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Modifications of reactively sputtered titanium nitride films by argon and vanadium ion implantation: Microstructural and opto-electric properties

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Polycrystalline titanium nitride (TiN) layers of 240 nm thickness and columnar microstructure were deposited at 150 °C by d.c. reactive sputtering on Si(100) wafers and then irradiated at room temperature with either 80 keV V^+ ions (at fluences of up to 2×10^{17} ions/cm^2) or 200 keV Ar^+ ions (at fluences of 5×10^{15}–2×10^{16} ions/cm^2). Rutherford backscattering spectroscopy, cross-sectional (high-resolution) transmission electron microscopy and X-ray diffraction were used to characterize ion-induced changes in the structural properties of the films. Their optical and electric properties were analyzed by infrared reflectance (IR) and electric resistivity measurements. After deposition, the stoichiometric TiN films had a (111) texture. Ion implantation generated a damaged surface layer of nanocrystalline structure, which extended beyond the implantation profile, but left an undamaged bottom zone of (111) orientation. This layer geometry determined from transmission electron microscopy was inferred in the analysis of IR reflectance data using the Drude model, and the variation of the electric and optical resistivity with the irradiation was deduced. The results were compared to those recently gained for ion-implanted reactively sputtered chromium nitride films.

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1. Introduction

Transition metal nitrides such as titanium nitride (TiN) present highly covalent bonds in simple, usually cubic (for TiN: rock salt) structures, which give them an extreme hardness, high corrosion resistance and excellent mechanical and high-temperature stability [1–6]. Due to their excellent tribological characteristics, they have become important materials for protective and abrasion-resistant coatings. TiN is inert, biocompatible and will tolerate temperatures of up to 480 °C in air; its coefficient of friction against other nitrided surfaces is 0.05–0.15. Its high infrared and optical reflectivity is similar to that of gold; thus it is frequently applied in scratch-resistant decorative coatings [7,8]. Furthermore, TiN films are known as antireflective coatings in optical lithography [9], as diffusion barriers in the aluminum and copper metallization, and as high-Q superconducting microresonator detectors [10]. Numerous investigations have been devoted to synthesizing TiN films and nano-composites via various sputtering and ion-beam-assisted techniques [1–6,11–14], e.g. plasma-immersion ion implantation, arc plating, or reactive sputtering. These studies aimed at optimizing the tribological properties and tailoring the orientation of the TiN columnar structure relative to the substrate [15,16]. Recent studies [17–21] have indicated that the presence of a few atomic percent of amorphous silicon or additional transition metals (Al, Fe, V, Cr, Nb) may change the mechanical properties dramatically and enhance the hardness of TiN coatings.

In various respects, the present work is an extension of previous microstructural analyses of Ar-ion irradiated polycrystalline TiN films [22–25]. By using vanadium as another transition-metal ion species, we have tried to distinguish between chemical effects and purely defect-related effects induced during Ar-ion implantation. When predicting the new final phase(s) to be generated, the heat of formation of the binary or ternary nitride has to be considered; at 298 K, the heat of formation is −336.6 kJ for TiN and −217.3 kJ for vanadium nitride (VN) [26–28]. A priori, one may expect the formation of either metallic V or Ti precipitates, or VN nanoparticles, or a solid solution of the type $Ti_{1-x}V_xN$ [28], provided the correct stoichiometry and sufficient mobility are available. Davies and collaborators [20] have recently produced homogeneous cubic $Ti_{1-x}V_xN$ alloys on Si by means of dual source pulsed cathode arc, over the full composition range $0\le x\le1$. They found the highest hardness and stress for $x\approx0.23$. Since TiN, VN and $Ti_{1-x}V_xN$ have similar microstructural parameters when analyzed with X-ray diffraction (XRD) and transmission electron microscopy (TEM), we have also used alternative techniques, such as infrared reflectance spectroscopy and electric resistance measurements, to characterize the samples after deposition and ion implantation. A similar recent study of V-implanted chromium nitride (CrN)

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films [29] has demonstrated the relevance of the opto-electric techniques and we shall compare here the results for both systems.

