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Strategy for silicon based hot-wire chemical vapor deposition without wire silicide formation

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ABSTRACT

Silicide formation of wires during hot-wire chemical vapor deposition (HWCVD) of silicon based coatings is a key challenge which has to be overcome before HWCVD can be transferred successfully into industry. Silicide formation of tungsten wires is not occurring at temperatures of approximately 1900 °C and above when maintaining a silane partial pressure below approximately 1 Pa. Proceeding silicide formation at the cold ends where the wires are electrically contacted was completely prevented by continuously moving the cold ends of the wires into the hot deposition zone, resulting in a retransformation of the tungsten phase. Thus the maintenance period of a HWCVD manufacturing tool can be freed from wire lifetime.

1. Introduction

Thin silicon films deposited by HWCVD, also known as cat-CVD, are regarded as a high rate, cost effective, environmental friendly and easy to scale up alternative to plasma deposited silicon thin films [1–3]. In the HWCVD deposition of silicon based films silane (SiH_4) is used as precursor gas and tungsten (W) or tantalum (Ta) as the wire material. This article focuses on the silicide formation of tungsten wires. Tungsten silicides W_5Si_3 and WSi_2 are likely to form at low wire temperatures of less than 1850 °C [4]. These temperatures appear in the region where the wires are electrically contacted. Both silicides are very brittle and have an increased total hemispherical emissivity compared to tungsten. The increased emissivity results in unstable process conditions due to an increased power radiated by the wire surface. The brittle nature of the silicides usually leads to an abrupt mechanical failure of the wire at the silicide growth regions after some hours of usage. As the short lifetime of the wires in SiH_4 atmosphere would determine the maintenance period of a HWCVD manufacturing plant, effort was made to increase the wire lifetime in recent studies: Honda [4] used a tube surrounding the cold ends and a nitrogen gas flow from inside the tube to decrease the intrusion of SiH_4 molecules into the tube and to the cold ends. Frigeri [5] used a tube without any additional gas flow to protect the cold end. Silane molecules are extracted from the gas phase and build up coatings on the interior walls of the tubes. Using these methods the maintenance period can be extended but the films on the tubes cause new problems due to blistering of film material or contacting to the wire and thus causing abrupt process failure. For this reason we made another approach based on moving the cold end region by moving the wire.

2. Experimental details

2.1. Experimental setup

Experiments were performed in a roots blower pumped cylindrical vacuum chamber with a volume of approx. 0.5 m^3. The gas flows of the purge and process gases are controlled using mass flow controllers. The chamber supports a feed-through for electrical contacts and gas feeding, respectively. Window ports are used for pyrometry. A scheme of the experimental setup that is used inside the vacuum chamber is shown in Fig. 1. The tungsten wire is represented by a thick black line. The electric contacts for the heating power supply are located at (A) and (B). A stepping motor (C) is constantly pulling the wire which is led over a roll (D) and fixed to a weight (E). During each experiment a wire temperature above 1900 °C at the hot zone of the wire (F) is kept constant by adjusting the constant power supply manually. The wire loses a non-negligible amount of power by heat conductance at both contacts (A and B) which cools down the wire near to the contacts. These regions of the wire are denoted as "cold ends" (G and H). Silicide formation at the cold ends cannot be prevented, but its negative effects can be circumvented: The wire moves parallel to the wire axis in the direction indicated by arrows in Fig. 1 using a constant velocity. This allows a continuous supply of "new" tungsten wire into both cold end regions either from the hot zone (F) or from the stock on the right side of contact (A). Using this procedure at a constant total pressure of approximately 1 Pa abrupt process failure is prevented. The two variables investigated in this study were the wire temperature of the hot zone and the velocity of continuous wire movement. Table 1 lists all

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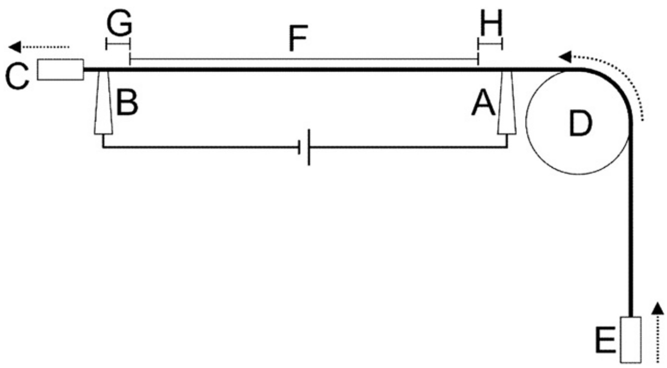

Fig. 1. Scheme of experimental setup showing one of five wires. (A) and (B) are electric contacts. (C) represents a stepping motor which pulls the wire in the direction indicated by the arrows. (D) is a guide pulley and (E) a weight to achieve straight wires. On the whole range of (F) the hot zone extends where the wire temperature exceeds a minimum of 1850 °C. The cold ends (G) and (H) are located near the electric contacts.

the process parameters applied. Additionally, static processes without any movement of the wire were made at identical wire temperatures.

