JOURNAL OF MATERIALS SCIENCE 35 (2000) 2689–2693

Preparation and characterization of superhard TiC/Mo multilayers

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Nanometer scale TiC/Mo multilayers have been prepared by ion beam assisted deposition (IBAD) at nearly ambient temperature. The modulation wavelength was in the range of 2 nm to 14 nm and the individual layer thickness was maintained to be equal. Two series (series A and series B) were prepared which were bombarded with different bombarding energy (0 eV and 50 eV) in order to investigate the bombardment effect on the nano-hardness of the multilayers. Low angle X-ray diffraction (LXRD) was used to analyzed the layered structure of multilayers. Mechanical properties of these multilayers were thoroughly studied using a nanoindentation facility. The nanohardness showed a strong dependence on the sharpness of the interlayer and the modulation wavelength. It was found that the multilayer hardness was greater than the volume weighted mean of the component hardness. With the modulation wavelength adjusted, the multilayer can be even harder than its hard component (TiC). A maximum hardness of 47.62 GPa, about 1.5 times larger than that of the TiC values, was found at $\lambda = 8$ nm multilayer deposited without ion beam bombardment. It was also found that the films without ion bombardment were much harder than those bombarded by 50 eV Ar^+ ion beam.

1. Introduction

There has been a great deal of interest regarding the mechanical properties of artificially multilayered thin films. A few publications have indicated that multilayer coatings may be superior to single layer coatings for some applications. It has been reported that larger increases in hardness and strength can be achieved in both nitride and metallic multilayer coatings [1–3]. For example, increase in the hardness values to more than twice those of homogeneous nitrides has been observed in transition-metal nitride multilayers such as TiN/NbN and TiN/VN, in both single crystal and polycrystalline forms [1, 4, 5]. However, little work on nanoscale metal/ceramic multilayers has been reported [6–8], while many investigations concentrated on metal/ceramic multilayered coatings covering periodic thickness into the micrometer range [9, 10]. As we know, nanometer materials have many unique properties due to the great amount of interfaces. The property of nanometer multilayers can be quite different from that of micron level multilayers even if they have the same component proportion.

In this paper, we prepared nanoscale multilayers of a hard component TiC with a soft component Mo using IBAD system at ambient temperature. IBAD is a combination of ion implantation and physical vapor deposition. The aim of this work was to investigate the influence of ion bombardment on the structural and mechanical properties of TiC/Mo nanoscale multilayers. During deposition, we used Ar^+ ions with different energy to bombard the multilayers in order to alter the sharpness of the interlayer of TiC/Mo multilayers. Mechanical properties of these multilayers with and without ion beam bombardment were thoroughly studied as well as the structures inside the multilayers. Both series exhibited substantial hardness enhancement over rule-of-mixture values over the investigated range of λ. A maximum hardness of 47.62 GPa, about 1.5 times larger than that of the TiC values, was found at $\lambda = 8$ nm multilayer deposited without ion beam bombardment. It was also found that the nano-multilayered films without bombardment were much harder than those bombarded by 50 eV Ar^+ ion beam.

2. Experimental procedure

TiC/Mo multilayers were prepared by an IBAD system which has been described elsewhere [11, 12]. The base vacuum of the equipment was 3×10^{-4} Pa. Film deposition was performed at about $(1.0–1.2) \times 10^{-2}$ Pa. Single crystal Si (111) wafer was used as the substrate to the film, which was cleaned with acetone and methanol, and then etched in a 20% HF solution prior to loading inside the chamber. Prior to deposition, the substrates were cleaned by Ar^+ bombardment with an energy of 3 KeV and beam density of 127 uA cm^{-2} for 10 min.

