Carbonized tantalum catalysts for catalytic chemical vapor deposition of silicon films

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ABSTRACT

Catalytic chemical vapor deposition (Cat-CVD) has been demonstrated as a promising way to prepare device-quality silicon films. However, catalyst ageing due to Si contamination is an urgency to be solved for the practical application of the technique. In this study, the effect of carbonization of tantalum catalyst on its structure and performance was investigated. The carbonized Ta catalyst has a TaC surface layer which is preserved over the temperature range between 1450 and 1750 °C and no Si contamination occurs on the catalyst after long-term use. Si film prepared using the carbonized Ta catalyst has a similar crystal structure to that prepared by uncarbonized Ta catalyst. Formation of the TaC surface layer can alleviate the ageing problem of the catalyst, which shows great potential as a stable catalyst for Cat-CVD of Si films.

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1. Introduction

Catalytic chemical vapor deposition (Cat-CVD), often called hot-wire CVD (HWCVD), has received considerable attention in recent years since it is a promising technique for preparing device-quality Si films at low cost as well as high deposition rate [1–7]. In this method, Si-containing source gases are decomposed by catalytic cracking reactions on electrically heated catalyst wires and then the produced species are transported to the substrate at a low temperature to form the Si film. To date, W and Ta metal wires have been the most commonly used catalysts [8–11]. However, the catalyst surface is easily converted to silicide during the reaction [12–16], which leads to a lower deposition rate for the film due to deactivation of the catalyst [17]. Worse still, quality of the prepared Si film declines with the duration of the reaction [17–19]. In addition, the temperature control for the catalyst becomes difficult because of the large changes in its resistivity and emissivity due to silicidation [13,20,21], which further varies the deposition rate of the film [18,21,22]. Finally, the catalyst wire is broken with a rather short lifetime [9,18]. Thus, catalyst ageing due to Si contamination becomes a bottleneck issue to the practical application of Cat-CVD technique for Si film deposition [5,15,23].

To solve the ageing problem and improve the stability and lifetime of the catalyst, some efforts have been made to suppress the silicide growth on the catalyst surface. Radio-frequency alternating current instead of direct current has been used to heat the Ta catalyst wire, which decreases the Si content in the catalyst bulk and suppresses the formation of thick Si deposits on its surface because of the skin effect of the alternating current [11,18]. Annealing of the catalyst in H_2 ambient or in vacuum at a high temperature is beneficial to increase its lifetime [24,25], but that still cannot avoid the silicide growth during the reaction. Recently, Honda and co-workers have reported on surface carbonization of W wire for Cat-CVD of Si films [20,26]. They found that the carbonized W catalyst with W_2C surface can suppress the silicide layer thickness to half of that for uncarbonized W catalyst, which is attributed to the less emissivity change from W_2C to WSi_x than that from W to WSi_x, and then W_2C exhibits better temperature stability than W.

For Cat-CVD of Si films, Ta catalyst has a relatively longer lifetime than W for the slower growth rate of tantalum silicide than tungsten silicide [10,27,28]. And TaC is more stable than Ta in terms of physical properties such as melting point and hardness, which is different from tungsten carbides (WC and W_2C) with the lower melting points than W. Consequently, we were motivated to prepare Si films using the TaC coated Ta catalyst. Laterally, we noted that a very recent publication briefly reported a stable catalyst for Cat-CVD of Si films: TaC covered graphite rod [29], which was fabricated by coating the graphite rod with a TaC layer. In our work, carbonized Ta catalyst with a TaC surface layer was obtained by simply carbonizing the Ta wire and the effect of carbonization on its structure and performance for Cat-CVD

of Si films was systematically investigated. It was found that the TaC surface structure was preserved at different reaction temperatures and no Si contamination was detectable for the catalyst even after used for several hours at 1600 °C.

2. Experimental details

2.1. Carbonization of Ta wires

A single-chamber Cat-CVD system was used for both carbonization of Ta wires and preparation of Si films. CH_4 gas diluted in H_2 ($CH_4 = 5\%$) at a flow rate of 10 sccm is used as the carbon source. Ta metal wire (Alfa Aesar, Purity > 99.95%) of 0.5 mm in diameter and about 12 cm in length is spanned straight in the Cat-CVD chamber for carbonization. Direct current is used to heat the Ta wire, and its temperature is measured in the middle part by a two-color infrared pyrometer (Raytek, MR1SCCF) with an accuracy of ± 20 °C. During the carbonization process, the wire temperature is kept constant at 1900 °C, while the applied voltage and current are allowed to vary. The chamber pressure is kept at about 4 kPa, which is monitored by a capacitance diaphragm gauge (Inficon, CDG025D). The carbonization time is 1 h.

2.2. Preparation of Si films

All Si films are deposited on glass substrates (Corning EAGLE 2000™) at a temperature of 150 °C. Both carbonized and uncarbonized Ta wires are used as catalysts for comparison. The distance between the catalyst and substrate is 3 cm. Prior to the film deposition, the Cat-CVD chamber is evacuated to a base pressure below 8×10^{-4} Pa. A gas mixture of SiH_4 and H_2 at a flow rate of 10 sccm is introduced into the deposition chamber to start the film deposition, while the catalyst wire is heated to a certain temperature. Pressure in the chamber is kept constant at 50 Pa, which is monitored by a resistance vacuum gauge. The typical deposition time is 1 h except where otherwise noted, and the obtained Si films are cooled down to room temperature in vacuum.

