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High-rate deposition of amorphous and nanocomposite Ti-Si-C multifunctional coatings

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Abstract

Amorphous (a) and nanocomposite Ti-Si-C coatings were deposited at rates up to 16 μ m/h by direct current magnetron sputtering from a Ti₃SiC₂ compound target, using an industrial pilot-plant system, onto high-speed steel, Si, and SiO₂ substrates as well as Ni-plated Cu cylinders, kept at a temperature of 200 or 270 °C. Electron microscopy, x-ray photoelectron spectroscopy, and x-ray diffraction analyses showed that TiC/a-C/a-SiC nanocomposites were formed consisting of textured TiC nanocrystallites (nc) embedded in a matrix of a-C and a-SiC. Elastic recoil detection analysis showed that coatings deposited at a target-to-substrate distance of 2 cm and an Ar pressure of 10 mTorr have a composition close to that of the Ti₃SiC₂ compound target, as explained by ballistic

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transport of the species. Increased target-to-substrate distance from 2 cm to 8 cm resulted in a higher carbon-to-titanium ratio in the coatings than for the Ti_3SiC_2 compound target, due to different gas-phase scattering properties between the sputtered species. The coatings microstructure could be modified from nanocrystalline to predominantly amorphous by changing the pressure and target-to-substrate conditions to 4 mTorr and 2 cm, respectively. A decreased pressure from 10 mTorr to 4 or 2 mTorr at a target-tosubstrate distance of 2 cm decreased the deposition rate up to a factor of ~7 as explained by resputtering and an increase in the plasma sheath thickness. The coatings exhibited electrical resistivity in the range 160-800 $\mu\Omega$ cm, contact resistance down to 0.8 m Ω at a contact force of 40 N, and nanoindentation hardness in the range 6-38 GPa.

Keywords: Nanocomposites, TiSiC coatings, Pilot plant, Magnetron sputtering, Resistivity, Electron microscopy

1. Introduction

Sputter deposited nanocomposite conductive ceramics challenge electroplated gold as a coating material for electrical contacts. Gold has low resistivity, but its poor wear resistance decreases the lifetime of the electrical contact substantially [1,2,3,4]. Another unsatisfactory condition is that electroplating of gold often requires preparation steps that are not environmentally friendly. TiC-based nanocomposite coatings are well known from tribological applications [5,6,7,8,9,10], but have only recently been adopted for electrical contacts [11,12,13,14,15]. Ti-Si-C based nanocomposites are particularly relevant, since these nanocomposites have been demonstrated to combine their known mechanical strength and low coefficient of friction [9,16,17,18,19,20,21] with high

conductivity and low contact resistance [11,15]. This far, mainly laboratory scale sputtering of Ti-Si-C nanocomposites has been performed [11,15,16,17,18,19,20,21]. However, further exploitation of such coating materials will require well-defined microstructure at high deposition rates and temperatures below 300 °C to meet industrial demands on high productivity.

In this study, we investigate the deposition of Ti-Si-C coatings from a Ti_3SiC_2 compound target in an industrial pilot-plant system under different Ar pressures and target-tosubstrate distances, using deposition temperatures of 200 and 270 °C. The main focus is to understand the coating microstructure formation, mechanical characteristics, and electrical properties. We demonstrate that coatings with microstructures ranging from predominantly amorphous to nanocrystalline TiC embedded in an amorphous SiC/C matrix can be deposited with compositions close to that of the Ti_3SiC_2 compound target, at deposition rates as high as 16 µm/h.

2. Experimental details

Table 1 presents the conditions applied to grow the Ti-Si-C coatings. They were grown by dc magnetron sputtering in a high vacuum industrial pilot-plant system with a base pressure of $\sim 7.5 \times 10^{-3}$ mTorr ($\sim 1 \times 10^{-3}$ Pa). The magnetron was operated with a 210x100 mm Ti₃SiC₂ compound target. The target was positioned at a distance of 2 or 8 cm directly in front of a fixed substrate holder. The magnetron was operated in currentcontrol mode (4 or 8 A), resulting in a dc power density of 4-10 W/cm². The deposition temperature was 270 °C, except in two experiments where it was 200 °C. The thermocouple and heater were mounted somewhat above the substrate, therefore, the deposition temperature is slightly higher than the actual substrate temperature. Depositions were carried out in an argon plasma using a total pressure of 2, 4 or 10 mTorr (~0.3, ~0.5 or ~1.3 Pa). The deposition time was 20 minutes in all experiments. Four different substrate materials were used: Si(100) and SiO₂(100) (both 15x10x0.5 mm) for resistivity, compositional, and structural characterization; high-speed steel (20x20x3 mm) for adhesion testing; and Ni-plated Cu cylinders (with a radius of 10 mm and a length of 20 mm) for contact resistance measurements. The substrates were placed on a substrate holder directly facing the target. All substrates were ultrasonically cleaned in acetone and isopropanol with 5 minutes in each solvent. Prior to deposition, the substrates were plasma etched for 15-20 min with a pulsed dc bias of -440 V at 250 kHz. During deposition, a constant dc bias of -50 V was applied.