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TiC layers were synthesized by Ar^+ ion beam sputtering of a Ti/C composite target which had been adjusted to produce stoichoimetric TiC. Mo layers were deposited by Ar^+ ion beam sputtering of an elemental molybdenum target. The typical film growth rates were 3 nm/min for TiC and 6.7 nm/min for molybdenum. Multilayers were obtained by alternating deposition of TiC and Mo. The thicknesses of TiC and Mo individual layers, denoted l_{TiC} and l_{Mo}, respectively, were maintained to be equal by controlling the deposition time. In the work reported here, some multilayers were prepared at a relatively low Ar^+ ion beam bombardment with ion energy of 50 eV in order to investigate the bombarding effect on the layered structure and the nanohardness. All multilayers were about 300 nm thick.

The layered structures of TiC/Mo multilayers were examined by low-angle X-ray diffraction (LXRD), which was performed by a Rigaku D/max-RB diffractometer. The operating voltage was 40 kV, and the tube current was 100 mA. The multilayer wavelength was calculated by measuring the angle θ of the low angle peaks, and using Bragg's equation, $n\Lambda = 2\lambda \sin\theta$, where n is the order of the peak, λ is the multilayer period, and Λ is X-ray wavelength.

The mechanical properties of multilayered TiC/Mo films, as well as homogeneous TiC and Mo films, were investigated using the nanoindentation facility. At least five indents were made on each sample. The spacing between indents was 50 um. In order to avoid the substrate effects [13], the load used in the hardness measurement was chosen to be sufficiently small (5 mN) so that the penetration depth was less than 20% of the total thickness of the films.

3. Results

3.1. X-ray diffraction

The architecture of the multilayers can be examined by low angle X-ray diffraction (LXRD) analysis. Fig. 1a and b show LXRD patterns obtained from TiC/Mo nanometer multilayers with and without Argon ion beam bombardment respectively. It can be seen clearly that higher order diffraction peaks were observed in the samples without ion bombardment than that bombarded by 50 eV Ar^+ ion beam, indicating a well-defined composition modulation.

XRD analyses were used to study the phase structure of TiC/Mo multilayers. It can be seen from Fig. 2 that in both series, policrystalline TiC and Mo layers were formed and textures existed in TiC and Mo layers. From the above XRD spectra, we can summarize that there was no apparent difference between the two series in the phase structure.

