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Reversibility of silicidation of Ta filaments in HWCVD of thin film silicon

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ABSTRACT

If tantalum filaments are used for the hot wire chemical vapour deposition (HWCVD) of thin film silicon, various types of tantalum silicides are formed, depending on the filament temperature.
Under deposition conditions employed for device quality amorphous and microcrystalline silicon ($T_{wire} \approx 1750$ °C) a Ta_5Si_3 (as determined by XRD) shell is formed around the Ta core. After 8 h of accumulated deposition time this shell has a thickness of around 20 μm. Upon annealing of the filament in vacuum at 2100–2200 °C the tantalum silicide shell becomes thinner, while a Ta layer is reappearing at the surface of the wire. After 4 h of annealing the silicide is completely removed, whereas the total diameter of the wire has not significantly changed. The resistance of the filament has been monitored and after the annealing procedure, it completely recovered to that of a fresh wire. This regeneration procedure greatly helps to avoid frequent replacement of the filaments.

1. Introduction

One of the main issues in the use of the hot wire chemical vapour deposition (HWCVD) technique for the fabrication of thin film silicon and its alloys, is the reaction of the silicon precursor (usually silane) with the filament metal. In case tantalum filaments are used, various types of tantalum silicides can be formed, depending on the filament temperature. This silicide formation may lead to a decreased filament lifetime, which in turn, may lead to undesirable down time and higher costs, when employed in industrial processes. Much effort is put in developing methods to increase the filament lifetime [1–3]. In this work we present an effective annealing procedure for removing the tantalum silicide from the filament.

2. Experimental details

In this study 99.9% pure Ta filaments were used with a diameter of 0.5 mm. After mounting two filaments of approx. 15 cm length, in electrical series connection, they were first annealed in vacuum (background pressure $<10^{-7}$ mbar) for 3 h at a constant current of 12.5 A (2050 °C) to remove impurities. Depositions were performed at a constant current of 10.5 A (~1750 °C) with a partial silane pressure of either 2 Pa during typically 10 min (a-Si:H [4,5]) or 0.25 Pa for almost 3 h (μc-Si:H [6]). Prior to every subsequent exposure to silane, the filaments were annealed for 30 min at a constant current of 12.5 A (1950–2050 °C). After an accumulated deposition time of between 6 and 8 h, the filaments were either annealed for 0 min, 10 min, ~1 h or 4 h at a constant current of 14 A.

During the annealing treatment the voltage at the output of the power supply was monitored at 1 s intervals by a Keithley 2000 multimeter, from which the resistance was calculated.

Cross-sections of the filaments were made by cutting and subsequent polishing with diamond lapping films and studied with optical microscopy and Scanning Electron Microscopy (SEM). The identification of the structural phases at the filament surface was obtained from X-ray diffraction (XRD) measurements.

3. Results and discussion

3.1. Ta_5Si_3 shell formation

In Fig. 1a an optical micrograph of a cross-section of the centre part of a Ta filament, which had an accumulated exposure to silane of 6 h, is shown. Fig. 1b shows a magnification of the same wire. It is clearly seen that a shell has formed. The shell has a thickness of around 20 μm. Fig. 2a depicts an XRD pattern of this filament, which indicates that the shell consists of Ta_5Si_3. The filament surface has become rougher as can be seen by comparing Fig. 3a and b, but is still rather smooth in comparison to Grunski et al. [7] and shows no deep fissures or voids. The cracks visible in Fig. 1b are most likely caused by thermal stress during the rapid cooling of the filament [7]. Also the shell is far thinner than in the case of Grunski (~20 μm vs. up to 100 μm).

Fig. 4 presents a SEM micrograph of the cross-section of the "cold end" at the electrode contact of the filament shown in Fig. 1a. The insert shows an optical micrograph at a lower magnification. Here the

