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Control of plasma flux composition incident on TiN films during reactive magnetron sputtering and the effect on film microstructure

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A hybrid plasma enhanced physical vapor deposition (PEPVD) system consisting of an unbalanced dc magnetron and a pulsed electron beam-produced plasma was used to deposit reactively sputtered titanium nitride thin films. The system allowed for control of the magnitudes of the ion and neutral flux, in addition to the type of nitrogen ions (atomic or molecular) that comprised the flux. For all deposition experiments, the magnitude of the ion flux incident on the substrate was held constant, but the composition of the total flux was varied. X-ray diffraction and atomic force microscopy showed that crystallographic texture and surface morphology of the films were affected by the plasma flux composition during growth. [DOI: 10.1116/1.2134706]

I. INTRODUCTION

Substantial research efforts over at least three decades have led to the broad industrial acceptance and commercial success of reactively sputtered transition metal nitrides in diverse applications. The literature contains many studies on process-structure relationships, including early works that identified ion energy[1] and flux[2] as critical parameters for TiN deposition processes. Later reports examined the effect of the energy deposited per atom.[3–5] The remarkable control of film structure and properties with ion bombardment has motivated the development of processes such as ionized PVD,[6] or inductively coupled plasma enhanced magnetron sputtering,[7–10] and high power pulsed magnetron sputtering.[11,12] All of these processes are designed to generate an increased fraction of ionized and dissociated species that are ultimately incorporated into the growing film. While increasing the total flux of reactive species to the substrate is beneficial for texture development or reduction of film porosity,[7–9] it might be more effective to increase the flux of only those species that are most effective in producing the desired microstructural response in the deposited material. For example, Chun *et al.*[13] Gall *et al.*,[14] and Petrov *et al.*[15] have observed that the steady-state coverage of N on TiN crystals with the polar (111) orientation is independent of the atomic nitrogen flux, whereas coverage increases for the (001) orientation, resulting in the development of (002) texture for TiN. The presence of texture due to the increased availability of reactive nitrogen is also likely to be accompanied by a reduction in film porosity, as reported by Hultman *et al.*[16] and Petrov *et al.*[15] for growth of NaCl structured transition metal nitrides under different nitrogen flux conditions.

The current work demonstrates a relationship between the composition of the incident nitrogen ion and neutral flux and the microstructure of reactively sputtered TiN films grown in a hybrid deposition system. The system combined a pulsed, electron beam-generated plasma[17,18] with a dc unbalanced magnetron in pure nitrogen gas.[19] The electron beam has been shown to produce large relative fluxes of atomic nitrogen ions (N^+)[20] compared to the glow discharge produced by an unbalanced magnetron.[21] Changing the duty factor of the electron beam thus provides a means to vary the nature and magnitude of the ion and radical fluxes at the film surface. An adjustable auxiliary magnetic field was used to confine the electron beam and also to reduce the ion flux from the magnetron discharge, so that the time-averaged total ion flux could be maintained for any electron beam duty factor. The hybrid PEPVD system used in this way allowed for a study in which the composition of the plasma-generated nitrogen flux was the primary variable, and other deposition parameters, such as gas flow rate, pressure and neutral titanium flux were essentially constant. Glancing angle x-ray diffraction and atomic force microscopy were used to demonstrate the relationship between TiN film microstructure and nitrogen flux composition.

II. EXPERIMENTAL PROCEDURE

Experiments were conducted in a stainless steel vacuum chamber pumped by a $1000\,\mathrm{l\,s^{-1}}$ diffusion pump to a base pressure of 5×10^{-7} Torr. The apparatus was configured as shown in Fig. 1, with the substrates 1.5 cm from the electron beam axis and 6.0 cm from the magnetron target, which was a 1.3 cm diameter disk of 99.99% pure titanium metal. A chamber pressure of 30 mTorr, measured with a capacitance manometer, was achieved with 110 sccm of 99.999% pure nitrogen during deposition. The sputtering target was powered by an Advanced Energy MDX power supply in dc current regulation mode at 0.10 A and a nominal voltage of 180–200 V. The electron beam originated from a $15\times1\times1\ \mathrm{cm^3}$ hollow cathode inside the chamber as shown in Fig. 1. The cathode was pulsed to −2 kV at 20%–50% duty with a maximum current of 50 mA. The pulse length was always 1 ms, and the frequency of the pulses was adjusted to produce the desired duty factor. The electron beam passed through a slot in a grounded anode before terminating at a

