Paul H. Mayrhofer, Markus Geier, Christian Löcker, Li Chen
Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, Austria

Influence of deposition conditions on texture development and mechanical properties of TiN coatings

Dedicated to Professor Dr. Franz Jeglitsch on the occasion of his 75th birthday

The influence of varying substrate temperature, N_2 partial pressure, ion energy, and ion-to-Ti flux ratio on the texture development and mechanical properties of TiN is investigated in detail. We show that during low substrate temperature ($T_s = 300\,^{\circ}C$) reactive sputtering of TiN in a mixed $Ar + N_2$ discharge a change from 111- to 001-oriented growth occurs when increasing the ion-to-Ti ratio J_i/J_{Ti} above 2.5 while using a low ion energy E_i of 30 eV. This texture change can be reversed to a 111-oriented growth by increasing the ion energy to 60 and 90 eV when using high ion-to-Ti ratios J_i/J_{Ti} of 2.5 and 9, without introducing strain. Thereby the hardness can be increased from $\sim$31 to 37 GPa with only minor changes in compressive stresses. Consequently, by defining the ion-to-Ti ratio and the ion energy during low substrate temperature reactive sputtering of TiN the texture development towards 111- or 001-oriented growth can be controlled. Based on previous studies and the texture development as a function of substrate temperature and N_2-partial pressure, we propose that varying the ion-to-Ti ratio and the ion energy result in different N-terminated surfaces and hence different Ti-fluxes from 111- to 001-oriented grains and vice versa.

Keywords: Titanium nitride; Ion bombardment; Adatom mobility; Texture development; Thin films

1. Introduction

Titanium nitride TiN_x, due to its unique properties such as high hardness, golden color, and chemical inertness is used for various applications, e. g., as a protective coating for machining tools and as a diffusion barrier in microelectronic devices [1–11]. Cubic B1-NaCl structure TiN_x is stable over a wide composition range, which includes the stoichiometric compound with $x = 1$, and temperatures up to $\sim$3290 °C. The N-rich boundary above 50 at.% N is undetermined, the Ti-rich boundary is at $\sim$42 at.% N for 500 °C [12, 13]. TiN is in favor as a model system for investigations on preparation–structure–property interrelations based on its unique properties. Magnetron sputtering, where various particle fluxes bombard and hit the substrate surface and consequently the film, provides a large variety in preparation conditions. Thereby, nucleation and growth kinetics and consequently the texture development are influenced as TiN shows anisotropies in surface energy, strain energy, and adatom mobilies [2–10].

Based on the opposing behavior of surface energy (preferred (001) planes for minimized energy) and the strain energy (preferred (111) planes for minimized energy) Pelleg et al. [7] suggested that the preferred orientation during growth of TiN is controlled by their competition to minimize the overall energy. If the surface energy term is dominant, the (001) planes are preferred and for conditions where the strain energy becomes dominant, the film will grow towards (111). As the strain energy increases with increasing film thickness and energy of ion irradiation there will be a tendency towards a change from 001- to 111-oriented growth. However, Greene, Hultman, and Petrov et al. [2, 3, 8, 9] showed that varying the flux of incident N_2^+ ions, having a low-energy of 20 eV, during reactive TiN deposition results in a pronounced texture change, without introducing strain, and attributed this to kinetic rather than thermodynamic effects. Growth at low temperatures and ion fluxes resulted in 111-textured TiN layers while increasing the ion-to-Ti flux ratio J_i/J_{Ti} to values above 5 resulted in fully 001-oriented films. This was confirmed by ab initio studies of various adatom mobilities and pathways on TiN(001) and (111) surfaces by Gall et al. [10], showing that the kinetics of the Ti adatoms in particular (being the slow species and therefore the growth-rate determining step) on the (001) and (111) surfaces during growth of TiN are strongly influenced by the presence of atomic N on the surface.

Under reactive magnetron sputtering conditions with negligible N_2^+ ion irradiation and atomic N flux incident at the growing film there is a net lateral Ti flux from 001 to 111 grains leading, during polycrystalline TiN deposition, to the more rapid growth of 111 grains at the expense of 001 grain growth. For deposition conditions with a high N_2^+ ion irradiation (i.e., high N_2 partial pressure and/or high J_i/J_{Ti}) there is a net atomic Ti flux from 111- to 001-oriented grains and the 001-oriented grains will win in competitive texture evolution [10]. Thus, N_2^+-ion irradiation results in a reversal of the net atomic intergrain flux and, hence, a corresponding reversal from 111 to 001 texture growth. Petrov et al. [2] showed that an 001-oriented growth can also be obtained by a low-flux ion irradiation ($J_i/J_{Ti} < 0.63$) when using substrate bias potentials above 1000 V, as in TiN the [111] direction exposes the densest array of atoms to the bombarding ions, while [001] is the most open channeling direction where the energy of impinging ions is distributed over larger volumes. Planes corresponding to easy channeling directions and lower sputtering yield have a higher survival-probability. Due to the very

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energetic ion bombardment these films have a high defect density and stresses [2].

