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Strain-free, single-phase metastable $Ti_{0.38}Al_{0.62}N$ alloys with high hardness: metal-ion energy *vs.* momentum effects during film growth by hybrid high-power pulsed/dc magnetron cosputtering

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ABSTRACT

A hybrid deposition process consisting of reactive high-power pulsed and dc magnetron cosputtering (HIPIMS and DCMS) from Ti and Al targets is used to grow $Ti_{1-x}Al_xN$ alloys, with $x \sim 0.6$, on Si(001) at 500 °C. Two series of films are deposited in which the energy and momentum of metal ions incident at the growing film are individually varied. In both sets of experiments, a negative bias V_s ranging from 20 to 280 V is applied to the substrate in synchronous, as determined by in-situ mass spectrometry, with the metal-ion-rich part of the HIPIMS pulse. Ion momentum is varied by switching the HIPIMS and dc power supplies to change the mass m and average charge of the primary metal ion. Al-HIPIMS/Ti-DCMS layers grown under Al^+ ($m_{Al} = 26.98$ amu) bombardment with $20 \le V_s \le 160$ V are single-phase NaCl-structure alloys, while films deposited with $V_s > 160$ V are two-phase, cubic plus wurtzite. The corresponding critical average metal-ion momentum transfer per deposited atom for phase separation is $\langle p_d^* \rangle \ge 135$ [eV-amu]$^{1/2}$. In distinct contrast, layers deposited in the Ti-HIPIMS/Al-DCMS configuration with Ti^+/Ti^{2+} ($m_{Ti} = 47.88$ amu) ion irradiation are two-phase even with the lowest bias, $V_s = 20$ V, for which $\langle p_d^* \rangle > 135$ [eV-amu]$^{1/2}$. Precipitation of wurtzite-structure AlN is primarily determined by the average metal-ion momentum transfer to the growing film, rather than by the deposited metal-ion energy. Ti-HIPIMS/Al-DCMS layers grown with $V_s = 20$ V are two-phase with compressive stress $\sigma = -2$ GPa which increases to -6.2 GPa at $V_s = 120$ V; hardness H values range from 17.5 to 27 GPa and are directly correlated with σ. However, for Al-HIPIMS/Ti-DCMS, the relatively low mass and single charge of the Al^+ ion permits tuning properties of metastable cubic $Ti_{0.38}Al_{0.62}$ N by adjusting V_s to vary, for example, the hardness from 12 to 31 GPa while maintaining $\sigma \sim 0$.

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1. Introduction

TiN, long a model compound for hard wear-resistant thin films [1], suffers from severe disadvantages in high-temperature applications stemming from the fact that it oxidizes very rapidly at temperatures above ~500 °C to form a layer that is predominantly composed of TiO_2 which continuously spalls and reforms due to its large molar volume (18.8 cm^3) compared to that of TiN (11.4 cm^3) [2]. This fact led to the development of metastable cubic NaCl-structure $Ti_{0.5}Al_{0.5}N$ alloys (the equilibrium structure of AlN is hexagonal wurtzite) [3], which exhibit greatly enhanced high-temperature oxidation resistance due to the formation of a stable passive bilayer oxide [2]. $Ti-_{1x}Al_xN$ alloys with AlN concentrations $x \ge 0.5$ are presently used as high-temperature wear-resistant coatings in a wide range of applications [4] including metal machining (cutting, turning, milling or drilling) [5], die casting [6], extrusion [7], and automotive components [8].

Despite the low equilibrium thermodynamic solubility of AlN in TiN, only 2 mol% at 1000 °C [9], single-phase metastable NaCl-structure alloys can be grown by kinetically-limited low-temperature physical vapor deposition [10]. The highest reported AlN concentrations in cubic $Ti_{1-x}Al_xN$ alloys, $x_{max} \sim 0.67$, were obtained by cathodic arc evaporation at growth temperatures $T_s = 500$ °C [11,12]. However, the layers have extremely high compressive stresses ranging up to -9.1 GPa [13].

