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Microstructures and properties of Si_3N_4/TiN ceramic nano-multilayer films①

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Abstract: The polycrystalline Si_3N_4/TiN ceramic nano-multilayer films have been synthesized on Si substrates by a reactive magnetron sputtering technique, aiming at investigating the effects of modulation ratio and modulation period on the microhardness and to elucidate the hardening mechanisms of the synthesized nano-multilayer films. The results showed that the hardness of Si_3N_4/TiN nano-multilayers is affected not only by modulation period , but also by modulation ratio. The hardness reaches its maximum value when modulation period equals a critical value λ_0, which is about 12 nm with a modulation ratio of 3∶1. The maximum hardness value is about 40% higher than the value calculated from the rule of mixtures. The hardness of nano-multilayer thin films was found to decrease rapidly with increasing or decreasing modulation period from the point of λ_0. The microstructures of the nano-multilayer films have been investigated using XRD and TEM. Based on experimental results, the mechanism of the superhardness in this system was proposed.

Key words: Si_3N_4/TiN; multilayer films; micro hardness; micro structures **Document code**: A

1 INTRODUCTION

In recent years, ceramic superhardness compositionally-modulated multilayer films have been actively investigated. The results showed that multilayers can combine the properties of the constituent materials and have more excellent properties than the single-layer film. Multilayers with optimized interface areas seem to be most promising with respect to an optimum hardness-to-toughness ratio[1~5]. Especially in ceramic nano-multilayer films, it has been attracting attention because the hardness of films exhibits maximum value, that is, so-called superhardness effects. There are several theoretical explanations for hardness anomaly effects[6~10], which are the Brillouin zone-Fermi surface interaction model, the interfacial coherent strain model and the theory of dislocation generation and movement. There are still significant deviations between the experimental results and the theories and more detailed research work needs to be done in order to well understand the superhardness effects[11]. It has potential technological application and theoretical significance to study on new kinds of superhardness nano-multilayer films.

So far no results are reported about PVD Si_3N_4/TiN nano- multilayers. In this paper, a new kind of Si_3N_4/TiN nano-multilayers has been fabricated by reactive magnetron sputtering process. The effects of modulation periods and modulation ratio on microhardness values have been investigated. The mechanisms of superhardness in this system were proposed.

2 EXPERIMENTAL PROCEDURE

The polycrystalline Si_3N_4/TiN ceramic nano-multilayer films were deposited using SPC-350 magnetron sputtering system. The sputtering targets were pure Si and Ti mounted on each of the r.f. cathodes. A mixed Ar-N_2 gas was used for reactive sputtering with Ar pressure of $(4.0\sim5.0)\times10^{-1}$ Pa and a N_2 partial pressure of $(0.1\sim1.0)\times10^{-1}$ Pa. Ground and

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polished single-crystal Si wafers were used as deposition substrates. They were ultrasonically cleaned in chemical solvents before being mounted on the substrate holder in the chamber. Compositionally-modulated structures were obtained by rotating the substrate holder, letting samples face Si and Ti targets. The different modulation periods and modulation ratios were obtained through exactly controlling the stopping times in front of Si and Ti targets. The source power of each target was 200 W. The total thickness of multilayer films were 2.0 μm. The substrates were not heated during deposition and their temperature was below 70 ℃.

The hardness of multilayer films was measured for 15 s at load of 0.245 N by using MM-6 microhardness tester. A Knoop diamond tip indenter was used. The crystal structure of multilayer films was determined by X-ray diffraction (XRD) in D/max-3A diffractometer with CuKα radiation. The JEM-200CX transmission electron microscope was used to study cross-sectional microstructure of samples.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

Low-angle X-ray diffraction (XRD) pattern of Si_3N_4/TiN multilayers with modulation period $\lambda = 7.5$ nm and modulation ratio $l_{Si_3N_4}/l_{TiN} = 3$ was shown in Fig. 1. The low-angle XRD can provide information of the interface state of short-period multilayer films. The characteristic interface sharpness can be estimated by $\lambda/(4n_{max})$, where n_{max} is the highest order of the observed low-angle peaks[10]. From Fig. 1, it is clear that the interface of Si_3N_4/TiN is sharp. The results of high-angle XRD showed that the crystal structure of single-layer TiN was cubic with (111) textures and single-layer Si_3N_4 was β-Si_3N_4 nano-polycrystalline structure or amorphours structure.