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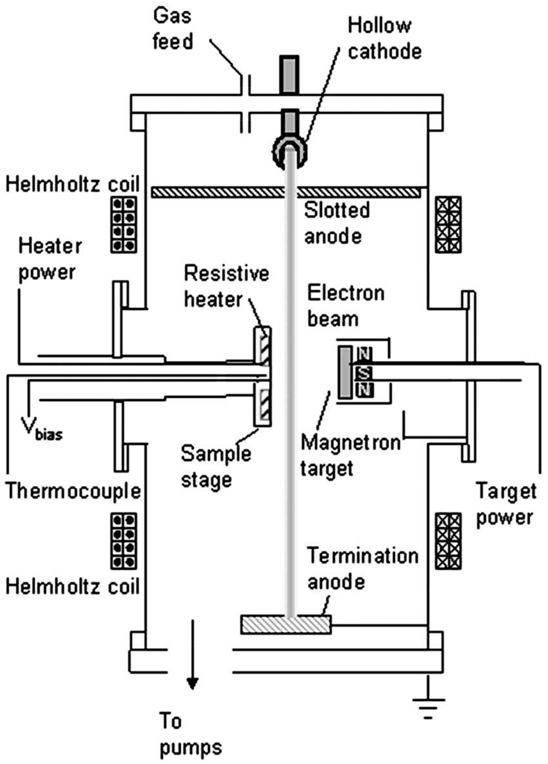

FIG. 1. Schematic of the processing chamber.

second grounded anode. A magnetic field between 125 and 165 Gauss (depending on electron beam duty factor) directed along the electron beam axis was generated with a pair of Helmholtz coils. The magnetic field was spatially uniform in the processing volume such that no variation was detected when measured over 0.5 cm steps along and across the beam axis; the field confined the electron beam to a uniform $60 \times 15 \times 1$ cm^3 sheet between the anodes.

Films were grown on (001) Si substrates clamped to an 11.5 cm diameter stainless steel disk. The substrates were heated to 250 °C and dc biased to −100 V. The total ion current to the substrate holder was calculated by measuring the voltage across a 100 ohm sense resistor on the substrate bias power supply with a digitizing oscilloscope during deposition. The substrate holder was imbedded in a 5 mm thick boron nitride insulator, allowing the current measurement to reflect only the incident positive ion flux from the plasma; the secondary electron yield from the stainless steel plate is assumed to be negligible when bombarded by ions with a kinetic energy of 100 eV or less.[22] The magnetic field produced by the Helmholtz coils was adjusted to maintain the time-averaged ion flux to the substrates for all experiments. All films were grown to a thickness of 500±25 nm as measured with a contact profilometer. Materials were characterized with a Rigaku ATX 18 kW x-ray diffractometer with θ fixed at 8° for all scans. A Digital Instruments atomic force microscope was also used to examine the surface morphology of the films.

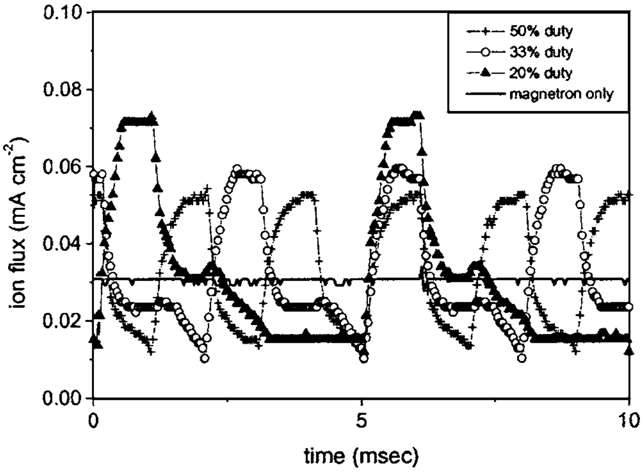

FIG. 2. Time-resolved ion flux at the substrate during operation of the magnetron and electron beam at different electron beam duty factors.

