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Arc deposition of Ti–Si–C–N thin films from binary and ternary cathodes — Comparing sources of C

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ABSTRACT

Ti–Si–C–N thin films with composition of 1–11 at.% Si and 1–20 at.% C have been deposited onto cemented carbide substrates by arcing Ti–Si cathodes in a $CH_4 + N_2$ gas mixture and, alternatively, through arcing Ti–Si–C cathodes in N_2. Films of comparable compositions from the two types of cathodes have similar structure and properties. Hence, C can be supplied as either plasma ions generated from the cathode or atoms from the gas phase with small influence on the structural evolution. Over the compositional range obtained, the films were dense and cubic-phase nanocrystalline, as characterized by X-ray diffraction, ion beam analysis, and scanning and transmission electron microscopy. The films have high hardness (30–40 GPa by nanoindentation) due to hardening from low-angle grain boundaries on the nanometer scale and lattice defects such as growth-induced vacancies and alloying element interstitials.

1. Introduction

Arc deposition of binary and ternary transition metal nitrides and carbides is a common method to protect and enhance properties of, for example, cutting tools. Multinary compounds are considered in order to achieve film materials with enhanced and optimized properties for various applications [1].

In this study, we report on different methods to synthesize Ti–Si–C–N thin films as potential material for wear and oxidation resistant coatings. The study of this quaternary system is inspired by the well-known ternaries Ti–Si–N [2–5] and Ti–C–N [6–8] and has been approached by different strategies for combining the four elements with quite different outcomes because of the reaction involved during thin film synthesis. First, chemical vapor deposition (CVD) [9–12] and plasma enhanced CVD [5–8] rely on reactions between gaseous precursors. In physical vapor deposition (PVD) ions and neutrals of the film forming species are generated through methods like magnetron sputtering from compound targets [13,14], multicomponent targets [15], or through plasma enhanced magnetron sputtering [16,17]. A hybrid approach combining magnetron sputtering and arc evaporation has also been demonstrated [18] as well as arcing Ti in a gas mixture containing N_2 and trimethylsilane [19,20]. These methods yield films ranging from highly crystalline TiN-based films with minor additions of Si and C, to films of high C content. In some cases of CVD-growth, the study of carbonitride thin films is motivated by the search for less harmful Si-precursors, that turn out to also include C [21]. There are examples of intended Ti–Si–N growth where the incorporation of C from precursors was not realized [22] until revealed by subsequent analysis [23]. The presence of C is important for film properties (influencing texture, hardness etc.), in conjunction with Si, as we show in the present publication.

To advance the field of Ti–Si–C–N reactive arc deposition, a versatile technique for rapid growth of dense and defect rich films [24], we concentrate studies on binary and ternary arc cathodes. Deposition from binary cathodes has the advantage of applying conventional and commercially available Ti–Si cathodes [25]. For deposition from ternary cathodes, only one reactive gas is employed and thus easier process control can be obtained, as recently shown using Ti_3SiC_2 cathodes to grow films with high Si and C contents [26]. Furthermore, carbon originating from the cathode will to a large extent be ionized and accelerated in contrast to CH_4 molecules, which only partially undergo electron impact ionization with a corresponding energy barrier [27]. The form that C has when contributing to film growth will thus be different and may affect film growth.

In this work we present a systematic comparison of structure and properties of arc deposited films grown from Ti–Si cathodes ($Ti_{90}Si_{10}$, $Ti_{80}Si_{20}$, and $Ti_{75}Si_{25}$) in a mixture of CH_4 and N_2, or Ti–Si–C cathodes ($Ti_{90}Si_5C_5$, $Ti_{80}Si_{10}C_{10}$, and Ti_3SiC_2) in pure N_2 atmosphere. We compare the methods and provide a systematic overview as a function of Si and C contents in the cathodes and films.

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2. Experimental details

Thin films were deposited in an industrial scale cathodic arc deposition system (Metaplas MZR 323) onto polished cemented carbide substrates of WC with 10 wt.% Co that were placed about 15 cm from the cathode on a cylinder rotating at 3 rpm. The system can be operated with several vertically separated cathodes in simultaneous operation, which was utilized for the depositions from binary cathodes. To obtain several samples with a gradient in Si composition, pure Ti was used along with alloyed $Ti_{90}Si_{10}$ and $Ti_{80}Si_{20}$ cathodes on one chamber side. The cathodes were operated with 50 A arc current. The ratio of CH_4 to N_2 was tuned to different set values between 2% and 20% through mass flow controllers, which were held constant during each deposition. The corresponding flow rates were in the interval of 3–55 standard cubic centimeter per minute (sccm) for CH_4 and 230–310 sccm for N_2. The total pressure was kept constant at 2 Pa. In a separate experiment, to attempt deposition of films with higher Si and C contents, motivated by previous results for films deposited from Ti_3SiC_2 cathodes rich in Si and C [26], a $Ti_{75}Si_{25}$ cathode was evaporated in an atmosphere of 50% CH_4 and 50% N_2, at a total pressure of 2 Pa and a corresponding flow rate of ~170 sccm for both gases.

Depositions from ternary cathodes were performed simultaneously from $Ti_{90}Si_5C_5$ and $Ti_{80}Si_{10}C_{10}$ cathodes (GfE, Gesellschaft für Elektrometallurgie mbH) placed on one chamber side in the top and bottom positions, respectively, while not using the center cathode position. This setup will minimize plasma overlap as shown by the deposition profile from one cathode [28]. Nitrogen was introduced at pressures between 0 and 6 Pa (hereafter abbreviated pN_2) to form a reactive atmosphere.