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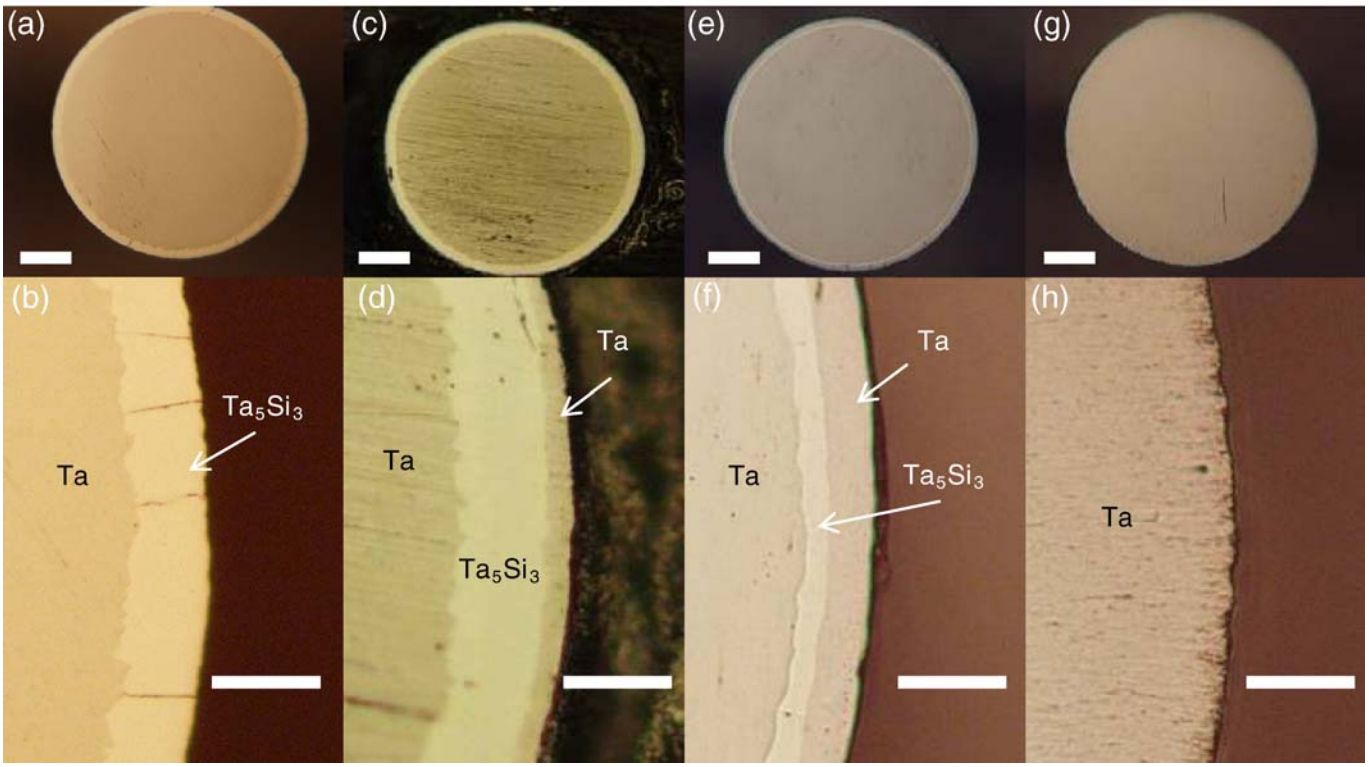

Fig. 1. Optical micrographs of cross-sections of 4 Ta wires with comparable deposition history, but annealed for different durations. The top row shows the total cross-section (scale bar 100 μm), whilst the bottom row corresponds to the outer regions at a higher magnification (the scale bar is 30 μm). The annealing time after deposition is 0 min (a, b), ~10 min (c, d), ~1 h (e, f) and ~4 h (g, h).

outer shell is significantly thicker compared to the hot centre (~33 μm vs. 20 μm) whilst the outermost ~10 μm of the shell are clearly porous. However, this is far less than in the case of Grunski [7] where only a small solid core remains. The deposition conditions used for this research, differ in two ways from those used by Grunski [7]. In this work the filaments were mainly exposed to a low partial silane pressure of only 0.25 Pa (diluted with hydrogen), as used in our laboratory for deposition of device-quality microcrystalline silicon, whereas Grunski [7] uses a silane pressure of 1 Pa. The other difference is the higher filament temperature during silane exposure, in this study (~1750 °C vs. 1600 °C). Thus by using higher temperatures, the filament is less affected, especially at the "cold ends". It was found by several groups that a lower filament temperature is beneficial for the material quality [8,9]. However, under the conditions used in this study, high quality a-Si:H [4,5] and μc-Si:H [6] material are obtained at high deposition rates (1 nm/s and 0.2 nm/s respectively).

3.2. Removal of the Ta_5Si_3 shell: regeneration of the filament

A different filament that underwent a similar silane exposure time, was annealed for 10 min at 14 A (2100–2200 °C) in vacuum, after the exposure to silane. Optical microscope images of its cross-section are shown in Fig. 1c and d. A second outer shell appears to have formed. Fig. 1e and f shows that this outer shell increases in thickness at the cost of the Ta_5Si_3 shell when a wire is annealed for 1 h. Fig. 2b depicts the XRD pattern of the wire that was annealed for 1 h. It appears that this outer shell consists of pure crystalline Ta again. Eventually, after 4 h of annealing, the inner Ta_5Si_3 shell has completely disappeared, as is shown in Fig. 1g and h. XRD (not shown) confirms that the wire consists of Ta. Fig. 3c shows that the morphology of the surface has hardly changed during the removal of the Ta_5Si_3 shell.

