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Coherent growth and mechanical properties of AlN/VN multilayers

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The growth condition of metastable cubic AlN (c-AlN) in AlN/VN multilayers and the effect of c-AlN on the mechanical properties of multilayers were investigated. A series of AlN/VN multilayers with different modulation periods were prepared by reactive magnetron sputtering. The microstructure and mechanical properties of multilayers were characterized with low-angle x-ray diffraction, high-resolution transmission electron microscopy, and nanoindentation. The results show that AlN exists as a metastable cubic phase in multilayers at small modulation periods due to the “template effect” and forms a superlattice with VN through coherent epitaxial growth. Correspondingly, multilayers show the superhardness effect with the enhancement of hardness and elastic modulus. With the increase of modulation periods, c-AlN transforms to the stable hexagonal structure (h-AlN) and multilayers demonstrate a “brick-wall” structure with nanometer grains. The hardness and elastic modulus of multilayers with large modulation periods are close to the value calculated from the rule of mixtures. The discussion indicates that the prerequisite for the formation of c-AlN is the low coherent interface energy. It is the difference of volume energy between c-AlN and h-AlN that primarily determines the critical thickness of c-AlN. The change of properties with the formation of c-AlN and the alternative strain field resulted from coherent growth of c-AlN and VN are likely reasons for the superhardness effect of AlN/VN multilayers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1630367]

I. INTRODUCTION

Multilayers consisting of very thin (1–10 nm) layers of nitride materials exhibit extremely high hardness, making them very attractive for tribological application. Some multilayer systems have been reported to have hardness in excess of 50 GPa,^{1,2} which is comparable to that of cubic-BN and is second only to diamond. This special class of thin films has been the subject of many recent studies to determine the mechanisms that give rise to this high hardness (superhardness effect). In the past 10 years, several explanations have been proposed including Hall–Petch strengthening,³ supermodulus effect,⁴ alternating strain effect at layer interfaces,^{5,6} and modulus difference hardening.^{7,8} These mechanisms were supported by experiments on corresponding systems and explained the experimental results with various levels of success. All the hardening mechanisms mentioned above are based on the isostructural multilayer systems which consist of two modulation layers with the same crystal structure through coherent epitaxial growth. However, recent research has shown that in nonisostructural multilayers, because of the “template effect” of one deposited layer, the other layer forms a metastable phase that can exist over a certain range of thickness. As the modulation period (Λ) increases, the metastable phase will transform to a stable phase. This transformation is accompanied by changes of mechanical properties, which makes it more difficult to investigate the hardening mechanism of multilayers. In this

work, AlN/VN multilayers are studied to investigate the effect of a metastable phase on the mechanical properties of multilayers.

AlN/VN multilayers were chosen for the following two reasons: first, AlN with a NaCl structure (c-AlN) is a high-pressure phase. At ambient temperature, it needs a pressure more than 22 GPa for AlN to transform from its stable hexagonal structure (h-AlN) to c-AlN;⁹ even at 1800 K, this transformation still needs a high pressure of 14–16.5 GPa.¹⁰ However, c-AlN can stably exist in some multilayers because of the template effect. Many works^{11–14} have studied the formation of c-AlN in TiN/AlN nanomultilayers and reported the superhardness effect in this multilayer system. Second, TiN was usually chosen as the template layer for the research of the metastable phase in multilayer systems, such as TiN/AlN,^{11–14} TiN/TaN,¹⁵ TiN/NbN,¹⁶ TiN/CrN_{0.6},¹⁷ cubic AlN, TaN, NbN, and CrN_{0.6} metastable phases can form and keep the cubic structure when their thickness is less than 2, 6, 9, and 6 nm, respectively, and multilayers show the superhardness effect with a corresponding modulation period. We substitute VN for TiN as a template layer in this work because VN has a stable face-centered-cubic structure like TiN and the lattice constant of VN is closer to that of c-AlN than that of TiN ($a_{\text{TiN}}=0.424$ nm,¹⁴ $a_{\text{VN}}=0.414$ nm,¹⁸ $a_{\text{c-AlN}}=0.404$ – 0.412 nm^{9,15}). It should be better for the formation and the growth of c-AlN.

