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Nanocomposite Ti–Si–N, Zr–Si–N, Ti–Al–Si–N, Ti–Al–V–Si–N thin film coatings deposited by vacuum arc deposition

P.J. Martin[a,*], A. Bendavid[a], J.M. Cairney[b], M. Hoffman[b]

[a]*CSIRO Telecommunications and Industrial Physics, P.O. Box 218, Lindfield NSW 2070, Australia*
[b]*Department of Materials Science and Engineering, The University of New South Wales NSW 2052, Sydney, Australia*

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Abstract

Thin films of Ti–Si–N, Zr–Si–N, Ti–Al–V–Si–N and Ti–Al–Si–N have been synthesized by reactively evaporating a metal or metal alloy cathode by a vacuum arc in a background of nitrogen gas and tetramethylsilane. The amount of silicon in the films was varied from 0 to 19 at.%. With increasing silicon content, the Ti–Si–N, Ti–Al–V–Si–N and Zr–Si–N films were found to increase in hardness, the maximum recorded value being 42 GPa. The Ti–Al–Si–N films showed either a slight increase or decrease in hardness with silicon content. Structural studies showed that the increased hardness was accompanied by a reduction in the grain size, in the case of Ti–Al–V–Si–N, from 24 to 7.7 nm. Transmission electron microscopy (TEM) studies confirmed the X-ray diffraction (XRD) results and showed that the major diffraction lines were associated with the nitride phases. X-ray photoelectron spectroscopy (XPS) studies indicated the presence of Si_3N_4 and also small amounts of carbide which may be amorphous and possibly located at the grain boundaries.
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1. Introduction

In recent years, there have been considerable advances in the development of new materials and thin film deposition technologies for use in hard, wear-resistant applications. Among the more significant developments in hard coatings has been the synthesis of the Ti–Si–N system with super-hardness values in excess of 40 GPa [1]. The enhanced properties of the Ti–Si–N system are attributed to the refinement of the grain size in which one or more phases are present at the nanoscale to form a nanocomposite layer. Nanocomposite coatings are a consequence of nanocrystalline grains of a transition metal nitride, e.g., TiN, immersed in an amorphous matrix of a second material phase, e.g., Si_3N_4. More generally, the material may be described as nc–Me_n/a–Si_3N_4 (where Me is a transition metal such as V, Ti, Nb, Zr, etc., in an amorphous silicon nitride matrix). Nanoscale crystallites are relatively free of dislocations and when high stress is applied any dislocation movement that may be present is trapped at the grain boundaries by the amorphous matrix resulting in an enhancement in the material strength.

Nanocomposite materials have been synthesised by PACVD, ion-assisted ion beam sputtering, vacuum arc deposition, magnetron sputtering and recently, by hybrid arc and magnetron sputter processing [1–6]. The vacuum arc process is an attractive production deposition technology but the requirement of silicon in the deposited nanocomposite films and the difficulty in arc-evaporating elemental Si has necessitated the use of special Me–Si alloy cathodes [7]. Alternatively, the silicon may be introduced into the coatings by concurrent operation of a titanium arc source and magnetron source operating with a silicon cathode. This approach has been successful both by

* Corresponding author. Tel.: +61 2 94137126; fax: +61 2 94137200.
E-mail address: philm@tip.csiro.au (P.J. Martin).

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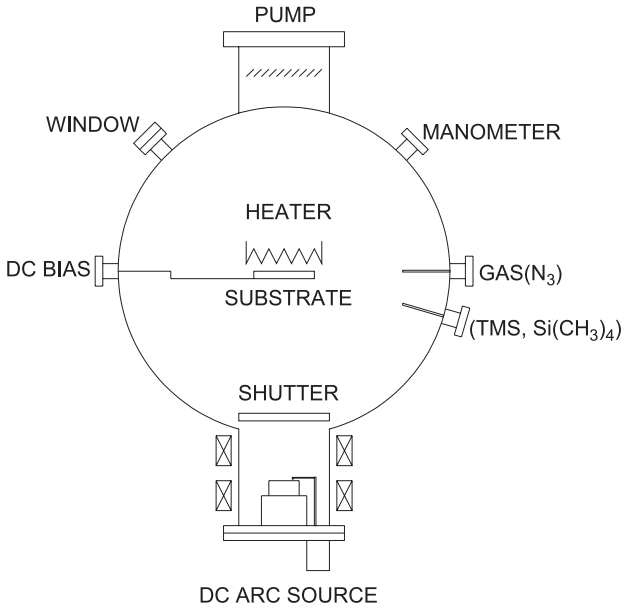

Fig. 1. Schematic diagram of the deposition system.

simultaneous deposition of the two fluxes and by alternating arc and magnetron deposition [2,8].

