Crystalline tantalum carbide and ditungsten carbide formation via hot wire chemical vapor deposition using the precursor of 1-methylsilacyclobutane

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An efficient method for the preparation of crystalline tantalum carbide (TaC) was reported using a new methyl-substituted precursor, 1-methylsilacyclobutane (MSCB), in the hot-wire chemical vapor deposition process with a tantalum filament. The ability of MSCB to produce methyl radicals on heated Ta filament allows for the formation of crystalline TaC (α=4.5) in a wide temperature range of 1600–2200 °C. This corroborates the key role of the radical species formed via the precursor's decomposition on the hot metal wire in the type of metal alloys formed on the wire surface. The growth rate of TaC achieved at 0.12 μm/min and 0.35 μm/min, respectively, for 1600 °C and 2200 °C is much higher than the value obtained from using CH₃H₂ mixtures as the C-containing precursor. Crystalline ditungsten carbide (W₂C) was formed by treating the tungsten filament with MSCB at the relatively high temperatures of 2200–2400 °C, with a deposition rate of 2.1 μm/min at 2400 °C. The method reported in this work is a useful method to produce crystalline TaC or W₂C without the use of the corrosive metal halide precursors.

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1. Introduction

Group IV–VI transition metal carbides (TMCs) are known for their unique physical and chemical properties of high melting point, high hardness, good thermal and electrical conductivity, and excellent resistance to chemical attack and oxidation [1,2]. These properties originate from the coexistence of metallic, ionic, and covalent bondings in their structures [3]. TMCs have therefore been widely utilized as cutting tools, high-temperature structural or functional materials, anti-wear and corrosion-resistant coatings. Furthermore, Group IV–VI TMCs have outstanding catalytic ability, similar to those of noble metals [4,5]. They have recently received a lot of attention for the application as electrocatalysts for numerous reactions, many of them are important in renewable energy devices such as fuel cells, electrolyzers, batteries, and electrochemical supercapacitors [6–10]. TMCs are also good choices for electrocatalyst supports due to the enhanced catalytic ability from the synergistic effect and the need to reduce the overall loading of the precious metal such as Pt, Pd and Ir [11–13].

Many methods have been developed for the synthesis of TMCs. These include chemical vapor deposition (CVD) [14–17], pulsed laser ablation [18,19], carbothermal methods [20], and reactive plasma [21,22]. Among these methods, CVD is a versatile technology to produce TMC films [14–17]. In a CVD process for the formation of TMC, typically separate sources for metal (e.g., metal hexafluoride, hexachloride, or metal carbonyl complexes) and carbon (e.g., methane, propane, or ethene) are used. Recently, reports of using hot wire CVD (HWCD), also known as hot filament CVD (HFCVD) or catalytic CVD (Cat-CVD), for the deposition of TMC materials have been found in the literature [23–28]. This method uses a metal filament as the metal source in the formation of TMCs, as a result, the use of the corrosive metal halide precursors is avoided. Other advantages of HWCD include a simple apparatus, high deposition rate, and high utilization efficiency of the precursor gases.

Aside from being the metal source, the filament also serves as a catalyst in HWCD to decompose the C-containing source gases to form active carbon species, which leads to the formation of metal carbide on the filament surfaces. Previous studies have shown that the difference in the radical species produced from hot wire decomposition of precursor molecules plays a key role in determining the type of metal alloys formed on the wire surface using HWCD [29–31]. CH₃ mixed with H₂ gas is the most commonly used carbon source [26,32,33]. The reaction chemistry of CH₄ in the presence of H₂ in a HWCD reactor has been extensively studied for the diamond growth. Based on the experimental results [34,35] and kinetic modeling [36,37], the main reactive species produced in the process has been found to be the methyl radical. In
our recent study of the reaction chemistry of organosilicon compounds on the metal wire surfaces [29,38], we have found that methyl-substituted silane and methyl-substituted (di)isilacyclobutane molecules produce methyl radicals quite efficiently upon decomposition on the heated metal wires with low activation energies. For parent silacyclobutane (SCB) and 1,3-disilacyclobutane (DSCB) molecules that do not have Si—CH₂ bonds, their decomposition is characterized, respectively, by ring-opening reactions forming silylene and silene reactive species [39], and acyclic H₂ elimination reactions forming a cyclic 1,3-disilacyclobutyl-1-yldiene species [40]. We have shown that SCB as precursors leads to the formation of tungsten silicides [41], whereas treating the Ta and W filament with DSCB gives rise to a mixture of tantalum (tungsten) carbides, SiC, and Ta₅Sn₄ (or W₅Sn₃) [42].