We recently demonstrated distinctly different film-growth kinetics for $Ti_{1-x}Al_xN$ alloys, deposited using a hybrid reactive high-power pulsed and dc magnetron co-sputtering (HIPIMS/DCMS) configuration, depending upon which target, Ti or Al, is powered by HIPIMS [14,15]. (The acronym HPPMS is also used for high-power pulsed magnetron sputtering) [16]. Al^+ ion irradiation of the growing film during Al-HIPIMS/Ti-DCMS with a synchronous negative substrate bias $V_s = 60$ V leads to single-phase NaCl-structure $Ti_{1-x}Al_xN$ films ($x \le 0.60$) with

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high hardness (>30 GPa) and low stress (0.2–0.7 GPa tensile). In contrast, $Ti_{1-x}Al_xN$ layers grown with Ti^+/Ti^{2+} metal ion irradiation and the same V_s value, via Ti-HIPIMS/Al-DCMS co-sputtering, are two-phase mixtures, NaCl-structure $Ti_{1-x}Al_xN$ plus wurtzite AlN, exhibiting low hardness (~18 GPa) with high compressive stress, up to −2.7 GPa.

There is a large literature on the use of rare-gas ion bombardment of the growing film during low-temperature sputter deposition in order to increase film density, improve film/substrate adhesion via interfacial mixing, enhance crystallinity through collisional increases in adatom mean free paths, form metastable phases through ion-irradiation-induced near-surface mixing, etc. [10,17,18]. However, at higher ion energies, a steep price is extracted in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice [18,19]. Early studies of these effects characterized differences in film growth kinetics as a function of the average ion energy per deposited atom $\langle E_d\rangle$ [20–22]. It was soon realized, however, that $\langle E_d\rangle$, the product of the ion energy E_i and J_i/J_{Me} (the ratio of the accelerated rare-gas ion flux J_i to the deposited metal atom flux J_{Me}) is not a universal parameter for describing the effects of low-energy ion irradiation on film microstructure [23–25]. In fact, as first shown for the growth of $Ti_{0.5}Al_{0.5}N$ alloys, ion-irradiation-induced changes in film microstructure, texture, phase composition, and nitrogen ion-to-metal ratio follow distinctly different mechanistic pathways depending upon whether E_i or J_i/J_{Me} is varied, resulting in quite different film properties for the same value of $\langle E_d\rangle$ [23,24]. Clearly, as is now commonly recognized, the kinetic pathway for optimizing the beneficial effects of rare-gas ion bombardment during film growth while minimizing deleterious effects, is to maintain E_i low (below the lattice displacement threshold which is ~20–50 eV, depending upon the ion and film species involved) while independently increasing J_i/J_{Me} as can be accomplished by, for example, magnetically-unbalanced magnetron sputter deposition [26].

Windischmann [27] proposed, based upon early studies of ion-bombardment-induced compressive stress, typically carried out using rather high ion energies, >100 eV, that the residual stress should scale with the average momentum transfer per deposited metal atom $\langle p_d\rangle$. Kester and Messier [28] demonstrated that as-deposited BN transforms from a hexagonal structure to the high-pressure sphalerite phase during ion-beam-assisted reactive evaporation of B with $\langle p_d\rangle > 200$ $[\text{eV-amu}]^{1/2}$, irrespective of the bombarding rare-gas ion: Ar, Kr, or Xe. However, stress levels in the cubic BN films were so high that the samples exhibited cracking and peeling, whereas hexagonal-structure BN films grown at lower $\langle p_d\rangle$ values were adherent and smooth. Similar results were later obtained using unbalanced rf magnetron sputtering with a pulsed dc bias ≥100 V applied to the substrate [29].

The use of HIPIMS, operated such that the substrate bias is synchronized to the metal-ion rich part of the sputter deposition pulse [30], provides yet another potential kinetic pathway for controlling film growth — the possibility of employing predominantly metal-ion, rather than rare-gas-ion, irradiation. In this case, the accelerated metal ion is incorporated as a film constituent; thus, the resulting ion-bombardment-induced film stress, and the corresponding residual lattice damage which exacerbates second-phase precipitation in metastable alloys, can be much less than that observed for equivalent rare-gas bombardment. In addition, for multi-target sputter deposition, momentum transfer to the growing film can be tuned.

Here, we present the results of an investigation of the effects of varying metal-ion energy E_i *vs.* momentum p_i on the nanostructure, phase composition, and stress of $Ti_{1-x}Al_xN$ alloys, with x ~ 0.6, grown by hybrid HIPIMS/DCMS co-sputtering from Ti and Al targets. Ion energy is varied by applying a negative bias V_s, ranging from 20 to 280 V, to the substrate in synchronous with the metal-rich part of the HIPIMS pulse. Concurrent gas-ion bombardment is minimized during the metal-ion portion of the pulse when the target current is maximum.