X-ray diffraction (XRD) using θ -2 θ -scans was performed in a Bruker D8 diffractometer. ω -scans were performed to determine the substrate curvature from which we estimate the intrinsic stress of the coating by means of Stoney's formula.

Time-of-flight energy elastic recoil detection analysis (ToF-E ERDA) measurements were performed using a 40 MeV $^{127}I^{9+}$ ion beam at 67.5° incidence and 45° scattering angle [22]. The obtained data were evaluated with the CONTES code [23].

X-ray photoelectron spectroscopy (XPS) measurements were performed in a Physical Electronics Quantum 2000 spectrometer using monochromatic Al K α radiation, with the binding energy calibrated against Ag, Cu, and Au [24]. High resolution XPS spectra were recorded after 90 seconds of sputter etching with 4 kV Ar⁺ ions over an area of 2 x 2 mm². Scanning electron microscopy (SEM) was performed in a LEO 1550, operated at accelerating voltages of 5-20 kV. Cross-sectional and plan-view images were obtained by secondary electron imaging. Coating thickness measurements were performed on the coatings deposited onto Si(100) substrates.

Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and high-resolution TEM (HRTEM) images were obtained in a Tecnai G² 20 Ultra Twin 200 kV FEGTEM. Cross-section samples for TEM were mechanically polished to a thickness of ~50 μ m, and then thinned to electron transparency using a Gatan Precision Ion Polishing System (PIPS) ion miller operated at 5 kV using Ar⁺ ions, with a final polishing step at 2.5 kV.

Mechanical properties were determined by nanoindentation with an Umis 2000 instrument equipped with a Berkovich indenter. The load was 7 mN and the hardness was an average calculated according to the Oliver-Pharr method [25] from 50 indents.

Room temperature four-point-probe measurements were performed using a Model 280C (Four Dimensions) instrument. The resistivity values were obtained by multiplying the sheet resistance with the coating thickness.

The contact resistance of the coatings deposited on Ni-plated Cu cylinders was measured using an in-house setup against an Ag counter part. Figure 1 shows a schematic drawing of the setup, in which the voltage drop over the coated cylinder and the Ag counter part is measured as a function of contact force. The contribution from the bulk material to the measured contact resistance is negligible.

3. Results and discussion

3.1 General observations

Rockwell indentation tests (not shown) revealed that all coatings were in the HF2 or HF3 regime, i.e., the adhesion of the coatings on steel substrates was good.

Figure 2 shows x-ray diffractograms from Coatings 1-12. TiC is observed to be the only crystalline phase. Angular shifts for the TiC peaks are observed, and the explanation of



Figure 1. Schematic drawing of the contact resistance measurement setup.

this shift is that the C fraction in the TiC_x phase can vary between 0.47-0.97 [26], which in our case corresponds to a 2 θ peak positions of TiC(111) in the range 35.87-36.18° (range is marked with a grey layer in Figure 2). A shift outside that range can also be seen in Figure 2 for some of the coatings, suggesting an additional contribution to the peak shift from residual stress. Thus, the stress was estimated for Coatings 1-12 by means of Stoney's formula to be in the range -0.2 to 2.2 GPa. The coatings deposited with 8 A (Coatings 1-6) show higher stresses than the coatings that are deposited with 4 A (Coatings 7-12), which have a stress <1 GPa. Consequently, the lower scattering angle of the TiC peaks from Coatings 4, 5, 7, and 11 is due to compressive residual stress, and a peak shift to higher scattering angle of the TiC peak for Coating 8 is due to tensile residual stress.



Figure 2. X-ray diffractograms from Coatings 1-12 deposited on SiO₂.

Coatings 1, 5, 7, 8, 10, and even 11 at a closer inspection have <111> preferred out of plane orientation, whereas Coating 6 has <100> preferred out of plane orientation, Coating 12 has a weak <100> preferred out of plane orientation, and Coatings 2, 3, 4, and 9 have a relatively random orientation. The strong <111> preferred out of plane orientation of Coating 1 is consistent with our previous work [11,12] for nc-TiC/a-SiC and nc-TiC/a-C coatings, all with C/Ti ratio larger than one (see Table 2). In contrast Coatings 2, 3, 4 with a C/Ti ratio smaller than one, has a relatively random preferred out of plane orientation. The <111> preferred out of plane orientation, indicating that the C/Ti ratio affects the orientation. The <111> preferred out of plane orientation of Coating 5 is an exception, probably due to the extreme deposition

conditions. The fact that Coatings 1 and 6 and also Coating 7 and 12 have different texture shows that the small decreased in deposition temperature from 270 °C to 200 °C affects the atom mobility during growth, which affects the preferred orientation.

