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# High-power impulse magnetron sputtering of Ti-Si-C thin films from a $Ti_3SiC_2$ compound target

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## Abstract

We have deposited Ti-Si-C thin films using high-power impulse magnetron sputtering (HIPIMS) from a $Ti_3SiC_2$ compound target. The as-deposited films were composite materials with TiC as the main crystalline constituent. X-ray diffraction and photoelectron spectroscopy indicated that they also contained amorphous SiC, and for films deposited on inclined substrates, crystalline $Ti_5Si_3C_x$. The film morphology was dense and flat, while films deposited with dc magnetron sputtering under comparable conditions were rough and porous. Due to the high degree of ionization of the sputtered species obtained in HIPIMS, it is possible to control the film composition, in particular the C content, by tuning the substrate inclination angle, the Ar process pressure, and the bias voltage.

# 1 Introduction

Highly ionized magnetron sputtering features a number of advantageous attributes making this an attractive deposition technique [1–5]. The characteristic difference between this technique and conventional approaches is that a high fraction of the sputtered material is ionized, while in traditional magnetron sputtering, the sputtered species are almost exclusively neutrals. This provides a possibility to tailor the microstructure of the growing film through alteration of the energy of the depositing species.

Several techniques have been developed for obtaining an ionized growth flux [5]; the plasma may be generated, for example, by electron cyclotron resonance [6] or by inductively coupled radio-frequency (rf) power [1,7]. A more recent approach to achieve a high ionization fraction of the sputtered material is high-power impulse magnetron sputtering (HIPIMS), also known as high-power pulsed magnetron sputtering (HPPMS) [4]. In this method, high-power pulses are applied to the cathode (target). Typically, the peak power of the pulses is of the order of hundreds of kWcm$^{-2}$. The requirements on low average power and low thermal load are fulfilled by using a low duty factor (typically lower than 1%), leading to an average power of the order of a few kWcm$^{-2}$ [4]. Plasma characterization of the discharge [8–10] has shown that by applying high-energy pulses to the target, a peak plasma density (electron density) higher than $1\times10^{19}$ m$^{-3}$ can be achieved, resulting in ionization of a large fraction of the sputtered material, e.g., up to 70 % for Cu [4]. The merits of the technique have been demonstrated in metallization for the use in high-aspect-ratio filling applications [4], as shown by the improvements in thickness homogeneity and density of films deposited on substrates with complicated geometries, compared to conventional

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magnetron sputtering [11]. Moreover, the applicability of HIPIMS to a reactive

sputtering-process has been demonstrated for CrN films deposited from a single metal

target and a $N_2$ precursor gas [12]. In these technologically important applications, the

technique offers process benefits not easily achieved by conventional approaches, as

exemplified by the improved mechanical properties, film density, and corrosion

resistance of the HIPIMS-grown CrN films compared even to contemporary arc-

evaporated CrN. While the arc-deposition techniques also have a high degree of

ionization, they suffer from macroparticle codeposition.


However, the use of HIPIMS to grow higher-order material systems, for

instance ternary compounds, is yet to be investigated. As a suitable candidate for

such ambitions, we choose the Ti-Si-C system. Our choice of materials system is

motivated by the significant attention it has attracted in recent years, as a response to

the challenge in exploring the wide range of phases in the ternary system, including

TiC, SiC, $Ti_5Si_3C_x$, and $Ti_3SiC_2$. The interest is also motivated by the exceptional

structural, electrical, and mechanical properties exhibited by $Ti_3SiC_2$, a material

belonging to the $M_{n+1}AX_n$-phase family (n=1 to 3) [13-15], and by other Ti-Si-C

compounds and composites [16–18]. Furthermore, given the fact that deposition of a

higher-order materials systems often requires sputtering from several sources, it is

highly beneficial that deposition of Ti-Si-C films can be carried out from a single

$Ti_3SiC_2$ target, an approach that has previously been employed for dc magnetron

sputtering (dcMS) [16,19] and pulsed laser deposition [20,21]. A further motivation is

that, due to the high degree of ion bombardment, HIPIMS has the potential to allow

synthesis of the MAX phases $Ti_3SiC_2$ and $Ti_4SiC_3$, as well as the structurally related

Nowotny phase $Ti_5Si_3C_x$ at lower temperature than what is required in dcMS [13,14].