II. EXPERIMENTAL PROCEDURE

AlN, VN single layers, and AlN/VN multilayers with modulation periods from 1 to 30 nm were deposited with reactive magnetron sputtering using an ANELVA SPC-350

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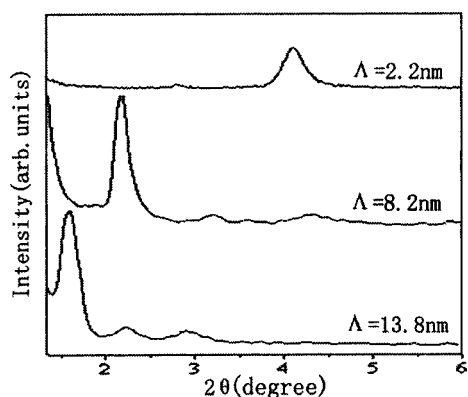


FIG. 1. Low-angle XRD patterns of AlN/VN multilayers.

magnetron sputtering system. The sputtering targets were pure Al (99.99%) and pure V (99.99%) with a diameter of 75 mm, which were mounted on the separately governed rf cathodes and dc cathodes, respectively. Si wafers were ultrasonically cleaned in acetone and absolute alcohol before being mounted on the rotatable substrate holder. After a base pressure of 3×10^{-4} Pa was obtained, Ar and N₂ gas mixture flowed into the vacuum chamber with an Ar partial pressure of 4.0×10^{-1} Pa and an N₂ partial pressure of 0.5×10^{-1} Pa. The sputtering powers for the Al target and the V target were 75 W and 420 V \times 0.12 A. The compositionally modulated structure of multilayers was obtained by rotating the substrate holder and letting the samples face the two targets, alternately. By precise control of the resident time in front of the Al and V targets, the AlN/VN multilayers with different modulation period were obtained. The thickness of films on each specimen was about 2 μ m.

The modulation periods of AlN/VN multilayers were determined by low-angle x-ray diffraction (XRD). A high-resolution transmission electron microscope (HRTEM) was used to characterize the modulation structure and the crystal-line structure of multilayers. Mechanical properties of these films were measured using a Fisherscope H100VP nanoin-denter.

III. EXPERIMENTAL RESULTS

A. Microstructure analysis

Low-angle XRD patterns of AlN/VN multilayers are shown in Fig. 1. It shows that AlN/VN multilayers form a modulation structure with compositionally periodic change. The modulation periods Λ of these multilayers are 2.2, 8.2, and 13.8 nm, respectively, calculated with a modified form of Bragg's law.¹⁹

The microstructures of AlN/VN multilayers with modulation periods Λ of 3.6 and 13.8 nm were investigated using HRTEM. Figure 2(a) shows the TEM image and selected area electron diffraction (SAED) pattern multilayer with Λ of 3.6 nm. It shows that the ratio of the thickness of the AlN layer (light layer) and VN layer (dark layer) is about 1:2. Multilayers form columnar crystal grains which are almost perpendicular to the modulation layers. The SAED pattern at the top left corner is indexed as an fcc structure. The HRTEM image and SAED pattern in Fig. 2(b) show that the lattice on the (001) crystal plane of the multilayer grows across several modulation layers. It indicates that under the template effect of VN, AlN exists as a metastable cubic structure and forms a superlattice through coherent epitaxial growth with VN in the multilayers at small modulation periods.

Figure 3 shows the TEM image and SAED pattern of the multilayer with a Λ of 13.8 nm. From Fig. 3, the multilayer shows a "brick-wall" structure with nanometer grains. The growth of the darker VN layer was restrained by the lighter AlN layer and the VN grains were limited within the width of its own layers. The SAED pattern in Fig. 3(b) shows that there exist fcc and hcp structures in the multilayer. It indicates that the existence of h-AlN restricts the coherent epitaxial growth of VN and AlN in AlN/VN multilayers with large modulation periods and results in the formation of the brick-wall structure.

B. Measurement of mechanical properties

Like other hard films, the measurement of mechanical properties for multilayers is very difficult due to the uncer-

