Thin Solid Films 578 (2015) 31–37

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effect of deposition conditions and post deposition anneal on reactively sputtered titanium nitride thin films

Nikhil K. Ponon *, Daniel J.R. Appleby, Erhan Arac, P.J. King, Srinivas Ganti, Kelvin S.K. Kwa, Anthony O'Neill

School of Electrical and Electronic Engineering, Newcastle University, Newcastle upon Tyne NE1 7RU, United Kingdom

ARTICLE INFO

Article history:
Received 29 May 2014
Received in revised form 17 December 2014
Accepted 3 February 2015
Available online 10 February 2015

Keywords:
Titanium nitride
Reactive sputtering
Resistivity
Annealing
X-ray photoelectron spectroscopy
X-ray diffraction

ABSTRACT

Titanium nitride (TiN_x) was deposited by reactive sputtering using a titanium target in a nitrogen ambient. Nitrogen flow rate during deposition was varied in order to investigate its effect on film resistivity. Conductivity is found to improve with increasing nitrogen content. Films were then annealed, varying the time and temperature of the anneal. Resistivity was found to decrease with longer annealing time and higher temperature during post deposition annealing. TiN_x films showed good thermal and electrical stability upon annealing and did not show any silicon diffusion. It was found that film orientation can influence the resistivity, with [111] oriented films more resistive than [200] oriented films. Moreover, re-crystallization effects brought on by post deposition annealing cause the resistivity to decrease. Films deposited above 20% nitrogen flow rates during deposition were all stoichiometric TiN. However, TiN_x deposited at very high nitrogen flow rate was found to be electrically, thermally and morphologically more stable than the ones deposited at low nitrogen flow rates.

1. Introduction

Titanium nitride (TiN) is an extremely hard material with high thermal and chemical stability and low electrical and thermal resistivity [1]. It has found many applications in the microelectronics industry as a diffusion barrier [2], gate material [3], Schottky barrier contact [4], adhesion layer [5], and as an electrode in dynamic random access memory cells as well as a back-end-of-line metal–insulator–metal capacitor electrode in integrated circuits [6]. With the increased use of metal nitrides in front-end-of-line processes, which may undergo a post deposition anneal at a temperature well above 500 °C, the stability of these materials at process-relevant temperatures is of paramount interest. The stability of titanium nitride is also key for high temperature electronic circuits as they can be used as capacitor electrodes and transistor gate electrodes in wide-gap semiconductor devices [7].

TiN_x can be deposited in a variety of ways [8–11]. One such method is direct current (DC) magnetron reactive sputtering. This inexpensive technique can deposit films that have high purity and uniformity, with a good control over stoichiometry. In reactive sputtering, the quality of the deposited films depends upon deposition parameters such as nitrogen content in the chamber during deposition, power, residual oxygen in the chamber, pressure, substrate temperature and substrate bias [11]. In the case of integrated circuit applications, TiN_x with better electrical properties may be preferred over stoichiometric TiN.

In microelectronic applications there are constraints on the use of high substrate temperatures during deposition. This is to avoid structural and compositional changes to other materials used in device manufacture and to prevent any uncontrolled diffusion or metal extrusion [12]. However, these structures may undergo a controlled high temperature rapid thermal process (RTP) for dopant activation, dielectric crystallization or metal–semiconductor interface activation. Hence, understanding the impact of post deposition annealing on TiN_x is crucial. To date, there are currently no detailed investigations reported in the literature on the role of post deposition annealing in an oxygen-free ambient above 500 °C on TiN_x deposited with various nitrogen contents. Many research groups have reported that the resistivity of sputtered TiN increases between 100 μΩcm and 1000 μΩcm [13–15] after annealing in a non oxidizing environment in the 500 °C–800 °C range, which is claimed to be due to the oxygen impurity in the annealing ambient [16]. A drastic increase in the sheet resistance after the RTP process would increase the parasitic resistance and resistor–capacitor circuit delays and is not generally desirable from a semiconductor device point of view. Moreover, a sheet resistance value below 400 μΩcm is typically preferred when they are used as the gate electrode of a metal–oxide–semiconductor field effect transistor (MOSFET). [14,17]. Here, we have annealed the samples in high vacuum conditions (1.3×10^{-4} Pa) at temperatures ranging from 500 °C to 900 °C and time varying from 1 min to 20 min in order to avoid the effect of oxygen impurity in the annealing process. The impact of nitrogen flow rate relative to that of argon (N_2 / N_2 + Ar) during deposition, and the post deposition thermal treatment of TiN_x are discussed in this paper. In comparison to other studies, results show that resistivity in fact decreases