Whereas there are numerous studies on the influence of varying substrate temperature, N_2 partial pressure, ion energy (for low $J_i/J_{Ti} = 0.63$), and ion-to-Ti flux ratio (for low ion energy $E_i \leq 30$ eV) on the texture development of TiN [1–10], there is no report on the influence of varying the ion-to-Ti flux ratio (with $J_i/J_{Ti} \leq 9$) at moderate ion energies E_i between 30 and 90 eV. To complete this study, we add this variation to our investigations on the influence of deposition conditions on texture development and mechanical properties of TiN thin films. We show that during low substrate temperature ($T_s = 300\,°C$) reactive sputtering of TiN in a mixed Ar + N_2 discharge a change from 111- to 001-oriented growth occurs when increasing the ion-to-Ti ratio J_i/J_{Ti} above 2.5 when using a low ion energy $E_i = 30$ eV. This texture change can be reversed to a 111-oriented growth by increasing the ion energy to 60 and 90 eV using ion-to-Ti ratios J_i/J_{Ti} of 2.5 and 9, without introducing strain. As a result, the hardnesses increase from ~31 to 37 GPa whereas the compressive stresses vary only between –2.66 and –3.66 GPa. Consequently, defining the ion-to-Ti ratio and the ion energy during low substrate temperature reactive sputtering of TiN allows controlling the texture development towards 111- or 001-oriented growth.

2. Experimental details

TiN films are grown on austenitic stainless steel and Si(001) substrates at 150, 225, 300, 400, and 500 °C by magnetically-unbalanced magnetron sputter deposition from a Ti target (99.5 % purity and 150 mm in diameter) in mixed Ar + N_2 (both 99.999 % purity) discharges. The N_2 partial pressure ratio, p_{N2}/p_T, was 17 % of the 0.4 Pa (3 mTorr) total pressure (Ar + N_2) and the power density at the Ti target was $3.0\ W \cdot cm^{-2}$ to obtain near-stoichiometric TiN coatings with N/Ti ratios of 1.09 ± 0.04 (see next paragraph). The deposition system with a base pressure of 0.1 mPa (7.5×10^{-7} Torr) used is a modified Leybold-Univex 300 equipped with a circular unbalanced planar-magnetron (∅ 152.4 mm, 6 inch, Gencoa PP 150 with NdFeB – permanent magnets). The substrates are centered parallel to the target and separated by 9 cm. An external pair of coreless electromagnetic coils (Helmholtz arrangement), are utilized, as indicated in the schematic of the equipment, Fig. 1, to create a uniform axial magnetic field B_{ext} with a maximum value of ±200 G (20 mT) in the region between the target and substrate. The positive or negative signs refer to B_{ext} fields aiding or opposing, respectively, the magnetic field of the outer magnetron pole. The incident metal flux J_{Ti} is estimated after [14] based upon measurements of the film composition (see next paragraph) and the deposition rate, which is obtained by the film thickness and deposition time and assuming bulk density. The ion flux J_i bombarding the growing film and the plasma potential V_p are determined using Langmuir-probe measurements (Hiden ESP Langmuir wire probe) following the procedures described in [14]. The J_i/J_{Ti} ratio was set to 1.3, 2.5, 4.5, 9, 17, 25, and 35 by adjusting the external magnetic field B_{ext} to –120, –80, –40, 0, +40, +80, and +120 G, see Fig. 2, and the ion energy E_i was varied between 30, 60, 90, and 120 eV in the experiments by adjusting the bias potential V_b applied to the substrates with respect to the plasma potential V_p. For single ionization, which is mainly valid for the plasma conditions used, the ion energy is therefore $E_i = e(V_p - V_b)$ [15]. The floating potential V_f as a function of B_{ext} is also added to Fig. 2 for comparison.

Film compositions are measured by wavelength dispersive electron probe microanalysis (MICROSPEC WDX-3PC) calibrated using a stoichiometric TiN coating standard whose composition was determined by Rutherford backscattering spectroscopy (RBS). The films exhibit no detectable impurities within the detection limit of approximately 0.1 at.%.

The biaxial compressive stresses σ with an accuracy of ±0.25 GPa were measured using the cantilever beam method [16] in films (thickness of around 1.0 µm) grown on Si(001). The hardnesses of our coatings (on steel substrates) are obtained with a Berkovich indenter attached to an ultra micro indentation system (UMIS). The maximum loads range from 4 to 16 mN to keep the indentation depth below 10 % of the film thickness of around 2.5 µm. The values for H were obtained from analysing the loading and unloading segments of the indentation curves after the Oliver–Pharr method [17].

Structural investigations of the coatings on steel substrates were performed by X-ray diffraction (XRD) with a

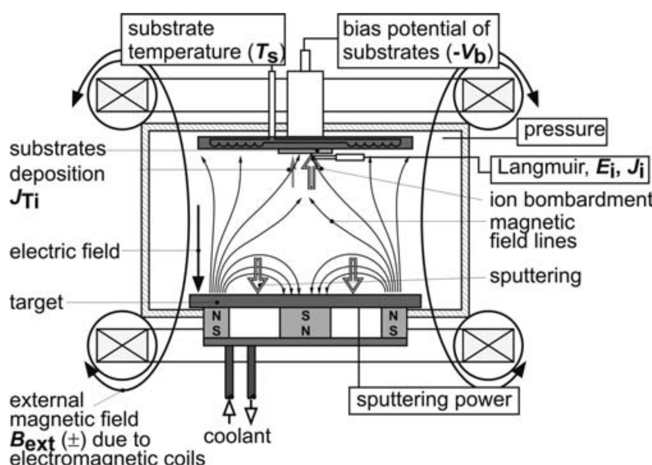

Fig. 1. Schematic of the unbalanced dc magnetron sputtering system used.