In the dcMS case, a significant amount of thermally activated diffusion, i.e., substrate heating, is required to form these large-unit-cell phases. The present study shows that at least the Nowotny phase can be grown by the HIPIMS technique.

The present work is a study of HIPIMS growth of Ti-Si-C films from a $Ti_3SiC_2$ compound target. We have deposited the films at two positions with respect to the target surface: i) facing the target, and ii) at a 90º inclination angle. We investigate the effect of substrate geometry, gas pressure, and target-to-substrate distance on the structure and composition of HIPIMS-deposited Ti-Si-C films, and compare with that obtained by dcMS. The results show that, as a consequence of the high degree of ionization and the difference in degree of ionization between the three elements of the target, the composition of the deposited films differs from the nominal target composition, and can be controlled to some extent by an appropriate choice of process parameters. Thus, HIPIMS provides means of tailoring the structure and composition of the grown films.

## 2    Experimental details

Figure 1 shows a schematic of the deposition system for the two different geometries used in the study, (a) with the substrate at a 90º angle with respect to the target surface, and (b) with the substrate facing the target (0º inclination angle). A weakly unbalanced planar magnetron was operated with a circular $Ti_3SiC_2$ compound sputter-source (Maxthal®, courtesy of Kanthal AB) of 50 mm in diameter. The target was located inside a stainless steel chamber of a radius of 22 cm and a height of 30 cm, and the cathode was driven by a pulsed power supply from Chemfilt Ionsputtering AB. Details about the power unit are available elsewhere [4, 9]. The sputtering gas was Ar, held at pressures in the range 2-20 mTorr. The target current

and voltage were monitored by a Tektronix TDS 520 C (500 MHz, 1 GS/s)

oscilloscope using a Tektronix P6015 high voltage probe (1000 × attenuation), a

Tektronix CT-04 high current transformer (20 kA peak current and bandwidth 20

MHz), and a TCP202 current probe (15A ac/dc and bandwidth 50 MHz). The load

voltage and peak current of the magnetron were $V_T = 1200$ V and $I_{Tp} = 30$ A,
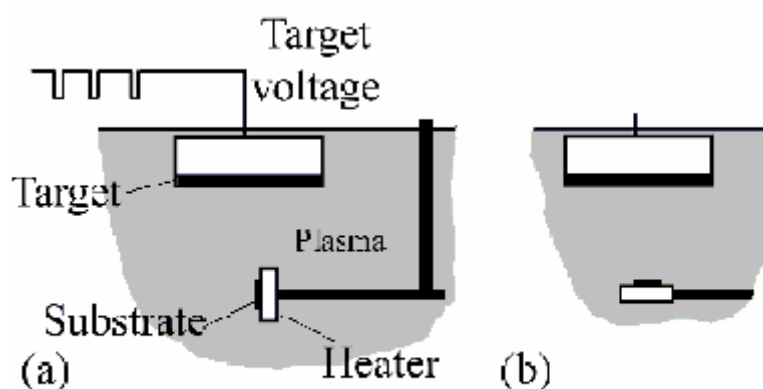
respectively.