Considering the efficient production of methyl radicals from the methyl-substituted silacyclobutane molecules, we explore, in this present work, the growth of tantalum carbide and tungsten carbide films using the method of HWVC as a new methyl-substituted silacyclobutane precursor, i.e., 1-methyl-1,3-disilacyclobutane (MSCB). The deposition of both Ta₂C and W₄C (x = 1.2) films was systematically studied at various filament temperatures ranging from 1200 to 2400 °C and deposition time of 1–4 h, X-ray diffraction (XRD), scanning electron microscopy (SEM), and in-situ resistance measurements were used to examine the layer growth, the crystallinity, and the phases of metal carbides produced in the process for an understanding of the alloy formation and phase transitions. Crystalline TaC and Ta₅C were found to form, depending mainly on the filament temperature used. A W₄C layer can also be formed at relatively high temperatures of 2200 and 2400 °C. A comparison of W₄C and Ta₅C formation using different organosilicon precursors will also be provided to shed light on the determining factor in the formation process.

2. Experimental details

Tantalum and tungsten carbides were prepared by treating the Ta and W wires, respectively, with MSCB samples in a HWVC reactor. Details of the HWVC setup have been described previously [29,43-44]. A straight Ta or W filament (99.9%, Aldrich) with a length of 10 cm and a diameter of 0.5 mm was housed in a cylindrical stainless steel reactor, which was pumped to a base pressure of 5 x 10⁻¹⁰ Torr. The filament was resistively heated by a DC power supply (Agilent, N5744A) and its temperature was monitored by a two-color pyrometer (Chino Works). To clean the filament surface and also the reactor chamber wall, each new filament (Ta or W) was annealed, prior to each deposition, at 2000 °C for 1 h in the atmosphere of 12 Torr of gaseous mixture of 1% H₂ in He (99.999%, Praxair). The filament was then treated with 12 Torr of 4% MSCB vapor seeded in He at various filament temperatures for different time duration. MSCB was synthesized according to an established method, where 1-chloro-1-methylsilacyclobutane was prepared from 3-chloropropylmethylchlorosilane (Gelset, 97%), followed by its reduction using LiAlH₄ (Alfa Aesar, 97%) [45-47]. The gaseous mixture of 4% MSCB in He was prepared in a 2.25 L sample cylinder by entraining the room-temperature vapor of MSCB in He after degassing the liquid MSCB sample using several cycles of freeze-pump-thaw. The MSCB/He gases were then introduced to the HWVC reactor via a mass flow controller (MKS, type 1179A) to maintain a constant pressure of 12 Torr. The flow rate was set at 1.00 scm. The partial pressure of MSCB in the reactor is therefore 0.48 Torr. For each deposition run, the filament temperature (in the range of 1200–2400 °C) was kept constant by adjusting the power supplied to the filament for the duration. The current and voltage supplied to the filament was monitored in situ with a LabView program, from which the power and resistance data was obtained. At the end of each deposition, the gas flow was stopped and the gas was pumped out of the reactor. The metal filaments were then cooled down to room temperature in the reactor setup, and were stored under vacuum after being removed from the reactor for further analysis.