Here we report on the deposition of nanocomposite films, by a new, simpler approach, in which TMS (tetramethylsilane), $Si(CH_3)_4$ is used as the silicon precursor in a hybrid PVD–CVD deposition process. This approach requires no special alloy cathodes, no secondary PVD source and is easily retrofitted to existing equipment [9].

2. Experimental details

2.1. Sample preparation

The deposition system is shown in Fig. 1. A cathodic arc source is used to provide a flux of metal ions from a 55-mm-diameter cathode (99.95% purity). Cathodes used in the arc source were Ti, Zr, $TiAl_{75:25}$, $TiAl_{50:50}$, $TiAl_{33:67}$ and Ti_6Al_4V. The arc source was fitted with an extended tubular anode to reduce the number of microdroplets ejected from the cathode depositing onto the substrate surface [2,3]. The arc source was operated at a DC arc current of approximately 135–145 A (electrodes floating) and adjusted to produce a positive ion current of 4 A, measured at the exit of the arc source with a shutter [3]. The substrates used in the study were semiconductor-grade polished (100)-conducting silicon (resistivity, 0.05 Ω cm) and aluminium foil for silicon concentration analysis. The TMS (99.9%; Aldrich) was introduced into the vacuum chamber through a mass flow control valve in which the flow rate could be varied from 0 to 60 sccm. High-purity nitrogen (99.99%) was introduced through a second mass flow control valve and the flow rate adjusted to a constant 28 sccm, producing a total pressure during deposition of 0.8 Pa. The substrate bias was fixed at −150 V DC with respect to the grounded vacuum chamber [3]. The substrate temperature was raised to 350 °C during film growth and was monitored with a J-type thermocouple. The deposition rate was approximately 3 μm h^{-1} and the film thickness typically 1.5 μm.

2.2. Characterization

The composition of the films deposited onto the aluminium foil was measured using Energy Dispersive X-ray Analysis (EDX). X-ray photoelectron spectroscopy (XPS) was performed on selected samples using a Specs SAGE 150 XPS system operated with Mg Kα X-ray source (10 keV and 10 mA). The structure of the films was assessed by X-ray diffraction (XRD) using a Phillips PW 1830 diffractometer operated with a Cu Kα source. The film hardness and elastic modulus were measured with a CSIRO UMIS 2000 indentation instrument fitted with a diamond Berkovich indentor. The optimum indentation load was determined to be 20 mN. The stress in the deposited coatings was determined from the bending of the silicon substrates [9]. Cross-sections were prepared and imaged using a FEI 200×P focused ion beam (FIB) system. Cross-sectional thin foils for transmission electron microscopy (TEM) were also prepared by FIB milling. Details of TEM specimen preparation of coatings in cross-section have been given previously [10].

3. Results

3.1. Si content

Fig. 2 shows the silicon content of the deposited films as measured by EDX as a function of the TMS flow rate. It can be seen that the degree of silicon incorporation increases with the aluminium content of the cathode material. The highest concentration of 18 at.% is seen for $Ti_{0.3}Al_{0.7}$ for a

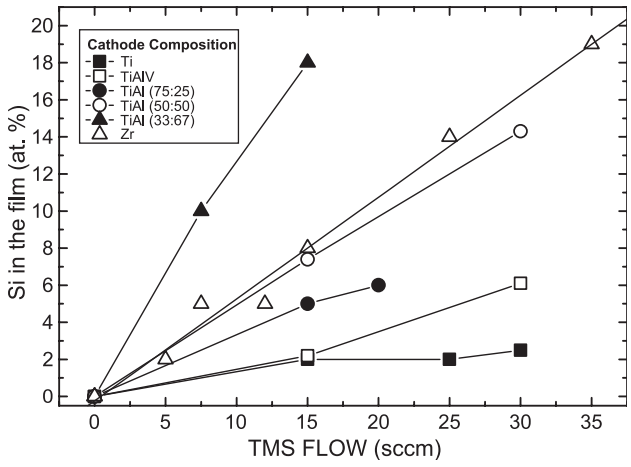

Fig. 2. Silicon content in the deposited films as a function of the TMS flow rate.

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