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Substrate and annealing temperature dependent electrical resistivity of sputtered titanium nitride thin films

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ABSTRACT

We have studied the electrical resistivity and the temperature coefficient of resistance (TCR) of titanium nitride (TiN_x) thin films deposited by radio-frequency (RF) reactive magnetron sputtering from a high purity titanium target in a nitrogen-argon gas mixture environment with high nitrogen-to-argon ratio (20:1). The electrical resistivity and TCR are measured from room temperature to 500 °C for films deposited with substrate temperatures of 25 °C, 350 °C and 600 °C. After deposition, some films are annealed at 600 °C for four hours either with or without breaking the vacuum. The structural stability of the films was examined by measuring electrical resistivity from room temperature to 500 °C repeatedly up to four cycles. Selected films were further characterized by Rutherford backscattering, X-Ray diffraction, and Raman spectroscopy. Our results show that RF sputtered TiN_x films with good electrical resistivity and temperature-stable TCR for high-temperature applications of conductive diffusion barrier and temperature sensing can be produced. We conclude that high substrate temperature, high annealing temperature, and annealing without breaking the vacuum yield optimal structural stability and electrical resistivity. High mass density is also important to prevent oxidation and degradation of electrical performance.

1. Introduction

Thin film titanium nitride (TiN_x), due to its extreme hardness, high melting point, low electrical resistivity, and excellent corrosion and diffusion resistance [1], has been of interest for many years in a variety of applications, such as ultrahard coatings [2], contacts [3], gate electrodes [4], MEMS resistors [5], and diffusion barriers [6]. The high melting point and metallic resistivity behavior of TiN_x films make them an intriguing material for high-temperature electronic and sensing applications, as exposing electronic devices containing silicon-based thin films to high temperature environment can cause silicide formation and inter-diffusion of silicon with metallic contacts. Most resistivity work on TiN_x films is conducted, however, below 100 °C [1], while fewer studies have examined the resistivity of TiN_x beyond this temperature range [5]. This is likely because many practical electronics applications already fall within this temperature range. Although there are reports on the effects of annealing [6, 8] or deposition at temperatures > 100 °C [7, 9], these studies do not consider the combined effects of annealing and high temperature deposition, nor do they consider repeated annealings. Additionally, most of them only examined room temperature resistivity. Several applications, such as MEMS hotplates [5] and thin-film nanocrystalline silicon thermoelectrics [10, 11] involve sustained operation at temperatures higher than 100 °C. Some TiN_x films have sheet resistances that do not have a linear or even reproducible temperature dependence as they are brought to temperatures higher than their deposition temperature [5, 7]. This suggests that TiN_x films are not structurally stable when they exceed their deposition or annealing temperatures and that, even with otherwise optimal deposition parameters, substrate temperatures during deposition and annealing are critical to high temperature performance. In addition to structural change, high temperature exposure, especially in atmospheric or poor vacuum environments, may also lead to oxidation of TiN_x, the degree of which varies depending on the quality of the films, such as film density [9, 12, 13].

While a variety of methods exist for depositing TiN_x such as atomic layer deposition [4], chemical vapor deposition [14], pulsed laser

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deposition [15], and cathodic vacuum arc deposition [12, 16], reactive magnetron sputtering is a well-established deposition method known to produce high structural quality and low resistance thin films. Sputtering techniques are also known to typically produce dense, uniform, and stoichiometric TiN_x films ($x = 1$), an especially important consideration for thin barrier layers. Fortunately, a large amount of literature is available on reactively sputtered TiN_x, examining the effects of reactive sputtering parameters such as nitrogen percentage [5, 6, 17–22], total pressure [17], sputtering gases [21], bias voltage [8], power [2], substrate temperature [8, 23, 24], and annealing [6, 13, 18, 25]. Studies on nitrogen partial pressures [5, 6, 17–19, 23] note that higher nitrogen partial pressure produces films having higher stoichiometry, lower resistivity, and thus better structural stability. As annealing and elevated substrate temperatures are known to lower resistance in most cases by improving crystalline structural order [6–8, 23, 24], we expect reactively sputtered stoichiometric TiN films that are stable at high temperatures to also be of high structural quality and low resistivity, and thus also possess a higher temperature coefficient of resistance (TCR). Therefore, we study the combined effects of substrate and annealing temperatures on electrical resistivity and TCR from room temperature to 500 °C as the TiN_x thin films go through repeated thermal cycles. In addition, we also examine the structural stability and oxidation resistance of the TiN_x films in combination with structural characterizations.

2. Experimental details

Thin film TiN_x was deposited on fused silica substrates using an AJA magnetron sputtering system at a base pressure of 3×10^{-5} Pa using a 5 N 2″ Ti target at a target-to-substrate working distance of 77 cm. Initially in a pure Ar environment, samples were pre-sputtered for 5 min, then an adhesion layer of 6 nm Ti was deposited on the substrate. These two steps help to remove oxide and nitride from the target surface and further reduce residual oxygen in the deposition chamber through oxidation. During TiN_x deposition, a radio frequency (RF) power of 100 W was used, resulting in a power density of 4.94 W/cm^2 in the presence of N_2 and Ar gases at 3 mTorr in a 20:1 ratio favoring N_2 to ensure that the sample was nitrogen saturated.