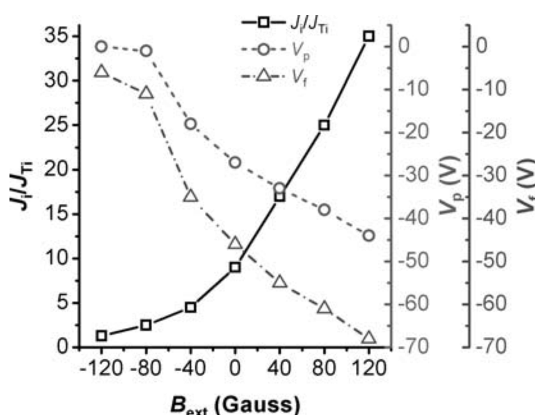

Fig. 2. Ion-to-Ti flux ratio J_i/J_{Ti} and plasma and floating potential (V_p, V_f) at the center of the substrate holder during reactive deposition of TiN with $p_{N2}/p_T = 17\%$ of the 0.4 Pa Ar + N_2 discharge as a function of the applied external magnetic field B_{ext}.

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Siemens D500 diffractometer in Bragg–Brentano ($\theta-2\theta$) geometry using Cu-K_α radiation, a step size of 0.02° and a scan rate of $1.2° \cdot s^{-1}$. The lattice parameters were obtained by the Cohen-Wagner [18] method yielding an accuracy of ±0.005 Å. Nanoscale morphological characterization of the films are determined using cross-section transmission electron microscopy (XTEM) performed in a JEOL 2010F instrument.

3. Results

The texture coefficients $TC_{(hkl)}$, calculated for the (111), (002), (022), and (113) XRD reflections after,

$$TC_{(hkl)} = \frac{I_{(hkl)}}{\sum I_{(111)} + I_{(002)} + I_{(022)} + I_{(113)}}$$

where $I_{(111)}$, $I_{(002)}$, $I_{(022)}$, and $I_{(113)}$ are their respective intensities, indicate a change from a preferred (111) orientation ($TC_{(111)} = 0.44$) to a preferred (001) orientation ($TC_{(002)} = 0.61$) with increasing substrate temperature T_s from 150 to 500 °C, using an ion energy E_i of 60 eV and an ion-to-Ti ratio J_i/J_{Ti} of 1.3 at a N_2 to total pressure ratio p_{N2}/p_T of 17 %, see Fig. 3a. Decreasing E_i to 30 eV at 300 °C (and keeping other parameters constant) results in a texture coefficient of $TC_{(111)} = 0.88$ and $TC_{(002)} = 0.05$. With increasing p_{N2}/p_T from 17 to 23 to 27 % (for $E_i = 30$ eV, $T_s = 300$ °C, $J_i/J_{Ti} = 1.3$) the texture coefficient $TC_{(111)}$ decreases from 0.88 to 0.72 to 0.11 and $TC_{(002)}$ increases from 0.05 to 0.14 to 0.87, see Fig. 3b. The biaxial compressive stresses in these films are below –1 GPa.

For further studies on the ion bombardment induced texture development during film growth, a low substrate temperature of $T_s = 300$ °C and a low N_2 to total pressure ratio p_{N2}/p_T of 17 % is used. Increasing the energy of the bombarding ions E_i from 30 to 60 to 90 eV while keeping the ion-to-Ti flux low ($J_i/J_{Ti} = 1.3$) results in a decrease of $TC_{(111)}$ from 0.88 to 0.41 to 0.06, while $TC_{(002)}$ changes from 0.05 to 0.44 to 0.42 and $TC_{(022)}$ increases from 0.04 to 0.11 to 0.49, respectively, see Fig. 4. For a further increase in E_i to 120 eV, the texture changes towards (111) again, with $TC_{(111)} = 0.96$ and $TC_{(002)} = 0.00$. The TEM cross-sectional investigations of this film, Fig. 5a, exhibit an extremely fine columnar and dense morphology. As the film has a pronounced (111) growth orientation with $TC_{(111)} = 0.96$, no (111) planes can be detected during selected area electron diffraction (SAED) studies of the cross-section, Fig. 5b.