The surface morphology and the layer thickness of the formed metal carbides were examined by SEM (Philips XL30), operating at 20.0 kV. The crystalline phases of the samples were characterized using a Bruker D8 Advance X-ray diffractometer with a Cu-Kα radiation source (λ = 1.54 Å) operated at 40 kV and 40 mA. Samples were scanned in the 20 range of 10–80°. Data were collected in a continuous mode with a step size of 0.05°/step. The metal films were placed on the glass slides for the XRD analysis. The room-temperature XRD data sets were refined by conventional Le Bail method using the GSAS package with the EXPGOL interface [48]. A Le Bail-like approach was used for the sample with highly preferred orientations, where background factor, zero-point position, cell parameters, preferred orientations, and profile coefficients for the pseudo-Voigt/FCT asymmetric peak shape function were refined until the convergence was achieved. The size of the crystallite particles, s, was evaluated using the Scherrer formula, s = λ / βₘ, where λ is 0.154 nm from the Cu Kα radiation source, K is the shape factor which is taken as 0.9, β is the peak broadening represented by full width at half maximum in radian corrected for instrument broadening, and θ is the Bragg angle. The average crystallite size was determined from the intense peaks in each phase.

3. Results and discussion

3.1. Formation of tantalum carbides

Formation of tantalum carbides by exposing the heated Ta filament to MSCB was studied at different filament temperatures and exposure time. The effect of filament temperature on the growth of tantalum carbides was examined for the range of 1200–2400 °C at an increment of 200 °C. Visible changes in morphology appeared in Ta films after exposure to MSCB, as shown in the representative surface SEM images of Ta films treated at different temperatures (See Fig. S1 in the Supplementary material). This indicates the formation of deposits on the surface of Ta films. Fig. 1 shows the cross-sectional SEM images of alloyed tantalum carbides prepared using 0.48 Torr of MSCB for 1 h at different temperatures of 1400, 1800, 2200 and 2400 °C. A thin layer was found on the outside of the filament after exposure to MSCB. The XRD patterns for the alloyed tantalum films prepared at different temperatures using 0.48 Torr of MSCB samples at a deposition time of 1 h were shown in Fig. 2. The XRD pattern for a new Ta film was also shown for comparison. The three XRD peaks for Ta observed at 28 = 38.5°, 55.5°, and 69.6° represent the body-centered cubic phase of Ta (ICDD 00–004-0788) [49]. At 1200 °C, new peaks characteristic of Ta₂C (28 = 33.3°, 36.3°, 38.1°, 50.1°, 59.5°, 66.5°, 71.7°, 72.9° - ICDD 01-071-2677) [49] and Ta₅C (28 = 34.9°, 40.5°, 58.6°, 70.0° - ICDD 00-035-0801) [49] were observed, indicating the formation of both Ta₂C and Ta₅C. When the temperature was raised to 1400 °C, the peaks from TaC became predominant. In addition, a peak was observed at 25.9°, which is attributed from the graphite formed on the Ta surface [50]. Furthermore, the XRD peaks from Ta disappeared at temperatures of 1400 °C and beyond. A TaC layer was formed for higher temperatures between 1600 and 2200 °C. Our previous study on the carburization of W filament using a different methyl-substituted disilacyclobutane precursor molecule, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB) [27], showed that the carbon content on the wire surface first increased with increasing filament temperature but decreased at higher temperatures, and a maximum C content was reached at 1600–1700 °C. The reason for this is due to the competition between the filament carburization and C diffusion into W filament. The observation of a graphite peak in this work at 1400 °C, but not at other temperatures, indicates that the maximum C content was reached at 1400 °C when using MSCB. At higher temperatures, the C diffusion rate into Ta filament increases, leading to the formation of a C-rich TaC phase at 1600–2200 °C. The Le Bail refinement performed for the XRD patterns at 1400 °C and 2200 °C confirmed that TaC phase was present, whereas Ta and Ta₂C
were absent. The lattice constants of the crystalline TaC from the refinement results of the 1400 °C and 2200 °C treated samples were determined to be \(a = 4.4491(4) \text{ Å} \) and \(a = 4.4474(1) \text{ Å} \), respectively, with the cubic \(Fm-3m\) space group. Details of the Le Bail refinement can be found in the Supplementary material (Figs. S2 and S3). It is also noted from Fig. 1 that the intensity of the TaC (111) peak (at \(2\theta = 34.9°\)) generally increases with temperature between 1200 and 2200 °C, except for 2000 °C, whereas the other TaC peaks maximizes at a particular temperature between 1200 and 2200 °C. Specifically, the TaC (200) peak (at \(2\theta = 40.5°\)), (220) peak (at \(2\theta = 58.6°\)), and (311) peak (at \(2\theta = 70.0°\)) reached their maximum intensities at 1400, 1600, and 1800 °C, respectively. As a result, the TaC (220) peak is the strongest of all at 1600 °C, and the (111) peak becomes the dominant one at 2200 °C. This possibly indicates a change in the preferred crystallization orientation to (111) at the high temperature of 2200 °C. When the temperature was further increased to 2400 °C, interestingly, TaC became the dominant phase. The sample treated at 2400 °C revealed the hexagonal P-3m1 space group for the crystalline TaC, where the cell parameters were found to be \(a = 3.0814(3) \text{ Å} \), \(c = 4.9110(8) \text{ Å} \), and \(V = 46.6(3) \text{ Å}^3\). (See Fig. S4, Supplementary material). The average size of the TaC and Ta2C crystallite was determined to be 42 ± 7 and 40 ± 6 nm, respectively.