3.2 The influence of the target-to-substrate distance and pressure

We start by considering the results for coatings deposited with a target current of 8 A. Table 1 shows that the thickness of the coatings is in the range 0.7-5.3 μ m. The highest deposition rate (~16 μ m/h) was obtained for the coating deposited at the shortest targetto-substrate distance of 2 cm and the highest process pressure of 10 mTorr, i.e. Coating 3, while an increase in the target-to-substrate distance to 8 cm (Coating 2) resulted in a reduction of the deposition rate by ~75%, to ~4 μ m/h. At the pressure of 4 mTorr, an increase in the target-to-substrate distance from 2 cm to 8 cm yielded an increase of the deposition rate by a factor of ~ 2 , from 2.4 μ m/h to 4.5 μ m/h. At the target-to-substrate distance of 2 cm, a decrease in pressure from 10 mTorr to 4 mTorr resulted in a reduction of the deposition rate of a factor \sim 7, and when the pressure is decreased even further to 2 mTorr, the deposition rate continues to decrease to 2.1 µm/h. At the target-to-substrate distance of 8 cm, a decrease in pressure from 10 mTorr to 4 mTorr resulted in an increase of the deposition rate of a factor by ~ 20 %. Finally, the similar deposition rate found for Coatings 1 and 6, and Coatings 7 and 12 shows that the deposition temperature does not affect the growth rate.

Table 2 shows ERDA results for Coatings 1-6. Normally, in sputtering it is difficult to achieve the same composition in the coating as in the target, and coatings are C-rich compared with the target, due to gas-phase scattering processes and difference in angular and energy distribution between species sputtered from the target [27]. H or O are also

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easily incorporated in the coating, which leads to differences. Here, Coatings 2 have a composition of 45.9 at.% Ti, 16.5 at.% Si, 37.6 at.%, and Coating 3 has a composition of 49.2 at.% Ti, 15.3 at.% Si, 35.5 at.%. This means that the difference in angular and energy distribution between species from the target is not that pronounced, and that the composition of Coatings 2 and 3 is close to the one of the Ti_3SiC_2 compound target, (50 at.% Ti, 16.7 at.% Si, and 33.3 at.% C). Coatings 1, 4, and 6 have a C content of ~40 at.%, i.e., these coatings are C-rich compared to the Ti₃SiC₂ compound target. The fact that the compositions of Coating 1 and 6 are similar shows that the decrease in the deposition temperature from 270 °C to 200 °C does not significantly affect the composition. The composition of Coating 5 is similar to that of Coating 3, but with higher O contamination content. The trend is that coatings deposited at a target-to-substrate distance of 2 cm exhibit a higher O content than coatings deposited at a target-to-substrate distance of 8 cm. Especially, Coating 3 is thick and porous as a consequence of the high deposition rate, and its O has probably been incorporated after the deposition when the coating is exposed to atmosphere. The high O content in Coating 5 is probably due to that it has flaked because of energetic backscattered neutrals that have hit the surface. By virtue of O adsorption on these flakes the apparent O content in the coating is increased in a similar way as in the porous Coating 3.

The observations on deposition rate and composition can be explained by difference in gas phase scattering, predominant at a target-to-substrate distance of 8 cm, and direct transfer of the sputtered material, predominant at a distance of 2 cm. For a target-to-substrate distance of 8 cm, the C enrichment in the coatings is due to more energy loss by collisions during the transport to the substrate for Ti and Si compared to C [27,28]. The mean-free paths at a pressure of 4 mTorr are estimated to be 7.3 cm, 3.5 cm, and 2.3 cm

for C, Si, and Ti, respectively [29]. Thus, the C content in such coatings is enriched compared to the Ti₃SiC₂ compound target, since Si and Ti species are thermalized while C is in the transition regime. In contrast, at a pressure of 10 mTorr all species are thermalized and the coating composition approaches that of the target. At a target-tosubstrate distance of 2 cm, and a pressure of 10 mTorr, the coating composition is very close to the one of the Ti_3SiC_2 compound target, due to direct transfer (ballistic transport) of all species. The same result would be expected at growth at 2 cm and pressure of 2 or 4 mTorr. We observe by ERDA, however, that Coatings 4 and 5 have a lower Ti content than Coating 3 (cf. Table 2). Since the sputtering yield of Ti in Ar is higher than for Si and C for elemental targets [30], we believe that this decrease in Ti content in Coatings 4 and 5 is caused by selective resputtering of Ti. We speculate that the observed decrease in deposition rate for the lower pressure at a target-to-substrate distance of 2 cm is an effect of both resputtering and a change of the plasma sheath thickness. This is because a decrease in pressure leads to a decrease in plasma density and an increase of the Debye length [31]. This means that the sheath region (including the pre-sheath) will extend outwards from the target and thereby move the negative glow region from the target. The sheath has been estimated by the Childs law [31] to 5 mm, when an electron temperature of 2 eV and an electron density of $1*10^{10}$ cm⁻³ are used. The pre-sheath thickness is difficult to estimate, hence, due to the small target-to-substrate distance, the substrate might partially be in the dark space region, where the plasma is not fully developed, which explains the decrease in deposition rate of a factor of \sim 7.