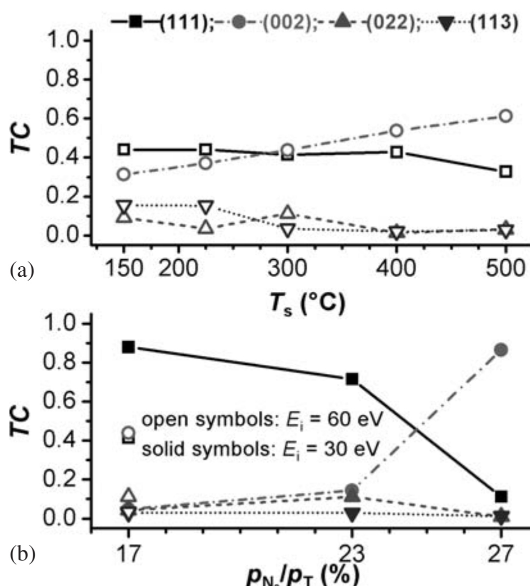

Fig. 3. Texture coefficients TC for the (111), (002), (022), and (113) planes as a function of (a) the substrate temperature T_s (with $J_i/J_{Ti} = 1.3$, $E_i = 60$ eV, and $p_{N2}/p_T = 17$ %) and (b) the N_2 to total pressure ratio p_{N2}/p_T (with $J_i/J_{Ti} = 1.3$ and $T_s = 300$ °C) used during deposition.

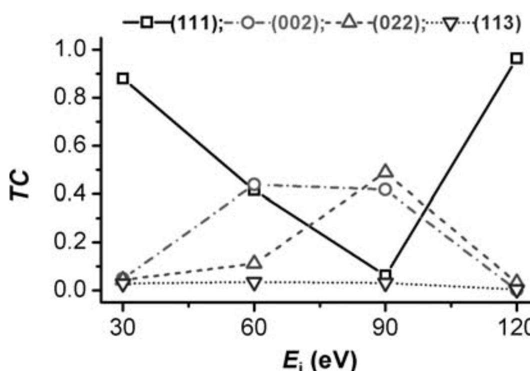

Fig. 4. Texture coefficients TC for the (111), (002), (022), and (113) planes as a function of the ion energy E_i (with $J_i/J_{Ti} = 1.3$, $T_s = 300$ °C, $p_{N2}/p_T = 17$ %) used during film growth.

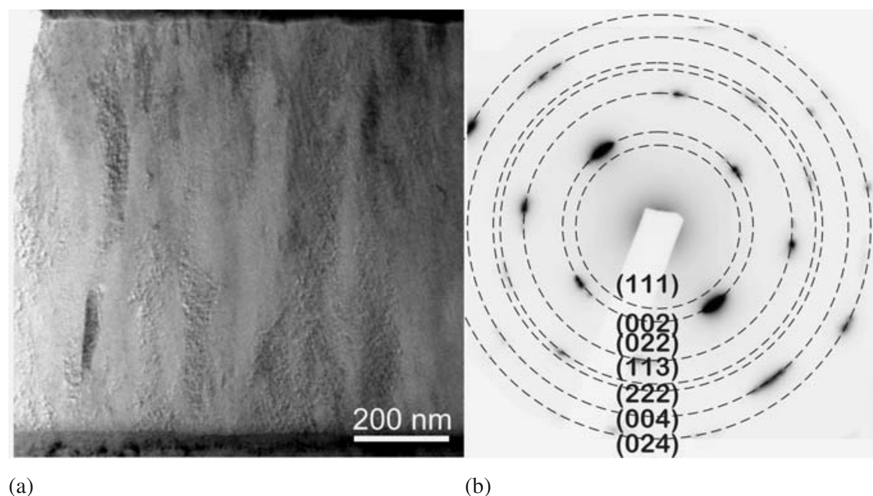

Fig. 5. Bright-field cross-sectional TEM image (a) and corresponding SAED (b) of the TiN film grown with $E_i = 120$ eV, $J_i/J_{Ti} = 1.3$, $T_s = 300$ °C, and $p_{N2}/p_T = 17$ %.

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With almost doubling the ion-to-Ti flux J_i/J_{Ti} from 1.3 to 2.5 the preferred growth orientation is (111) with $E_i \geq 60$ eV. The same is valid for an even higher ion-to-Ti flux of 9, see Fig. 6a. In contrast, with low ion energy, $E_i = 30$ eV, the preferred growth orientation changes from (111) towards (001) while increasing the ion-to-Ti flux J_i/J_{Ti}, see Fig. 6b. The $TC_{(002)}$ increases from 0.05 to 0.70 to 0.99 and $TC_{(111)}$ decreases from 0.88 to 0.17 to 0.01 with increasing J_i/J_{Ti} from 1.3 to 2.5 to 35, respectively.

The stress measurements of our films indicate that their biaxial compressive stresses increase (for low values of $J_i/J_{Ti} = 1.3$, $T_s = 300\,^\circ$C, and $p_{N2}/p_T = 17\,\%$) from −0.57 to −2.74 to −4.83 to −5.82 GPa with increasing ion energy E_i from 30 to 60 to 90 to 120 eV, respectively, see Fig. 7a.

