Topic Area: CMMSP

Synthesis and Characterisation of Titanium Vanadium Nitride Thin Films

M. B. Taylor[1], K. E. Davies[2], B. K. Gan[2], D. R. McKenzie[2], M. M. M. Bilek[2], D. G. McCulloch[1], B. A. Latella[3], P. A. Wilksch[1], M. McPherson[1] and R. A. van den Brink[1].

[1] *Applied Physics, School of Applied Sciences, RMIT University, GPO Box 2476V, Melbourne, 3001, Australia*

[2] *School of Physics, University of Sydney, 2006, Australia*

[3] *Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, 2234, Australia*

E-mail of corresponding author: matthew.taylor@rmit.edu.au

Introduction

Many transition metal nitrides form very hard and wear resistant thin film coatings. Alloying of transition metal nitrides creates the possibility of producing films with even higher hardness and wear resistance. In this paper we look at alloying TiN and VN utilising a dual source pulsed cathodic arc. TiN and VN both form face centred cubic structures, have similar lattice parameters [1] and are completely miscible over the entire range in bulk form [2]. Of interest is the correlation between intrinsic stress, indentation hardness, microstructure and optical properties of $Ti_{(1-x)}V_xN$ films over a range of compositions from $x = 0$ to $x = 1$.

Previous work by Knotek [3] using magnetron sputtering showed that thin films of $Ti_{(1-x)}V_xN$ made using a metal target of 25 atomic percent V and 75 atomic percent Ti showed the best wear resistance in a pin-on-disc test and the highest Vickers microhardness. In this work we vary the ratio of pulses applied to each cathode in the dual source filtered cathodic arc system to change the composition of the resultant film in a controllable manner. In this way, the properties over a range of composition can be evaluated.

In addition to hardness, this work will explore the variations in optical properties of the alloys. Nitrides frequently exhibit attractive colours; for instance, the colour of TiN thin films deposited by plasma immersion ion implantation has been found to vary widely with the conditions of deposition [4]. However, little has been published on the optical properties of the $Ti_{(1-x)}V_xN$ alloy.

Methods

A dual pulsed filtered cathodic arc vapour deposition system, described previously [5], was used to deposit $Ti_{(1-x)}V_xN$ films onto silicon substrates. Pure cathodes of titanium and vanadium were used and the pulse rates of each were varied to control the deposition rate of TiN and VN, and thus control the final composition of the films.

Indentation hardness of the films was measured using the CSIRO Ultra Micro Indentation System (UMIS 2000), configured with a Berkovich diamond tipped indenter. A minimum of five indents was made on each film and the results averaged. In order to minimise the effects of the substrate on the measurements, an indentation depth of less than 25% of the film thickness was used. The intrinsic stress of each film was determined by measuring the change in curvature of the substrate and applying Stoney's equation as outlined elsewhere [6].

Electron microscopy was performed on the films using a Philips SEM 505 at 10kV and a Jeol 2010 TEM, operating at 200kV, equipped with a Gatan Imaging Filter (GIF). EDS was conducted on the samples in the SEM to obtain information on the composition of the samples over a large area. Cross sectional transmission electron microscopy (X-TEM) was performed on samples prepared by tripod polishing and ion-beam thinning. Electron energy loss spectroscopy (EELS) was conducted on the X-TEM samples to confirm mixing of the TiN and VN and to confirm the composition of each film.

Optical properties were measured with a Gaertner L116B ellipsometer, operating at the helium-neon laser wavelength of 633 nm, and at angles of incidence of 50, 60, 65, 70 and 75 degrees. The complex refractive index of each film was derived from the ellipsometric psi and delta values in a fitting procedure that took account of thin-film interference effects, using the film thickness measured by TEM.

Results and Discussion

Table 1 compares the composition found as measured by EDS and EELS with that calculated by the ratio of pulses applied to each target. There was excellent agreement between expected and experimental values. Further electron microscopy on these samples can be found elsewhere [7]. The indentation hardness and stress as a function of composition are presented in Figure 1. The data shows a correlation between the level of intrinsic stress in the film and the indentation hardness. The highest hardness was found with the alloy $Ti_{0.77}V_{0.23}N$, and was significantly higher than 15GPa for untreated TiN reported elsewhere [8]. This composition at which the highest hardness was observed compares well with that found by Knotek [3].