*FIG. 1 Experimental setup. The substrate was placed at a $90^o$ angle with respect to the target (a), or facing it (b).*

Ti-Si-C films were deposited on single-crystal $Al_2O_3(0001)$ and $MgO(111)$

substrates that were ultrasonically cleaned in methanol and isopropanol baths, and

blown dry in $N_2$ before being introduced into the vacuum chamber. The substrates

were held by pointed Mo clips and placed on a heated rotatable plate, and were

negatively biased at 20 V. The substrate temperature was measured and calibrated

with the heater temperature using a thermocouple glued onto the surface of the

substrate using silver paste. All depositions were carried out at a substrate temperature

of 680 ºC. Samples were grown with a deposition time of 2 h at different distances (in

the range 6.5–14 cm) from the sputter source, and the deposition rates were

determined by measuring the film thickness using cross-sectional scanning electron

microscopy (XSEM) in a LEO 1550 Gemini FEGSEM. The crystal structure of the

as-deposited films was assessed with X-ray diffraction (XRD), using grazing

incidence geometry with an incidence angle of $4^{\circ}$ in a Philips Bragg-Brentano

diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were

performed in a Phi Quantum 2000 using monochromatic Al Kα radiation. The energy

scale was calibrated against the Cu 2p peak. Sensitivity factors determined from a

reference sample of sintered $Ti_3SiC_2$ were used for quantitative XPS analysis. XPS

depth profiling was performed by sputtering with 2 kV Ar ions corresponding to ~10

nm/min. Plasma characterization was performed using an electrostatic cylindrical

Langmuir probe, placed at 10 cm from the target surface. Details of the Langmuir-

probe setup can be found elsewhere [9].

## 3 Results and discussion

### 3.1 Plasma characterization

The results of the Langmuir-probe measurements, with the probe at a substrate

position 10 cm from the target surface, revealed that $V_d$, the difference between the

plasma potential, $V_p$, and the floating potential, $V_f$, (i.e., $V_d = V_p - V_f$) reached a peak

value of ~10 V during the pulse-on time, and was ~1 V for the rest of the measured

time. $V_d$ corresponds to the maximum energy gained by bombarding and depositing

ions reaching a floating substrate. The plasma density (electron density) peaked at

~$5\times10^{18}$ m$^{-3}$, a value typical for HIPIMS, although somewhat lower than the plasma

density obtained for pure metals like Ti and Ta, ~$1\times10^{19}$ m$^{-3}$ [8-10]. The electron

temperature was a few electron volts during the pulse-on time, but decreased after the

pulse ended to a plateau value of ~0.2 eV. The high plasma density can be expected to

result in enhanced ionization of the sputtered material, as shown by Kouznetsov *et al.*

[4]. However, the ionization fraction depends on the target element. When sputtering

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from a single-element target, we have previously shown that the ionization fraction in the plasma increased with increasing target power [22], with the peak ionization-fraction reaching 90 % for Ti [23]. On the other hand, DeKoven *et al.* [24] showed that elements such as C ionized to a lesser extent (~4.5 %). The ionization potential of Si is higher than that for Ti and lower than for C. Therefore, we expect the degrees of ionization of Ti, Si, and C vapors from the $Ti_3SiC_2$ target to vary accordingly, i.e. highest for Ti and lowest for C.

## 3.2   Thin film deposition

### 3.2.1      Deposition rate

Deposition rate measurements were performed with XSEM on films deposited using HIPIMS and dcMS from a $Ti_3SiC_2$ target, with the substrate at 0º and 90º inclination angles. The measurements were performed with the substrate at a distance of 14 cm from the target. For both HIPIMS and dcMS, it was observed that the deposition rate at 0º inclination angle was higher than that at 90º inclination angle. For dcMS, the deposition rates were 11.1 nm/min and 4.2 nm/min at 0º and 90º inclination angle, respectively, which corresponds to a 62 % decrease in film thickness. For HIPIMS, the corresponding values were 6.7 nm/min and 4 nm/min, i.e., a 40 % decrease in film thickness. The smaller difference in deposition rate between the 0º and 90º angles observed for HIPIMS than for dcMS can be explained by the much higher ionization fraction of the sputtered species in HIPIMS. In the case of dcMS, the depositing species are virtually exclusively neutrals and will be largely restricted to deposition on surfaces in the line of sight of the target. In the case of HIPIMS, a large amount of the depositing species consists of ions that are attracted by the negative bias and the sheath voltage at the substrate. It should be noted that a