MSCB has been shown to decompose on the heated W and Ta surfaces via three pathways, respectively, to form CH3/silacyclobutane-1-yl radicals, ethene/methylsilene (H2CSH=CH2), and propene/methylsilylene (\(\text{SiH}(\text{CH}3)\)) [45]. According to literature studies using CH3/H2 gaseous mixtures, CH3 radical is an efficient precursor species for the growth of metal carbides on a metal surface [34-37]. Therefore, the exclusive formation of tantalum carbides, including both TaC and Ta2C, should be originated from the ability of MSCB to produce CH3 radicals. As is shown above, a TaC or Ta2C layer can be formed, depending on the filament temperature. Previous studies reported on using CH3/H2 gas mixtures as the source gases in HWCDV to synthesize tantalum carbide films [23,24,29]. The products are usually a mixed phase of TaC, Ta2C, and Ta. Using a different four-membered-ring organosilicon molecule, DSCB, has led to the formation of TaC and Ta2C contaminated by SiC and Ta5Si3 [42]. Therefore, the employment of MSCB molecules in HWCDV has the advantage of being able to form a TaC layer at a relatively low temperature of 1600 °C. According to the layer thickness measurement from the cross-sectional SEM images, the growth rate for TaC with MSCB samples was found to be 0.12 \(\mu\text{m}/\text{min}\) at 1600 °C, and it increased with temperature, reaching 0.35 \(\mu\text{m}/\text{min}\) at 2200 °C. This rate is much higher compared to TaC formation by Dai et al. at 8.4 \(\mu\text{m}/\text{min}\) at 2000 °C [25] when using CH3/H2 gas mixtures with a flow rate ratio CH3/H2 of 1:250 and a total pressure of 20 Torr. The

![XRD patterns of alloyed Ta filaments prepared using 0.48 Torr of MSCB sample at various temperatures in the range of 1200-2400 °C for a deposition time of 1 h. Indexing labels: TaC (blue) and Ta2C (red).](image-url)
main reason for the higher TaC formation rate with MSCB may be attributed to the fact that MSCB produced CH4 radicals on the Ta filament very efficiently, whereas the formation of CH radicals from CH4/H2 gas mixtures was not as efficient.

