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High rate hot-wire chemical vapor deposition of silicon thin films using a stable TaC covered graphite filament

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ABSTRACT

We grow silicon films by hot-wire/catalytic chemical vapor deposition using a new filament material: TaC-coated graphite rods. The filaments are 1.6 mm diameter rigid graphite rods with ~30 μm thick TaC coatings. Whereas heated W or Ta wire filaments are reactive and embrittle in silane (SiH_4), the TaC/graphite filament is stable. After >2 h of exposure to SiH_4 gas at a range of filament temperatures, the full length of a TaC/graphite filament retains its shiny golden color with no indication of swelling or degradation. In comparison, a W wire exposed to SiH_4 under the same conditions becomes swollen and discolored at the cold ends, indicating silicide formation. Scanning electron microscopy images of the filament material are nearly identical before and after SiH_4 exposure at 1500–2000 °C. This temperature-independent chemical stability could enable added control of the gas phase chemistry during deposition that does not compromise the filament lifetime. The larger surface area of the 1.6 mm diameter TaC coated graphite filament (compared to the 0.5 mm W filament) allows for a ~2× increase in the deposition rate of Si thin films grown for photovoltaic applications.

1. Introduction

Hot-wire chemical vapor deposition (HWCVD) (also known as catalytic CVD, or hot filament CVD) is a demonstrated technology for high-rate deposition of high-quality thin films [1]. HWCVD can be scaled to large areas and efficiently convert process gases into film; this has led to the commercial production of a number of materials [2,3]. The main drawback of the technology is the durability of the filament material itself, which typically degrades as it interacts with process gases at extremely high temperatures. Previous research has shown that W and Ta filaments react with silane (SiH_4) and methane (CH_4) deposition precursors to form silicides or carbides, which cause the filaments to break after 2–20 h, depending on the processing conditions. During SiH_4-based HWCVD, brittle tungsten and tantalum silicides form most quickly at the colder regions of the filament, typically close to the electrical contacts [4]. Thick silicon deposits (TSDs) also form on the hot regions of filament, altering the filament surface temperature, T_{fil} [5], and therefore the gas chemistry [6].

In order to extend the life of the various filament materials, it is best to operate in a narrow range of T_{fil} or to perform specific treatments before and/or after growth. For 0.5 mm diameter Ta wires, the optimal T_{fil} is $\geq$1900 °C, resulting in filament lifetimes as long as 8 h [4]. Alternately, growth with T_{fil} ~1600 °C coupled with pre- and post-deposition annealing of the hot filament in hydrogen can significantly extend the filament lifetime by reducing the outer silicide layer into a protective Si shell [7]. Heating with 13.56 MHz current (AC) may also extend filament lifetimes [5,8] by concentrating the current flow near the filament surface, preventing TSDs and reducing the Si indiffusion responsible for silicide formation [8]. For W wires, it is also possible to engineer special reactor geometries that reduce exposure of the cold ends of the filament to process gases [4]. All of these lifetime-extending approaches increase the complexity of the otherwise simple HWCVD technology and restrict the available process conditions.

In this article, we report the use of a new filament material for HWCVD silicon growth: TaC coated graphite, developed by Momentive Performance Materials. A photograph of a typical TaC coated graphite (TaC/C) filament is shown in Fig. 1a. We find that the surface of the TaC/C filament is stable in SiH_4 over a wide range of T_{fil} and that prolonged exposure does not lead to extensive silicide formation.

2. Experimental

The TaC coating on the graphite core is formed by chemical vapor deposition (CVD). The graphite rods are mounted in a hot wall CVD reactor (Fig. 1b) and heated to >2200 °C. This process is commonly used to coat graphite for a variety of applications, such as wafer carriers and heaters used in the metal organic CVD of SiC and GaN. The