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comparison of the deposition rates for substrates facing the target surface shows that when using HIPIMS, the film thickness was only 60 % of the value achieved with dcMS for the same applied average power. It has been proposed [22] that the lower deposition rate for HIPIMS than dcMS is mainly due to that many of the ions are attracted back to the target surface by the cathode potential, resulting in a decrease of the sputtering yield. On the other hand, DeKoven *et al.* [24] showed that, for elements with low ionization fraction, such as carbon, the deposition rate was not substantially influenced by HIPIMS (compared to dcMS), but the film density was improved due to the high flux of bombarding Ar ions.

### 3.2.2    Structural analysis

For structural and compositional analysis, Ti-Si-C films were deposited on substrates heated to 680 ºC, in the two geometries shown in Fig. 1 (90º and 0º inclination angles). SEM images (Fig. 2) of the films grown by HIPIMS [Fig. 2 (a)] and dcMS [Fig. 2 (b)] facing the target surface revealed that both methods resulted in columnar growth. However, the HIPIMS films exhibited a dense structure with a relatively flat surface, while the dcMS films were rough and porous. The findings for the dcMS films could be expected for the large substrate-to-target distance of 14 cm, the high Ar discharge pressure of 20 mTorr, and the relatively limited substrate temperature of 680 ºC. The respective microstructures can be understood in light of the high degree of ion bombardment (from metal and Ar species) obtained in HIPIMS. Further, it has recently been shown that the sputtered species have a considerably higher energy in HIPIMS than in dcMS [25]. This was exemplified for sputtering of pure Ti [25], where it was observed that ~50 % of the sputtered Ti species had an energy of more than 20 eV compared to a few electron volts in the case of dcMS.
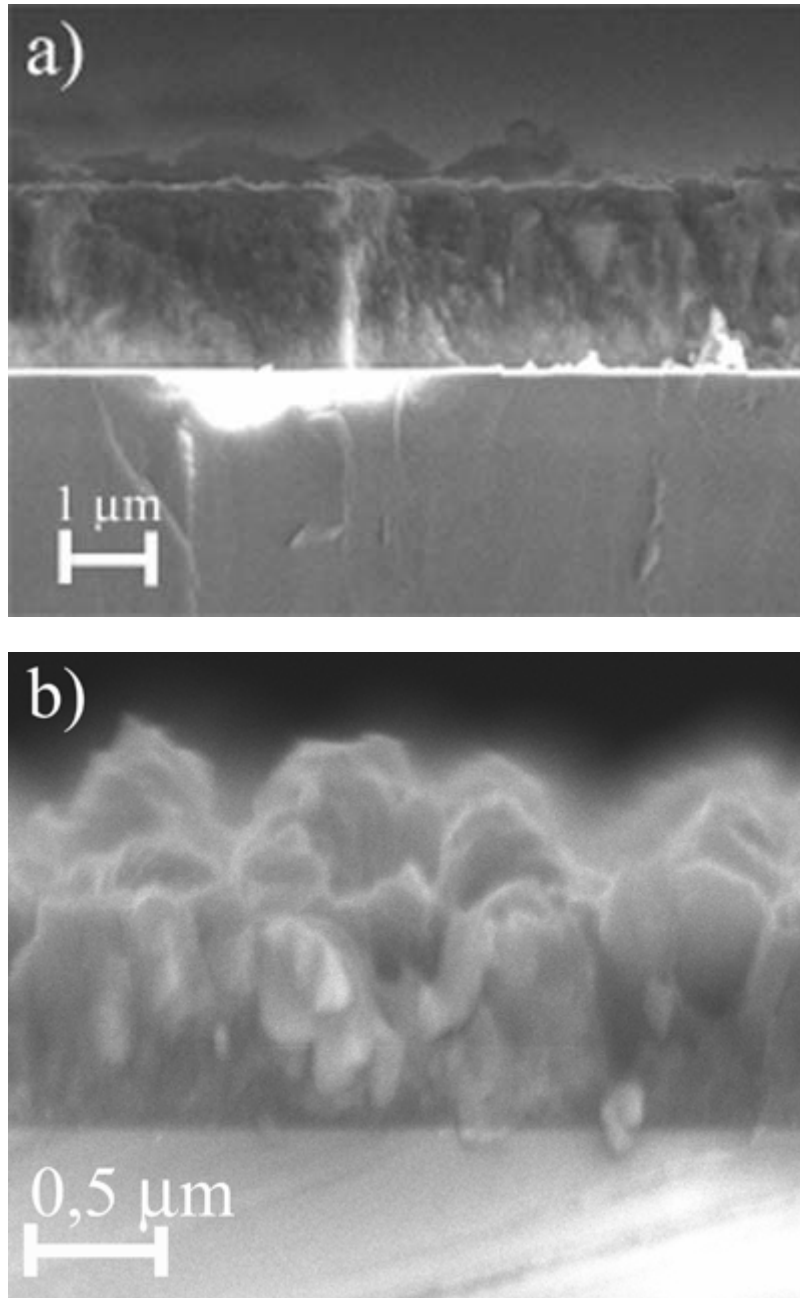
*FIG. 2 SEM micrographs from Ti-Si-C films grown facing the target surface by HIPIMS (a) and dcMS (b), using 20 mTorr Ar a sputtering gas and a substrate bias of -20 V.*