* Corresponding author.
E-mail address: nikhil.ponon@ncl.ac.uk (N.K. Ponon).

http://dx.doi.org/10.1016/j.tsf.2015.02.009

with increase in nitrogen flow rate during deposition, annealing temperature and time. It was found that there is more than one factor which affects the resistivity of the film. Based on these results, reasons for the drop in resistivity with increase in nitrogen flow rate and with a post anneal are assessed in section 3.

1.1. Experimental details

TiN_x was sputtered in an Oxford plasma 400 DC magnetron sputtering system using an eight inch high purity (99.995%) titanium target in a mixture of argon and nitrogen gas. 80 nm thick thermally oxidized silicon dioxide on <100> oriented silicon was used as the substrate. The system was baked out at 100 °C for 12 h which reduced the chamber pressure to 1.3×10^{-4} Pa. Further improvement in the vacuum was achieved by depositing titanium on a dummy wafer in two steps of 15 min each, which reduced the vacuum of the system to 1.3×10^{-5} Pa. The sputtered titanium is believed to react with the remaining oxygen in the chamber creating oxides and thereby reducing the gas pressure inside the chamber.

The deposition time was set to 10 min with the chamber pressure kept at 0.5 Pa. The base pressure was 1.3×10^{-5} Pa and the power used was 800 W for all experiments based on the initial optimization experiments. Step height, measured using atomic force microscopy (AFM), showed that the thickness variation was from 130 nm to 170 nm corresponding with the variation in nitrogen content. The flow rate of nitrogen relative to that of argon was varied from 20% to 95% in order to produce samples of varying stoichiometry. The substrate temperature was limited to 250 °C in order to closely mimic the fabrication condition for both front and back end of line integration. In order to examine the role of high temperature processing on TiN_x thin film properties, as-deposited samples deposited at different nitrogen flow rates were annealed in high vacuum (1.3×10^{-4} Pa). Annealing processes were carried out at 500, 700 and 900 °C for 1, 2, 10 and 20 min.

Sheet resistance was measured at room temperature by a standard four point probe measurement technique. Phase composition and crystallinity were characterized by X-ray diffraction (XRD) with Cu-K_α X-ray radiation having a characteristic wavelength of 1.5418 Å. The powder X-ray diffractometer was set up in the Bragg–Brentano geometry. The X-rays were generated from a Cu anode supplied with 40 kV and a current of 40 mA. Ar ions with beam current 5 mA, an acceleration of 5 kV and a square raster of 1 mm were used to etch the sample for X-ray photoelectron spectroscopy (XPS) depth profiling. The X-ray spot size was 110 μm for the XPS measurements. Raman spectroscopy was used to identify vacancies in the film. A 514 nm laser was used for Raman spectroscopy measurements. The acquisition time was 30 s and the confocal aperture was set to 300 μm. Surface roughness of the deposited film was measured using Park Systems XE 150 AFM in non contact mode. The majority of the material analyses were carried out on samples deposited at lowest nitrogen content (20%) and highest nitrogen content (95%), in order to isolate the physical/structural origins of any observed differences in resistivity.