In this study the Ta_5Si_3 shell was completely removed while the diameter of the filaments, which shows a small increase after the formation of the Ta_5Si_3 shell, was restored (to within 1%) to its value before exposure to silane. This shows that the silicidation process was truly reversed.

Knoesen et al. [2] use a hydrogen treatment for their filaments to extend the lifetime. Indeed they managed to extend it to 322 h accumulated exposure time and end up with a smooth surface, but the silicide shell is not removed, which possibly leads to differences in the deposited materials.

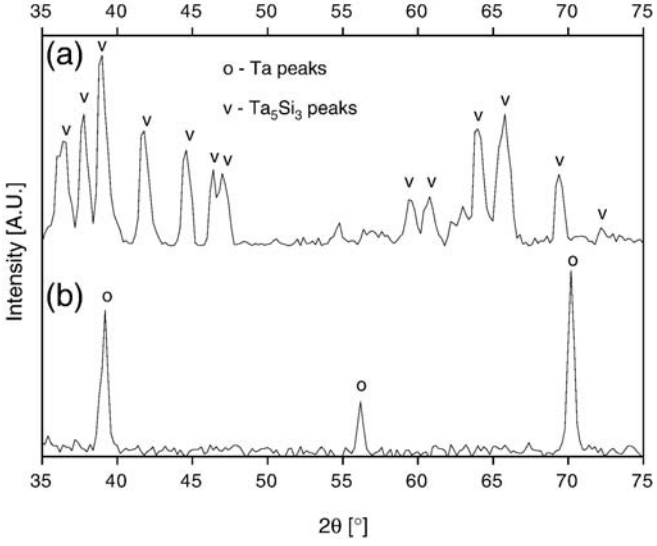

Fig. 2. XRD pattern of a filament exposed to silane for 6 h (a) and with an anneal treatment of 1 h (b).

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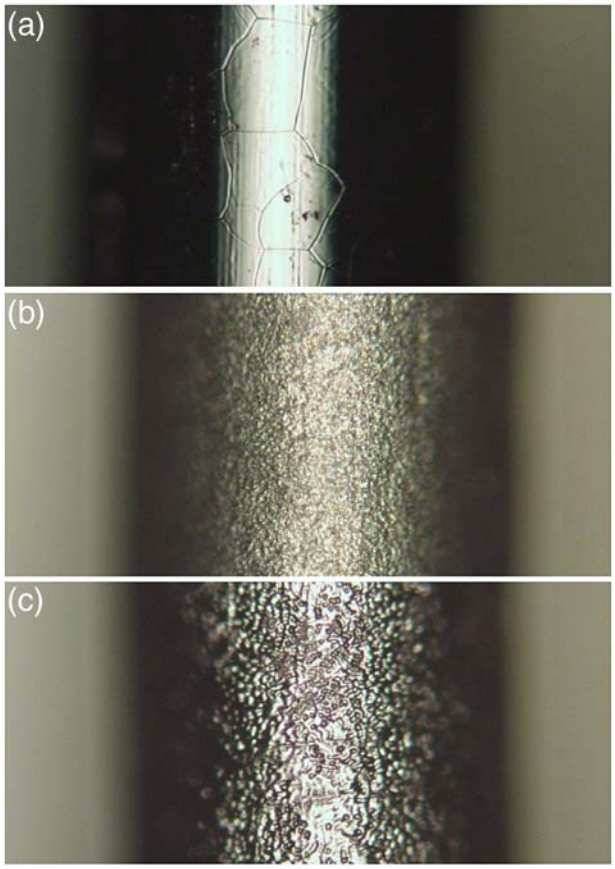

Fig. 3. Optical micrographs of the filament surface after 3 hour pre-annealing in vacuum without exposure to silane (a), after ~6 h accumulated exposure to silane (b) and after ~6 h accumulated exposure to silane and subsequent vacuum annealing for 4 h (c).

3.3. Resistance monitoring

During the annealing of the silicidised filaments the voltage over the filaments was monitored with a sample frequency of 1 Hz. In this way the resistance of the wires (including an invariable contact resistance) was monitored. In Fig. 5 this resistance is plotted vs. the annealing time for the filaments which were annealed during 4 h. The trend was similar for the filaments that were annealed during 10 min and 1 h, respectively.