During the 1 h deposition process, the resistance of the alloyed Ta filaments was found to increase continuously with time. The increase in filament resistance is a common observation in alloyed filament due to carboxylation and silicidation [28,42,51,52]. The room-temperature resistivity of TaC and Ta2C at 8.0 \times 10^{-5} \, \Omega \, cm and 2.5 \times 10^{-5} \, \Omega \, cm [50], respectively, is higher than that for the pure Ta at 1.245 \times 10^{-5} \, \Omega \, cm [53]. The increase in resistance therefore, agrees with the observation of TaC and TaC signals from the XRD analysis in Fig. 2. We have also determined the temperature coefficient of resistance (TCR), defined in the equation of \( (R - R_0)/R_0 = \alpha (T - T_0) \), where \( R \) and \( R_0 \) are resistances at temperatures \( T \) and \( T_0 \), respectively. Fig. 3 shows a plot of \( (R - R_0)/R_0 \) as a function of \( (T - T_0) \) for the alloyed filaments prepared in our experiments in the temperature range of 1200–2400 °C. \( T_0 \) was set at 1200 °C and \( R_0 \) was the corresponding terminal resistance at the end of the 1 h deposition at this temperature. The \( (R - R_0)/R_0 \) increases linearly with \( (T - T_0) \) in the temperature range with a TCR of 5.6 \times 10^{-4} \, ^\circ \mathrm{C}^{-1}. \) This value is lower than the reported TCR of 3.83 \times 10^{-3} \, ^\circ \mathrm{C}^{-1} for pure Ta [53], which is mainly due to the formation of tantalum carbides.

Formation of different phases of tantalum carbides was also studied for different deposition times ranging from 1 to 4 h at two temperatures of 1200 °C and 2400 °C, respectively. Fig. 4 shows the XRD patterns for the alloyed Ta filaments prepared for different deposition times of 1–4 h at 1200 °C. At this temperature, TaC formed at 1 h time was converted to Ta2C with increasing deposition time. At the longer time of 4 h, the outer layer is dominated by the TaC formation. However, the Ta phase was still present under these conditions. There is also an unknown peak observed at 41.9° in Fig. 4. For the highest temperature tested in this work at 2400 °C, Ta2C is the main product formed at 1 h. As the deposition time was extended to 2 h, interestingly, the dominant phase became the TaC with no presence of either Ta or Ta2C. This is confirmed by the LeBail refinements of the XRD data obtained under this condition (see Fig. S5, Supplementary material). Same was observed for the filament prepared at 4 h. These were shown in the XRD analysis in Fig. 5. Therefore, heating the Ta filament to 2400 °C in the environment of 0.48 Torr of MSCB sample for longer deposition time of 2–4 h would also produce a Ta2C outer layer. The deposition rate of the TaC layer at 2400 °C when using MSCB is determined to be 1.1 μm/min. Okoli et al. reported the use of 0.5% or 1% CH4 in H2 mixtures as the source gases to carburize the Ta filament [51]. At a total pressure of 40 Torr and 2400 °C, the deposition rate of TaC using either 0.5% or 1% CH4 in H2 mixture was obtained at 0.33 μm/min, which is slightly lower than the rate achieved in this work when using MSCB. This again shows that MSCB is a more efficient source gas for the production of CHx radicals.

3.2. Formation of tungsten carbides

Formation of tungsten carbides by exposing the heated W filament to MSCB was also studied under the same experimental conditions. Representative surface SEM images of W filaments after exposure to MSCB (Fig. S6, Supplementary material) showed visible changes in the morphology at different temperatures. Fig. 6 shows the cross-sectional SEM images of alloyed W filaments prepared using 0.48 Torr of MSCB at different filament temperatures and deposition times.

