reduces the silane gas by a thermal catalytic process[1–3] to various ions that impinge on a heated substrate where film growth will occur.

The filament normally operates at above 1600 °C in a silane, or mixtures of silane and hydrogen gases in a low pressure environment. The thermal catalytic reaction occurring at the filament surface reduces the silane to Si–H-ions that on reaching the substrate surface bond with the surface atoms and formed a hydrogenated silicon film. At lower temperatures the catalytic reaction does not occur and the filament rapidly forms a metal silicide [4]. Within a few heating cycles the filament becomes too brittle and breaks, giving it an operating lifetime of a few hours.

The normal procedures used is to heat the filament to the operating temperature in vacuum and then first expose it to hydrogen gas, to react with any silicide on the surface of the filament and remove it by reduction, leaving the metal behind in a relative pure state [5].

However the H-gas treatment only reduces the surface silicide. During the initial heating stage the filament goes through the temperature range where rapid silicidation occurs at the surface. Silicide growth will continues to occur deeper into the metal, till eventually the filament is weakened sufficiently and it breaks. The filament ends at the electrode contact are in any case cooler even during the deposition process, and silicide formation occurs most rapidly there. We have studied the reactions occurring on the tantalum filaments and varied the pre- and post-deposition conditions to determine what primarily determines the breakage and thus lifetime of the filament.

2. Experimental details

The filament studies were performed using an MVSystems Inc. hot wire CVD system at our department of Physics, University of the Western Cape. Ta filaments of 7 cm length and 0.5 mm diameter were heated to 1600 °C in high vacuum ($<8\times10^{-8}$ mbar) before exposing to any reaction gases, and again expose to the same high vacuum before switching the current off. The standard lifetime before breakage was then 3 to

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5 h of deposition time, requiring filament replacement every 2 weeks. We introduce a hydrogen gas treatment processes before and after deposition runs with the filament at its operational temperature and arrived at a process that reduces silicide formation and increases the filament life extensively. The heated filament is first exposed to pure hydrogen for a minimum of 5 min, before any of the reacting gases (silane and hydrogen in our case) is allowed into the chamber. On completion of a deposition run, the filament is again exposed to pure hydrogen for a minimum of 5 min, the chamber then again evacuated to a vacuum better than 8×10^{-8} mbar before cutting the power to the filament.

This has resulted in a filament life of 11 months, with an accumulated operating time of 322 h. Such a filament has been studied and compared to the previous filaments, using microscopy and elemental analysis to determine the silicide/metal presence on the surface and filament interior. Cross-sections of the Ta filaments were also prepared from regions at the filaments centre and the ends. Analyses were done on the Hitachi SEM at the EM Unit at UWC equipped with a Genesis 2000 EDAX system for elemental analysis. EDS elemental analysis and X-ray mapping were performed at various positions along the filament length, as well as on the cross-sections to determine the occurrence of silicides at the surface and the interior of the filaments.

3. Results and discussions

Filaments as used in the hot wire CVD process only treated by annealing before a deposition run, did not last long, and typically broke after 3 to 5 h of accumulated deposition time. Silicide formation is found along the full length of these tantalum filaments, with severe structural changes especially at the ends. This includes cracks running along the length of the filaments, and the formation of a granular structure inside these cracks. In Fig. 1 (a) a Ta filament that was only heated in vacuum with no exposure to the gas is shown as reference. Fig. 1 (b) shows a centre section of a filament that was exposed to silane gas for about 3 h accumulated before breakage occurs. Cracks along the filament length are clearly visible, and a granular structure is apparent inside the cracks. In Fig. 1 (c) a section near the edge of the filament close to the electrical electrodes is shown. The structural disintegration of the filament is most severe at these ends, and this is where the breakage eventually occurs.