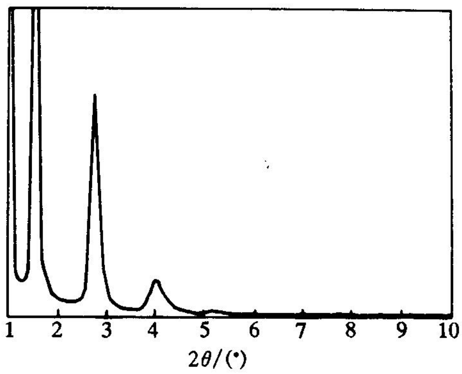

Fig.1 X-ray small angle diffraction scans of Si_3N_4/TiN nano-multilayers

The high-angle XRD patterns of Si_3N_4/TiN nano-multilayers with diffrent modulation periods at modulaton ratio $l_{Si_3N_4}/l_{TiN} = 3$ were shown in Fig. 2. The 2θ peak position of TiN (111) was shown variating with the change of modulation periods. The 2θ tends to increase with the decreasing of λ and reaches its maximum value at the range of $\lambda = 7.5 \sim 16.3$ nm. Then 2θ tends to decrease with the decreasing of λ. It is indicated that the TiN (111) lattice plane spacing in multilayers has a relation with the modulation period (λ).

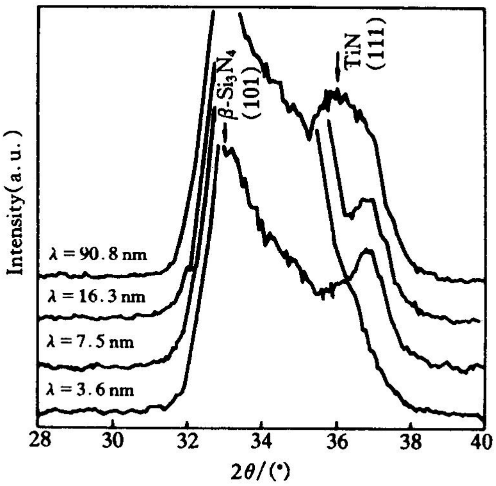

Fig.2 High-angle X-ray diffraction of Si_3N_4/TiN nano-multilayers with different modulation periods

3.2 Transmission electron microscopy study

Fig. 3(a) is the bright-field cross-sectional transmition electron micrograph of Si_3N_4/TiN multilayers. The modulation structures is clearly shown, where TiN layers are bright and Si_3N_4 layers are grey. The interface is very sharp and plain, which is coincident with the results of low-angle XRD. Fig. 3 (b) is a cross-sectional TEM diffraction pattern of Si_3N_4/TiN multilayers with $\lambda = 16.3$ nm and $l_{Si_3N_4}/l_{TiN} = 3$. The polycrystalline circles are cubic crystal for TiN layers. Si_3N_4 layers did not show crystal diffraction patterns. Based on the results of high-angle XRD, it may be considered that Si_3N_4 layers were mainly amorphous structure.

3.3 Microhardness

Fig.4 shows the microhardness values of Si_3N_4/TiN multilayers as a function of modulation periods with $l_{Si_3N_4}/l_{TiN} = 3$. The hardness values of single-layer TiN and Si_3N_4 films were 23.13 GPa and 22.42 GPa, respectively. In Si_3N_4/TiN multilayers, hardness values increase with the decreasing of modulation periods. Hardness reaches its maximum value at a critical modulation period λ_0, which is about 16.3 nm. The maximum hardness value is about 37.00 GPa. Then with the decrease of λ, the hardness values also rapidly decrease. At $\lambda = 3.6$ nm, hardness is equal to 22.50 GPa. The maximum hardness value is about 40% higher than the value calculated from the rule of mixtures. When modulation ratio $l_{Si_3N_4}/l_{TiN} = 1$, the hardness values increase slightly with the modulation periods decreasing. The superhardness effect did not occur till modulation period $\lambda = 5.0$ nm.

Helmersson *et al*[6] considered that there may be at least two reasons for explaining the hardness anomalies observed in TiN/VN and TiN/NbN ceramic multilayers. One is related to the generation and motion of dislocations, the other might a supermodulus effect. After having researched the lattice-matched single-crystal $TiN/V_{0.6}Nb_{0.4}N$ superlattices, Mirkarimi *et al*[7] proposed that coherency strains do not play the major role in enhancing the hardness of these nitride superlattices. In Si_3N_4/TiN nano-multilayers, the variational tendency of hardness with the change of modulation period is different at different modulation ratio. When modulation ratio $l_{Si_3N_4}/l_{TiN} = 3$, there is superhardness effects. Hardness had a maximum value at $\lambda =$ 16.3 nm or so. When layer thickness ratio $l_{Si_3N_4}/l_{TiN} = 1$, there is only small hardness enhancement with the decrease of λ. No hardness anomalous effects have been found. Hence the mechanism of dislocation generation and motion does not play a main role in the hardness anomalous effects of Si_3N_4/TiN nano-multilayers at