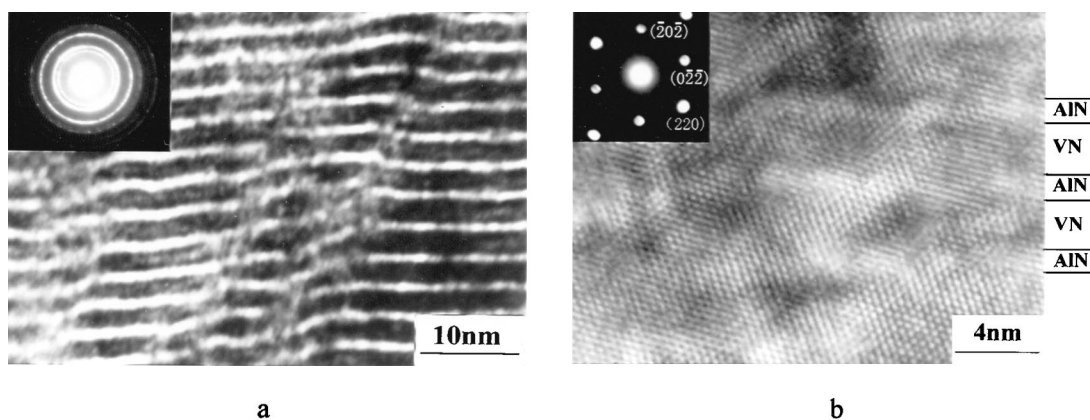


FIG. 2. Cross-section TEM image (a), HRTEM image (b), and SAED patterns of the multilayer with a modulation period of 3.6 nm.

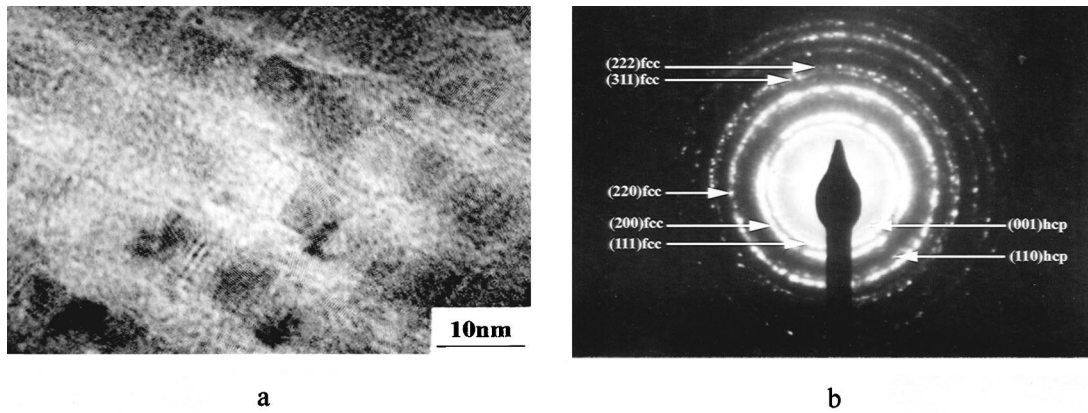


FIG. 3. Cross-section HRTEM image (a) and SAED patterns (b) of the multilayer with a modulation period of 13.8 nm.

tainty in finding the proper penetration load. It has been reported that the depth of indentation should be less than $1/5$,²⁰ $1/10$,²¹ or $1/20$ (Ref. 22) of the film thickness in order to avoid the influence of substrate deformation. To get a reliable value of hardness, a two-step penetration method²³ was used to measure the hardness and elastic modulus of AlN/VN multilayers. The first step of this method employs a large enough load in penetration experiment to get the curve of HU (universal hardness²⁴) versus penetration load calculated from the loading curve of the film/substrate composite. Figure 4 shows the HU of AlN/VN multilayers as well as AlN and VN single layers as a function of the load. The platform stages with high hardness values in the figure indicate that when the penetration load is in the range of 4 to about 20 mN, the deformation under the indenter tip is within the films and not spreading to the substrate. Therefore 15 mN was selected as a substrate free load carrying out the second step of measurement. The Vickers hardness HV and the elastic modulus E of films can be calculated according to Oliver's formula.²⁴

Figure 5 shows the hardness and the elastic modulus of AlN/VN multilayers as a function of the modulation period and also the mechanical properties of h-AlN, and VN single layers. Combined with the results of microstructure analysis, the following characters can be seen: (1) The hardness of multilayers rises monotonically with decreasing Λ and increases rapidly since $\Lambda=10$ nm (the thickness of the AlN

layer is about 3 nm correspondingly); (2) the elastic modulus of multilayers changes similarly to the hardness, which indicates that there exists a supermodulus effect in AlN/VN multilayers; and (3) multilayers with large Λ form nanocrystalline structures, and their hardness and elastic modulus are close to the value calculated from the rule of mixture. However, the hardness and the elastic modulus increase at small Λ when the multilayers form a columnar crystal superlattice due to the formation of c-AlN and its coherent growth with VN.