2. Results

2.1. Variations in resistivity

Changes in resistivity as a function of nitrogen flow rate during TiN_x deposition and for different annealing temperatures for a 1 minute anneal are shown in Fig. 1. The resistivity of the as-deposited samples is also shown and is highest when the nitrogen flow rate is lowest (20%). Resistivity reduces with increasing nitrogen content during TiN_x deposition and reaches the lowest value of 80 μΩcm for the highest nitrogen content of 95%. The resistivity of the films reduces with increasing annealing temperatures for all nitrogen contents, and falls to 35 μΩcm for the sample deposited at 95% nitrogen content when annealed at 900 °C for 1 minute. Resistivity values for different annealing times at fixed annealing temperatures of 500 °C, 700 °C and 900 °C are shown in Fig. 2. Resistivity drops with annealing time and the lowest value of 30 μΩcm was obtained when annealing the highest nitrogen content sample for 20 min. It can be clearly observed that the resistivity is inversely proportional to nitrogen content during deposition, annealing time and annealing temperature. The highest resistivity was present for the as-deposited samples deposited in 20% nitrogen ambient. The lowest resistivity was obtained when the nitrogen flow was at its highest (95%) and when annealed at 900 °C for 20 min. The variation in the material properties after a post deposition anneal is discussed in the following sections.

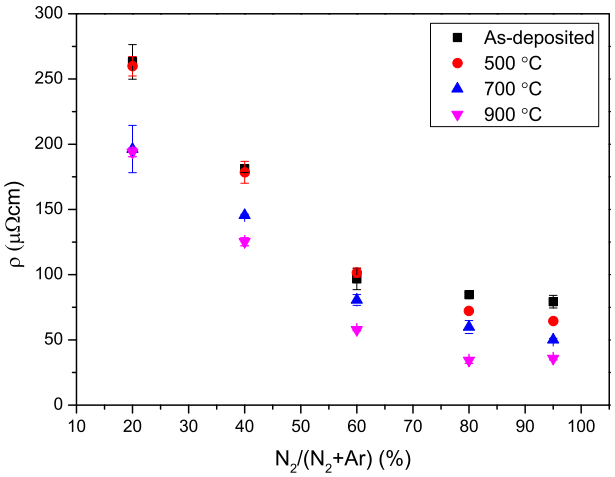

Fig. 1. Variation of TiN_x resistivity with annealing temperature for a fixed annealing time of 1 min. Resistivity decreases with increase in annealing temperature for all nitrogen flow rates.

2.2. Variations in orientation

The XRD patterns of TiN_x deposited at 20% or 95% nitrogen ambient and then annealed at 700 °C for 1 min and 10 min are shown in Fig. 3. The 20% sample shows a main peak associated with the [111] orientation at around 36.7°, whereas the 95% sample shows a weaker peak for [111] orientation and a predominant peak for [200] orientation around 42.8°. The XRD peak positions confirm that samples deposited at various nitrogen pressures are all TiN phases [18]. The relative intensity (I[111]/I[200]) from the XRD patterns is shown in Fig. 4. TiN_x films with the highest I[111]/I[200] intensity in XRD patterns demonstrate the highest resistivity; these are also the films deposited at lowest nitrogen content. The I[111]/I[200] XRD peak intensity and the resistivity decrease with increasing nitrogen flow rate for the as-deposited samples. These results demonstrate that the resistivity of TiN_x depends on the phase orientation. However, after post deposition annealing, the change in I[111]/I[200] intensity was not proportional to the annealing time even though the resistivity decreased with increasing annealing time. Moreover, the I[111]/I[200] XRD peak intensity increased when compared to that of the as-deposited sample deposited in 60% nitrogen ambient. This would suggest that there is more than one factor directly influencing the resistivity of the film. These other factors affecting the resistivity of the film are investigated in the following sections.

2.3. Variations in vacancies

Raman spectra of the as-deposited and annealed samples (10 min, 700 °C) for 20% and 95% nitrogen flow rate during TiN_x deposition are shown in Fig. 5. Refractory materials such as TiN_x contain both titanium and nitrogen vacancies even for stoichiometric samples. Due to these vacancies, defect induced first-order Raman scattering is possible even though TiN has a symmetric cubic lattice [19]. Raman spectra for TiN_x