With the hydrogen pre-treatments, a different structure of the filament is observed. The filaments show minimal change at the centre regions as in Fig. 2 (a), where the temperature remains above 1600 °C, but at the cooler end regions the filaments develop an outer layered structured as in Fig. 2 (b) that start flaking off after only a few hours of exposure and lead to film burn out, as also reported by Grunsky [6].

Cross sections of the filament that was operating for 322 h were prepared to observe the internal structure. The centre region as shown in Fig. 3 (a) has a central metal core of Ta with a high concentration of absorbed Si, while the outer layer appears to be a $TaSi_2$ silicide, as can be deduced from the Ta:Si ratio of 27:73 as determined by EDS analysis.

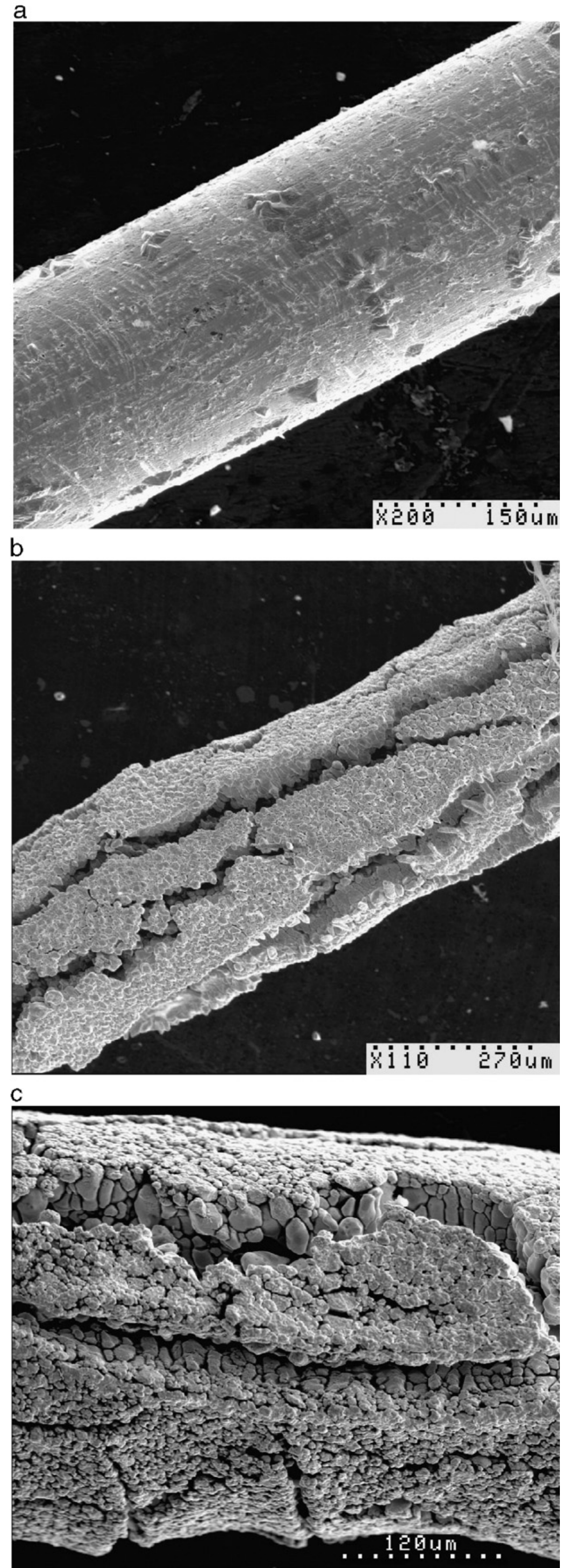

Fig. 1. (a) A Ta filament heated only in vacuum with no gas exposure, (b) a centre section of a filament after 3 h gas exposure, and (c) the end section of this filament.

