



## Layer formation by resputtering in Ti–Si–C hard coatings during large scale cathodic arc deposition

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### ABSTRACT

This paper presents the physical mechanism behind the phenomenon of self-layering in thin films made by industrial scale cathodic arc deposition systems using compound Ti–Si–C cathodes and rotating substrate fixture. For the as-deposited films, electron microscopy and energy dispersive X-ray spectrometry reveals a trapezoid modulation in Si content in the substrate normal direction, with a period of 4 to 23 nm dependent on cathode configuration. This is caused by preferential resputtering of Si by the energetic deposition flux incident at high incidence angles, when the substrates are facing away from the cathodes. The Ti-rich sub-layers exhibit TiC grains with sizes up to 5 nm, while layers with high Si-content are less crystalline. The nanoindentation hardness of the films increases with decreasing layer thickness.

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### 1. Introduction

Cathodic arc is a powerful technique for thin film synthesis, where the plasma originates from so called cathode spots of very high current, power, and plasma density [1]. The resulting energetic and highly ionized plasma can be used for rapid growth of stable as well as metastable compounds, hence frequently used for tribological, decorative, protective, and functional coatings. Cathodic arc is in particular used extensively for commercial wear resistant coatings such as TiAlN [2], AlCrN [3], and TiSiN [4].

In a variety of applications, particularly at industrial scale, the aim is to coat large areas with high uniformity. As with other PVD-methods, arc deposition is a line of sight method, which necessitates rotation to equally expose all areas to the deposition flux when substrates are large or numerous. Substrate rotation, however, may induce an artificial layering of the coatings, see e.g. Ref. [5] and Ref. [6], due to anisotropic growth conditions. For many applications, this is used advantageously to create multilayers [7], where the large number of interfaces contributes to enhanced mechanical properties [8]. However, in most cases, the layering is unintentional and not even recognized. The underlying conditions during film growth, and the effects on the film properties have, so far, not been given much consideration. An improved understanding of these phenomena could have implications on the design of coatings as well as deposition

systems. Sample fixture rotation and variation of coating flux by angular position have also been pointed out as an important underexplored factor for improved performance of coated products [9].

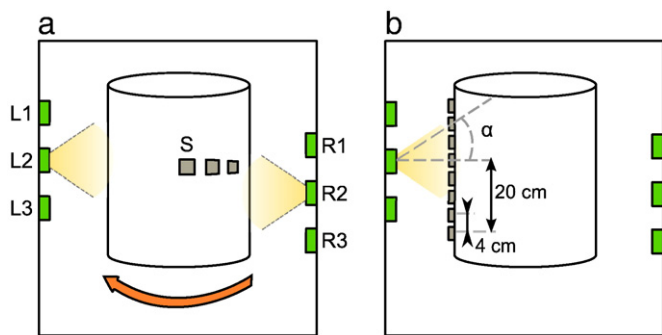
There are few studies focusing on properties of arc plasma originating from compound cathodes, despite their common use in a wide range of applications to enable synthesis of multi-element films through rational utilization of existing coating equipment. Here, we examine arcing from ternary Ti<sub>3</sub>SiC<sub>2</sub> cathodes and the self-layering in the resulting Ti–Si–C coatings. The investigated cathodes are of relevance for exploration of, e.g., the Ti–Si–C–N system providing a path to coatings rich in both Si and C when used in reactive N<sub>2</sub> atmosphere [10]. We study the variation in film composition and structure with substrate position and cathode configuration, enabling analysis of the spatial deposition profile of each of the three elements. In conjunction with analysis of temporal changes in deposition conditions due to substrate rotation, we identify likely mechanisms for the layer formation. The findings emphasize the complex nature of material transfer from cathode to substrate during cathodic arc deposition, particularly when employing compound cathodes combining lighter and heavier elements.

### 2. Experimental details

Thin films were deposited using a Sulzer Metaplas MZR 323 industrial scale cathodic arc evaporation system, see schematic in Fig. 1. The chamber can hold up to six cathodes (diameter 63 mm) in simultaneous operation, placed on the left (L1–L3) and the right (R1–

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**Fig. 1.** (a) Schematic drawing of the deposition chamber holding six cathodes, L1–L3 and R1–R3, and substrates S on a rotating metal cylinder. (b) A non-rotating chamber configuration for investigation of film thickness and compositional distribution.

R3) side. The vertical cathode positions on opposite sides, i.e. L1 relative to R1 etc., are displaced about 10 cm relative to each other, to attain film thickness uniformity. Ternary  $\text{Ti}_3\text{SiC}_2$  cathodes (Maxthal) were used in different configurations, and polished  $12 \times 12$  mm cemented carbide substrates, WC with 10 wt.% Co, were placed on a cylinder rotating at 3 rpm about 15 cm in front of the cathodes. During one revolution the substrates (S) experience passage in front of one cathode, L2, on one chamber side and in the space between two cathodes, R1 and R2, on the opposite side, see Fig. 1a. Further complex sample fixturing, such as three-fold rotation, is often used for specific applications. The present configuration was chosen to isolate one type of rotation and provide flexibility in substrate positioning.

The films were deposited using 50 A dc arc current at  $\sim 1 \times 10^{-3}$  Pa base pressure. An addition of  $\sim 0.1$  Pa Ar was necessary to sustain the arc. The substrates were negatively biased at  $-30$  V, and the chamber was heated through resistive heating element located on the far chamber side, to approximately  $400^\circ\text{C}$  on the rotating cylinder.

