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# Tantalum carbide-graphite composite film synthesized by hot-filament chemical vapor deposition\*

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*Abstract*: A composite film of tantalum carbide (TaC)-graphite was synthesized on etched Si using thermal evaporation of Ta followed by C/H chemical vapor deposition (CVD). In the present study, Ta wire 0.5 mm in diameter was electrically heated without carburizing. Under high current conditions, filaments were thermally evaporated and interacted with chemically decomposed C, forming a composite film of TaC-graphite deposits on the substrates. The influence of chamber pressure, substrate temperature, and methane concentration on the film properties has been studied. By increasing chamber pressure from 25 to 100 torr in a gas mixture of H and methane (containing 3 % methane), the morphology of films changed with an increased growth rate and surface roughness. Increasing the methane concentration in the mixture resulted in broadening of X-ray diffraction (XRD) peaks, increase in film thickness, and coarsening of grains, along with formation of clusters. The growth rates of the films produced at a substrate temperature of 950 °C were lower than those deposited at 850 °C. Their grain sizes were bigger and exhibited a dense structure with higher surface roughness.

*Keywords*: chemical vapor deposition; composite materials; crystal structures; interfaces; materials science.

## INTRODUCTION

Tantalum carbide (TaC) is a promising material, particularly in applications where tolerance toward high temperature is an essential requirement. TaC is an extremely high melting point material (3983 °C), and displays high hardness (15–19 GPa) and resistance to chemical attack [1]. Owing to these attractive properties, TaC offers promise for high-temperature applications, such as rocket nozzles and scramjet components. As a stoichiometric compound, TaC is also inert to C up to its melting temperature and has high resistance against corrosion [2] and chemical attack [1].

TaC films have been prepared by various methods, for example, reactive dc magnetron sputtering [3], chemical vapor infiltration [4], thin-film solid-state reaction [5], ion-beam-assisted deposition [6], isothermal chemical vapor deposition (CVD) [7], cold-wall low-pressure CVD [8] and pulsed laser ablation [9].

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By contrast with the foregoing methods, hot-filament CVD possesses many advantages. It is costeffective, easy to scale up to large-area deposition, and, no less important, the understanding of its chemical and deposition processes is possible by simple kinetic modeling [10]. The main ingredients for TaC deposition in hot-filament CVD are a Ta filament and methane gas. We could find only one published report on TaC coatings produced via hot-filament CVD [11]. In another study, Soto et al. [12] grew diamond on in situ deposited TaC, simply by switching from hot-filament physical vapor deposition (PVD) to hot-filament CVD. In this process, the filaments work not only as a source of heat for substrate and decomposition of precursor gases, but also act as the material source for growing films. In this study [12], a TaC layer could only be achieved when the system was operated at lower pressures (4–10 torr). Secondly, the filament's power supply was run at constant-current instead of constant-voltage mode, so that metallic emission from the filament remained almost constant [12].

In the present study, we disclose methods for producing composite structures of TaC-graphite on etched-Si surfaces at various process parameters, working under conditions that do not allow diamond deposition. The resulting films are expected to offer potential for a variety of applications, particularly at high temperature. The presence of soft material (graphite) in this TaC structure suggests that a major opportunity may exist in those applications of TaC-graphite composite films where surface wear and material embrittlement are impediments. In very recent published work, we have shown the growth of composite structure of TaC-graphite on Si substrate [13], in which prior etching of the substrate was avoided.

## **EXPERIMENTAL DETAILS**

Detailed description of substrate material and filament arrangement is provided elsewhere [14]. The substrate was etched with hydrofluoric (HF) and deionized (DI) water (50:50) for 2 min. The substrate-to-filament distance was set to 7.0 mm, and the heating of substrates was provided by filament radiation. After evacuation of the chamber  $(4 \times 10^{-3} \text{ Pa})$ , gas flow was started. The filament temperature was around  $2200 \pm 25$  °C measured with optical pyrometer, whereas substrate temperature was measured with both B- and K-type thermocouples. These temperature values were recorded at source current of 280 amp (±5 amp). The precursor flow rates of 300 sccm (3.0 and 6.0 vol % CH<sub>4</sub>) were controlled by mass flow controllers. The filament was arranged in 16 consecutive wires with a distance of 7 mm (±1 mm) from each other.