Figure 3(a) shows the grazing-incidence X-ray diffractogram from a film

deposited by HIPIMS on a MgO(111) substrate facing the target, at an Ar pressure of

20 mTorr and a target-to-substrate distance of 14 cm. The TiC 111, 200, 220, 311,

and 222 diffraction peaks can be observed, indicating that the films have one

crystalline constituent, TiC, which is the preferential crystalline phase forming in the

Ti-Si-C system at low deposition temperature (typically below 500 ℃) [14-17].

Depositions with lower Ar pressures and/or different distances from the target

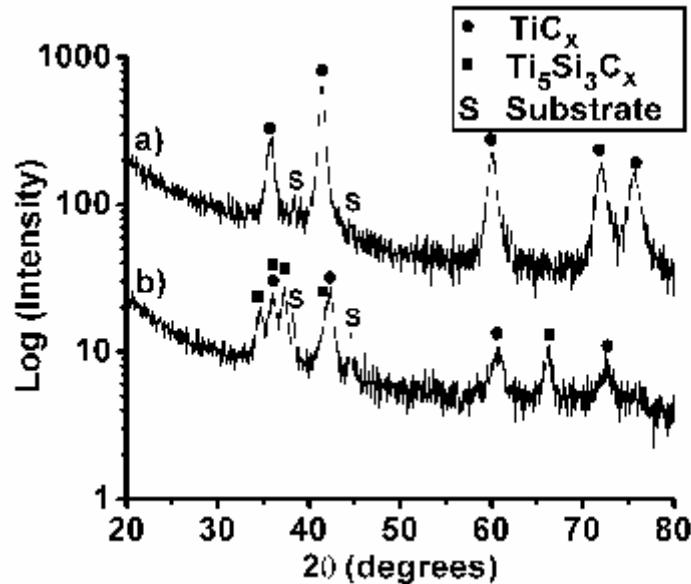resulted in similar XRD patterns, exhibiting no diffraction peaks other than the TiC

peaks.



FIG. 3 X-ray diffractogram of Ti-Si-C films grown by HIPIMS with the substrate a) facing the target surface and b) at a 90º inclination angle.