In the initial film growth five cathodes, L1–L3 and R1–R2, were operated, with substrates at position S, see Fig. 1a. In a second set of experiments, one cathode on either left (L2) or right (R2) side, or on both sides (L2 + R2) simultaneously, was used with substrates fixed at position S. In a final experiment, thicker films were deposited from one cathode (L2) without rotation of the cylinder. Substrates were then placed at approximately every 4 cm vertically covering a range of 20 cm below and above the cathode, see Fig. 1b. The latter stationary experiment was used for two purposes: i) to grow sufficiently thick films for compositional characterization, also on substrates placed far from the cathode within reasonable time, and ii) to isolate effects of relative cathode–substrate placement in the vertical direction only, as rotation would infer constantly changing horizontal positions.

Compositional characterization of the films, along with a cut-out piece from the cathode bulk, was carried out by elastic recoil detection analysis with a time-of-flight and energy detector (TOF-E ERDA), using a 40 MeV  $^{127}\text{I}^{9+}$  ion beam at  $67.5^\circ$  incidence angle relative to the surface normal and  $45^\circ$  scattering angle. The resulting time-of-flight versus recoil energy spectra were evaluated using the CONTES code to obtain elemental composition spectra [11]. Structural characterization was performed through transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), using an analytical FEI Tecnai G2 TF 20 UT microscope equipped with an energy dispersive X-ray spectrometer (EDS). Cross sectional TEM samples were prepared through mechanical polishing and ion milling. X-ray diffractometry (XRD) for phase analysis was performed using a Bruker AXS D8-advanced X-ray diffractometer with a line-focus  $\text{Cu K}\alpha$  X-ray source. Film thickness was determined using a LEO 1550 Gemini scanning electron microscope (SEM), also equipped with Oxford Link EDS, on polished cross-sections. Film hardness was measurement on polished tapered cross sections using a UMIS nanoindenter equipped with a Berkovich diamond tip. Approximately 20 indents were made

for each sample to an indentation depth of  $\sim 0.2$   $\mu\text{m}$ , corresponding to a maximum applied load of 25 mN. Hardness was evaluated using the method proposed by Oliver and Pharr [12].

### 3. Results and discussion

Films deposited using the conventional five cathode setup features alternating bright and dark layers in a trapezoid wave pattern in bright field TEM, see Fig. 2a–b. The layering is even better revealed by z-contrast in STEM imaging, see Fig. 2c, together with EDS elemental mapping in a  $50 \times 50$   $\text{nm}^2$  area, as shown in the inset. The amount of Si and Ti vary, with every second layer richer in Si (corresponding to bright region in the Si map) and with less of Ti. An EDS line profile (S  $\rightarrow$  F), covering approximately six periods, was recorded and is presented for Ti and Si in Fig. 2d as relative deviation from the respective average EDS signal. There is an anti-correlation between Si and Ti, with the Si oscillations being most pronounced, up to  $\pm 20\%$  of measured EDS signal. The profiles resemble a square wave with substantial noise. The segments where Si has positive deviation correspond to the dark regions in the STEM image, also indicated at the bottom of Fig. 2d (tolerating single deviating data points). The Si-rich regions are on average 12.4 nm thick, calculated over three 150 nm scans, compared to 10.9 nm regions where Ti has positive deviation. The Ti-rich zones also have larger crystalline grains as evident from dark field and high-resolution TEM, see Fig. 3a and b, respectively. In STEM the grains appear bright, see Fig. 2c, which together with the selected area electron diffraction (SAED) pattern inset in Fig. 3c indicate that these are TiC. Si has a known effect as grain refiner [4,13] explaining the nanocrystalline grains in the Si-rich regions. The sub-layers within the Ti-rich regions, visible in Fig. 2b and c, are related to passage between off-axis cathodes (R in Fig. 1a), and is discussed in detail below.

The layered structure is present also in single cathode (L2) depositions, see Fig. 4a, when the substrate is placed on the rotating fixture directly in front of the cathode. STEM-imaging in Fig. 4b shows repeating broader bright and narrower dark segments, indicating compositional modulation similar to the five cathode case. Samples placed on the cylinder at 10 cm vertical displacement relative to the cathode center, under otherwise identical deposition conditions, have no discernible layering, see Fig. 4c. This result is confirmed by repeated analysis for a second off-axis sample from a different deposition under the same conditions. In the case where two cathodes were used (L2 and R2 in Fig. 1a), the layers are again present, see Fig. 4d, though with an increased thickness as compared to the one cathode case.

We conclude that layering with a characteristic appearance in terms of compositional modulation occurs in all cases when the substrate path includes passage directly in front of a cathode. The periodicity can be correlated to substrate rotation by knowing the film thickness and deposition time, hence growth rate, together with rotation speed of the substrate holding cylinder. The growth during one full revolution corresponds to the size of the repeating motif.

All the investigated films are nanocrystalline with a grain or domain size generally below the thickness of the layer period. X-ray diffraction reveals only one identifiable film peak at a  $2\theta$ -angle of  $41^\circ$ , see Fig. 5. This is in the vicinity of the reference position for the Ti 101 reflection at  $40.2^\circ$  and the TiC 200 reflection at  $41.7^\circ$  [14]. Scans at  $2\theta$ -angles in the range  $2$ – $30^\circ$  did not show any peaks originating from  $\text{Ti}_3\text{SiC}_2$  MAX phase, which is the predominant phase in the cathode.

We suggest that the layering is primarily caused by selective re-sputtering in high plasma incidence angle segments of the rotation, after consideration of three potential factors: 1) spatial variations in plasma composition prior to deposition, 2) ion-surface interaction with resulting re-sputtering from the growing film, and 3) material transfer through post deposition processes, as outlined below. For analysis of these factors, we initially assess the deposition profile from

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