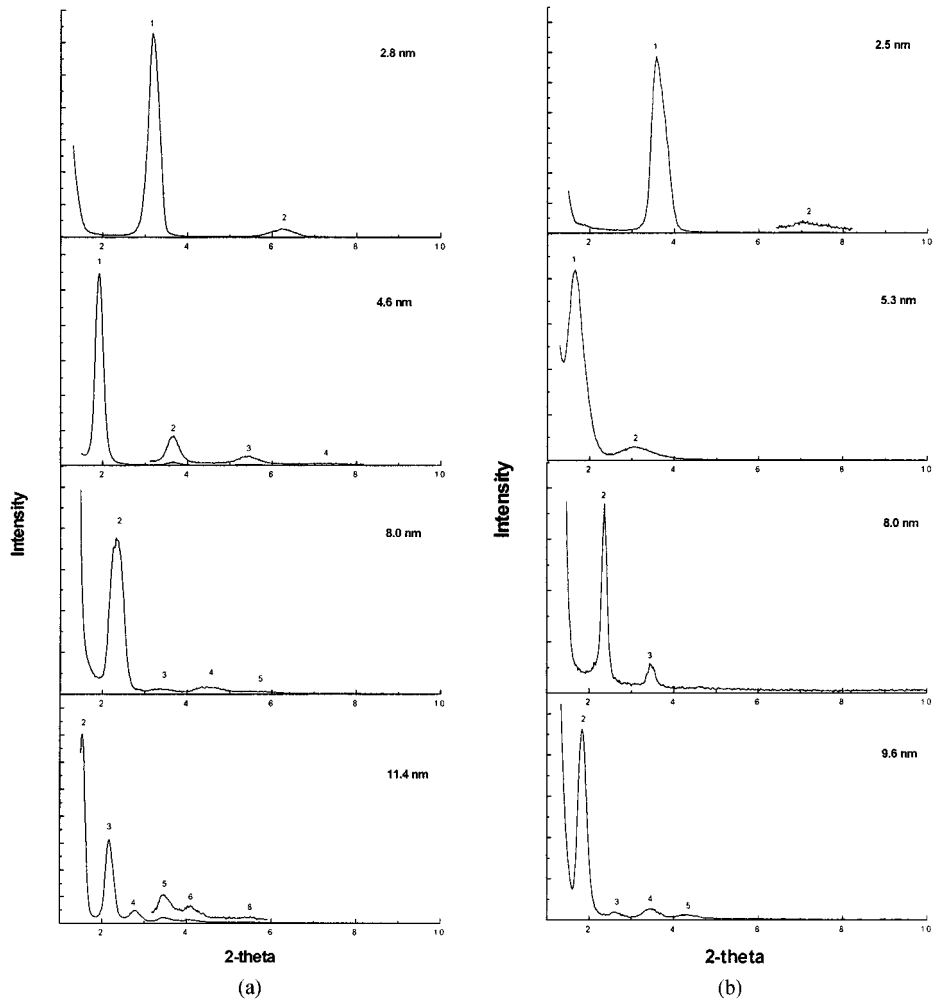

Figure 1 Low angle XRD (LXRD) patterns for TiC/Mo multilayered films, (a) without bombardment; (b) bombarded by 50 eV Ar^+ ion beam.