Figure 3a-f shows the surface morphology of Coatings 1-6, respectively. Coatings deposited at a target-to-substrate distance of 8 cm (Coatings 1, 2, and 6) have a similar nodular surface morphology. For a target-to-substrate distance of 2 cm, Coating 3 has a



Figure 3. Plan view SEM images from a) Coating 1, b) Coating 2, c) Coating 3, d) Coating 4, e) Coating 5, and f) Coating 6.

rough flake-like surface morphology, whereas Coating 4 has a featureless smooth surface, and Coating 5 has a "brush-painted" surface morphology. The differences in surface morphology between Coatings 3-5 most likely depends on the degree of resputtering and deposition rate. A comparison of the surface morphology and thickness results for coatings deposited at a target-to-substrate distance of 2 cm (Coatings 3-5) shows that a lower deposition pressure results in thinner and smoother coatings.

XPS showed that the positions of Ti2p and Si2p peaks (not shown) were identical for these coatings. Observed peaks at 454.6 eV (Ti2p_{3/2}) and 460.6 eV (Ti2p_{1/2}) with the difference between the Ti2p_{1/2} and Ti2p_{3/2} of 6.0 eV correspond to Ti-C bonds [32,33], and a peak at 100.3 eV (Si2p) corresponds to Si-C bonds [34]. Figure 4 shows the C1s peaks for Coatings 1-4. The C1s peaks at 281.8 eV and 284.6 eV corresponds to C-Ti and C-C bonds (free carbon), respectively [33,35,36]. Between these contributions C-Si bonds, at 282.5 eV, are expected. For nanocomposite Ti-C materials additional contributions have also been reported in this region [37,38,39,40,41,42,43,44], which have been associated with several different causes, including ion beam sputtering damage

[42], and an interfacial state between nc-TiC and a-C phase [12,40,41,43]. Such contribution can hence not be excluded in the present samples, and is indicated in Figure 4 by TiC*.



Figure 4. XPS C1s regions from Coatings 1-4.

The XPS results thus show that the coating materials grown in this study mainly consist of Ti-C and Si-C bonds with a C-C feature (cf. Figure 4), consistent with the XRD results (cf. Figure 2) showing a structure with the only crystalline phase being TiC, i.e. a nc-TiC/a-C/a-SiC nanocomposite.

The correlation between the C-C feature and the deposition parameters is not clear. Coating 3 deposited at a target-to-substrate distance of 2 cm and with the lowest C content has the largest C-C feature in the coating, and Coating 1 deposited at a target-tosubstrate distance of 8 cm and with the largest C content has the smallest C-C feature in the coating, and Coatings 2 and 4 deposited at different distances and pressures have only the C-C feature on the coating surface which corresponds to contamination. The composition values determined by ERDA and XPS (not shown) are similar to each other, except for Coating 3, where ERDA gave 47 at.% Ti, 15 at.% Si, and 34 at.% C, and XPS gave 32 at.% Ti, 13 at.% Si, and 55 at.% C. The reason for this discrepancy is that Coating 3 has a large amount of free C on the surface with a decreased content inwards in the coating, and the depth profile sputtering in XPS was insufficient to reach a composition representative for the bulk of the coating. In contrast, ERDA measures the average composition in the whole coating.

Figure 5 shows cross-sectional SEM images of Coatings 1 and 3. Coating 1 (Figure 5a) represents the general appearance of the nanocomposite coatings and has a dense columnar structure, where the width of the columns increases with coating thickness, which is expected for such coatings deposited with dc magnetron sputtering [45,46]. Coating 3 (Figure 5b) has a similar appearance, however, with intercolumnar porosity, probably due to the high deposition rate and the low adatom mobility.

Figure 6a shows cross-sectional TEM and HREM images with corresponding SAED patterns from Coating 2. The SAED pattern shows that Coating 2 is polycrystalline with a random preferred out-of-plane orientation, consistent with XRD. The TEM image shows that Coating 2 exhibits a columnar morphology that represents the general appearance of the nanocomposite coatings. This columnar microstructure is indicative of a competitive growth mode.



Figure 5. Cross sectional SEM images of a) Coating 1 and b) Coating 3. Note that the scale bars are different in (a) and (b).



Figure 6. TEM images, a) overview, high resolution images and SAED pattern of Coating 2, b) overview, high resolution images and SAED pattern of Coating 4, and c) STEM overview, high resolution images and SAED pattern of Coating 3.

Figure 6b shows cross-sectional TEM and corresponding SAED patterns from Coating 4. According to the SAED and the TEM image Coating 4 is clearly amorphous in the investigated areas. The XRD finding of some TiC diffraction intensity (cf. Figure 2) indicates, however, the presence of isolated TiC-crystallite clusters in Coating 4, which where not found in the localized TEM images. There are only a few previous examples in the literature on the amorphization of such carbides. Naka et al. observed that Ti-Si-C coatings can be grown amorphous by dc magnetron sputtering if the Si content is high (46 at.%) [47], and Wilhelmsson et al. observed that Ge induces an amorphous structure of VC_x coatings [48]. Here, the effective amorphization is explained by the deposition conditions, where a target-to-substrate distance of 2 cm and a pressure of 4 mTorr yield concurrent ion-bombardment that destroys most of the crystalline clusters at the coating surface in combination with the low deposition temperature, which effectively quenches diffusion and hinders crystallization in the bulk [49,50].