III. RESULTS

The ion flux from the magnetron alone to the substrate decreased monotonically with increasing magnetic field strength over the 125–165 G range investigated. By increasing the magnetic field (to reduce the ion flux from the magnetron) and simultaneously increasing the electron beam duty factor, a constant time-averaged ion flux could be maintained. Figure 2 shows the ion flux collected at the biased substrate holder during the deposition experiments. When the magnetron was operated alone with an auxiliary magnetic field of 125 G, the positive ion flux was constant at 0.031 mA cm^{-2}. When the electron beam source was introduced at various duty factors, the time-averaged positive ion flux was controlled by adjusting the auxiliary magnetic field from the Hemholtz coils to be within 3% of 0.031 mA cm^{-2}.

Titanium nitride films were grown with the electron beam operated at 0, 20, 33, and 50 percent duty for 180 min. Figure 3(a) shows x-ray diffraction patterns for selected film samples, and Fig. 3(b) shows the normalized (002)/(111) X-ray diffraction peak ratios for the crystalline TiN detected in the films. The ratio increased from 0.68 to 0.91 with increasing electron beam duty factor. Atomic force micrographs in Fig. 4 show the surface morphology of the TiN films grown with the electron beam off [Fig. 4(a)] and operating at 50% duty [Fig. 4(b)]. The films grown with the magnetron only exhibited an average grain size of approximately 25 nm, compared to ≈60 nm for TiN grown with both plasma sources. The root-mean-square (rms) roughness also decreased from 4.0 to 2.5 nm with exposure to the electron beam generated plasma during growth.

IV. DISCUSSION

The auxiliary magnetic field from the Helmholtz coils was directed parallel to the magnetron target surface and was sufficient to perturb the trajectories of electrons produced by the magnetron, especially those that followed the diverging field lines of the unbalanced magnetron. Varying the auxiliary field strength thus provided control over plasma genera-

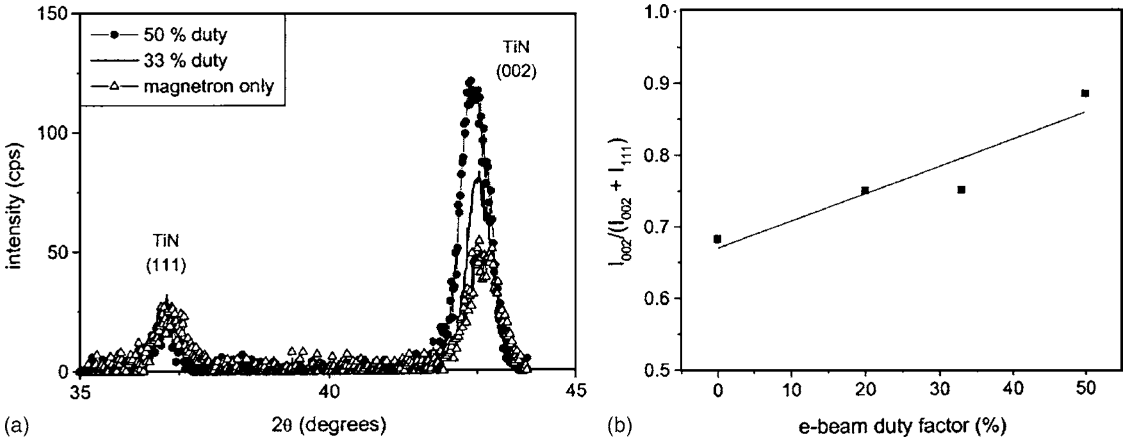

FIG. 3. X-ray diffraction data showing (a) raw diffractograms and (b) linear approximation of the normalized integrated (002)/(111) peak intensities for TiN films deposited with different electron beam duty factors.

tion near the substrate, while having little influence on the discharge at the target surface. Indeed, the ion flux to the magnetron target was constant, as it was maintained by its power supply, and the target voltage was only weakly dependent on the magnetic field. This provided a nearly constant Ti flux, and thus TiN deposition rate for all experiments. While increasing the auxiliary magnetic field reduced the ion flux from the magnetron discharge to the substrate, the time-averaged total ion flux was maintained by increasing the flux of species from the electron beam source. Thus, at least two critical deposition parameters were altered with increasing electron beam duty factor: The time-dependent ion-to-atom flux ratio, and the composition of the nitrogen ion flux.