Six samples were studied in this work; they vary in substrate temperatures and the methods of annealing, see Table 1. Sputtering time was controlled based on deposition rate as a function of substrate temperature, to produce films varying in thicknesses ranging from 57.1 to 78.2 nm. For sample A-E, depositions took approximately 2 h while sample F was given only 1 h, due to the elevated deposition rate. Substrate temperatures of 25 °C, 350 °C, and 600 °C were used. Samples B, D and E were annealed in the sputtering chamber in vacuum for 4 h at 600 °C. While samples B and E were removed from the sputtering chamber and were later loaded back in for their annealing steps, sample D was annealed in the sputtering chamber without breaking vacuum. Samples A and C are from the exact same deposition as sample B and E, respectively, except that they were not returned to the sputtering chamber and were thus left unannealed.

An ellipsometer was used to measure film thicknesses and the results were confirmed using a step profilometer. Rutherford backscattering (RBS) measurements were performed by EAG laboratories to determine the mass density and Ti:N ratio of samples C and F, where the thicknesses from ellipsometer measurements were used to obtain the density. The results, included in Table 1, show that the samples are nearly stoichiometric, but less dense than bulk TiN and many reported TiN_x thin films in the literature. Square pieces were cut using a laser cutting tool and aluminum wire bonds were made directly to the four corners of TiN_x samples. After this, each sample was placed in a Janis VPF-800 cryostat and a four point Van der Pauw method was used to determine electrical resistivity at each preset temperature between room temperature and 500 °C in the order of increasing temperature. At each temperature point, the sample was held for as long as it took for its resistance to be reasonably stabilized. Only the final and stable resistance value was used for analysis.

After resistance measurements, samples were characterized by grazing-incidence X-ray diffraction (XRD) measurements using a Rigaku SmartLab X-ray diffractometer equipped with fixed CuKα radiation in parallel-beam mode. The angle of incidence was set to 0.5° θ and the detector was rotated to measure from 20 to 70° in increments of 0.02° 2θ and counts were accumulated for 1 s at each step. Sample height alignment was conducted via Rigaku's automated height-alignment function for flat samples. The Raman spectra were acquired with a home-built confocal micro-Raman setup composed of a 0.5-m single spectrometer using a 1800 groove/mm grating; a liquid nitrogen cooled back-thinned/deep-depleted CCD sensitive in the visible-near IR spectral range; and a single-mode 488 nm laser with typical spot size < 1 μm and intensity ~2 mW at the sample.

3. Results and discussion

Fig. 1 shows the results of two consecutive resistivity measurements from room temperatures to 500 °C for sample A and B. Due to the fact that sample A was deposited at room temperature and not annealed, the film underwent an irreversible structural relaxation with increasing temperature in the first run. This caused its resistivity to drop 35%. Note that at each temperature point, we allowed a sufficient amount of time (~45 min) for the film to reach thermal equilibrium with the stage and to allow some structural relaxation of the film to take place. At the second run, sample A started with a much lower resistivity and showed a sign of positive TCR, a signature of metallic resistivity. The slight drop of resistivity at the highest temperature is a sign of further structural relaxation of the film. Because of the 4 h annealing at 600 °C, sample B started with a resistivity similar to that of sample A at the second run with a positive TCR. The decrease of resistivity at higher temperature (~300 °C) shows that structural relaxation continues despite of the annealing, indicating the effect of annealing is limited for room temperature deposited TiN_x films. For the second run, its resistivity started at a 10% lower value and shows a positive TCR throughout the investigated temperature range. These results demonstrate that TiN_x films deposited at room temperature undergo structural changes with increasing temperature, resulting in a reduction in resistivity as observed previously [7]. Annealing helps but is still far from enough as we will

Table 1
Sputtered TiN_x names, deposition parameters, and some characterizations in comparison with the bulk.

Sample	N_2:Ar	Substrate °C	Annealing °C	Thickness nm	Deposition rate nm/s	Crystal size nm	Ti:N	Density g/cm^3
A = TiN/25	20:1	25	–	78.2	0.01086	–	–	–
B = TiN/25/600[air]	20:1	25	600*	78.2	0.01086	5.5	–	–
C = TiN/350	20:1	350	–	57.1	0.00758	–	–	–
D = TiN/350/600[vac]	20:1	350	600	62.5	0.0086	12.4	1:1.04	3.78
E = TiN/350/600[air]	20:1	350	600*	57.1	0.00758	–	–	–
F = TiN/600	20:1	600	–	58.0	0.0161	15.6	1:0.98	4.14
Bulk	–	–	–	–	–	–	1:1	5.22

* Exposed to air.

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