Prior to initial experiments, it was confirmed that the temperatures of substrate and filaments remained constant throughout the deposition process except for the time when the gases entered the chamber, for the initial 5 min. For keeping the substrate temperature at the required level without changing the substrate-to-filament distance, various experiments were executed by placing insulating material between the substrate material and height-adjustable water-cooled Cu holder. Similarly, for achieving substrate temperature of 950 °C, high-quality 1-mm alumina plate was placed below the substrate, while for the film deposited at 100 torr, four alumina caps were placed below the substrate. The purpose of this whole exercise was to control the substrate temperature at constant value by tailoring the insulating properties of materials put between the water-cooled Cu holder and the Si substrate. The flow of gases was commenced once the substrate temperature reached 850 °C. First, H<sub>2</sub> was admitted, followed by  $CH_4$  after an interval of 5 min. In this manner, carburization of filaments was avoided. On the contrary, in the case of diamond deposition in hot-filament CVD, carburization of filaments was mandatory prior to growing high-purity diamond films. On opening of cool gases, a slight decrease in both filament and substrate temperatures occurred, which was adjusted by increasing source current up to 5 amp, for the initial 5 min. Total deposition time in each experiment was set at 2 h excluding the initial 15 min for establishing the substrate temperature. The main process parameters are listed in Table 1. The films so produced were characterized and analyzed by atomic force microscopy (AFM), field emission scanning electron microscopy (SEM), and X-ray diffraction (XRD).

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| Sample # | Chamber<br>pressure<br>(torr) | Substrate<br>temperature<br>(°C) | Vol %<br>CH <sub>4</sub><br>(sccm) | Total mass<br>flow rate<br>(sccm) | Surface<br>roughness<br>(nm)                      | Scan<br>area<br>(4 µm <sup>2</sup> ) |
|----------|-------------------------------|----------------------------------|------------------------------------|-----------------------------------|---|--------------------------------------|
| 1        | 25                            | 850                              | 3                                  | 300                               | $R_{a}$<br>$R_{ms}$                               | 6.34<br>8.00                         |
| 2        | 60                            | 850                              | 3                                  | 300                               | $R_{a}$<br>$R_{ms}$                               | 6.19<br>7.98                         |
| 3        | 100                           | 850                              | 3                                  | 300                               | $egin{array}{c} R_{ m a} \ R_{ m ms} \end{array}$ | 15.46<br>19.46                       |
| 4        | 60                            | 950                              | 3                                  | 300                               | $egin{array}{c} R_{ m a} \ R_{ m ms} \end{array}$ | 22.21<br>26.29                       |
| 5        | 60                            | 850                              | 6                                  | 300                               | $egin{array}{c} R_{ m a} \ R_{ m ms} \end{array}$ | 11.50<br>14.85                       |

 Table 1 Surface roughness of TaC-graphite composite films synthesized at various process parameters.

## **RESULTS AND DISCUSSION**

At the lowest chamber pressure (25 torr), the coating is composed of nail-shaped grains, which are shown in Fig. 1a. By increasing chamber pressure from 25 to 60 torr, grains transformed into fine spherical-shaped particles, having an average grain size of 35 nm (Fig. 1b). Further increase in the chamber pressure (100 torr) led to coalescence of the particles, and coarse-shaped grains are produced (Fig. 1c), showing termination of boundaries around the coarse-shaped grains/clusters. By increasing the substrate temperature to 950 °C, the average grain size became almost 45 nm (Fig. 1d) compared to the film synthesized at a substrate temperature of 850 °C, while the grain retained a spherical shape. Again, with an increase in the CH<sub>4</sub> concentration (from 3 to 6 % in H<sub>2</sub>), the composite film led to a mixed morphology, covering nano-sized grains, coalescence of nano-sized grains, voids, coarse-shaped grains, and non-homogeneity in the overall structure, which is shown in Fig. 1e.

