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


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Titanium nitride (TiNₓ) 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 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 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.

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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]. TiNₓ 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, TiNₓ 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 TiNₓ 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 TiNₓ 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 anneal 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 (N₂ / N₂ + Ar) during deposition, and the post deposition thermal treatment of TiNₓ are discussed in this paper. In comparison to other studies, results show that resistivity in fact decreases.

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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

TiNx 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 \(1.3 \times 10^{-3}\) 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 \(1.3 \times 10^{-5}\) 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 \(1.3 \times 10^{-5}\) 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 processes. In order to examine the role of high temperature processing on TiNx thin film properties, as-deposited samples deposited at different nitrogen flow rates were annealed in high vacuum \((1.3 \times 10^{-4}\) 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-Kα X-ray radiation having a characteristic wavelength of 1.5418 A. 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 TiNx 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 TiNx 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.

2.2. Variations in orientation

The XRD patterns of TiNx 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 of [111]/[200] from the XRD patterns is shown in Fig. 4. TiNx films with the highest [111]/[200] intensity in XRD patterns demonstrate the highest resistivity; these are also the films deposited at lowest nitrogen content. The [111]/[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 TiNx depends on the phase orientation. However, after post deposition annealing, the change in [111]/[200] intensity was not proportional to the annealing time even though the resistivity decreased with increasing annealing time. Moreover, the [111]/[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 TiNx deposition are shown in Fig. 5. Refractory materials such as TiNx 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 TiNx...
show two broad bands in the 150 cm\(^{-1}\)–300 cm\(^{-1}\) region and one around 550 cm\(^{-1}\). The bands below 300 cm\(^{-1}\) (titanium peaks) arise due to acoustic transitions (LA and TA) and the band around 550 cm\(^{-1}\) (nitrogen peak) is due to optic modes (LO and TO)\(^{[19,20]}\). Raman scattering in the acoustic range is characterized by vibrations of the relatively heavy titanium ions, and the scattering at the optic range is due to lighter nitrogen ions. The presence of titanium modes indicates nitrogen vacancies, and the existence of nitrogen modes indicates titanium vacancies\(^{[21]}\). The slight variations in the peak positions in Fig. 5 correspond with small variations in vacancy concentrations\(^{[22]}\). The intensity ratio of the titanium to nitrogen peak is a semi-quantitative method to analyze the deviations in vacancy concentrations. The titanium/nitrogen peak intensity ratio is near unity for the as-deposited samples deposited at various nitrogen levels. However, after annealing, the titanium/nitrogen peak intensity decreases considerably for all the samples. An increase in the nitrogen peak intensity would indicate the creation of titanium vacancies. It is possible that the titanium slightly oxidizes due to the presence of residual oxygen in the chamber, creating titanium vacancies in the TiN\(_x\) lattice. Nevertheless, the influence on resistivity from oxidation is minimal and, as such, the resistivity in the annealed films does not increase. The increase in oxygen concentration after annealing is confirmed through XPS and is discussed in detail in the next section.

### 2.4. Variations in stoichiometry

The variations in stoichiometry were analyzed using XPS spectra. A top layer of TiN\(_x\) was etched away in the XPS chamber in order to remove contamination at the surface. High resolution XPS spectra of N 1s, O 1s and Ti 2p as-deposited and annealed samples are shown in Fig. 6. The Ti 2p3/2 for TiN occurs at around 455.0 eV for all nitrogen to argon flow ratios. This is consistent with literature values for stoichiometric TiN\(^{[23]}\). The binding energy for Ti 2p3/2 remains the same after annealing. The variations in binding energy between different nitrogen to argon flow rates and between as-deposited and annealed samples are less than 0.02 eV. This indicates that there is minimal variation in stoichiometry for TiNx between these samples. The high shoulder regions in Fig. 6(c) for the Ti 2p1/2 and the Ti 2p3/2 peaks correspond with the nitrogen/titanium atom ratio and found to be the highest for stoichiometric TiN\(^{[23]}\). However, the oxide phases and oxynitride phases of titanium also occur at the same binding energy. This means that the presence of small amounts of oxide cannot be confirmed through XPS spectra of titanium as the peaks are masked. Similar to the titanium spectra, N 1s spectra also do not vary between the samples under
investigation, again indicating the consistency in stoichiometry before and after annealing for samples deposited at different gas flow rates. The N 1s spectra of TiN$_x$ are observed at 397.3 eV, consistent with previous studies for stoichiometric TiN [24]. The low intensity, high binding energy peak can be attributed to the oxynitride phases. O 1s spectra (Fig. 6(b)) are contributed by oxygen atoms from the oxides.