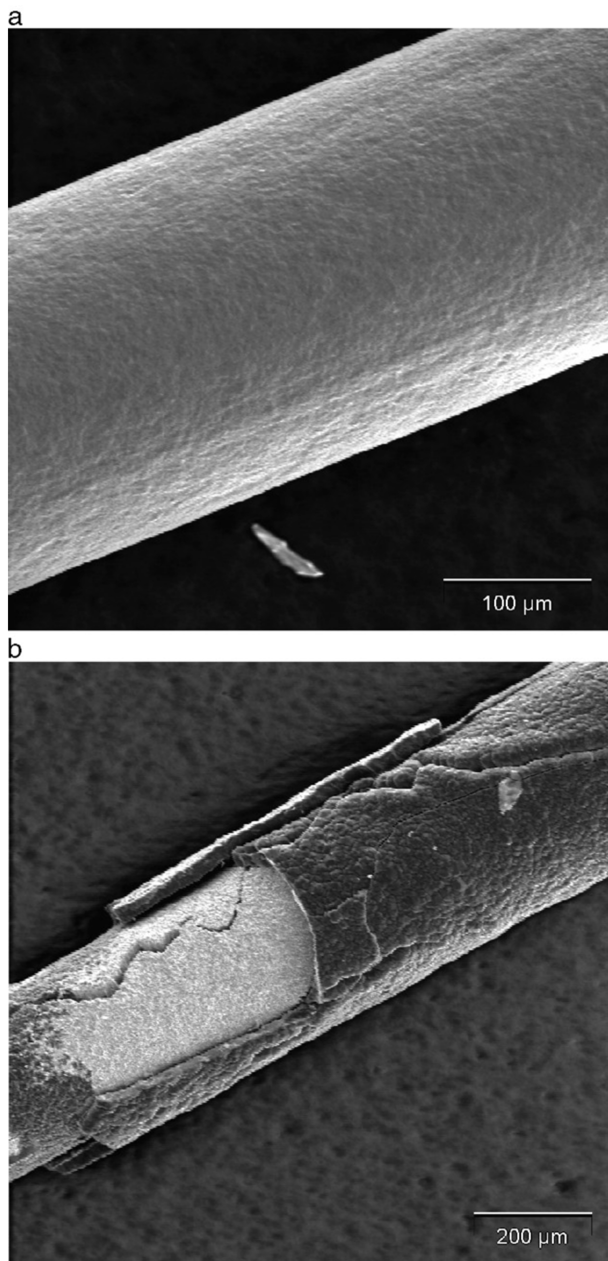

Fig 2. Filament after exposure to silane: (a) from the centre region, and (b) from the end region.