The surface roughness data of deposited films (TaC-graphite composite films) collected from AFM are shown in Table 1. It is evident that the values for both average surface roughness ( $R_a$ ) and root mean square surface roughness ( $R_{ms}$ ) decrease slightly as we go from 25 to 60 torr, whereas they are significantly higher when TaC-graphite composite film is synthesized at a chamber pressure of 100 torr. The higher values of surface roughness are mainly associated with the presence of defects along with growing film, as the mean-free path of species responsible for film growth prolonged. This indicates that the film produced at a chamber pressure of 60 torr has a relatively smoother texture, as it provides suitable time for adjusting C and Ta species and hence diffusion of reactive C remained almost in line with the Ta grains within the growing composite film. Increasing substrate temperature from 850 to 950 °C led to increased surface roughness (owing to increased grain size), while increasing CH<sub>4</sub> concentration also increased the surface roughness compared to the film produced at 3 % of CH<sub>4</sub>.

Chen et al. [7] studied the effect of substrate temperature on properties of TaC films produced on C fibers by chemical vapor infiltration and found that grain size increased with temperature. Our results also indicate increase in grain size with increase in substrate temperature.

SEM fracture cross-sections and thickness of synthesized films are shown in Figs. 2a–e; exhibiting that structures produced at chamber pressure of 100 torr and 6 vol % of  $CH_4$  are porous (Figs. 2c,e), while at substrate temperature of 950 °C they are dense (Fig. 2d). Again, the lowest growth rate was observed for film synthesized at the lowest chamber pressure, 25 torr (Fig. 2a), whereas higher growth rates are mainly associated with the porosity of synthesized films. Higher rates of growth result in



**Fig. 1** 3D AFM images over  $2 \times 2 \mu m$  areas of TaC-graphite composite films for samples 1, 2, 3, 4, and 5 [deposited at (a) 25 torr, (b) 60 torr, (c) 100 torr (d) 950 °C, and (e) 6 vol % CH<sub>4</sub>].

higher porosity, as revealed by the cross-sectional SEM micrographs (in Fig. 2). At interface, all the films reveal that coating is well adhered with the substrate, which was the result of the etching treatment to Si substrate, prior to synthesized composite film. This is an important feature from the adhesion point of view, as the compactness of deposited films with base material will enable us to solve adhesion-related problems, while using these for various applications.

The observed variation of film thickness with pressure indicates the highest growth rate at a chamber pressure of 100 torr, while the lowest at a chamber pressure of 25 torr. Increasing  $CH_4$  concentration increases the growth rate. However, increasing chamber pressure results in porous film. The

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**Fig. 2** SEM fracture cross-sections showing thickness of TaC-graphite composite films for samples 1, 2, 3, 4, and 5 [deposited at (a) 25 torr, (b) 60 torr, (c) 100 torr, (d) 950 °C, and (e) 6 vol % CH<sub>4</sub>].

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improvement in growth rate at higher  $CH_4$  concentration and chamber pressure is mainly because of transfer of mass in a higher amount, while an increase in grain size at higher substrate temperature is due to grain growth phenomena. The decreased growth rate at lower pressure and  $CH_4$  concentration may be due to deficiency of metallic element at these parameters. It appears from the AFM 3D topography images that at higher chamber pressure and  $CH_4$  concentration the mean-free path of structure formation species decreases and deteriorates the features of resulted coatings.