IV. DISCUSSION

A. The growth of AlN

The growth of AlN in the multilayers can be thermodynamically analyzed as follows. The total energy of h-AlN and c-AlN layers growing on a cubic template can be simply expressed as

$$E_T^h = E_i^h + tE_b^h,$$

$$E_T^c = E_i^c + tE_b^c,$$

where E_T^h and E_T^c are the total energy of unit area h-AlN and c-AlN at the thickness of the AlN layer (t), respectively; E_i^h and E_i^c represent the interface energy of unit area of h-AlN/

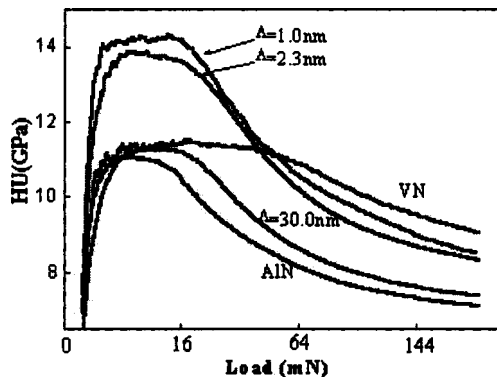


FIG. 4. Universal hardness of the films as a function of the load.

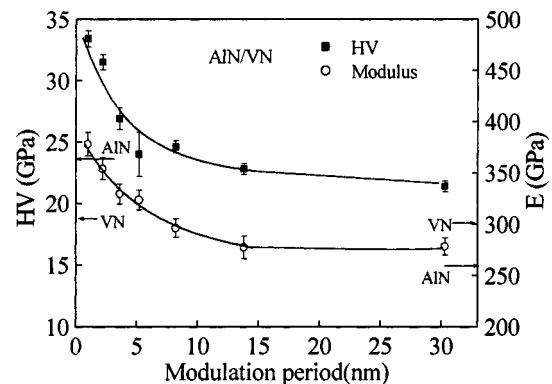


FIG. 5. Hardness and elastic modulus of the AlN/VN multilayers as a function of the modulation period.

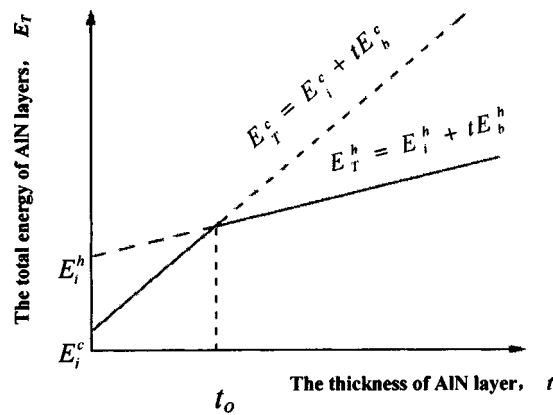


FIG. 6. The total energy of c-AlN and h-AlN layers vs the thickness of the AlN layer.

cubic template interfaces and c-AlN/cubic template interfaces; E_b^h and E_b^c are the volume energy of h-AlN and c-AlN per unit area and per unit thickness.

Figure 6 illustrates the total energy E_T^h and E_T^c as a function of t when AlN is deposited at the surface of the template. The values of two lines at $t=0$ are interface energy, E_i^h and E_i^c . Although interface energy will increase with t at the initial deposition of AlN, it would quickly reach a fixed value and here the interface energy is considered as a constant for simplification. At the initial deposition of the AlN layer, the volume energy has little influence on the total energy because thickness t is very small and thus the total energy is mainly controlled by the interface energy. Since a coherent structure has much lower interface energy than a noncoherent structure ($E_i^c < E_i^h$),¹⁴ E_T^c is lower than E_T^h at the very beginning and the formation of c-AlN is much easier than that of h-AlN when t is very small. With the increase of t , the difference between volume energy of c-AlN and h-AlN layers increases quickly because E_b^c is much larger than E_b^h , which is implied by a high transformation driving force when h-AlN transforms to c-AlN. Therefore the two lines must intersect at some point (defined as t_o) because of their different slopes due to their different volume energy. In order to meet the principle of the lowest energy, the growth of AlN should follow the trend indicated by the solid lines in Fig. 6: for $t < t_o$, AlN exists as c-AlN; when $t > t_o$, h-AlN is formed. In fact, a new interface will appear when the structure transforms from c-AlN to h-AlN, which will increase the total energy of the system and make the critical thickness of c-AlN slightly larger than t_o .