For films deposited with the substrate normal to the target surface, i.e., at 90º

inclination angle, the structure and phase composition varied depending on the Ar gas

pressure. At 20 mTorr, only TiC peaks could be observed. However, when the Ar gas

pressure was decreased to 10 and 5 mTorr, extra peaks were observed at the

diffraction angles 34.5º, 37.4º, and 66º, as shown in Fig. 3 (b) for a pressure of 5

mTorr. These peaks can be attributed to the Nowotny phase $Ti_5Si_3C_x$ [14,26,27]. This

phase can be regarded as a solid solution of carbon in the binary silicide $Ti_5Si_3$, where

the value of $x$ can be in the approximate range of 0 to 1, i.e., corresponding to a

carbon content of up to ~10 at. % [26]. The individual peaks can be identified as 002

(34.5º), 210 (~36º, overlapping with TiC 111), 102 (37.4º), 211 (~41º, partially

overlapping with TiC 200). The broad peak at ~66º can be interpreted as three overlapping peaks from $Ti_5Si_3C_x$: 321, 141, and 213. It should further be noted that the peaks originating from TiC are broader and of lower intensity than for the films deposited at 0º inclination angle, where no $Ti_5Si_3C_x$ was observed. We therefore conclude that the films deposited at 5-10 mTorr at 90º inclination angle are phase mixtures of the crystalline phases TiC and $Ti_5Si_3C_x$, probably with some amorphous-phase content as well. This interpretation is further supported by the XPS results (section 3.2.3).

### 3.2.3        Chemical-bonding and compositional analysis

XPS analysis of the C1s, Si2p, and Ti2p photoelectrons showed that both films deposited at 0º and 90º inclination angles exhibited strong C-Ti interaction, with the C1s peaks located at 282.0 eV, see Fig. 4(a) and 4(b), respectively. Also, a smaller contribution from C-Si bonding at 282.9 eV was present, as observed from the deconvoluted spectra in Fig 4. The Ti2p chemical bonding energies (not shown) were determined to be 454.5 eV for $Ti2p_{3/2}$, and 460.5 eV for $Ti2p_{1/2}$, which corresponds to Ti-C bonding as in TiC [15]. Together with the XRD results, this shows that crystalline TiC is present in all films. For the Si2p peak, films deposited at 0º inclination angle exhibited a typical Si-C interaction [16,17] with a broad peak centered at ~100.3 eV [Fig. 5(a)], thus supporting that these films probably consist of nanocrystalline TiC and amorphous SiC. This conclusion is supported by previous reports [16-18]. However, XPS analysis of the films deposited on inclined substrates at Ar pressures of 5–10 mTorr showed a Si2p peak position of 99.1 eV, as shown in Fig. 5(b). Deconvolution of the spectrum revealed two peaks at 98.8 eV and at 99.8 eV. The position of the former component agrees with $Ti_5Si_3C_x$ [27], in consistence with XRD, The latter component, however, indicates that there is still amorphous SiC

present in the film, which is supported by the fact that a component corresponding to C-Si bonding was present in the C1s spectrum. The difference between the positions of the Si-C component in Figs. 5(a) and 5(b) can tentatively be explained by interface effects and/or preferential sputtering of C.
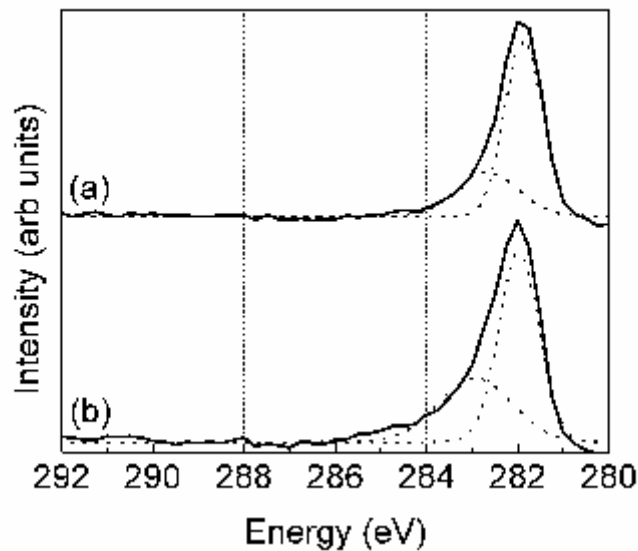