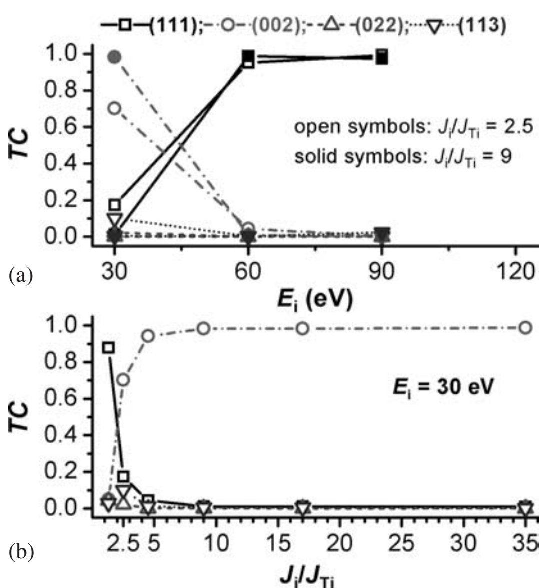

Fig. 6. Texture coefficients TC for the (111), (002), (022), and (113) planes as a function of (a) the ion energy E_i (with $J_i/J_{Ti} = 2.5$ and 9, $T_s = 300\,^\circ$C, $p_{N2}/p_T = 17\,\%$) and (b) the J_i/J_{Ti} (with $E_i = 30$ eV, $T_s = 300\,^\circ$C, $p_{N2}/p_T = 17\,\%$) used during deposition.

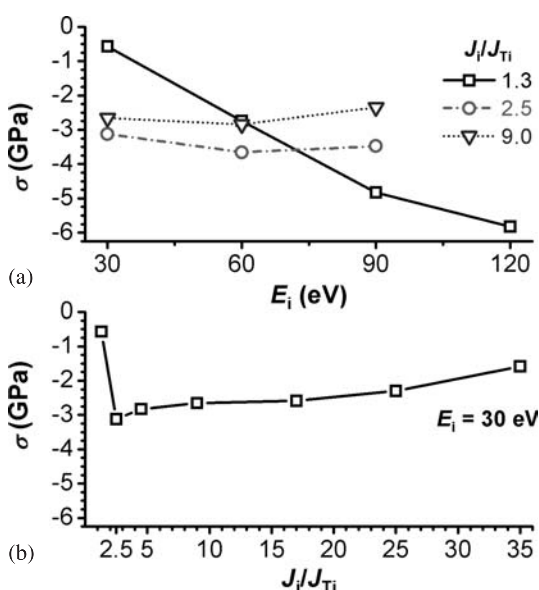

Fig. 7. Biaxial stresses s in our TiN films as a function of (a) the ion energy E_i with $J_i/J_{Ti} = 1.3$, 2.5, and 9, and (b) the ion-to-Ti flux J_i/J_{Ti} with $E_i = 30$ eV used during deposition at $T_s = 300\,^\circ$C and $p_{N2}/p_T = 17\,\%$.

Varying the ion energy between 30 and 90 eV at higher ion densities results in minor changes of the compressive stresses between −3.12 and −3.66 GPa for $J_i/J_{Ti} = 2.5$ and −2.66 and −2.84 GPa for $J_i/J_{Ti} = 9$. Increasing the ion-to-Ti flux J_i/J_{Ti} from 2.5 to 35 at low energy ($E_i = 30$ eV) during film growth results in decreasing compressive stresses from −3.21 to −1.59 GPa, see Fig. 7b. The only exception from this trend is the film prepared with $J_i/J_{Ti} = 1.3$ having a compressive stress of −0.57 GPa, which can be explained by its open columnar structure (not shown here). Using low energies at a low substrate temperature requires a higher ion-to-Ti flux (in our experiments J_i/J_{Ti} has to be 2.5 for $T_s = 300\,^\circ$C and $E_i = 30$ eV) to form a dense film.

The dependence of the biaxial stresses in our films on the deposition conditions used is in excellent agreement with the variations in lattice parameter a and the full width at half maximum (Γ_{002}) of the (002) XRD reflection presented in Figs. 8 and 9. Generally, the full width at half maximum increases when the grain size decreases and/or the microstresses increase. Only if the ion-to-Ti flux is low with $J_i/J_{Ti} = 1.3$ there is a pronounced increase in a from 4.239 to 4.295 Å (Fig. 8a) and Γ_{002} from 0.76 to 0.89° (Fig. 8b) with increasing ion energy E_i from 30 to 120 eV, corresponding to the increase in σ, compare Fig. 7a. If the ion-to-Ti flux is high with $J_i/J_{Ti} = 2.5$ or 9 there is almost no change in a with values of 4.281 ± 0.005 or 4.273 ± 0.003 Å and Γ_{002} with values of 0.78 ± 0.07 or $0.79 \pm 0.03°$, respectively, when increasing E_i from 30 to 90 eV, see Fig. 8a and b. This is in agreement with the small variation in σ, compare Fig. 7a. Keeping the ion energy at a low level of 30 eV while increasing the ion-to-Ti flux J_i/J_{Ti} from 2.5 to 35 during film growth results in decreasing a from 4.285 to 4.254 Å and decreasing Γ_{002} from 0.85 to 0.47°, see Fig. 9a and b, respectively. Corresponding results, with a decrease in a from 4.283 to 4.264 Å and a decrease in Γ_{002} from 1.01 to 0.47°, are obtained for our TiN coatings when increasing the substrate temperature from 150 to 500 °C using an ion bombardment with $J_i/J_{Ti} = 1.3$ and $E_i = 60$ eV. A decrease in a towards the stress free lattice parameter a_0 of 4.242 Å for bulk TiN [19] combined