2. Experiments

Titanium nitride films were deposited at a rate of about 8 nm/min by d.c. reactive sputtering from a Ti target of 99.9% purity, using Ar for sputtering, reactive N_2 gas and a Balzers Sputtron II system operated at 1.5 kV. The base pressure in the chamber was around 1×10^{-4} Pa, the argon and nitrogen partial pressures during deposition were 1×10^{-1} Pa and 3×10^{-2} Pa, respectively. The substrates used were 550 μm thick Si(100) wafers, which were cleaned in diluted hydrofluoric acid and deionized water, and were kept at 150 °C during deposition. After 30 min of deposition TiN films had a thickness of 240 nm, as verified by TEM. A previous study had confirmed that homogeneous and polycrystalline TiN films of the correct atomic stoichiometry are produced in this way [22–25].

The samples were implanted at room temperature and under a pressure of 1×10^{-4} Pa with 80-keV V^+ ions or 200-keV Ar^+-ions provided by the 500-kV implanter at Vinča. The V-implantations were performed at fluences of 1×10^{17} and 2×10^{17} ions/cm^2, the Ar-implantations at fluences of 5×10^{15}–2×10^{16} ions/cm^2. The implanted area was 2×2 cm^2, homogeneously covered by means of an xy sweeping system. The beam current was maintained at around 1 μA/cm^2. The chosen V-ion energy guaranteed that the average projected range, $R_P=38$ nm, and full width at half maximum (FWHM), $\Delta R_P=14$ nm, estimated with the SRIM2010 [30] and TRIDYN codes [31], should be well separated from the TiN/Si interface in order to avoid any ion beam mixing and interface reactions. In the case of Ar ions, SRIM2010 predicts an implantation profile characterized by $R_P=109$ nm and $\Delta R_P=38$ nm.

Structural and compositional characterizations were performed with Rutherford backscattering spectroscopy (RBS), XRD, cross-sectional and high-resolution transmission electron microscopy (XTEM and HRTEM). Optical and electric properties were measured by means of infrared reflectance spectroscopy (IR) and electrical resistivity measurements. The RBS analyses were performed with a 900 keV He^{++} ion beam provided by the Göttingen IONAS implanter [32] and with 1.2 MeV α-particles provided by the SAFIR facility of the Institut des Nanosciences in Paris [33]. The backscattering spectra were taken at normal beam incidence in two Si surface barrier detectors positioned at ±165° to the beam. The concentration profiles of the various components were analyzed with the WIN-DF and RBX codes [34,35] by assuming successive layers of homogeneous, but varying element compositions.

XTEM was carried out on a JEOL 100CX microscope operated at 100 kV, and we also used the micro-diffraction technique to study the crystalline structure. The specimens for XTEM examination were prepared by gluing samples together face-to-face in a sandwich structure and then cutting a vertical section, which was thinned by polishing it to a thickness of ~50 μm. The final thinning to electron transparency was done by 5-keV Ar-ion beam milling on a Gatan PIPS-691 ion-miller. Microstructural HRTEM characterization of selected samples was performed at a Philips CM200-FEG microscope operated at 200 keV. In order to investigate the structure of crystalline regions, the image was analyzed by fast Fourier transformation. Most of the samples were analyzed by XRD in Bragg–Brentano geometry using a BRUKER D8 Advance diffractometer and the CuK_α radiation; the scanned angular range extended between $2\theta=30°$ and 65°, in 0.03° steps. From the positions and widths of the diffraction peaks, we determined the lattice constants and average crystallite size of the films [36,37].