The variations in concentration of nitrogen, oxygen and titanium based on the XPS analysis are given in Fig. 7. The 20% as-deposited sample is nitrogen deficient and the 60% and the 95% as-deposited samples are nitrogen rich. The 20% sample contains greater concentrations of oxygen impurities, compared to the nitrogen rich films which have 13% oxygen impurity concentrations. After post deposition annealing, oxygen levels have increased slightly for all samples. Oxygen may have been introduced from the remaining oxygen in the vacuum chamber which was maintained at a pressure of 1.3 × 10$^{-4}$ Pa. This oxygen would react with titanium in TiN$_x$ to make oxides. This oxide formation creates titanium vacancies in the lattice, causing an increase in nitrogen mode peak intensity in the Raman spectra as discussed earlier. There is no variation in the titanium concentration after annealing, as expected. The nitrogen content also remains the same for the 20% sample after annealing. The nitrogen content for the nitrogen rich samples (60% and 95%) reduces after the annealing process. This could be due to the release of nitrogen which was precipitated at the grain boundaries [25] while annealing. However, these samples remain slightly nitrogen rich even after annealing at 900 °C for 20 min.

The XPS depth profile of the 95% sample annealed at 700 °C for 10 min is shown in Fig. 8. On the surface, the elemental contributions are different compared to the bulk. The sample surface has a high concentration of carbon and oxygen. This is due to contributions from hydrocarbons and/or surface hydration. After an initial etching cycle, these contaminants reduce. Carbon was not observed in the bulk of the film. The concentration of nitrogen is higher than that of titanium throughout the film, similar to the high resolution spectra results discussed in the earlier section. It is also apparent that there is no diffusion of silicon from the bottom SiO$_2$ showing good barrier properties. Diffusion of silicon dioxide into TiN$_x$ during annealing at temperatures above 500 °C is a known issue [26]. However, here we have shown that the TiN$_x$ deposited at high nitrogen content prevents the diffusion of SiO$_2$. Oxygen concentration is almost 15% throughout the film, which might have been introduced by the contamination in the nitrogen source during deposition [27].

2.5. Variations in surface morphology

The variations in the surface roughness as a function of nitrogen to argon flow for the as-deposited sample and one annealed at 900 °C for 20 min are presented in Fig. 9. The root mean square (rms) roughness decreases with increasing nitrogen flow rate after the anneal, the variation in surface roughness is more than double for lower nitrogen flow rate samples compared to the ones deposited at higher nitrogen content. Surface roughness of TiN$_x$ deposited at high nitrogen flow does not vary greatly after an anneal, showing good stability. Fig. 10 shows the AFM topography scan of as-deposited samples deposited in 20% and 95% nitrogen flow rates. The surface roughness on the 20% sample in Fig. 10(a) is found to be much larger than the 95% sample shown in Fig. 10(b).

Fig. 5. Raman spectra of as-deposited and annealed (700 °C, 10 min) TiN$_x$ deposited at 20% and 95% nitrogen flow rate.

Fig. 6. High resolution XPS spectra of (a) N 1s, (b) O 1s and (c) Ti 2p of as-deposited and annealed (900 °C, 20 min) deposited at 20% and 95% nitrogen content.

Fig. 7. Variation in nitrogen, oxygen and titanium concentration obtained from XPS spectra for TiN$_x$ deposited at various gas flow rates, before and after anneal.
which was obtained by varying the very small, given the large variation in nitrogen partial pressure, for high nitrogen content samples. The variations in stoichiometry are the nitrogen which was believed to be precipitated at grain boundaries samples is 0.96 which increases to 1.04 for 95% samples, after deducting phases and are all stoichiometric. Based on the XPS data shown in and the XPS binding energy of titanium and nitrogen spectra indicate position, defects (impurities) and microstructure, provided that the increase in conductivity. AFM topography scans shown in Fig. 10 confirm the variation in the surface structure with differences in crystallographic orientation. The sample which showed predominant [200] orientation (95% nitrogen flow) is found to have a much smoother surface than the one with [111] orientation (20% nitrogen flow). A smoother surface helps in the reduction of electron scattering and improves the conductivity. In addition, the resistivity of TiNx can also depend on film stoichiometry. Since the variation in stoichiometry is negligible, the reason for the decrease in resistivity with nitrogen flow rate for the as-deposited samples is the variation in the crystallographic orientation.