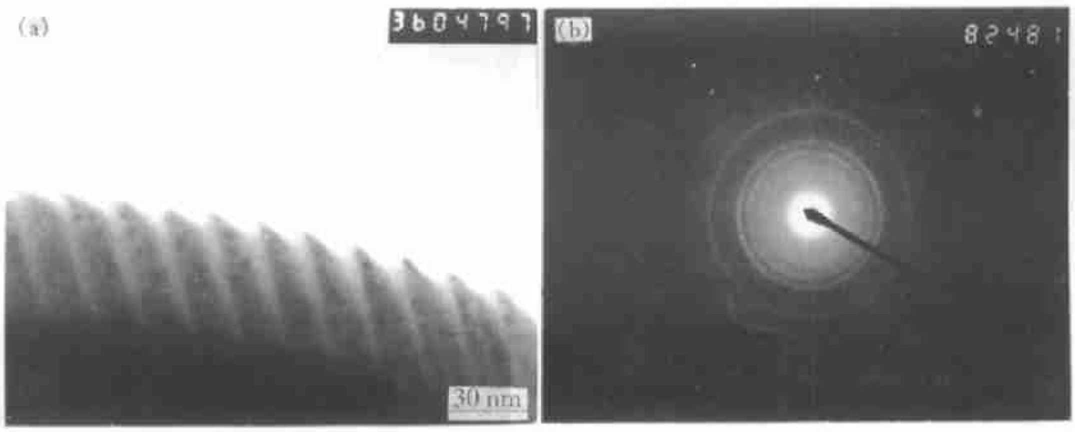

Fig.3 TEM bright-field cross-sectional image and electron diffraction pattern of Si_3N_4/TiN multilayer with period $\lambda = 16$ nm and $l_{Si_3N_4}/l_{TiN} = 3$

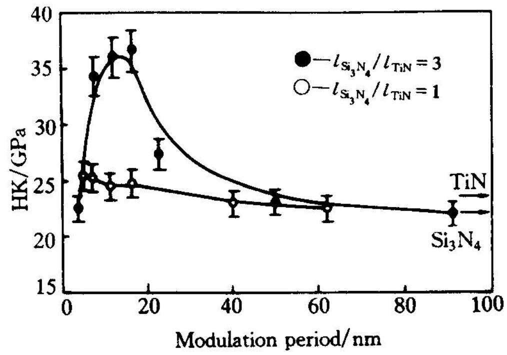

Fig.4 Knoop microhardness of Si_3N_4/TiN nano-multilayers with modulation ratio 3 and 1 as a function of the modulation period λ

layer thick ratio $l_{Si_3N_4}/l_{TiN}=3$.

The above experimental results indicate that modulation ratio has strong effect on the hardness change. Comparing Fig. 2 and Fig. 4, we can find that the variation tendency of TiN(111) peak positions with modulation periods is the same as that of hardness with modulation periods. The peak positions and hardness increase with the increasing of modulation periods till maximum values, and then decrease with further increase of λ. The modulation period of the maximum hardness value is the same as the modulation period of maximum 2θ value. Based on the experiment results, we can concluded that hardness of Si_3N_4/TiN nano-multilayers is related to lattice spacing of TiN (111). The stress state of multilayers at different modulation ratio may contribute to the hardness anomalies. Further work is performing in our laboratory related to the sources of the stresses and the relationships between the stress and the hardness value. Mechanism of hardness anomalies of Si_3N_4/TiN nano-multilayers with $l_{Si_3N_4}/l_{TiN}=3$ can thus be primarily explained as follows:

(1) When modulation period is longer, the main reason of hardness enhancement with decreasing λ is the action of interface stresses, which leads to the hardness anomalies.

(2) When λ is smaller than λ_0, the reason of hardness decreasing is because the TiN layer is too thin. Interface effects lost due to composition intermixing between Si_3N_4 and TiN layers.

4 CONCLUSIONS

(1) The polycrystalline Si_3N_4/TiN ceramic multilayers were synthesized by reactive magnetron sputtering technique. TiN layer has a cubic crystal structure and Si_3N_4 layer is amorphous in Si_3N_4/TiN ceramic multilayers. The Si_3N_4/TiN interfaces are plain and sharp.

(2) Superhardness effects were found in Si_3N_4/TiN multilayers with modulation ratio $l_{Si_3N_4}/l_{TiN}=3$. The maximum value of hardness is about 40% higher than the value caculated from the rule of mixtures. The superhardness effect was absent in this system when the modulation ratio $l_{Si_3N_4}/l_{TiN}$ equals one. It is considered that interface stresses play a major role in the effect of superhardness.

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