From the discussion above, the prerequisite for the formation of metastable phases in the multilayer is that the multilayer should form a coherent interface with lower interface energy. The critical thickness of metastable phase is primarily determined by the difference of volume energy between the stable and metastable phases. The larger the difference between their volume energy, the smaller the critical thickness. Compared with previous research on AlN/TiN multilayers, VN was chosen as the template in this work based on the fact that it has the same fcc structure as TiN and its lattice constant is closer to c-AlN. Therefore it is expected that a VN template is better for the formation and growth of

c-AlN. However, because of the large difference of the volume energy between c-AlN and h-AlN, though the critical thickness of metastable c-AlN can be increased, the increase is very limited.

B. Mechanisms of the superhardness effect in multilayers

1. Modulus difference hardening

According to Koehler's theory,⁷ the elastic modulus difference between two layers can lead to the increase of hardness in multilayers. The previous results^{9,25} showed that when h-AlN transforms to c-AlN, the volume of AlN would decrease by 18% and the elastic modulus would increase by about 30% (from 205 to 270 GPa). In this work, the elastic modulus of h-AlN and VN are about 260 and 302 GPa, respectively. When h-AlN transforms to c-AlN, if calculated by a 30% rise, though the elastic modulus of c-AlN is higher than that of VN, the modulus difference between these two materials does not increase but decrease. So the modulus difference hardening mechanism cannot give a satisfying explanation to the superhardness effect in AlN/VN multilayers.

2. Hall–Petch strengthening

Lehoczy²⁶ once applied the Hall–Petch relationship to explain the increase of hardness in multilayers. By replacing the grain size with the modulation period, the form of the relationship between the hardness of multilayers and the modulation period was given by

$$H = H_0 + k\Lambda^n,$$

where H is the hardness of multilayers with modulation period Λ , H_0 is the hardness of the multilayer calculated from the hardness of two ingredient materials according to the rule of mixture, and k is a constant related to the material. Anderson and coworkers³ used this Hall–Petch approach to model the mechanical behavior of multilayer materials with layer thickness as low as 1 nm. In their model, deformation of the multilayers is accomplished by dislocation loops moving within a given layer. In this work, though the grain size of AlN/VN multilayers is less than 10 nm at $\Lambda=13.8$ nm, the hardness of the multilayer is not increased obviously. By contrast, the multilayers show the superhardness effect when the grains grow because of coherent growth at small Λ . This result implies that the coherent interface appears to be one likely reason for the increase of hardness in multilayers and the effect of grain size refinement is not obvious.

3. Effects of the property change of AlN and coherent strain field

It can be seen in Fig. 5 that the hardness and elastic modulus of AlN/VN multilayers increase rapidly when $\Lambda < 10$ nm (the thickness of the AlN layer is about 3 nm) and rise monotonically with decreasing Λ . These changes of mechanical properties correspond to the critical thickness of coherent structure formed by AlN and VN, so the superhardness effect of multilayers may result from the following two reasons: first, when h-AlN transforms to cubic structure, its elastic modulus is increased, so is its hardness. This property

change of modulation layers will cause the increase of the hardness of multilayers. On the other hand, since the coherent interface is formed by epitaxial growth of AlN and VN, there exists the alternative strain field in multilayers due to lattice misfit. This alternative strain field will block the motion of dislocations and induce the strengthening of multilayers.^{5,6}

V. CONCLUSIONS

(1) Due to the template effect of VN layers, AlN layers exist as a metastable cubic structure in AlN/VN multilayers at a small modulation period and grow coherently with VN layers. As the modulation period increases, metastable c-AlN transforms to the stable hexagonal structure which blocks the coherent growth. The multilayers thus form a brick-wall structure with nanometer grains. It is better for the growth of c-AlN because the lattice constant of VN is closer to that of c-AlN than that of TiN, the critical thickness of c-AlN will not increase obviously.

(2) The hardness and the elastic modulus of AlN/VN multilayers rise monotonically with decreasing Λ and increase rapidly at $\Lambda=10$ nm. It reaches the highest hardness of 33.4 GPa and the highest elastic modulus 377.8 GPa at $\Lambda=1.0$ nm. The increase of the hardness and the elastic modulus of AlN/VN multilayers is due to the property change of AlN modulation layers and the alternative strain field resulted from the coherent growth of c-AlN and VN.

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