The ion-to-atom ratio has been shown by other authors to affect the texture evolution and other microstructural features of titanium nitride and similar thin films. Specifically, Petrov *et al.*[15] have shown, that increasing the ion-to-atom ratio results in growth of the (002) orientation over the closely packed (111) orientation for NaCl structured transition metal nitrides.

Voevodin *et al.*[23] and Muratore *et al.*[24] also showed that intermittent spikes of high ion-to-atom ratios during pulsed deposition processes can effectively inhibit growth of closely packed planes, resulting in preferred growth of other orientations in other materials. For the analogous case of TiN deposition studied here, larger pulses of high ion flux should have resulted in increased growth of (002) crystals at the expense of those with the (111) orientation. Table I shows the peak ion-to-atom ratios for the deposition experiments that employed the pulsed electron beam source. The values in the table were calculated using the peak ion flux values shown in Fig. 2 and assuming the deposition rate provides a reasonable estimate of the neutral metal flux. The table indicates that the normalized (002) diffraction peak intensity

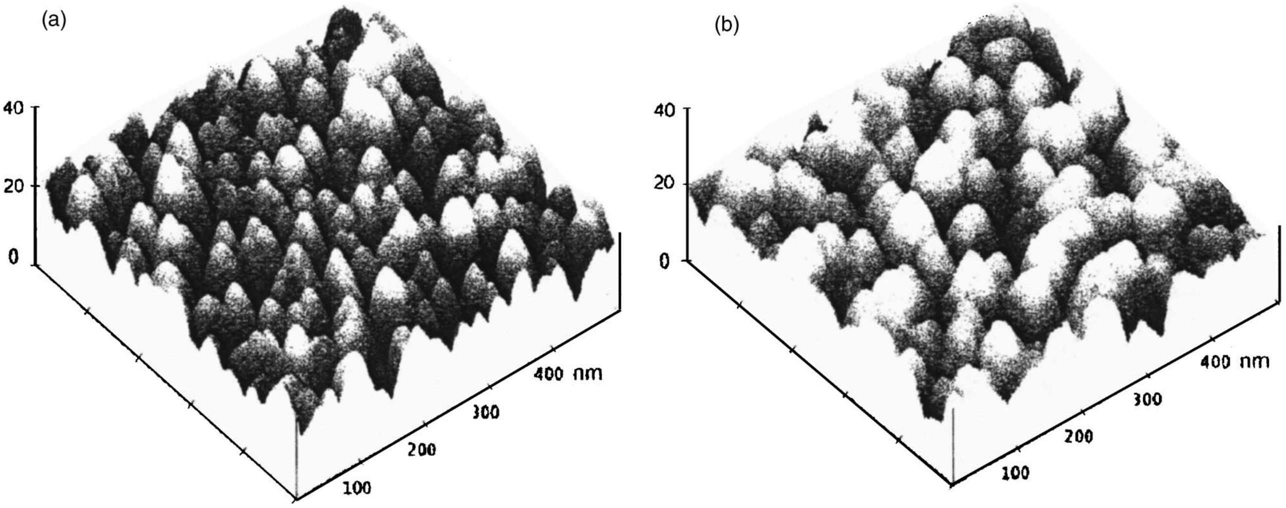

FIG. 4. Atomic force micrographs for the TiN films deposited with (a) the magnetron only and (b) the magnetron and electron beam plasma source at 50% duty. Units are in nanometers.

TABLE I. Calculated ion-to-atom ratios for peak ion fluxes at different electron beam duty factors and normalized x-ray diffraction peak intensities.

Duty factor (%)	Peak ion-atom ratio	Normalized (002)/111 intensity ratio
20	3.6	0.75
33	3.0	0.77
50	2.6	0.91

decreased with an increased peak ion-to atom ratio, but increased with electron beam duty factor. This suggests that TiN film texture was less dependent on the magnitude of the ion flux pulses than on other deposition parameters.