*FIG. 4 The C1s region of the XPS spectrum from Ti-Si-C films deposited at a) 0º inclination angle and b) 90º inclination angle.*

Table 1 shows the results of a compositional analysis with XPS on films grown at 90º inclination angle at different Ar pressure (5 mTorr, 10 mTorr, and 20 mTorr), with the composition of films grown at 20 mTorr and 0º inclination angle shown for comparison. As can be seen, the film deposited at 0º inclination angle has a relatively high C content (40 %) and a relatively low Si content (10 %) compared to the composition of the target, which is 50 % Ti, 17 % Si, and 33 % C. This effect has been observed previously for dcMS [16]. The films deposited at 90º inclination angle show a significant effect of Ar pressure, with the Ti content changing from 50 at. % (for 20 mTorr) to 58 at. % (for 5 mTorr), and the C content changing from 36 at. % (for 20 mTorr) to 28 at. % (for 5 mTorr). It is not surprising that the C content in films

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deposited at 90º inclination angle is lower than that in films deposited at 0º inclination angle. C ionizes weakly in HIPIMS and, consequently, is less active in the ion-deposition process than Ti and Si since ions, but not neutrals, are accelerated towards the film surface by the electric field in the sheath between the discharge and the substrate. For an Ar pressure of 20 mTorr, the composition is still relatively close to that of films deposited at 0º inclination angle. This may be due to resputtering of Ti and Si and/or gas-phase scattering of C, the latter resulting in C neutrals being scattered onto the substrate. Both these effects are expected to decrease with decreasing Ar pressure, which is consistent with our observations. We can therefore infer that it is, in principle, possible to control the film composition at the very least in the range 50 at % – 58 at. % (Ti content) and 28 at. % – 40 at. % (C content) by appropriate choices of substrate inclination angle, substrate bias, and Ar pressure.

*TABLE 1. XPS compositional analysis of HIPIMS-deposited Ti-Si-C films at 90º inclination angle with Ar pressures of 5, 10, and 20 mTorr, with the composition of films deposited at 0º inclination angle and an Ar pressure of 20 mTorr shown for comparison. The target-to-substrate distance was 14 cm. The O content of all films was lower than 4 at. %.*

| Inclination angle (degrees) | Ar pressure (mTorr) | Ti relative content (at. %) | Si relative content (at. %) | C relative content (at. %) |
|---|---|---|---|---|
| 90 | 5 | 58 | 14 | 28 |
| 90 | 10 | 55 | 14 | 31 |
| 90 | 20 | 50 | 14 | 36 |
| 0 | 20 | 50 | 10 | 40 |

The variation in composition also provides an explanation as to why $Ti_5Si_3C_x$ is formed in films deposited at low Ar pressure and at 90º inclination angle. As it is Si-rich, this phase requires a relatively high Si content and a relatively low C content to form. When this is not the case, it is more favorable to form the binary nanocomposite of nc-TiC and a-SiC. The formation of $Ti_5Si_3C_x$ is therefore