2.3. Characterization of Si films and catalysts

The as-prepared Si films are characterized by Raman spectroscopy and scanning electron microscope (SEM, Quanta 200 F). Raman scattering measurement is performed using a home-made Raman spectrometer equipped with a 532-nm laser source. Crystalline volume fraction (X_c) of the Si film is calculated using the integrated intensity of the deconvoluted Raman spectrum in the range of 350–550 cm^{-1} [30,31]. The film thickness is measured by cross-section SEM analysis. For SEM characterization, the accelerating voltage is 20 kV and the working distance is 10 mm.

Structures of the catalyst samples are identified by X-ray diffraction (XRD) characterization using Rigaku MiniFlex diffractometer with a Cu Kα radiation source. The measurements are performed between 2-theta angles of 30 to 90°. Cross-section SEM analysis is used to identify the outer layer thicknesses of the catalysts after used. Then energy dispersive X-ray spectroscopy (EDX) analysis is carried out to identify the chemical composition of the samples. For the SEM and EDX characterization, catalyst wire is first cut off and embedded in epoxy for solidification, then polished by emery paper and burnishing powder successively, finally the sample is ultrasonic cleaned. All the samples are sputter-coated with gold for 30 s prior to the tests. The quantity of Si embedded in the catalyst is detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu, ICPS-8100), then the mass ratio of Si to Ta is quantitatively calculated. The wire is dissolved in a mixture of nitric acid and hydrofluoric acid for the ICP-AES measurement (Hydrofluoric acid is an extremely dangerous chemical and should be handled with the utmost caution).

3. Results and discussion

Fig. 1a shows the XRD pattern of a typical carbonized Ta catalyst, and only TaC (JCPSD Card No. 65–8795) peaks are observed, which indicates the TaC surface layer is thick enough to cover the whole wire [20,32]. The catalyst exhibits a yellow color corresponding to TaC, as presented in the inset. Fig. 1b and c show the cross-section SEM images of the catalyst, which reveal a coaxial core-shell structure. EDX analysis confirms the catalyst core is pure Ta (not shown here). The shell layer has a uniform thickness of about 22 μm, which is suggested to be composed of TaC and Ta_2C annularly [32–34], and the Ta_2C is not identified by the direct XRD characterization for its existence in the inner side of the carbide layer.

Fig. 2a and b show the XRD patterns of both carbonized and uncarbonized Ta catalysts after used at temperatures ranging from 1450 to 1750 °C, respectively. 5% SiH_4 diluted in H_2 is used as the precursor gas. Interestingly, all the carbonized Ta catalyst samples demonstrate TaC peaks consistently, which are remarkably different from those of tantalum silicides (Si_3Ta_5 and $SiTa_2$) formed on the Ta catalysts. And no Ta peaks are observed for the Ta samples. The surface of Ta wire transforms into Si_3Ta_5 (JCPSD Card No. 65–2780) at temperatures below 1550 °C, and $SiTa_2$ (JCPSD Card No. 65–2696) peaks appear at about 1600 °C. With the increase of reaction temperature, $SiTa_2$ becomes the dominant species on the catalyst surface above 1700 °C. The preservation of TaC surface structure for the carbonized Ta catalyst indicates its much higher stability than the commonly used metal catalysts.

Raman spectra of the Si films prepared using the two kinds of catalysts at different temperatures are presented in Fig. 3a and b. With the increase of catalyst temperature from 1450 to 1700 °C, the obtained Si film transforms from amorphous to microcrystalline. Crystallinities (X_c) of the Si films are evaluated by Gaussian deconvolution of each spectrum into three components. X_c is defined as $(I_c + I_m)/(I_c + I_m + I_a)$, where I_c, I_m and I_a are the integrated peak
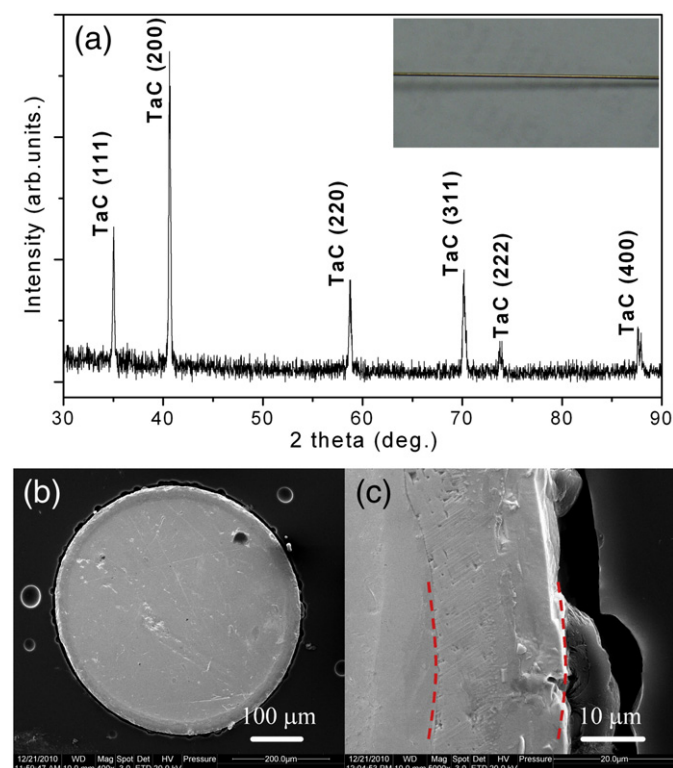

Fig. 1. (a) XRD pattern of a typical carbonized Ta catalyst. Inset shows the corresponding photograph. (b), (c) Cross-section SEM images of the carbonized Ta catalyst. Dash lines in (c) denote the outer carbide layer.