Figure 6c shows STEM images used to enhance the contrast from the columnar structure from Coating 3. The corresponding SAED pattern shows that the coating is polycrystalline with random preferred out of plane orientation, consistent with XRD. The high resolution STEM image from an area close to the coating-substrate interface shows that the crystallite size is ~10 nm. The STEM image shows that Coating 3 exhibits a columnar growth similar to the general appearance except that the crystallites continue to grow larger closer to the surface. This coating is more porous than those deposited at lower deposition rates, due to kinetically-limited growth conditions leading to vacancy trapping.

3.3 Electrical and mechanical properties

Table 3 presents the resistivity results for Coatings 1-6, together with literature values for the related materials nc-TiC/a-SiC, polycrystalline TiC_x, epitaxial Ti₃SiC₂, and nc-TiC/a-C. The resistivity of Coating 1-6 varies between 160-800 $\mu\Omega$ cm. At a target-to-substrate distance of 8 cm the resistivity values were $\sim 250 \ \mu\Omega cm$, regardless of deposition conditions. At 2 cm, the coatings resistivity varied from 160-800 $\mu\Omega$ cm. The resistivity values from the coatings 1-6 are comparable with data for nc-TiC/a-SiC [11], and in the same range as for TiC_x [51], but the resistivity values are much higher than for epitaxial Ti₃SiC₂ [52], and much lower than for nc-TiC/a-C [12]. An increased resistivity is normally connected with grain boundary scattering, where coatings with smaller grains have higher resistivity. Coatings 1-6 have an average grain size estimated in the range 11-19 nm with Scherrer's formula. Coating 3 has the highest resistivity (769 $\mu\Omega$ cm) and it cannot, however, be fully explained with grain boundary scattering, since the average grain size is similar as for Coatings 4-6 (~12 nm). Instead, the high resistivity in Coating 3 can be explained by the porosity, O content, and high amount of free C [40]. Coatings 1, 2, 5, and 6, have none or a small fraction of free C, resulting in a similar resistivity of $\sim 250 \ \mu\Omega cm$. The low resistivity for Coating 4 is surprising and interesting, because of its predominantly amorphous structure. For the binary TiC/a-C it has been seen that the resistivity increases radically when the thickness of the poorly conducting matrix increases in volume fraction [40]. For the present coatings, we have estimated the amount of the less conductive matrix (SiC and free C) from the XPS results (Figure 4), and it is clear that the coatings with high amount of Si-C and C-C bonds compared to the amount of C-Ti bonds have higher resistivity. Coating 4 has the lowest ratio of Si-C and C-C bond, therefore, we suggest that a conductive Ti-Si-C network is formed in this

predominantly amorphous coating, instead of only nc-TiC in an a-SiC matrix, which may explain how Coating 4 can be the better conductor.

Table 3 also presents the contact resistance for Coatings 1-6 against Ag as a counter part and an Ag-Ag reference. The contact resistances of the coatings deposited at a target-tosubstrate distance of 8 cm at a contact force of 40 N are 24.6, 3.8, and 3.2 m Ω for Coatings 1, 2, and 6, respectively. The contact resistances for coatings deposited at a target-to-substrate distance of 2 cm at a contact force of 40 N are 1.5, 0.8, and 1.9 m Ω for Coatings 3, 4, and 5, respectively. To a first approximation the contact resistance depends on the mechanical contact area of the contact spots [53]. However, in electrical contacts, the electrical contact area differs from the mechanical contact area (not for Au), since there is an insulating oxide present on the surface. In Coatings 1-6 there were up to ~ 29 at.% O on the coating surface according to XPS, which indicates the presence of an native oxide. A rough surface morphology of the coating usually decreases the contact resistance since the rough surface helps penetrating the oxide layer. Therefore, the contact resistance depends on the surface roughness, the hardness, and the resistivity of the contacting materials. Coatings 3-5 deposited at a target-to-substrate distance of 2 cm have the lowest contact resistance. The contact resistances for Coatings 1-6 were higher than 0.8 m Ω at 40 N, i.e., an order of magnitude higher than the Ag-Ag reference. The differences between Coatings 3-5 in contact resistance are explained by means of the sputter profile from a depth XPS profile of the O content (not shown). The contact resistance depends on the native oxide, and also the O content deeper down in the bulk. Coating 4 has a small amount of O in the bulk, therefore, when the native oxide is penetrated Coating 4 has a lower contact resistance than Coatings 3 and 5. Coating 5 has higher O content closer to the surface than Coating 3, but has a lower O content further

down in the bulk than Coating 3. Hence, Coating 5 has higher contact resistance at low applied force than Coating 3, due to higher O content at the surface, but lower contact resistance at higher applied force, due to a thinner insulating oxide than Coating 3.