Incident ion momentum is varied in our experiments by switching the HIPIMS and dc power supplies to change the mass m and average charge of the metal ions. During Al-HIPIMS/Ti-DCMS deposition, Al^+ ($m_{Al} = 26.98$ amu) is the primary ion incident at the growing films, as determined by in-situ mass spectroscopy, yielding single-phase NaCl-structure alloys, with low stress, for $20 \le V_s \le 160$ V. In contrast, layers deposited in the Ti-HIPIMS/Al-DCMS configuration with Ti^+/Ti^{2+} ($m_{Ti} = 47.88$ amu) ion irradiation are two-phase, cubic plus wurtzite, with high compressive stress even at the lowest bias, $V_s = 20$ V. We show that for a given value of J_i/J_{Me} and a particular choice of metal-ion incident at the growth surface, film properties are primarily a function of the average metal-ion momentum per deposited atom $\langle p_d\rangle$ transferred to the film surface rather than the average metal-ion energy deposited per atom $\langle E_d\rangle$. Single-phase NaCl-structure $Ti_{1-x}Al_xN$ alloys with x ~ 0.6 are only obtained with $\langle p_d\rangle \le 135$ $[\text{eV-amu}]^{1/2}$ which corresponds, for our growth conditions, to $V_s \le 160$ V for Al-HIPIMS. In the case of Ti-HIPIMS, $\langle p_d\rangle \le 135$ $[\text{eV-amu}]^{1/2}$ corresponds to $V_s \le 8$ V, which is less than the floating potential during HIPIMS, and explains why single-phase alloys are only obtained with Al-HIPIMS/Ti-DCMS.

2. Experimental procedure

$Ti_{1-x}Al_xN$ films are grown in a CC800/9 CemeCon AG magnetron sputtering system equipped with cast rectangular 8.8 × 50 cm^2 Ti and Al targets. Si(001) substrates, 3 × 1 cm^2, are mounted symmetrically with respect to the targets, which are tilted toward the substrate, yielding a 21° angle between the substrate normal and the normal to each target. Target-to-substrate distance is 18 cm and the system base pressure is 3.8×10^{-7} Torr (0.05 mPa). The substrates are cleaned sequentially in acetone and isopropyl alcohol and mounted with clips such that their long axis is parallel to the long axis of the targets. The growth chamber is thoroughly degassed before deposition using a two-step heating cycle: 10 kW is applied to each of two resistive heaters for 1 h, resulting in a chamber temperature of 600 °C; the power is then reduced to 7.3 kW/heater for 1 h (chamber temperature = 500 °C) and maintained at this level during film deposition. Ar flow is set at 350 cm^3/min, while the N_2 flow is controlled by an automatic pressure regulator via a feedback loop to maintain the total pressure P_{tot} constant during deposition at 3 mTorr (0.4 Pa).

A hybrid target power scheme is employed in which one of the magnetrons is operated in HIPIMS mode, while the other is operated as a conventional dc magnetron [15]. Two series of films are deposited as a function of the negative substrate bias V_s, which is varied from 20 to 280 V and synchronized with the metal-ion-rich portion of the HIPIMS pulse. In the first set, the Al target is powered with HIPIMS and the Ti target is operated with DCMS (Al-HIPIMS/Ti-DCMS); the positions of the targets are then switched for the second set of experiments (Ti-HIPIMS/Al-DCMS). In Al-HIPIMS/Ti-DCMS configuration, the average power to the Al HIPIMS target is 2.5 kW (5 J/pulse, 500 Hz), and the DCMS power (Ti target) is set at 2.4 kW resulting in $Ti_{1-x}Al_xN$ films with AlN concentrations $x = 0.62 \pm 0.01$. For the Ti-HIPIMS/Al-DCMS mode of operation, a higher average HIPIMS power, 5 kW (10 J/pulse, 500 Hz), is necessary in order to obtain films with the desired composition since the Ti sputtering rate is approximately half that of Al. dc power to the Al target is 1.0 kW, yielding films with $x = 0.58 \pm 0.01$. The shapes of the high-power pulses are controlled by the size of the power-supply capacitor bank. For Ti-HIPIMS, the target current density rises steeply during the first 40 μs to reach a maximum of 1.34 A/cm^2; over the next 60 μs, it decreases more gradually to 0.02 A/cm^2 and remains at this level throughout the remaining 100 μs of the preset 200 μs pulse. In the case of Al-HIPIMS, the initial current density rise, as well as the decay, is somewhat slower. A maximum current density of 0.41 A/cm^2 is achieved after 50 μs and the current density decays to reach a constant value of 0.03 A/cm^2 over the period from 120 to 200 μs. Between HIPIMS metal-ion pulses, the substrate is at floating potential, V_f ~ −10 V. The deposition time is maintained constant at 90 min

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