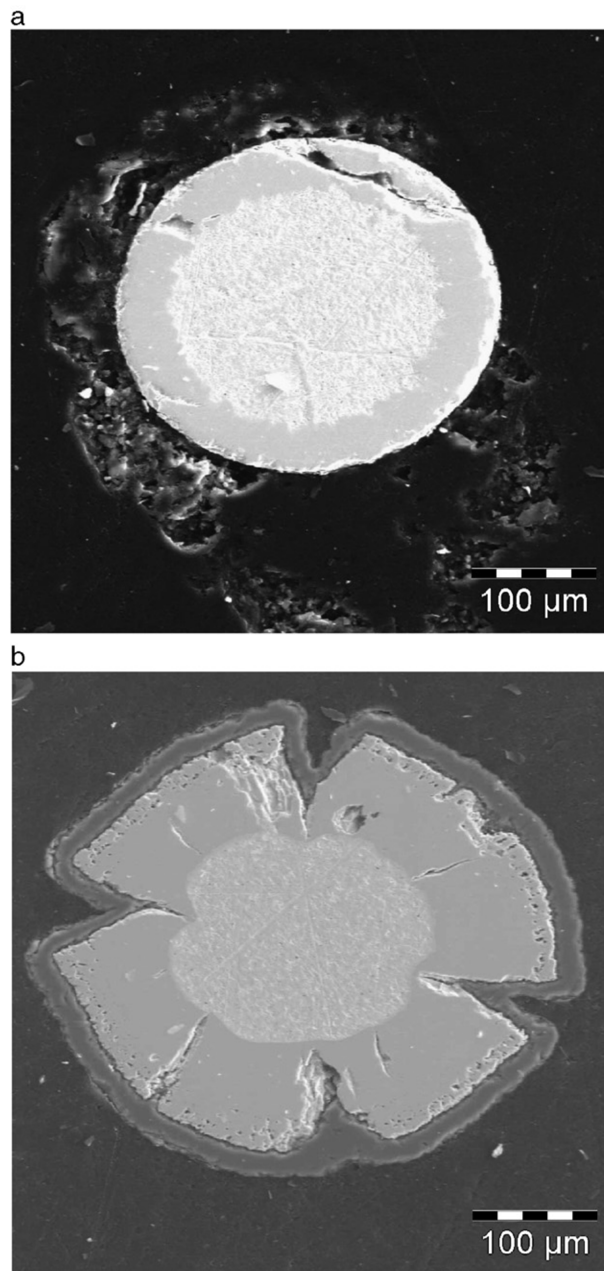

Fig 3. Cross-sections of filaments, with (a) from the centre section and (b) from an end region.

The filament from the centre section that is always at or above 1600 °C develops a stable configuration, with a silicide outer layer with an inner core of Ta (Si). At regions near the power mountings with lower temperatures there will be also a chemical reaction and silicide formation occurring.

Table 1 summarises results from the EDS analysis that were performed on the three clearly different regions of the filament in Fig. 3 (b). The interesting result here is the pure Si outer shell that completely covers the filament. The suggestion is that the Si that is reduced during the hydrogen treatment accumulated on the outer surface at this lower temperature ends, and forms a barrier for further catalytic reactions. Once formed it is stabilized by the pre- and post-hydrogen and prevents any further Si absorption into the metal. The filament from the middle Fig. 3(a) contained Si right though, with the outer layer containing sufficient Si to form the tantalum disilicide, $TaSi_2$.

Table 1
EDS analysis of Si and Ta from the different layers in Fig. 3 (a) and (b)

	Si: at.%	Ta: at.%
End section layers		
Central core	40.6	59.4
Silicide layer	59.9	40.1
Outer shell	100	0
Centre section layers		
Central core	68.9	31.1
Silicide layer	73.1	26.9

To prevent and reduce the degradation of the filament, most researchers exposed the hot filament to pure hydrogen prior to a deposition run to cause a reduction process of removing the silicon and reduce the metal to its metallic form. With this process the lifetime of the filament can be extended to several hours and deposition sequences, but it still required regular replacement. The problem is that after a deposition run with the system evacuated to its highest vacuum (better than 8×10^{-8} mbar) before reducing the power to the filament, there still remain some silicon at the filament surface, and as the filament cools down it went through the reactive temperature range where rapid silicide formation occurs. When next time the filament is heated again this reaction continues deeper into the filament, and the hydrogen exposure then only reduces the top surface layers. What we then introduce is another hydrogen purging after the deposition run, and before the power to the filament is cut. This exposure removes the remaining silicon on the surface, even at the cooler parts of the filament near the electrode mounts. The normal procedure is then followed to evacuate the chamber to a vacuum better than 8×10^{-8} mbar, before cutting the power to the filament. This resulted in a tremendous increase in lifetime, to the point where we measure it in terms of months instead of hours.

4. Conclusion

By using a pre- and post-deposition annealing in hydrogen at the same filament temperature as used for film growth, the lifetime of the Ta filament was extended substantially. The analyses show that the centre region of the filament developed a thin outer silicide region, while retaining a Ta metal core. At the colder regions near the filament ends, a Ta core remains covered by a metal silicide layer, and a pure Si outer shell. It is suggested that this Si shell prevents further catalytic reaction of the gas vapor, and acts as a protection for further silicide growth. At the high temperature centre region a balance is reached with a constant amount of silicon, which is stabilized with the pre- and post-hydrogen annealing.

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