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# Multilayer composite ceramic-metal thin film: Structural and mechanical properties

Sharmistha Anwar, Shahid Anwar*

*CSIR – Institute of Minerals and Materials Technology, Bhubaneswar 751013, Odisha, India*

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## ABSTRACT

Multilayer coatings with combination (10 BL, 20 BL and 30 BL) of transition-metal nitride (tungsten nitride, $W_2N$) and ductile interlayers (Ti, Ni) were deposited by reactive DC magnetron sputtering technique on silicon substrates. Structural and mechanical properties of the deposited samples were analyzed by grazing incidence X-ray diffraction (GIXRD), field emission scanning electron microscope (FESEM), energy dispersive X- ray analysis (EDX) and nanoindentation tests. GIXRD result confirms the presence of cubic $W_2N$ phase. FESEM image shows periodic arrangement of $W_2N$ and (Ti, Ni). Mechanical parameters like hardness, elastic modulus and resistance to plastic deformation were calculated. The effect of different factors e.g. ceramic/ metal ratio, interlayer material and interface on mechanical properties were discussed. These results indicate that these factors play a dominant role in defining mechanical properties. The best mechanical properties were observed for 20 BL in comparison with 10 BL and 30 BL coating and has been attributed to higher ceramic to metal thickness ratio.

## 1. Introduction

Protection of materials by applying hard coatings over it is one of the important and versatile application. Its improving component performance by reducing friction, increasing wear resistance, lifetime and hardness of coated cutting tools have shown improved behavior than uncoated tools. Better adhesion to the substrate, which is a fundamental requirement for coating applications, is a result of good toughness of the coating. [1] Wear resistance, the consequence of the favorable combination of hardness with toughness, which is very difficult to obtain with a single layer coating. The low toughness of hard ceramic coatings can be improved by incorporation of a ductile layer in between them. Multilayer concept, the deposition of alternate layers of different materials, has recently been paid much attention due to its enhanced mechanical properties. [2,3] In multilayered coatings strain hardening generally occurs when dislocations slip and interact in a single layer and higher stresses are required to transfer them into the other layer. Hardness is affected by several factors, like the thickness of the metal layer and the thickness ratio between ceramic and metal layers. There are several explanations for enhancement of hardness in multilayer coating like dislocation blocking by layer interfaces and change in the elastic properties of the different layers. [4] A dislocation while moving along a material, encounters with an energy barrier at the interface between a layer with alternative layers of lower and higher elastic modulus. As a consequence, in a multilayered structure, the movement of dislocations and propagation of cracks can be strongly reduced, resulting in increased wear resistance of the coating. A number of transition metal based multilayer combinations, like metal/metal, ceramic/metal and ceramic/ceramic have been recently investigated. [2,5–9] Physical vapor deposition techniques are favored to deposit such hard multilayer coatings; in particular, magnetron sputtering is an effective tool to fabricate the multilayer due to its versatility. [4–6] The sputtering technique has advantages over other deposition techniques like better adhesion, good line of sight, less contamination with improved crystallinity of deposited sample resulting in a good quality film. One of the main advantages of sputter deposition is that even materials with high melting points are easily sputtered. Various reports are presented in the literature that multilayer films composed of ceramic and metal layers show superior mechanical properties such as high hardness, adhesion, toughness, etc. [10] It is suggested that this improvement is due to following mechanisms (or a combination): crack deflection due to weak interfaces, or differences in elastic modulus of individual layer materials, favourable gradients in residual stresses, and deformation in combination with strong interfaces, crack deflection and reduced bending stress under load in the stiffer layers, compared to single layer. [10]

Transition metal nitrides based ceramic material e.g. tungsten nitride has important properties like low thermal expansion coefficient, good electrical and thermal conductivity with a high melting point. [11–13] WN has three phases $W_2N$ (FCC), WN (hexagonal), $WN_2$

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* Corresponding author.
*E-mail address:* shahid@immt.res.in (S. Anwar).

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(rhombohedral), among which $W_2N$ is the most stable phase. The ductile metal layer chosen were titanium and nickel. This choice was made in order to study the ceramic to metal thickness ratio effect on mechanical properties of multilayer coatings with same ceramic layer and two different metallic interlayers. Parameters like the number of layers, periodic thickness, total thickness and relationship between the thicknesses of the two deposited materials have shown interesting properties of multilayer coatings. [14] The atomic displacements are the source of internal stress near a dislocation. The stress fields that result from the compressive and tensile forces around different dislocations interact with one another. Experimentally, it was also observed that in various ceramic-metal multilayer systems, the hardness, corrosion resistance, adhesion of metal substrate can be significantly improved, when the modulation period or metal interlayer approaches to very low thickness (few nanometres).

In our study, two sets of ceramic metal multilayer thin films were deposited on Si (100) by reactive DC magnetron sputtering technique with the different metallic interlayers. We have deposited total six samples of 10 BL, 20 BL and 30 BL with titanium and nickel as metal interlayer was deposited. During deposition we had varied the individual thickness of the layers in such a way that the thickness of all the overall multilayers are same. This work was aimed to study the effect of different factors like geometrical factor (ceramic layer to metallic layer thickness ratio), interlayer material and interface on the microstructural and mechanical properties of multilayer coatings.