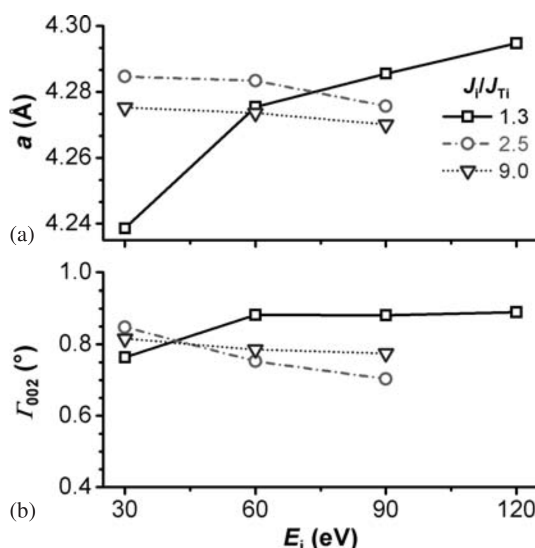

Fig. 8. Lattice parameter a (a) and full width at half maximum Γ_{002} of the (002) XRD reflection (b) of TiN films as a function of the ion energy E_i with $J_i/J_{Ti} = 1.3$, 2.5, and 9, used during deposition at $T_s = 300\,^\circ$C and $p_{N2}/p_T = 17\,\%$.

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with a decrease in Γ_{002} suggests a decrease of macro- and micro-stresses in the films.

The hardness measurements of our coatings follow a similar dependency on the deposition conditions used (T_s, J_i/J_{Ti}, and E_i) as the results obtained for TC, σ, a, and Γ_{002}, see Fig. 10. With increasing substrate temperature from 225 to 500 °C the hardness decreases from 30.7 ± 2.1 to 26.1 ± 1.8 GPa, as the stresses decrease. Also, the decrease in H from ~31 to 25 GPa while increasing J_i/J_{Ti} from 2.5 to 35 at a low ion energy of E_i = 30 eV is mainly due to the reduction in compressive stresses from $\sigma = -3.12$ to -1.58 GPa and the texture change from (111) to (001), respectively, compare Figs. 10a and 7b. The low hardness value of 22.9 ± 2.5 GPa for the film grown with J_i/J_{Ti} = 1.3

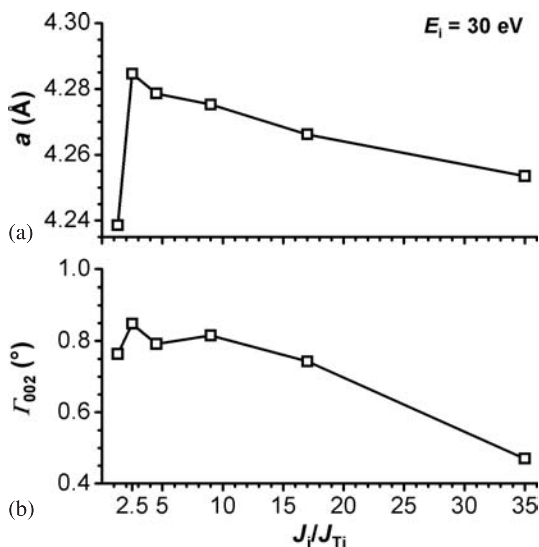

Fig. 9. Lattice parameter a (a) and full width at half maximum G_{002} of the (002) XRD reflection (b) of TiN films as a function of the ion-to-Ti flux J_i/J_{Ti} used during deposition with E_i = 30 eV, T_s = 300 °C, and p_{N2}/p_T = 17 %.

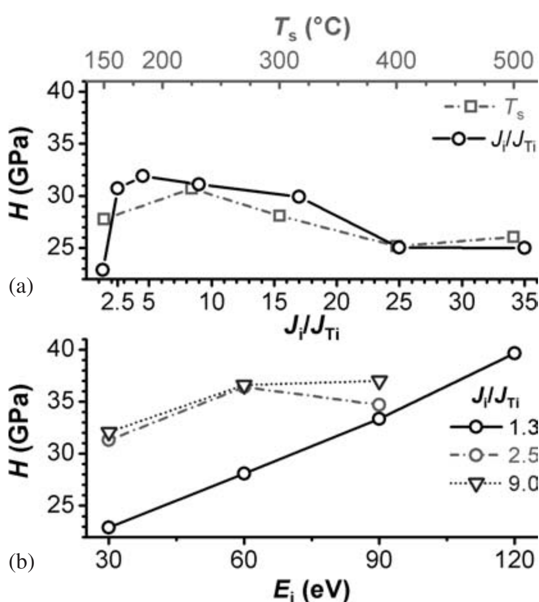

Fig. 10. Hardness H of TiN films with respect to (a) the substrate temperature T_s (J_i/J_{Ti} = 1.3, E_i = 60 eV) and ion-to-Ti flux J_i/J_{Ti} (E_i = 30 eV), and (b) the ion energy E_i (J_i/J_{Ti} = 1.3, 2.5, and 9) used during deposition at T_s = 300 °C and p_{N2}/p_T = 17 %.