Furthermore, Table 3 lists the mechanical properties of Coatings 1-6 together with literature values for the related materials nc-TiC/a-SiC [11], polycrystalline TiC_x [54], Ti₃SiC₂ [52], and nc-TiC/a-C [40]. Generally, all coatings, Coating 3 as an exception, have a similar hardness as TiC_x , and are harder than the other related materials mention above. Coatings 1 and 2, which were deposited at a target-to-substrate distance of 8 cm, a pressure of 4 or 10 mTorr respectively, have a hardness of 27 GPa. Coating 3, deposited at a target-to-substrate distance of 2 cm and a pressure of 10 mTorr has a hardness of 6 GPa. The lower hardness in Coating 3 compared to the other coatings is expected due to the porous microstructure. Coating 4, deposited at a target-to-substrate distance of 2 cm, a pressure of 4 mTorr has a hardness of 38 GPa. Coating 5, deposited at the same conditions as Coating 4 except that the pressure was decreased even further to 2 mTorr, has a hardness of 36 GPa, i.e. these coatings are harder than TiC_x . For Coatings 4 and 5, the compressive residual stress contributes to the high hardness. This is explained by the deposition conditions, which involves an intensive ion-bombardment of the substrate. A similar hardness of Coating 1 and Coating 6 shows that a decrease in deposition temperature from 270 °C to 200 °C did not affect the hardness.

3.4 The influence of the deposition rate

Finally, we consider the results for coatings deposited at a target current of 4 A (i.e., at the lower deposition rates). We used two different currents (4 and 8 A), to show that similar coatings could be deposited at different currents, and that the deposition rate is

proportional to the current, both for target-to-substrate distance of 8 cm and for a more "extreme" condition in this context, where the target-to-substrate distance was 2 cm. The coating thickness was measured to be 0.2-1.7 μ m, corresponding to a deposition rate of 0.6-5.1 μ m/h, compared with deposition rates of ~2-16 μ m/h at a target current of 8 A. Coatings deposited under the same conditions that resulted in the highest respectively the lowest deposition rate at a target current of 8 A, had the same trend at a target current of 4 A, i.e. the deposition rate is proportional to the target current. The electrical resistivity was in the range 233-325 μ Ωcm (160-800 μ Ωcm at 8 A) and the electrical contact resistances were in the range 2.5-102 mΩ (0.8-25 mΩ at 8 A) at a contact force of 40 N. Coatings deposited with a lower deposition rate, i.e. at 4 A, exhibit a similar resistivity, and higher contact resistance as the coatings deposited at 8 A.

4. Conclusions

Coatings consisting of nanocrystalline TiC embedded in an amorphous C and SiC matrix (nc-TiC/a-C/a-SiC) can be deposited by dc magnetron sputtering from a Ti_3SiC_2 compound target, using an industrial pilot-plant system at deposition temperatures of 200-270 °C.

Deposition rates up to ~16 μ m/h can be obtained at a target-to-substrate distance of 2 cm and a pressure of 10 mTorr.

The Ti_3SiC_2 compound target composition can be retained in 5 µm thick coatings for two deposition condition windows: 1) sufficient gas phase scattering operating at 8 cm and 2) direct transfer of the sputtered material operating at 2 cm.

Both the C/Ti ratio and the deposition temperature affected the preferred orientation in the coatings. Specifically, <111> preferred out of plane orientation is promoted in C-rich coatings.

The coatings have a resistivity of 160-800 $\mu\Omega$ cm, a contact resistance of >0.8 m Ω at 40 N, and a hardness of 6-38 GPa.

Finally, predominately amorphous Ti-Si-C coatings can be produced exhibiting the highest hardness and lowest resistivity, among the studied samples.

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- [1] Z-K. Chen, IEEE Trans. Comp. Hybrids. Manuf. Technol. vol. 15, no. 3 (1992) 378.
- [2] H. Tian, N. Saka, E. Rabinowicz, Wear 142 (1991) 57.
- [3] M. Antler, Thin Solid Films 84 (1981) 245.
- [4] Z-K. Chen, Wear 155 (1992) 353.
- [5] U. Jansson, E. Lewin, M. Råsander, O. Eriksson, B. André, U. Wiklund, Surf. Coat. Technol. (2010) doi: 10.1016/j.surfcoat.2010.06.017.
- [6] B. Feng, D. M. Cao, W. J. Meng, J. Xu, R. C. Tittsworth, L. E. Rehn, P. M. Baldo,
 G. L. Doll, Surf. Coat. Technol. 148 (2001) 153.