## 2. Experimental

$W_2N/Ti$ and $W_2N/Ni$ multilayers were deposited on single crystalline Silicon (100) substrates in ultra-high vacuum using DC sputtering unit (Minilab Deposition System) with Model ES60A supplied by Moorfield, UK. Sputtering was carried out in grounded substrate bias condition. Prior to deposition substrates were cleaned properly with soap solution and then ultra-sonicated in alcohol and distilled water for 10 min each. The sputtering chamber is equipped with four targets of 50 mm diameter each. Magnetrons were fixed at an angle of 20° with substrate normal. Three targets of tungsten (W), nickel (Ni) and titanium (Ti) of 50 mm diameter with 99.999% purity were used for sputtering. During the deposition process, Ar (99.999%) gas was introduced into the chamber at a constant flow rate of 20 sccm for all the samples with nitrogen as a reactive gas with a flow rate 5 sccm. Optimization study of tungsten nitride such as the partial pressure of nitrogen, substrate temperature, and the power has been extensively investigated in our previous work [15]. In order to optimize the $N_2$ flow rate, it was varied as 5, 10, 15, 20 and 25 sccm, with a constant argon flow rate of 20 sccm at 150 W of sputtering target power. Among which 20:5 flow rate was found to be the best for the formation of $W_2N$ phase. Such optimization of $W_2N$ phase was given elsewhere [15]. The partial pressure of $N_2$ was 0.12 Pa and for Ar, it was 0.48 Pa. Prior to deposition, the targets were sputter cleaned for 5 min each with shutter closed condition in order to prevent contamination. Details of deposition parameters are given in Table 1. Rotation of substrate holder was controlled in order to maintain the uniformity of films. A set of three samples (10 BL, 20 BL and 30 BL) with Ti interlayer was deposited for a constant time of 400 min only by varying the number of bilayers. With the same geometrical arrangement, another set was deposited with Ni as the ductile layer. For better adhesion of the coating with the substrates, a seed layer of Tungsten nitride was coated for 10 min each. The overall thickness of 10 BL, 20 BL and 30 BL were kept almost same by varying the individual layer deposition corresponding to the number of bilayers. A series of 10 BL, 20 BL, and 30 BL was deposited. Thus in this work, we have kept total deposition time constant for each sample with varying individual layer deposition time. Detail descriptions of samples are given in Table 2.

**Table 1**
Deposition parameters of $W_2N/Ti$ and $W_2N/Ni$ multilayer.

| | $W_2N/Ti$ | $W_2N/Ni$ |
|---|---|---|
| Substrate rotation | 4 rpm | 4 rpm |
| Substrate temperature | 150 °C | 150 °C |
| Working pressure | $6.1*10^{-3}$ mbar | $6.1*10^{-3}$ mbar |
| Base pressure | $4*10^{-6}$ mbar | $6*10^{-6}$ mbar |
| Argon flow rate | 20 sccm | 20 sccm |
| Nitrogen flow rate | 5 sccm | 5 sccm |
| W power density (DC) W/cm$^2$ | 7.397 | 7.397 |
| Metal (Ti/Ni) power density (DC) W/cm$^2$ | 3.698 | 3.452 |
| Deposition time | 400 min | 400 min |
| Substrate bias | Grounded | Grounded |

**Table 2**
Description of samples.

| Sample | $W_2N/Ti$ | $W_2N/Ni$ |
|---|---|---|
| **1** | 10 BL (267:35) nm | |
| **2** | 20 BL (138:15) nm | |
| **3** | 30 BL (85:12) nm | |
| **4** | | 10 BL (251:65) nm |
| **5** | | 20 BL (115:25) nm |
| **6** | | 30 BL (69:20) nm |

## 3. Characterizations

Phase analysis of deposited samples was performed by GIXRD, using a D8 Advance *X*-ray diffractometer equipped with a Cu–$K_\alpha$ source. Cross-sectional images were taken by Zeiss Olympus FESEM, attached with an EDS microprobe. Elemental analysis was carried out by energy dispersive *X*-ray analysis (EDX). Mechanical parameters were evaluated since the mechanical properties of hard coatings are significant criteria for their use in practical applications. Hardness and elastic modulus data of the multilayers were obtained by using UMIS Nano-indention system (Frisher Cripps, Australia), employed with a Berkovich diamond indenter with face angle 65.3° and tip radius 150 nm. Indentations were made on the film surface. To measure the hardness and elastic modulus of deposited films Oliver–Pharr method was used [15]. Load-displacement data were obtained during loading and unloading. A typical loading vs unloading curve is shown in Fig. 1. In the plot, $P$ is the applied load, $h$ is the indention depth, $h_{max}$ is the maximum indentation depth and $P_{max}$ is the maximum applied load. From the loading

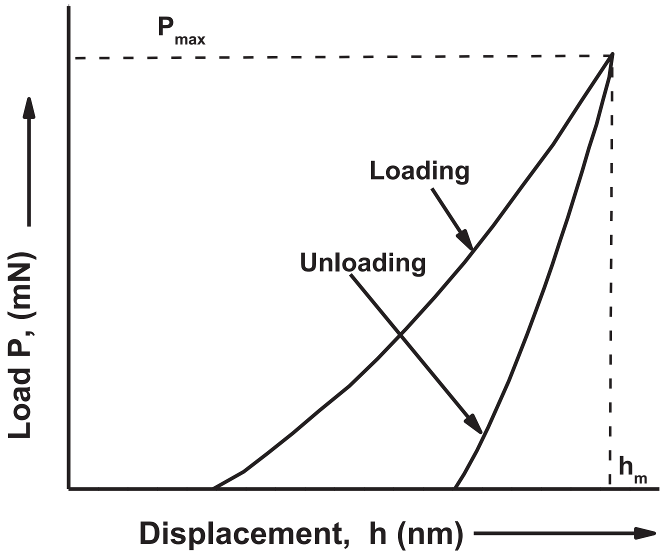

**Fig. 1.** Typical loading unloading plot during nanoindentation test.