Plasma flux composition was also altered by the presence of the electron-beam-generated plasma. While no characterizations were performed in the current hybrid PEPVD system, previous measurements have shown that the composition of the ion flux is different compared to a magnetron alone. Mass spectrometric measurements of magnetron discharges with titanium cathodes in nitrogen have shown that nearly all of the ion flux consists of N_2^+ ions at low pressures.[21] Electron beam-generated plasmas have been characterized under similar operating conditions,[20,25] and were shown to generate a much higher fraction of atomic nitrogen ions, so increasing the beam duty factor in the hybrid system (while maintaining a constant ion flux) served to increase the flux of atomic nitrogen ions. Similarly, the flux of nitrogen atoms should be dependent on the presence of the electron beam produced plasma. For the high-energy electron beam employed for this work, approximately one N atom per electron-ion pair is expected to result from interaction of the electron beam with the ambient gas.[26] Also, the electron temperature in the beam-generated plasma was approximately 0.5 eV,[25] compared to 1–10 eV in unbalanced magnetron discharges[27–29] and low electron temperatures promote dissociative recombination of molecular nitrogen ions into pairs of nitrogen atoms.[30] Therefore, the flux of both atomic nitrogen ions and atoms was likely to increase with the electron beam duty factor.

Figure 3 shows the effect of the electron beam duty factor on texture evolution for the reactively sputtered titanium nitride films. As is evident, increasing the duty factor increased the normalized (002)/(111) x-ray diffraction intensity ratios. The increase in (002) texture was accompanied by the presence of shorter, broader grains and smoother films. These results are similar to those observed with an increase in ion flux, substrate bias or temperature in other works.[31–35] Here, however, all of those factors were held constant. As mentioned earlier, other authors have reported comparable microstructural responses for TiN when the nitrogen partial pressure or total nitrogen ion flux was increased.[13–16]

The TiN microstructure and texture observed in the present work might also reflect that atomic nitrogen ions deliver more energy to the growing film due to their longer mean free path. The charge exchange mean free path for 100 eV N_2^+ ions in 30 mTorr nitrogen is ≈0.3 cm, but is ≈3.4 cm for the N^+ ion.[36] From the flux measurements, the plasma density at the sheath edge is estimated to be $\sim 10^9$ cm^{-3} (Ref. 37), and for a sheath potential of 100 V, the sheath width is ≈0.6 cm (Ref. 38). Therefore, a large number of the molecular nitrogen ions arrived at the substrate with energies below 100 eV, while nearly all of the atomic nitrogen ions arrived with an energy equal to 100 eV, which was sufficient to cause resputtering[39] and enhanced diffusion at the film surface. Moreover, the molecular nitrogen ions had to share incident kinetic energy between both atoms comprising the molecule, further reducing the energy available to induce atomic rearrangements at the film surface.

V. CONCLUSION

The effect of nitrogen flux composition on reactive deposition of titanium nitride was studied by varying the composition of the ion flux in a hybrid PEPVD system during film growth. At the same time, the metal deposition rate, time-averaged ion flux, substrate bias, nitrogen pressure and nitrogen flow rate were all held constant. Increasing the flux of atomic nitrogen ions and neutrals resulted in smoother film surfaces and an increase of the normalized (002)/(111) x-ray diffraction peak intensities from 0.68 to 0.91.

The (002) texture for TiN has previously been associated with an increase in ion flux, substrate bias or temperature, but all of those factors were held constant in the present experiment. This result suggests that the flux of atomic nitrogen species, rather than the ion-to-atom flux ratio, can be used to control texture evolution in reactively sputtered titanium nitride. According to other authors, the surface kinetics of the atomic nitrogen neutrals and ions should lead to the observed texture development. In this work, the additional kinetic energy imparted to the growing film by N^+ ions (because of their longer mean free path and atomic nature) was also considered. The correlation between ion flux composition and film microstructure suggests that the use of an auxiliary plasma source that efficiently generates atomic nitrogen ions and neutrals can alter film properties more effectively than techniques that simply increase the molecular nitrogen ion flux for TiN deposition. Substrates subject to damage from heating or other effects of excessive ion bombardment are especially likely to benefit from efficient atomic species generation. Additionally, increasing the atomic nitrogen ion and neutral flux might be useful for improving the step or surface coverage of very thin transition metal nitride layers, as the (002) grains grow outward more rapidly than upward.

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