and E_i = 30 eV can be explained by its open columnar structure, as mentioned before. The pronounced increase in H from 28.1 ± 1.7 to 39.6 ± 2.5 GPa with increasing ion energy from 60 to 120 eV during film growth can be explained by the observed pronounced increase in compressive stresses from –2.74 to –5.82 GPa and the pronounced change in texture with changing $TC_{(002)}$ from 0.44 to 0.00 and $TC_{(111)}$ from 0.41 to 0.96, respectively. As the biaxial compressive stresses in films prepared with high J_i/J_{Ti} vary only between –3.12 and –3.66 GPa (J_i/J_{Ti} = 2.5) and –2.66 and –2.84 GPa (J_i/J_{Ti} = 9) with increasing ion energy from 30 to 60 to 90 eV, the observed pronounced increase in H from 31.3 ± 2.1 to 36.4 ± 1.5 to 34.7 ± 2.2 GPa (J_i/J_{Ti} = 2.5) and from 32.1 ± 2.0 to 36.6 ± 2.2 to 37.0 ± 2.1 GPa (J_i/J_{Ti} = 9), can only be explained by the concomitant pronounced change in texture from (001) to (111), respectively, compare Figs. 10b, 7b, and 6a. The textures of these films change by decreasing $TC_{(002)}$ from 0.70 to 0.04 to 0.00 and increasing $TC_{(111)}$ from 0.17 to 0.95 to 0.99 with increasing E_i from 30 to 60 to 90 eV (with J_i/J_{Ti} = 2.5), respectively. For an even denser ion bombardment with J_i/J_{Ti} = 9 the observed texture change is even more pronounced with a decrease in $TC_{(002)}$ from 0.98 to 0.01 to 0.00 and an increase in $TC_{(111)}$ from 0.01 to 0.99 to 0.98 with increasing ion energy from 30 to 60 to 90 eV. The results show that hardness values above 32 GPa are only obtained for 111-oriented TiN films, where the film with the highest compressive stresses of –5.82 GPa exhibits also the highest hardness of 39.6 ± 2.5 GPa. This film is characterized by a fine and dense columnar growth with a smooth surface, Fig. 5a.

4. Discussion

The texture developments of our TiN films towards (001) with increasing T_s follows the major trend that the orientation with the lowest surface energy ($\gamma_{(111)} > \gamma_{(011)} > \gamma_{(001)}$) is preferred if adatom mobilities during growth are sufficient, as reported in [2, 3]. Consequently, as the substrate temperature increases, and thereby the mobilities, the probability for a (001) growth orientation also increases. For conditions where kinetics rather than thermodynamics control texture formation (e. g., substrate temperature below 450 °C) the system is sensitive to changes in the environment. As mentioned in the introduction, the kinetics of the Ti adatoms in particular (being the slow species and therefore the growth-rate determining step) on the (001) and (111) surfaces during growth of TiN are strongly influenced by the presence of atomic N on the surface [10]. The mechanisms towards an 001-oriented growth with increasing T_s and p_{N2}/p_T are further assisted by a concomitant decrease in biaxial stresses which would favor a 111-oriented growth as the (111) planes have the lowest strain energy. As TiN has a strain anisotropy with $\varepsilon_{(001)} > \varepsilon_{(011)} > \varepsilon_{(111)}$ [4, 6] and a Young's modulus anisotropy with $E_{(001)} > E_{(011)} > E_{(111)}$ the strain energy also has an anisotropy with $U_{(001)} > U_{(011)} > U_{(111)}$. Hence, (111) planes are preferable for high strains to minimize the strain energy in TiN.

Whereas the texture development of our TiN films as a function of the ion-to-Ti ratio J_i/J_{Ti} during growth can also easily be explained by well known mechanisms if the ion energy is low (E_i = 30 eV), the situation is more complex

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if ion energies of 60 and 90 eV are used. Increasing J_i/J_{Ti} from 1.3 to 35 at low E_i of 30 eV results in a change from 111-oriented to 001-oriented growth with $TC_{(002)} \geq 0.94$ for $J_i/J_{Ti} \geq 4.5$. As described in [10] increased N_2^+ irradiation (due to increased J_i/J_{Ti}) promotes the Ti flux from 111- to 001-oriented grains and hence results in 001-oriented growth. This mechanism is further assisted by a concomitant decrease in compressive stresses (reduction in strain energy and hence reduction in driving force towards 111-oriented growth) with increasing J_i/J_{Ti}, see Fig. 7b.