Infrared spectroscopy in reflection mode was performed by means of a BRUKER Vertex 70 interferometer and under an incidence of 30° in the 500–4000 cm^{-1} range, using a mercury cadmium telluride detector with an instrumental resolution of 4 cm^{-1}. A gold mirror was used as reference, i.e. the reflectance of each TiN/Si bilayer sample was calculated relative to the intensity of the beam reflected by the mirror. Finally, the electric resistivity of the films was measured by the four-point probe method. Note that the electro-optical techniques as well as XRD provided information over the whole sample depth. How the relevant optical and electric parameters for the ion-modified layers were extracted will be explained in Section 3.4.

3. Results and discussion

3.1. RBS analyses

Fig. 1a and b shows experimental and fitted RBS spectra for samples after deposition and Ar-ion implantation. Both spectra are consistent with a Ti:N atomic ratio of ~1:1 over the full depth of the film having an areal density of 2.41×10^{18} atoms/cm^2. Combining this number with the layer thickness measured by XTEM, $d=240$ nm, provides a density of 1.0×10^{23} atoms/cm^3 or 5.2 g/cm^3, which is close to the bulk density of 5.40 g/cm^3 for stoichiometric TiN. Note that the weak signal from N surface atoms (near the backscattering energy of 250 keV) overlapped with the signal arising from the Si substrate and thus prevented us from directly determining the nitrogen concentration profile. After Ar-implantation the spectrum (b) remained essentially unchanged, except for a small dip in the Ti backscattering yield around the backscattering energy of 580 keV, i.e. near the depth of the maximum Ar yield. The spectrum confirmed that Ar implantation does not induce any major redistribution of components in the film nor any intermixing at the TiN/Si interface.

Fig. 1c shows RBS spectrum after V-ion implantation at a nominal fluence of 2×10^{17} ions/cm^2; the spectrum accumulated for 1×10^{17} V-ions/cm^2 was qualitatively similar to the ones shown. The Ti, V and Si concentration profiles deduced from RBS at the two α-particle energies and presented in Fig. 2a and b are almost identical. We note an increase in total layer thickness, which most probably is due to surface oxidation and overcomes the expected reduction in layer thickness due to sputtering. For sputtering TiN with 150-keV Ar ions, a sputtering yield of 0.4 atoms/ion [38,39] was measured, with about equal values for both elements and no preferential sputtering observed. This result can be reproduced by either TRIDYN [31] or SRIM2010 [30], if the surface binding energy is adjusted to about 8 eV, on the basis of the high TiN binding energy of 4.89 eV and its high melting point of 2930 °C. Then one finds rather low and similar sputtering yields of $Y\approx0.6$ atoms/ion for Ti and N. For 80 keV V ions, we arrive at sputtering yields of $Y(Ti)\approx Y(N)\approx0.9$ atoms/ion. As expected, the V concentration rose in the implantation region, by up to 20 at.% in the maximum. The V, Ti and N profiles were simulated at the fluence of 2×10^{17} V-ions/cm^2, by means of TRIDYN [31], resulting in concentrations of about 30 at.% for V, 35 at.% for Ti, and 35 at.% for N at maximum overlap (see Fig. 2c). Combining the results from RBS and TEM, we arrive at an average atomic density of 1.02×10^{23} atoms/cm^3 in the damaged region, which has the thickness $y=120$–170 nm.

3.2. XTEM and HRTEM analyses

The depth-dependent structural evolution of the films was monitored via XTEM and HRTEM. Fig. 3a shows the cross-sectional bright-field image and corresponding micro-diffraction pattern of an as-deposited film, while Fig. 3b and c illustrates a bright-field and an HRTEM image of a sample implanted with 2×10^{16} Ar-ions/cm^2. The as-deposited sample exhibits a polycrystalline, columnar structure throughout the complete film with (111), (200) and (220) reflections visible. Ar-ion irradiation at this moderate fluence destroyed the columnar structure within the 160 nm top layer, roughly the dimension of the ion range + width, $R_p+\Delta R_p$, but did not affect the deeper sublayer adjoining the Si wafer. The damaged top layer exhibits nanocrystalline grains, 7–10 nm in diameter, which is in agreement with the XRD data. The interplanar distances of 0.245, 0.212 and 0.149 nm correspond

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