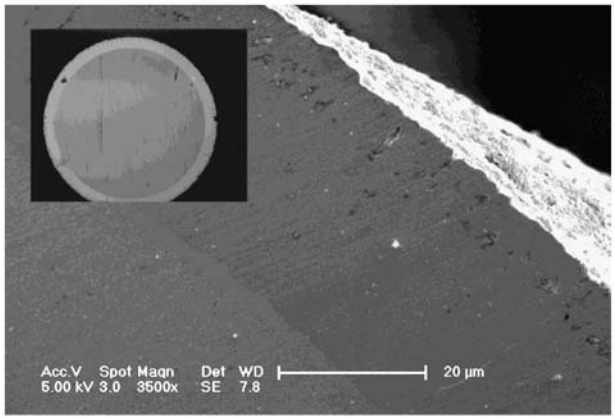

Fig. 4. SEM image of a part of the cross-section of the "cold end" of the filament shown in Fig. 1(a) and (b). The insert is an optical micrograph of the total cross-section of the same wire.

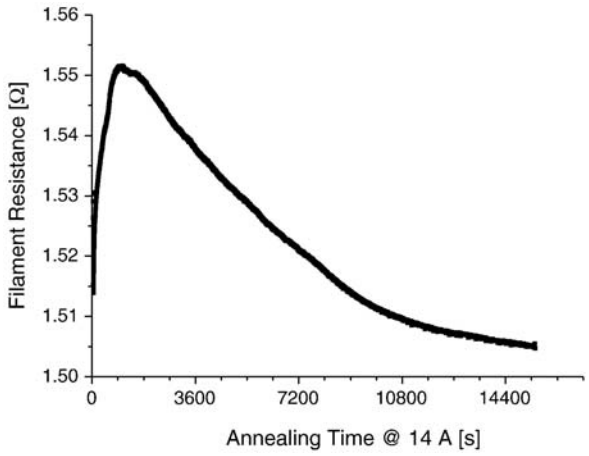

Fig. 5. The filament resistance vs. the annealing time for a filament with an accumulated silane exposure time of ~6 h.

During the first 15 min of annealing, an increase in the filament resistance is observed. This increase can be due to an increase in temperature caused by a decrease in emissivity of the filament surface, a decrease in filament diameter, or an increase in resistivity of the filament. After 10 min of annealing a Ta outer layer has formed on the filament and the diameter has decreased. The emissivity of Ta is expected to be lower than that of Ta_5Si_3 [10]. Together with the decrease in filament diameter this might explain the increase in resistance, which is observed despite the fact that the resistivity of Ta is lower than that of Ta_5Si_3 [11]. Another possibility (not investigated) is that Si dissolved in the Ta core [7] diffuses in the direction of the Ta_5Si_3 shell which then thickens at the inner shell interface at the expense of the Ta core, resulting in a larger resistance.

After 15 min the resistance starts to decrease. The diameter is still decreasing, whereas the emissivity is not likely to change, since the filament surface consists of pure Ta already (see Fig. 1d). Most likely the Ta_5Si_3 dissociates into Ta and Si. The Si then diffuses out of the filament into the ambient, since the Si concentration in the vacuum is virtually zero and the temperature provides enough thermal energy to desorb the Si. The Ta_5Si_3 shell, with its higher resistivity, thus decreases in thickness, causing a decrease in resistance. After 4 h the shell has disappeared.

The resistance of the filament was measured directly before the first exposure to silane at a current of 10.5 A, with the reactor in thermal equilibrium. After the 4 hour anneal the reactor was again brought in thermal equilibrium, with a current of 10.5 A through the filaments. It appeared that the resistance was completely restored (within 2%) to its original value. This also supports the statement that the silicidation of the Ta filament is truly reversible.

4. Conclusion

Under the conditions used in this study, a Ta_5Si_3 shell of approximately 20 µm was formed, when a Ta filament was exposed to silane. On the "cold end" of the filament this shell was around 30 µm thick of which the outermost 10 µm was porous.

The Ta_5Si_3 shell can be removed by annealing the filament at 2100–2200 °C without a significant change in filament diameter, confirming that no significant evaporation of Ta takes place in this annealing procedure.

Resistance monitoring shows an increase in filament resistance during the first 15 min, probably caused by a change in emissivity and a small decrease in diameter. After this 15 min a gradual decrease of the resistance is observed when Si is released from the Ta_5Si_3 shell and diffuses out of the filament. Eventually the resistance recovers to its initial value.

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By using this annealing procedure, the silicidation of the Ta filament can be truly reversed and thus the Ta filament can be regenerated. Similar regeneration procedures could be employed in industrial applications, to help avoiding frequent replacement of the filaments.

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