From the XRD patterns shown in Fig. 7 for the alloyed W filaments prepared at a deposition time of 1 h for various filament temperatures, it can be seen that both WC (2θ = 34°5, 38°0, 39°6, 52°3, 61°9, 69°8, 75°0, 76°0) and WC (2θ = 31°6, 35°7, 48°4, 64°2, 73°3) (ICDD 03-065-3890) were formed at the lowest...
temperature tested at 1200 °C, similar to the results with the Ta filaments. As the temperature was raised, the signals from WC became stronger, reaching a maximum at 1600 °C. At the same time, the peak intensity from W (body-centered cubic phase, 2θ = 40.3°, 58.3°, 73.2° - ICDD 00-001-1203) [49] decreased significantly with increasing temperature. A peak at 25.9°, originating from graphite [50], appeared very weakly at this temperature when the WC signals were the strongest. This agrees with our previous study that the maximum C content was reached at 1600–1700 °C when a W filament was exposed to 0.48 Torr of TMDCB [27]. Therefore, similar to the observation with Ta, it is the diffusion of C into W filament that forms the C-rich WC phase. At temperatures higher than 2000 °C, signals from W₂C were predominant, which is in agreement with our previous observations with TMDCB [27]. It is also noted that at these high temperatures, the peaks from W disappeared. The Le Bail refinement for the XRD pattern further confirmed that only W₂C phase was present at 2200 and 2400 °C, whereas W and WC were absent. The cell parameters of the crystalline W₂C were determined to be a = 5.1695(2) Å, c = 4.6943(8) Å, and V = 125.4(5) Å³ with the space group of P-31m (see Figs. S7 and S8, Supplementary material). The average size of the WC and W₂C crystallite was determined to be 42 ± 5 and 43 ± 5 nm, respectively.

Compared with our previous study on the alloying of the W filaments when exposed to the 1,3-disilacyclobutane (DSCB) molecule, a notable difference is that the utilization of MSCB precursors leads only to the carburization of W filaments, whereas formation of 3C-SiC and W₅Si₅ in addition to W₂C, was also observed with DSCB at temperatures lower than 1800 °C [42]. The reason for this can be explained by the different decomposition chemistry assumed by the two organosilicon molecules. MSCB molecule was able to form •CH₂ radicals upon its decomposition on heated W filaments [45]. On the other hand, the decomposition of DSCB is dominated by an exocyclic H₂ elimination to form 1,3-disilacyclobut-1-ylidene, a cyclic silylene reactive species [40]. Therefore, the use of MSCB as the C-containing precursor in the process of HWCVD carburizes the W filament efficiently, without the contamination of SiC and tungsten silicides. Similar observations were

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**Fig. 6.** Cross-sectional SEM images of alloyed W filaments prepared using 0.48 Torr of MSCB at a) 1200 °C, 1 h, b) 1200 °C, 3 h, c) 2200, 1 h, and d) 2400 °C, 1 h.

**Fig. 7.** XRD patterns of alloyed W filaments prepared using 0.48 Torr of 1-methyl-silacyclobutane (MSCB) sample at various temperatures in the range of 1200–2400 °C for a deposition time of 1 h. Indexing labels: WC (blue) and W₂C (red).
obtained with TMDSB, which decomposed on the hot W filament to form CH₃ predominantly [27].

Similar to what was observed for the Ta filaments, the electrical resistance of the alloyed W filaments increased continuously with time during the 1-h deposition process. The increase in resistance indicated the structural changes in the W filament at the room-temperature resistivity of W₂C and WC at 8.0 x 10⁻⁵ Ω cm and 2.2 x 10⁻⁵ Ω cm [51], respectively, is different from that for the pure W at 5.65 x 10⁻⁶ Ω cm [51]. This also agrees with the results from previous studies of the carburation process of W filaments [51,52]. In addition, the resistance increased with temperature as shown in Fig. 8, with the TCR determined as 9.8 x 10⁻⁴ °C⁻¹ for the temperatures between 1200 and 2400 °C. Compared to the reported TCR value for pure W at 5.5 x 10⁻³ °C⁻¹ [54], the one determined from our study is lower, which agrees with the formation of tungsten carbides as shown in the XRD analysis.