Increasing the ion energy at a low ion-to-Ti ratio of $J_i/J_{Ti} = 1.3$ results in a texture change from (111) for $E_i = 30$ eV to mixed (111) + (001) for $E_i = 60$ eV to mixed (001) + (011) for $E_i = 90$ eV to pronounced (111) for $E_i = 120$ eV. Here, the compressive stresses continuously increase with E_i from −0.57 to −5.82 GPa, Fig. 7a. This texture evolution (against the strain energy) suggests that with increasing E_i from 30 to 90 eV the N_2^+-ion irradiation increases, as thereby the texture growth reverses from 111 to 001, see Fig. 4. With a further increase in E_i from 90 to 120 eV again the (111) growth texture is preferred, corresponding to the increased compressive stresses, indicating changes in growth determining processes. At higher ion-to-Ti ratios of $J_i/J_{Ti} \geq 2.5$ this texture change from 001- to 111-oriented growth occurs already with increasing E_i from 30 to 60 eV. As for these conditions the compressive stresses vary only between −3.12 and −3.66 GPa for $J_i/J_{Ti} = 2.5$ and −2.66 and −2.84 GPa for $J_i/J_{Ti} = 9$, changed strain energy terms are not responsible for the observed transition from (001) towards (111). Our observations show that using an ion bombardment combining high ion-to-Ti ratios, $J_i/J_{Ti} \geq 2.5$, with moderate ion energies, E_i of 60–90 eV, results in a preferred (111) growth texture. We propose that resputtering events are responsible for this texture transition from (001) to (111) with increasing the ion energy from 30 to 60 eV when using high ion-to-Ti ratios of $J_i/J_{Ti} \geq 2.5$. The adsorption energy E_{ad} of Ti adatoms on TiN(111) with 10.09 eV is ∼3 times that on TiN(001) with 3.30 eV [10]. Therefore, resputtering of Ti atoms from 001-oriented grains would be preferred as compared to 111-oriented grains. As already mentioned above and discussed in [10] the presence of atomic N on the TiN(001) results in a dramatic reduction in Ti adatom diffusion length and therefore, in a net atomic Ti flux from 111- to 001-oriented grains. (Therefore, the 001 texture develops with increasing J_i/J_{Ti} at low ion energy of 30 eV, Fig. 6b). Hence, higher ion energies with preferential resputtering of N would reduce this effect and lead to a net atomic Ti flux from 001- to 111-oriented grains, as is the case for low J_i/J_{Ti} and p_{N2}/p_T. Consequently, 111-oriented grains will win in a competitive texture evolution. Argon in our films could only be detected with 0.35, 0.40 and 0.26 at.% if an ion energy E_i of 90 eV (with $J_i/J_{Ti} = 2.5$ and 9), or 120 eV (with $J_i/J_{Ti} = 1.3$) is used during deposition. Thus, channeling of energetic ions is minimal and therefore also texture development driven by anisotropic collision cascade effects.

The hardness development of our films with varying of the deposition conditions used follows the thereby induced changes in texture, morphology of the films, and compressive biaxial stresses. Hardness values above 32 GPa are only obtained for 111-oriented TiN films, where the film with the highest compressive stresses of −5.82 GPa also exhibits the highest hardness of 39.6 ± 2.5 GPa.

5. Conclusions

We have studied the effect of varying the substrate temperature T_s (150–500 °C), ion energy E_i (30–120 eV), ion-to-Ti ratio J_i/J_{Ti} (1.3–35), and N_2 to total pressure ratio p_{N2}/p_T (17–27 %) on the texture development and mechanical properties of face centered cubic TiN films sputtered from a metallic Ti target. The overall chemical composition of our films with $TiN_{1.09}$ is independent of the deposition conditions used, where an Ar content of 0.26, 0.35, and 0.40 at.% could only be detected in the films prepared with the highest ion energy used of 120 eV (combined with $J_i/J_{Ti} = 1.3$) and 90 eV (combined with $J_i/J_{Ti} = 2.5$ and 9). Consequently, the influence of chemical variations on texture development and mechanical properties are minimal. The texture development of our films towards (001) with increasing T_s and p_{N2}/p_T are fully in line with the well-known mechanisms of minimizing the surface energy term (preferred (001) orientation) and changes in the Ti-fluxes from 111- to 001-oriented grains. With increasing p_{N2}/p_T from 17 to 27 % the texture changes from (111) to (001) as the Ti-flux from 111- to 001-oriented grains become larger than those from 001- to 111-oriented grains. Hence, the (001) orientation wins in a competitive texture evolution. Corresponding mechanisms are responsible for the texture development of TiN, from 111- to 001-oriented growth, when increasing the ion-to-Ti ratio J_i/J_{Ti} from 1.3 to 35 while keeping the ion energy low with 30 eV.

The change in texture of our TiN films from pronounced (001) to pronounced (111) with increasing ion energy from 30 to 60 eV combined with a high ion-to-Ti ratio $J_i/J_{Ti} = 2.5$ can not be explained by an increased strain energy term, which would favor a 111-oriented growth as thereby the strain energy can be minimized. The compressive stresses in these coatings are almost independent of the increase in ion energy. We propose that with increasing E_i to 60 eV preferential resputtering of Ti and N occurs. As the adsorption energy of Ti atoms is ∼3 times smaller on TiN(001) than on TiN(111), resputtering would preferentially occur for Ti adatoms on TiN(001). Additionally, preferential resputtering of atomic N would reverse the effect of increased J_i/J_{Ti} at low E_i and result in a net atomic Ti flux from 001- to 111-oriented grains. Hence, both resputtering of Ti and N result in a 111 texture during competitive growth. This mechanism allows control of the texture formation from 001- to 111-oriented growth by simply increasing the ion energy from 30 to 60 eV while using high ion-to-Ti ratios $J_i/J_{Ti} = 2.5$, without increasing the compressive stresses.

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Correspondence address

Priv. Doz. Dr. Paul H. Mayrhofer
Department Physical Metallurgy and Materials Testing
Montanuniversität Leoben
Franz Josef Strasse 18, A-8700 Leoben, Austria
Tel.: +4 33 84 24 02 42 11
Fax: +4 33 84 24 02 42 02
E-mail: paul.mayrhofer@unileoben.ac.at

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