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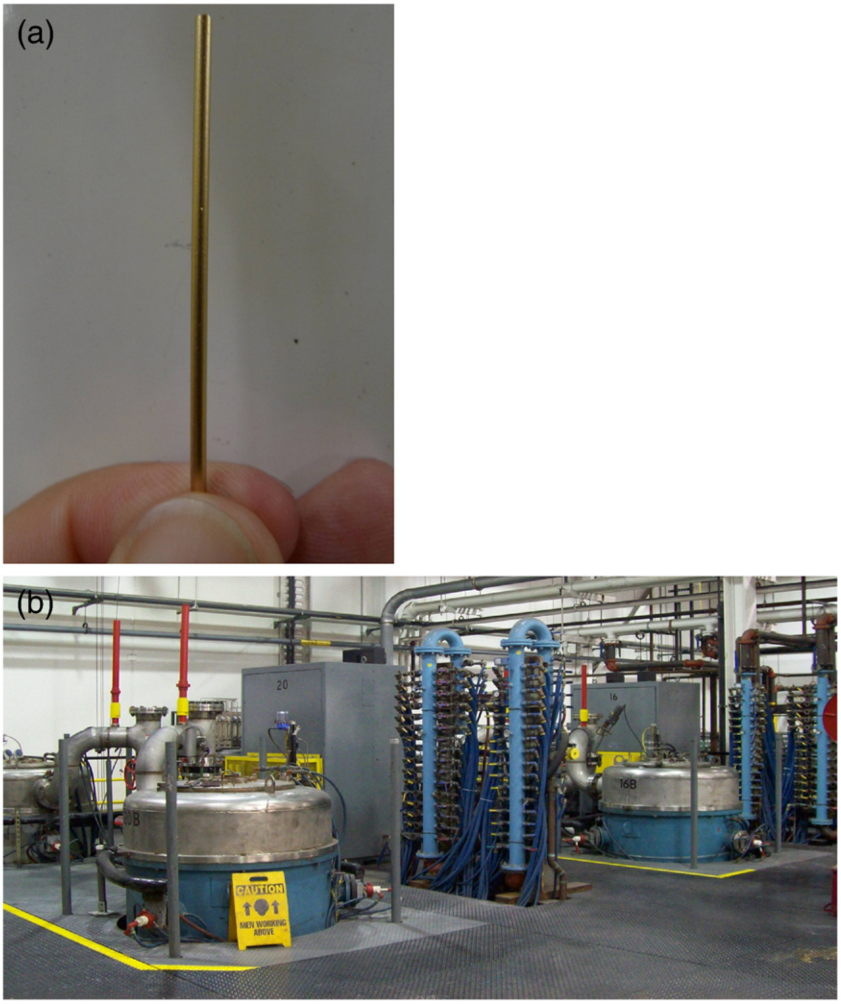

Fig. 1. Photographs of a) a virgin TaC/C filament and b) the CVD reactor used to fabricate the TaC/C filaments.

coating is conformal and uniform regardless of the shape of the initial graphite piece.

To test the stability of the ~0.3 Ω TaC/C filaments during the HWCVD process, we grow silicon films from pure SiH_4 gas over a range of T_{fil}. The TaC/C filament is a 10 cm-long, 1.63 mm-diameter rod and the TaC coating is ~30 μm thick. The ends of the TaC/C filament were wrapped in a thin graphite foil (to improve electrical contact) and clamped in an inconel holder. During film growth, the filament current was varied from 24–39 A (160–450 W). All of the data presented here are from a single filament. Deposition was started and stopped several times and the SiH_4 flow and chamber pressure were varied over the total SiH_4 exposure time of ~2 h. The T_{fil} of the TaC coated graphite filaments was calculated using:

$$T_{fil}\left[\frac{P_{rad}}{\sigma\varepsilon A}\right]^{1/4} \tag{1}$$

where P_{rad} is the filament power, A is the filament area, ε is the emissivity of TaC, and σ is the Stefan–Boltzman constant (5.67×10^{-8} $Wm^{-2}K^{-4}$) [9,10]. The emissivity value used in the calculation is based on the work of Ozaki and Zee, who report $\varepsilon = 0.6$ for both rough TaC surfaces, and smooth TaC surfaces that have been exposed to hot hydrogen at high temperatures [11]. Because we cannot directly compare the roughness of our filaments to those of Ozaki and Zee, we discuss the uncertainty in the emissivity value in section 3. The filament power, P_{rad}, is derived from

$$P_{in} = IV \cong P_{rad} + P_{SiH_4}, \tag{2}$$

where P_{in} is calculated from the current and the voltage of the filament, and

$$P_{SiH_4} = n\left(T_{gas}, p\right)\alpha(T)E_{SiH_4}A. \tag{3}$$

For (3), P_{SiH4} is a measure of power dissipated from the filament via SiH_4 decomposition, n (T_{gas}, p) is the number of collisions between the SiH_4 molecules and the filament surface ($s^{-1}m^{-2}$), α is the silane dissociation probability on the filament, E_{SiH4} (1380 kJ/mol) is calculated from the binding energy of Si–H bonds, and A is the filament area [9,10]. Assuming a maximum α of 0.3, P_{SiH4} is <10 W.

We also grow silicon films using a 25.4 cm long, 0.51 mm diameter W filament for comparison; the current on the W filament is set at 16 A (~2100 °C). Substrates were high resistivity (100) p-type c-Si wafers (625 μm thick, ~50 Ω cm, $10^{14}/cm^{-3}$ B) that are cleaned with a Piranha solution (3:1 H_2SO_4:H_2O_2) for 15 min at 120 °C and then rinsed in deionized water and blown dry with nitrogen. Immediately prior to deposition, substrates are dipped in 4% HF to remove the native oxide and produce a hydrogen-terminated surface. SiH_4 flow into the chamber was fixed at either 20 or 30 sccm, and the chamber pressure was fixed at either 10 or 20 mTorr. The substrate temperature (T_{sub}) and film quality are monitored by previously calibrated real-time spectroscopic ellipsometry (RTSE) [6,12]. T_{sub} is also monitored by an optical pyrometer, and a thermocouple contacted to the rear of the substrate heater; the substrate temperature is ~440 °C for amorphous Si (a-Si:H) growth and ~775 °C for epitaxial Si