- [7] D. Martinez-Martinez, C. Lopez-Cartes, A. Justo, A. Fernández, J. C. Sánchez-López, A. Garcia-Luis, M. Brizuela, J. I. Onate, J. Vac. Sci. Technol. A 23 (2005) 1732.
- [8] Y. T. Pei, D. Galvan, J. Th. M. DeHosson, A. Cavalerio, Surf. Coat. Technol. 198 (2005) 44.
- [9] T. Zehnder, J. Matthey, P. Schwaller, A. Klein, P. -A. Steinmann, J. Patscheider, Surf. Coat. Technol. 163-164 (2003) 238.
- [10] A. R. Phani, J. E. Krzanowski, J. J. Nainaparampil, J. Vac. Sci. Technol. A 19 (2001) 2252.
- [11] P. Eklund, J. Emmerlich, H. Högberg, O. Wilhelmsson, P. Isberg, J. Birch, P. O. Å. Persson, U. Jansson, L. Hultman, J. Vac. Sci. Technol. B 23 (2005) 2486.
- [12] E. Lewin, O. Wilhelmsson, U. Jansson, J. Appl. Phys. 100 (2006) 054303.
- [13] P. Eklund, T. Joelsson, H. Ljungcrantz, O. Wilhelmsson, Zs. Czigány, H. Högberg, L. Hultman, Surf. Coat. Technol. 201 (2007) 6465.
- [14] P. Isberg, P. Eklund, J. Emmerlich, L. Hultman, H. Högberg, H. Ljungcrantz, International Patent no. WO2005/038985 A2 (18 October 2004).
- [15] P. Eklund, Surface Engineering 23 (2007) 406.
- [16] M. Rester, J. Neidhardt, P. Eklund, J. Emmerlich, H. Ljungcrantz, L. Hultman, C. Mitterer, Mat. Sci. Eng. A 429 (2006) 90.
- [17] C. Lopes, N. M. G. Parreira, S. Carvalho, A. Cavaleiro, J. P. Rivière, E. Le Bourhis,F. Vaz, Surf. Coat. Technol. 201 (2007) 7180.
- [18] D. Munteanu, C. Ionescu, C. Olteanu, A, Munteanu, F. Davin, L. Cunha, C. Moura,F. Vaz, Wear 268 (2010) 552.

- [19] J. E. Krzanowski, S. H. Koutzaki, J. Am. Ceram. Soc., 84 (2001) 672.
- [20] W. Gulbinski, A. Gilewicz, T. Suszko, B. Warcholinski, Z. Kuklinski, Surf. Coat. Technol. 180 (2004) 341.
- [21] S. H. Koutzaki, J. E. Krzanowski, J. J. Nainaparampril, J. Vac. Sci. Technol. A 19(4) (2001) 1912.
- [22] Y. Zhang, H. J. Whitlow, T. Winzell, I. F. Bubb, T. Sajavaara, J. Jokinen, K. Arstila, J. Keinonen, Nucl. Instrum. Methods Phys. Res. B 149 (1999) 477.
- [23] M. S. Janson, CONTES instruction manual, 2004.
- [24] M. P. Seah, Surf. Interface Anal. 31 (2001) 721.
- [25] W. C. Oliver, G. M. Pharr, J. Mater. Res. 7 (1992) 1564.
- [26] H. O. Pierson, Handbook of refractory carbides and nitrides, Noyes Publication (1996).
- [27] P. Eklund, M. Beckers, J. Frodelius, H. Högberg, L. Hultman, J. Vac. Sci. Technol. A 25(5) (2007) 1381.
- [28] P. Eklund, M. Beckers, U. Jansson, H. Högberg, L. Hultman, Thin Solid Films 518 (2010) 1851.
- [29] A. Roth, Vacuum Technology, North-Holland, 1982, equation 2.57.
- [30] Y. Yamamura, H. Tawara, Atomic Data Nucl. Data Tables 62 (1996) 149.
- [31] B. Chapman, Glow discharge processes Sputtering and plasma etching, John Wiley & Sons, 1980.
- [32] J. Alami, P. Eklund, J. Emmerlich, O. Wilhelmsson, U. Jansson, H. Högberg, L. Hultman, U. Helmersson, Thin Solid Films 515 (2006) 1731.

- [33] J. Chastain, R. King, Jr., Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Eden Prarie, MN, 1995.
- [34] J. J. Nainaparampil, J. S. Zabinski, J. Vac. Sci. Technol. A 17 (1999) 909.
- [35] A. A. Voevodin, J. S. Zabinski, J. Mater. Sci. 33 (1998) 319.
- [36] S. Zhang, X. L. Bui, J. Jiang, X. Li, Surf. Coat. Technol. 198 (2005) 206.
- [37] J. Luthin, H. Plank, J. Roth, Ch. Linsmeier, Nucl. Instrum. Methods Phys. Res. B 182 (2001) 218.
- [38] G. Li, L. F. Xia, Thin Solid Films 396 (2001) 16.
- [39] W. Gulbinski, S. Mathur, H. Shen, T. Suszko, A. Gilewice, B. Warcholinski, Appl. Surf. Sci. 239 (2005) 302.
- [40] E. Lewin, E. Olsson, B. André, T. Joelsson, Å. Öberg, U. Wiklund, H. Ljungcrantz,U. Jansson, Plasma Processes and Polymers 6 (2009) S928.
- [41] E. Lewin, P. O. Å. Persson, M. Lattemann, M. Stüber, M. Gorgoi, A. Sandell, C. Ziebert, F. Schäfers, W. Braun, J. Halbritter, S. Ulrich, W. Eberhardt, L. Hultman, H. Siegbahn, S. Svensson, U. Jansson, Surf. Coat. Technol. 202 (2008) 3563.
- [42] E. Lewin, M. Gorgoi, F. Schäfers, S. Svensson, U. Jansson, Surf. Coat. Technol. 204 (2009) 455.
- [43] M. Magnuson, E. Lewin, L. Hultman, U. Jansson, Phys. Rev. B 80 (2009) 235108.
- [44] M. Stüber, H. Leiste, S. Ulrich, H. Holleck, D. Schild, Surf. Coat. Technol. 150 (2002) 218.
- [45] Y. T. Pei, C. Q. Chen, K. P. Shaha, J. Th. M. De Hosson, J. W. Bradley, S. A. Voronin, M. Cada, Acta Materialia 56 (2008) 696.