contingent upon obtaining a Si-rich composition, as is the case at 90° inclination angle and low Ar pressure. Note that the XPS bonding configuration (Fig. 5) indicates that some a-SiC appears to be present also in the films containing TiC and $Ti_5Si_3C_x$, which would not be expected according to the phase diagram [28], which states that $Ti_5Si_3C_x$ should co-exist with TiC and possibly $Ti_3SiC_2$. However, the phase diagram must be interpreted with great care, as it is determined at thermodynamic equilibrium and at temperatures above 1100 ℃. Sputtering processes in general, and HIPIMS in particular, operate far from equilibrium. Additionally, the temperature here is lower, 680 ℃. It is further worth noting that $Ti_5Si_3C_x$ has commonly been found as a minority phase in epitaxial $Ti_3SiC_2$ [14,15, 19]. The latter typically requires synthesis temperatures of ~800 ℃, while $Ti_5Si_3C_x$ can be synthesized at 650 ℃ [15], a temperature which is essentially the same as what was used in the present work. We can therefore conclude that synthesis of $Ti_5Si_3C_x$, albeit in phase-mixtures, is possible using HIPIMS from a $Ti_3SiC_2$ compound target, provided that the process parameters are tuned to give the appropriate composition. The synthesis temperature required for the Nowotny phase is also similar to what has been observed for dcMS. Based on the present results, it is therefore reasonable to assume that the temperature required for synthesis of $Ti_3SiC_2$ (which has a more complex and anisotropic unit cell than $Ti_5Si_3C_x$) using HIPIMS is similar to what has been used for dcMS [15, 19].
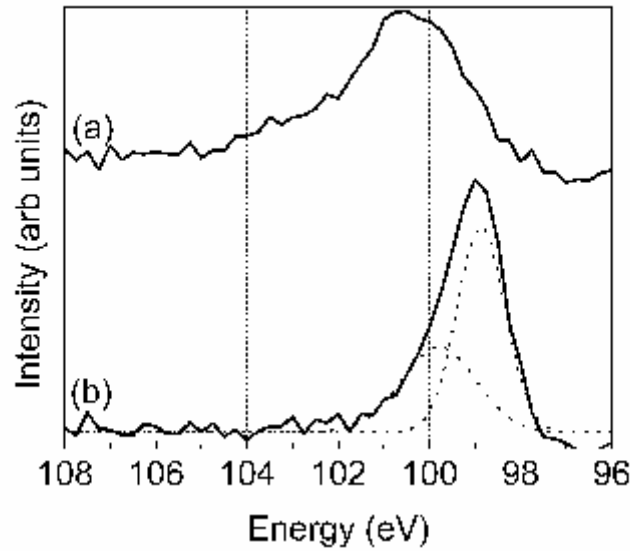
*FIG. 5 The Si2p region of the XPS spectrum from Ti-Si-C films deposited at a) 0º inclination angle and b) 90º inclination angle.*

# 4  Conclusions

Ti-Si-C composite thin films were deposited by high-power impulse magnetron sputtering (HIPIMS) from a $Ti_3SiC_2$ target. TiC was the main crystalline constituent of the Ti-Si-C films, as indicated by XRD. The film morphology was dense and flat, while films deposited with dc magnetron sputtering under comparable conditions were rough and porous. It was shown that the film composition, particularly with respect to carbon content, in principle could be controlled by appropriate choices of substrate inclination angle, bias voltage, and Ar pressure. In films deposited with the substrate at an inclination angle of 90º, XRD and XPS showed presence of the Nowotny phase $Ti_5Si_3C_x$.

The route towards $Ti_3SiC_2$ synthesis by HIPIMS may require that the energy and momentum transfer from the bombarding ions to the growing film surface be optimized to provide further enhanced adatom mobility to enable $Ti_3SiC_2$ phase

formation under the apparent kinetic limitations. However, it is clear that the film quality in terms of smoothness and density can be much improved by the use of HIPIMS compared to dcMS. That is a clear signature of the beneficial ion-surface interactions. Future experiments should focus on obtaining conditions for low-energy ion bombardment (~20 eV) and avoiding high-energy tail in order to avoid near-surface collisional mixing or renucleation of a growing $Ti_3SiC_2$ film.

## Acknowledgments

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