In the used experimental setup the wire stock is limited to 180 mm which corresponds to the maximum drop height the weight (E) has in the given mounting position. Depending on the velocity of wire movement the maximum duration of each experiment was limited to a few hours, which is sufficient for the fundamental studies presented in this article. To overcome silicide formation at the cold ends conclusively, a technological solution with a larger wire stock is necessary (i.e. a feeding system with a set of wire coils).

2.2. Characterization techniques

The wire temperature was measured by a two-color pyrometer (Type Ircon Modline 3R with adapted optical system). The wire surface was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). For comparison, the length $l_{WSi}(v)$ of the WSi_2-zone at position (H) in Fig. 1 of a dynamic process with velocity v was related to the length $l_{WSi}(v = 0)$ of the WSi_2-zone of a static reference process at the same temperature and in the same apparatus, respectively. For characterizing the effect of wire movement the resulting quotient $Q_{WSi2} = l_{WSi}(v) / l_{WSi}(v = 0)$ is instructive.

2.3. Thermodynamic calculations

Tabulated phase diagrams of the Si–W system are only available for standard pressure [6] and, therefore, not applicable to HWCVD process conditions. Hence, thermodynamic calculations on the Si–W system were performed using version 6.3 of FactSage® thermochemical software and data from the SGTE database around a pressure of 1 Pa. Due to the comparatively low vapor pressure of tungsten, the total pressure of the considered system corresponds largely to the partial pressure of silicon. For best comparison with the experiments only calculations for a pressure of 1 Pa are presented. Further information on the software and the databases is provided by [7,8].

Table 1
Process parameters for static and dynamic processes.

Parameter	Value or Range	Unit
Wire temperature	~1900 to ~2200	°C
Movement velocity	0 to 0.63	mm/min
Contacts distance	222	mm
Wire diameter	0.25	mm
Wire to wire distance	30	mm
Number of wires	5	
Process duration dynamic	~3	h
Process duration static	2	h
Pressure	1	Pa
Silane flow	8	sccm

3. Results and discussion

3.1. Silicide formation on moved wires

In Fig. 2 a series of SEM pictures of a wire surface is shown. The first picture (A) shows the surface topography of a wire at the cold end taken from a dynamic process. Because the wire is moved by a step motor also the growth of WSi_2 starts stepwise as indicated by the three lines perpendicular to the wire axis (A). In the second picture (B) the surface of the wire at the transient from the cold end to the hot zone is shown. WSi_2, which was built up at the cold end, is now transformed into W_5Si_3 at the transient position. The stoichiometries of the silicides were analyzed using EDX. As the temperature increases further by continued movement of the wire to the hot zone, W is reconstituted from W_5Si_3 (C). Surface roughness is increased compared to the as drawn surface of unused tungsten. Depending on the extent of preceding WSi_2 growth, former cracks remain visible after W reconstitution.

Fig. 3 shows the values for Q_{WSi2} for each experiment depending on the experimental variables. A quotient of less than unity shows, that the

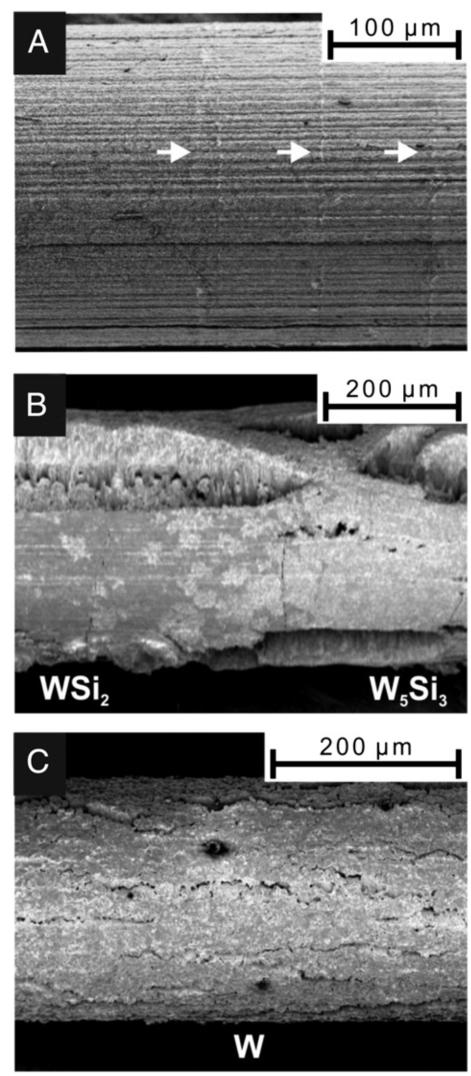

Fig. 2. SEM pictures of used wires in a dynamic process. The wires in the pictures move from cold to hot as indicated by the arrows. (A) Wire surface with a thin layer of WSi_2. Arrows indicate single steps of stepping motor. (B) First step of W reconstitution by phase transformation from WSi_2 to W_5Si_3. (C) Totally retransformed W wire.