In all cases the substrates were biased at −30 V and the chamber was heated through resistive heating elements located on the far chamber side to a temperature of approximately 400 °C on the rotating cylinder. The base pressure was ~10^{-3} Pa and all films were deposited to a thickness in the range of 3–5 μm.

Film composition was determined through time-of-flight energy elastic recoil detection analysis (TOF-E ERDA), using a 36 MeV $^{127}I^{9+}$ ion beam at 22.5° incidence angle relative to the surface and 45° recoil angle [29]. The resulting time-of-flight versus recoil energy spectra were evaluated using the CONTES code [30].

X-ray diffractometry (XRD) for phase analysis was performed using a PANalytical X'PERT X-ray diffractometer with a line-focus Cu K_α X-ray source where θ–2θ scans were recorded in the 2θ-range from 2° to 140°. Residual stress was measured by the $\sin^2\psi$-metod and the 220 diffraction peaks using a PANalytical Empyrean X-ray diffractometer, assuming an X-ray elastic constant based on a Young's modulus of 450 GPa and a Poisson's ratio of 0.22 similar to TiN [31]. Structural characterization was also performed through transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS), using an analytical FEI Tecnai G2 TF 20 UT microscope. Cross sectional TEM (XTEM) samples were prepared through mechanical polishing and ion milling. Surface morphology was characterized using a LEO 1550 scanning electron microscope (SEM) operated at 5 kV. Chemical bonding states were analyzed through X-ray photoelectron spectroscopy (XPS) using monochromatic Al K_α (1486.6 eV) radiation. The XPS measurements were performed in the Kratos Axis Ultra system. The binding energy scale of all XPS spectra presented here were calibrated against the Fermi-edge (E_f), which was set to a binding energy of 0 eV, and normalized at the background on the low binding energy side of the main peak/peaks. Contaminations on the sample surface were removed through sputtering using Ar^+ at 4 keV for 3 cycles of 20 s each: XPS spectra were acquired between every cycle and no indications of beam damage were observed.

Film hardness was measured on polished tapered cross sections using a UMIS nanoindenter equipped with a Berkovich diamond tip. At least 15 indents were made for each sample to an indentation depth of ~0.2 μm, corresponding to a maximum applied load of 20–50 mN. Hardness was evaluated using the method by Oliver and Pharr [32].

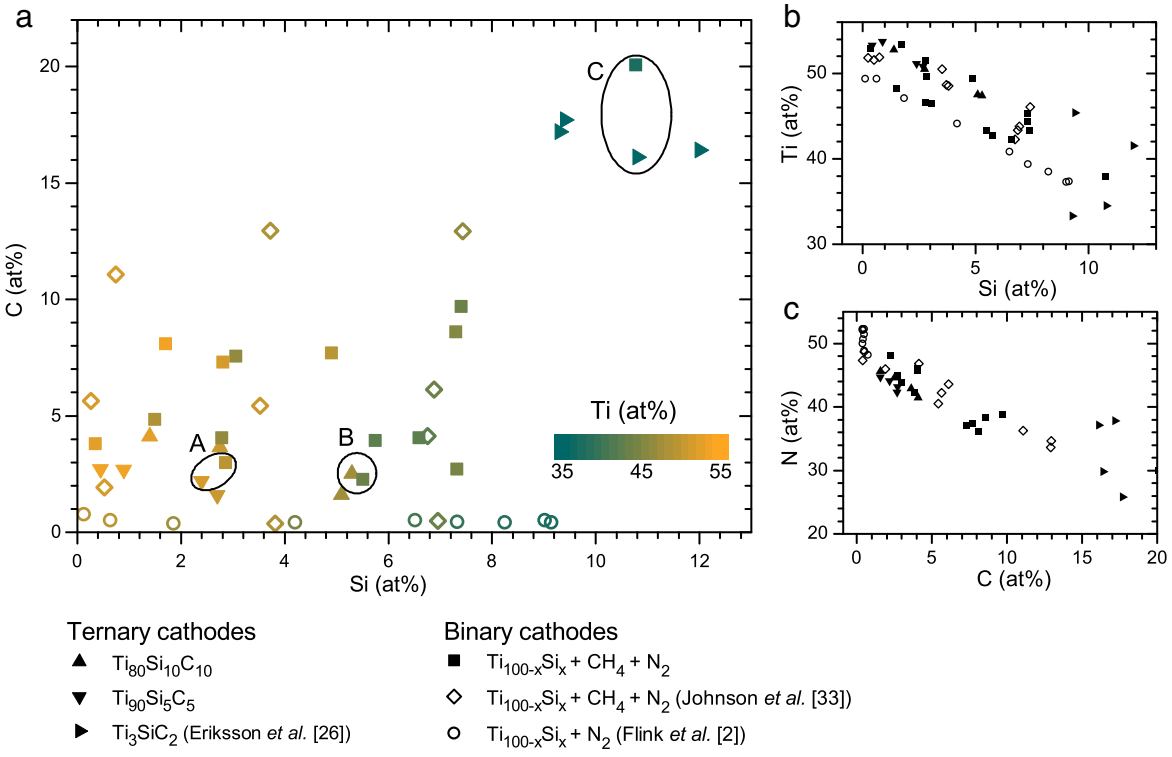

Fig. 1. (a) Overview of film composition obtained through deposition from binary or ternary cathodes (at.% N = balance). $Ti_{100-x}Si_x$ indicates that a setup with multiple binary cathodes of different Si contents ($x \in \{0, 10, 20, 25\}$) was employed. The encircled samples (A, B and C) are included in comparison of films from binary and ternary cathodes. (b) The Si content correlates with Ti as well as (c) N with C.