XRD patterns for the composite films of TaC-graphite synthesized on etched-Si substrates are shown in Figs. 3a–e. The XRD patterns at a glazing incidence angle of  $0.5^{\circ}$  of TaC films deposited at various process parameters demonstrate approximate peaks at diffraction angles 20 of 34.934, 40.558, 58.703, 70.166, 73.782, 87.770, 98.111, 101.615, and 116.207, which correspond to the (111), (200), (220), (311), (222), (400), (331), (420), and (422) reflections of TaC, respectively. The diffraction peaks are in accord with PDF No. 01-075-3086; thus, the material is identified as the face-centered cubic (f.c.c.) TaC, space group Fm3m. Apart from the simply recognized TaC and graphite, a minor fraction of Ta<sub>2</sub>C is discernible in all XRD patterns. The inward diffusion of graphite along with thermal evaporation of Ta led to the formation of TaC and Ta<sub>2</sub>C.



**Fig. 3** XRD patterns of TaC-graphite composite films for samples 1, 2, 3, 4 and 5 [deposited at (a) 25 torr, (b) 60 torr, (c) 100 torr, (d) 950 °C, and (e) 6 vol %  $CH_4$ ].

As shown in the XRD patterns (Figs. 3c,e), the composite films of TaC-graphite represent slightly a higher level of intensity peaks of C phases and hence indicate a higher level of porosity, which is also confirmed by (physically) the AFM 3D topography images. In Fig. 3e, the diffraction peaks of TaC are broad with lower intensity at higher  $CH_4$  concentration and become narrow with higher peak intensity at lower  $CH_4$  concentration (Fig. 3b). These are an indication of grain change and variation in coating thickness and are shown in Figs. 1 and 2.

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The presence of small amount of graphite along with TaC and Ta<sub>2</sub>C is believed to be enhanced by the material properties (ductility). Again, the presence of C in TaC does not degrade the thermal properties of TaC, as the sublimation temperature of graphite is 3527 °C, which is close enough to that of TaC (3985 °C). Additionally, it is flexible but not elastic, and is highly refractory and chemically inert. Ta<sub>2</sub>C has a structure based on a hexagonal closest-packed metal lattice with the C atoms filling one-half of the octahedral holes [15], while TaC has a f.c.c. crystal structure where the C atoms are located inside the octahedral sites. This compound is also featured by a high melting point (3327 °C), and it was found to possess a higher oxidation resistance in comparison to TaC [16].

The reason for the  $Ta_2C$  phase along with TaC is related to the mechanism of film formation. In fact, the film is formed mainly by particles directly ejected from the hot Ta filaments as the result of thermal evaporation and their chemical reaction with methyl radicals. When they leave the filaments, these particles are transformed into TaC. During the initial process stage, admit of  $CH_4$  gas was avoided so that the filament could not be carburized. As a result, the affinity of C with metallic element halted during that period and at a later stage inward diffusion of C led to the formation of the Ta<sub>2</sub>C phase.

Chen et al. [7] studied the influence of pressure on phase composition and morphology of TaC coating on C fibers by chemical vapor infiltration at substrate temperature of 850 °C and found that the films were composed of TaC and C phases when deposited at chamber pressures of 4.5, 15.0, 30.0, and 60 torr, respectively. Their calculated grain size of TaC as a function of pressure falls in the size range of 9.7–13.4 nm [7]. In the present work, the grains fall in the size range of 40–100 nm; the grains are bigger than the cited ones and mainly suggest variation in the shape and size of grains due to the nature of the substrate and variation in the coating system/process.

#### CONCLUSIONS

Variation of chamber pressure has a significant effect on the morphology of the produced structure. At 25 torr, the film has a pyramidal shape that transforms to a spherical shape at 60 torr. Further increase in pressure to 100 torr leads to bigger and coarser grains. The increase in substrate temperature and  $CH_4$  concentration leads to increase in the grain size and non-homogeneity in texture, respectively. Spherical-shaped grains of TaC with smooth texture film is formed at a chamber pressure of 60 torr, whereas the films grown at a chamber pressure of 100 torr and 6 vol % of methane exhibit the best growth rate but at the cost of film quality. The XRD patterns show the TaC film along with Ta<sub>2</sub>C and C phases and are believed to enhance the material's properties. The presence of two stable phases (Ta<sub>2</sub>C and graphite) in TaC film produced at selective parameters ensures the thermal stability of material along with other properties, owing to composite film in nature.

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