- [46] Y. T. Pei, K. P. Shaha, C. Q. Chen, R. van der Hulst, A. A. Turkin, D. I. Vainshtein, J. Th. M. De Hosson, Acta Materialia 57 (2009) 5156.
- [47] M. Naka, H. Sakai, M. Maeda, H. Mori, Mater. Sci. Eng. A226-228 (1997) 774.
- [48] O. Wilhelmsson, P. Eklund, H. Högberg, L. Hultman, U. Jansson, Acta Materialia 56 (2008) 2563.
- [49] H. Abe, S. Yamamoto, H. Naramoto, Nucl. Instr. Meth. Phys. Res. B 127/128 (1997) 170.
- [50] H. Abe, H. Naramoto, A. Iwase, C. Kinoshita, Nucl. Instr. Meth. Phys. Res. B 127/128 (1997) 681.
- [51] F. Santerre, M. A. El Khakani, M. Chaker, J. P. Dodelet, Appl. Surf. Sci. 148 (1999)24.
- [52] J. Emmerlich, J.-P. Palmquist, H. Högberg, J. M. Molina-Aldareguia, Zs. Czigány,
 Sz. Sasvári, P. O. Å. Persson, U. Jansson, L. Hultman, J. Appl. Phys. 96 (2004)
 4817.
- [53] P. Slade, Electrical contacts –Principles and applications, Marcel Dekker, Inc. New York 1999.
- [54] H. Högberg, J. Birch, M. Odén, J-O. Malm, L. Hultman, U. Jansson, J. Mater. Res. 16 (2001) 1301.

Coating	Distance	Pressure	Current	Temp.	Thickness	Dep. rate
	(cm)	(mTorr)	(A)	(°C)	(µm)	(µm/h)
1	8	4	8	270	1.5	4.5
2	8	10	8	270	1.2	3.6
3	2	10	8	270	5.3	15.9
4	2	4	8	270	0.8	2.4
5	2	2	8	270	0.7	2.1
6	8	4	8	200	1.5	4.5
7	8	4	4	270	0.6	1.8
8	8	10	4	270	0.7	2.1
9	2	10	4	270	1.7	5.1
10	2	4	4	270	0.6	1.8
11	2	2	4	270	0.2	0.6
12	8	4	4	200	0.7	2.1

Table 1. Experimental conditions and thickness of the coatings.

Coating	1	2	3	4	5	6
Ti content (rel. at. %)	40.0	45.2	47.3	43.9	42.2	40.8
Si content (rel. at. %)	17.1	16.2	14.7	14.8	16.8	15.8
C content (rel. at. %)	41.5	37.0	34.2	39.7	35.0	41.8
O content (rel. at. %)	1.4	1.5	3.5	1.5	6.0	1.6
C/Ti ratio	1.04	0.82	0.72	0.90	0.83	1.02

Table 2. ERDA composition of Coatings 1-6.

Table 3. Hardness and resistivity values for as-deposited nc-TiC/a-C/a-SiC coatings, and literature values for nc-TiC/a-SiC [11], TiC_x [51,54], epitaxial Ti₃SiC₂ [52], and nc-TiC/a-C [12,40]. Contact resistance values for as-deposited nc-TiC/a-C/a-SiC coatings and Ag against an Ag counter part.

								nc-			nc-
							Ag-	TiC/a-		Epitaxial	TiC/
Coating	1	2	3	4	5	6	Ag	SiC	TiC _x	Ti ₃ SiC ₂	a-C
Hardness	27	27	6	38	36	30	-	20	15-	~18	8-18
(GPa)									28		
Resistivity	260	247	769	160	268	223	-	250-	80-	25-33	1200-
(μΩcm)								1160	140		5000
Contact	24.6	3.8	1.5	0.8	1.9	3.2	0.07				
resistance	7.2	1.6	0.7	0.3	1.3	1.7	0.05				
(at 40, 100,	2.2	0.7	0.3	0.1	0.2	0.8	0.03				
300N)											
$(m\Omega)$											