Table 1: Calculated, EDS and EELS compositions of the series

Calculated Composition of Alloy	no. pulses V/Ti	Film Thickness (nm)	atomic% VN Calculated	atomic% VN EDS (± 5%)	atomic% VN EELS (± 5%)
TiN	-	-	0	-	-
$Ti_{0.87}V_{0.12}N$	-	61	12.9	13.3	13.8
$Ti_{0.84}V_{0.16}N$	13/51	76	15.9	18	-
$Ti_{0.77}V_{0.23}N$	20/50	59	22.8	24.2	21.2
$Ti_{0.63}V_{0.37}N$	24/30	69	37.2	36	38.7
$Ti_{0.43}V_{0.57}N$	78/44	68	56.8	52	58.4
$Ti_{0.22}V_{0.78}N$	78/16	63	78.3	78.8	77.4
VN	-	58	100	-	-

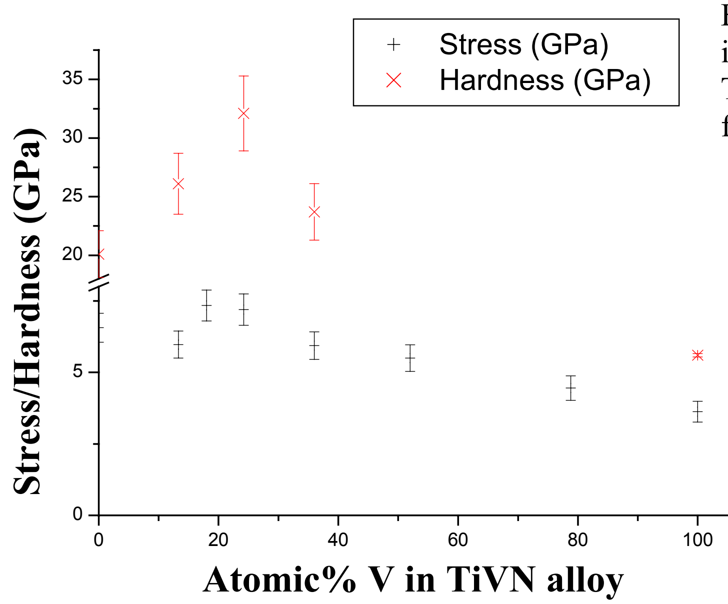

Figure 1: Stress and indentation hardness of $Ti_{(1-x)}V_xN$ alloy films as a function of x

Figure 2 shows the real and imaginary parts of the refractive index plotted against composition for the films. The error bars show the spread of the values over the different angles of incidence. The large imaginary component of the refractive index indicates high absorption. The influence of thin film interference was found to be slight.

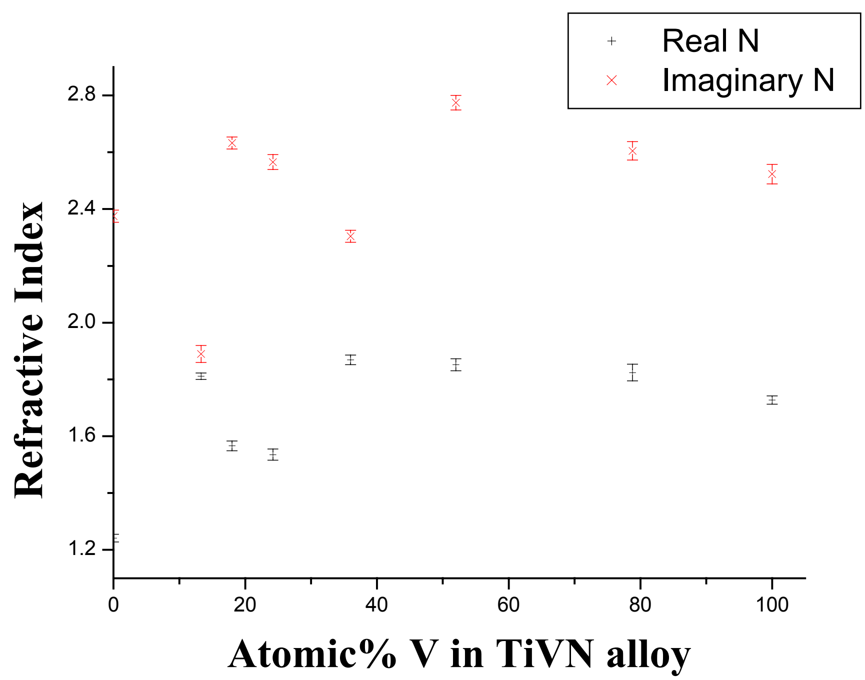

Figure 2: Real and imaginary parts of the complex refractive index measured by ellipsometry

The observed variation of the refractive index with composition is not simple. Samples were cleaned and measurements repeated to see if surface contamination had occurred, but results before and after cleaning were very similar. There is an indication of large changes in refractive index at small concentrations of VN, around the peak of stress and hardness, with a levelling out of the variations at large VN. These changes were found to be consistent over a number of measurements. The properties of the pure TiN film are consistent with measurements on other TiN samples made at this laboratory [4].

Conclusion

In this work, we show that a dual source pulsed cathodic arc can be used to generate alloys of TiVN with controllable compositions. The composition of $Ti_{0.77}V_{0.23}N$ showed the highest intrinsic stress and the highest hardness. Optical properties varied significantly with composition, but not in a simple way: the dependence was found to be very strong in the region from 0% to 40% VN.

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