Fig. 9 shows the XRD analysis of the alloyed W filaments prepared for different deposition time of 1–4 h at the same temperature of 1200 °C. According to the phase diagram of W-C [55], W₂C is unstable at temperatures below 1250 °C. Therefore, at 1200 °C, it is noted that the W₂C phase gradually converts to WC with increasing time. In our previous work when using DSCB as the precursor gas, similar behavior was observed. However, DSCB decomposes to form predominantly the 1,3-disilacyclobut-1-ylidene species and is not able to produce CH₃ radical, therefore a conversion from the W₂C phase to WC was not observed, but the unstable W₂C was converted to SiC instead [42].

As mentioned before, at temperatures higher than 2000 °C, the layer grown on the outside surface of W after 1 h deposition time was mainly W₂C, with no presence of WC. Fig. 10 shows the XRD patterns for the alloyed filaments prepared at 2400 °C for longer deposition time. Clearly, the predominance of W₂C phase was preserved at all deposition time between 1 and 4 h. The LaB₆ refinement confirmed a W₂C layer under these conditions (See Figs. S9 to S10, Supplementary material). Therefore, exposure of W filament to MSCB at the high temperature of 2400 °C for 1–4 h is able to produce a crystalline W₂C layer. This is similar to what can be achieved with the TMDSB sample at the same temperature but short deposition time of 1–2 h [28]. The deposition rate of the W₂C layer using the MSCB sample at 2400 °C was determined to be 2.1 μm/min, which is lower than the rate at 4.4 μm/min obtained with TMDSB. Another difference when using these two different methyl-substituted silacyclobutane molecules is observed at longer deposition time of 4 h at 2400 °C. Exposure to MSCB for 4 h leads to a W₂C layer, whereas treating the filament with TMDSB at 3 h produces a layer composed of both W₂C and WC. A deposition time of 4 h when using TMDSB, on the other hand, was able to produce a pure C-rich WC phase [28]. All these suggest that TMDSB is a more efficient precursor than MSCB for the carburation of W filaments. Although both chemicals have the ability to produce CH₃ upon their decomposition on the heated W wire surfaces, this exocyclic Si—CH₃ bond cleavage is the dominant pathway for TMDSB [56], whereas for MSCB, two other endocyclic ring-opening reactions, i.e., cyclonversion and 1,2-H shift-initiated ring opening, compete with the formation of CH₃ [45]. This is due to the presence of one additional Si atom in the four-membered-ring in TMDSB as compared to MSCB, which introduces ring stabilization, leading to a much less puckered ring in TMDSB with lower ring strain energy [29].

4. Conclusions

The formation of both tantalum carbides and tungsten carbides was studied in this work by using a new methyl-substituted silacyclobutane precursor, i.e., 1-methylsilacyclobutane (MSCB), in a HV/CVD process. Due to its ability to produce methyl radicals on the heated metal filaments, MSCB leads to the formation of tantalum (or tungsten) carbides
on the metal surfaces, with no contamination of SiC and tantalum (or tungsten) silicide. This is more advantageous over another organosilicon precursor, 1,3-disilacyclobutane (DSCB). It has also been shown that crystalline TaC (cubic Fm-3m) is formed in a wide film temperature range of 1600–2200 °C for a deposition time of 1 h. The growth rate of TaC when using the MSBC samples determined at 0.12 μm/min and 0.35 μm/min, respectively, for 1600 °C and 2200 °C is much higher than the value of 8.4 nm/min achieved when using CH₃H₂ mixtures at 2000 °C. Treating the W film with MSBC at the high temperatures of 2200 and 2400 °C for 1–4 h was able to produce a crystalline WC layer (hexagonal P-3m). The deposition rate of the WC layer with the MSBC sample obtained at 2400 °C was 2.1 μm/min, lower than the rate of 4.4 μm/min from using 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSBC). The predominant exocyclic Si—CH₂ bond cleavage in TMDSBC due to the ring stabilization explains the lower deposition rate of WC with TMDSBC. Overall, HWVCVD with the organosilicon precursor MSBC and metal film (Ta/W) provides an excellent alternative method to produce crystalline metal carbides (TaC/WC) without the use of the corrosive metal halide precursors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.surfcoat.2017.07.047.

References