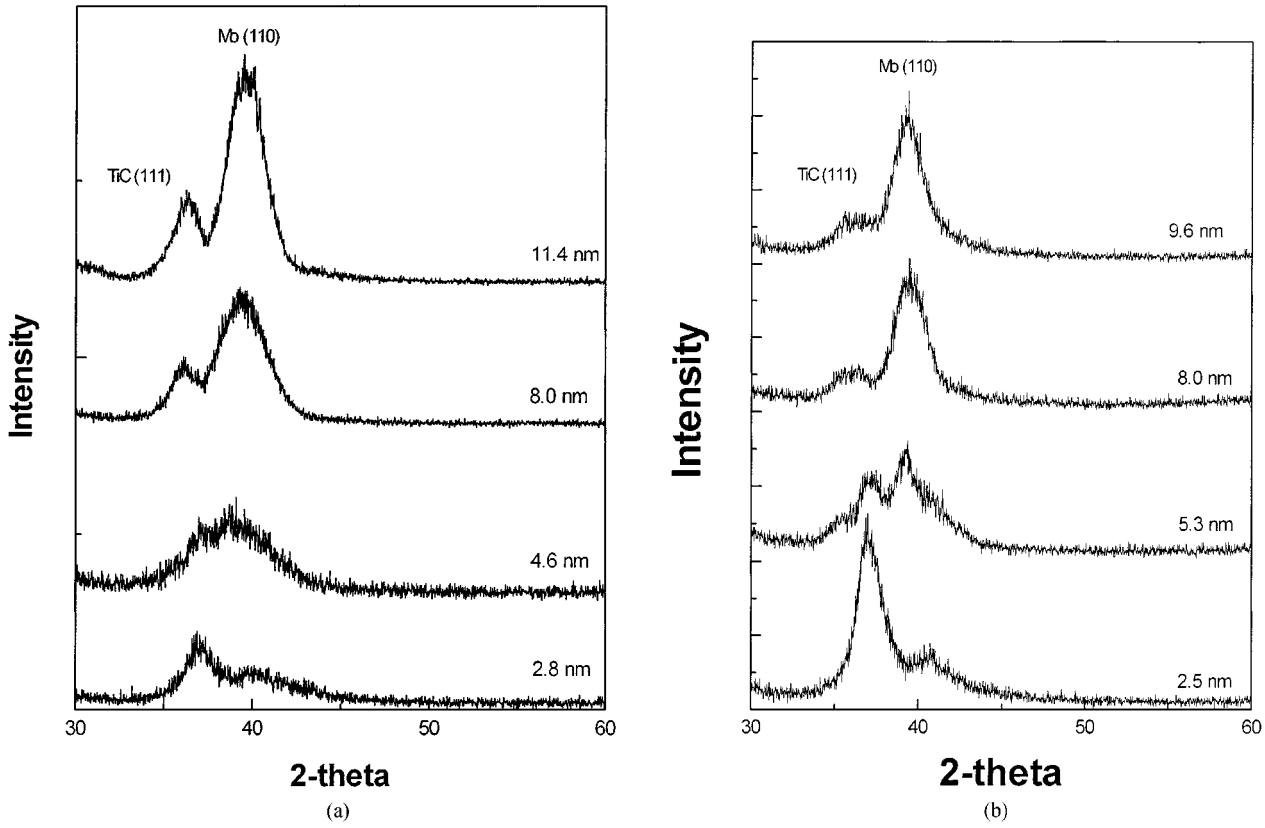

Figure 2 High angle XRD patterns for TiC/Mo multilayered films, (a) without bombardment; (b) bombarded by 50 eV Ar^+ ion beam.

TABLE I Hardness and elastic moduli of TiC/Mo multilayers

Sample number	λ (nm)	Hardness (GPa)	Elastic modulus (GPa)
A1	2.8	27.2	158.0
A2	4.6	32.7	148.7
A3	8.0	47.6	156.3
A4	11.4	36.7	164.9
A5	13.7	25.4	154.6
B1	2.5	21.4	158.0
B2	5.3	19.2	160.2
B3	8.0	18.2	181.1
B4	9.6	16.8	170.6
B5	13.7	12.4	145.9
TiC	—	18.5	138.3
Mo	—	3.0	184.5

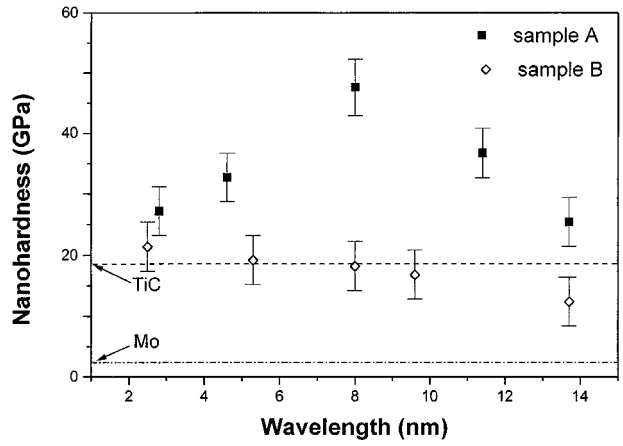

Figure 3 Hardness of TiC/Mo multilayred films as a function of bilayer thickness.

3.2. Hardness measurements

The nanohardness of TiC/Mo multilayers with and without ion bombardment are summarized in Table I. The hardness of pure TiC and Mo films are 3.0 and 18.5 GPa, respectively. The nanohardness of the multilayered films with different periods as a function of bilayer thickness is shown in Fig. 3. As can be seen, all the films displayed an increase in hardness over the rule-of-mixtrues values. The film with a multilayer thickness of 8.0 nm without ion bombardment gave almost 150% increase over the homogeneous hard component (TiC).

It is indicated that the multilayer hardness has a strong dependence on the sharpness of the interlayers. All the nano-multilayered films without ion bombardment were much harder than those bombarded by 50 eV Ar^+ ion beam.

It can be found that the wavelength arrangement also has much influence on the multilayer hardness. It can be seen from Fig. 3 that when λ is increasing from 2.8 to 8.0 nm, the hardness of the multilayer without ion bombardment steadily increases with the increasing multilayer wavelength. After reaching a maximum, it decreases with further increase the multilayer wavelength.

3.3. Elastic moduli measurements

The elastic moduli of pure TiC and Mo films are 184.5 and 138.3 Gpa, respectively. Elastic moduli of the multilayers as a function of bilayer thickness are given in

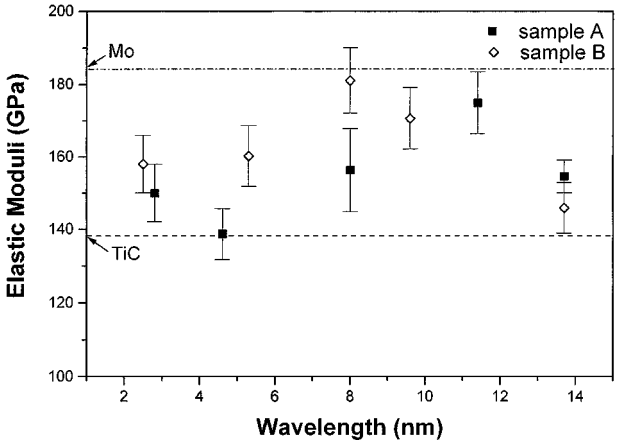

Figure 4 Elastic modulus of TiC/Mo multilayed films as a function of bilayer thickness.

Fig. 4. Within the accuracy of the measurement, there was no large difference from the volume weighted mean of the elastic moduli of the two components with different modulation wavelength. This agrees well with several recent results [14–16].

4. Discussion

In Fig. 3, it is observed that the TiC/Mo nanoscale multilayers exhibited hardness enhancements over rule-of-mixture values. For the series without ion bombardment, when λ is increasing from 2.8 to 8.0 nm, the multilayer hardness steadily increases with the increasing multilayer wavelength. After reaching a maximum, it decreases with further increase the multilayer wavelength. The highest hardness was observed to be 1.5 times greater than the hard component (TiC) with the multilayer wavelength about 8.0 nm.

It is possible therefore to understand the enhanced hardness behavior as owing to dislocation pinning mechanism as analogous to grain boundary hardening found in polycrystalline materials [17]. In the nanoscale multilayers, interfaces can limit dislocation motion. So introduction of interfaces can weaken the multilayer deformability, thus increasing its hardness. When individual layer thickness is decreased, more interfaces will be produced in the multilayer. Consequently, the multilayer is likely to exhibit a high hardness. On the other hand however, if the individual layer is too thin, it forms either a discontinuous layer or a weakly interbonded one. Both the interface strength and the layer's intrinsic strength are weakened. As a result, the multilayer will show a decrease in hardness. The two factors simultaneously exert influences on the multilayer hardness. Their competition accounts for the hardness behavior of TiC/Mo multilayers when individual layer thickness arrangement varies.

From the above results, we can draw another conclusion that the multilayers without ion bombardment are much harder than those bombarded by 50 eV argon ion beam. High angle XRD analyses showed that there is no apparent difference between the two series. So the different mechanical properties must come from the different interlayer structure induced by the bombardment effect. From LXRD results, we can see clearly that the nanoscale multilayers without argon bombardment have sharper interlayers than those bombarded by ion beam. When the multilayer wavelength is in the range of nanoscale, low energy bombardment may lead to severe mixture of the two nanolayers and the multilayer hardness will reduce.

5. Conclusions

TiC/Mo multilayers were prepared using IBAD method. Nanoindentation experiments were performed to study the structural and mechanical characteristics as a function of multilayer wavelength and bombarding energy. No elastic anomalies characteristic of the supermodulus effect were seen, but enhancements in the hardness were observed. It was found that the multilayer hardness was greater than the volume weighted mean of the component hardness. With the modulation wavelength adjusted, the multilayer was even harder than its hard component (TiC). A maximum hardness of 47.6 GPa, about 1.5 times larger than its hard component (TiC), was found at $\lambda = 8.0$ nm sample without ion bombardment. It was suggested that these enhancements could be understood as owing to an interphase boundary hardening mechanism analogous to grain boundary hardening found in polycrystalline materials. Another conclusion was that when the multilayer wavelength was in the range of nanoscale, the ion bombardment can alter the sharpness of the interlayers, lead to severe mixture effect, and reduce the hardness.

Acknowledgement

This project was supported by Natural Science Foundation of China (NSFC No.59832070).

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Received 29 July
and accepted 13 December 1999