XPS results have confirmed that TiNx deposited at various nitrogen flow rates are all stoichiometric TiN, although there are differences in the nitrogen concentration of the film. However, the observed decrease in resistivity after annealing cannot be explained by the orientation of the film as the variation in relative intensities after annealing shows a random behavior (Fig. 4). This indicates the possibility of a secondary mechanism which is contributing towards the decrease in resistivity for all samples after annealing. A post-deposition anneal typically results in re-crystallization and crystal growth of the as-deposited amorphous material. All the samples have shown an increase in crystallization after annealing, as it is evident from the XRD patterns (Fig. 3). An increase in grain size would reduce the number of scattered conducting electrons at grain boundaries, in turn reducing the resistivity. An increase in the anneal temperature or duration will increase grain size, leading to a reduction in electron scattering, which can explain the annealing temperature and time dependence on resistivity as shown in this study.

The values for nitrogen content used for TiNx deposition in the literature are varied, with the majority using nitrogen content lower than 50% [11]. Higher nitrogen content had resulted in diffusion of excess nitrogen to the surface and subsequent desorption, nitrogen precipitation in grain boundaries [25] or superstructure formation [31]. However, here we have shown that higher nitrogen content is in fact beneficial to achieve low resistivity, making the films more suitable for microelectronic applications. Stoichiometrically, films deposited at various nitrogen contents are all TiN. However, these films show variations in electrical, material and morphological properties based on the nitrogen flow rate used during deposition. TiN deposited at high nitrogen content showed least variation in resistivity after annealing, offering better electrical stability compared to the TiN deposited at low nitrogen content. The nitrogen rich films also prevented the diffusion of silicon during annealing, showing good thermal stability. Moreover, the films deposited at higher nitrogen content showed the lowest variation in surface roughness upon annealing, demonstrating better mechanical stability. We have also shown that the slight oxidation of the film during annealing did not affect the resistivity adversely. The reduction in resistivity due to grain growth during annealing superseded the effects due to oxidation or the increase in surface roughness of the film.
Fig. 10. AFM topography scan of as-deposited film deposited with (a) 20% and (b) 95% nitrogen flow. The surface irregularities on the 20% sample are much larger than the 95% sample.

4. Conclusions

We have investigated the effect of post deposition annealing in an oxygen free environment on the material and electrical properties of reactive sputtered TiN. As-deposited TiN resistivity showed a gradual decrease with increase in nitrogen flow rate during deposition. The lowest resistivity of 80 μΩ cm was obtained for nitrogen rich films. The variations in orientation and therefore the surface roughness are found to be the reason for this decrease in resistivity. TiN films sputtered at various nitrogen contents showed good stability and improved stoichiometry after a post deposition RTP in vacuum, without showing any silicon diffusion. Resistivity of these films decreased from the as-deposited levels upon annealing, and went down with annealing time and temperature. The re-crystallization and grain growth led to a further reduction in resistivity. XPS results showed that films deposited at various nitrogen flow rates are all TiN phases. However, films deposited with lower nitrogen content (20%) are titanium rich compared to films deposited with higher nitrogen content which are nitrogen rich. The nitrogen rich films showed least variation in resistivity and morphology. It was also observed that small traces of oxygen do not impact the resistivity of the film. Resistivity of TiN is found to reduce after annealing in an oxygen free environment showing a good thermal and electrical stability. This study concludes that, though variation in the nitrogen flow rate and thereby the nitrogen partial pressure during deposition do not have a large influence on the stoichiometry of the film, the nitrogen partial pressure can influence the orientation and the morphology. Films deposited at higher nitrogen partial pressures are electrically, thermally and morphologically more stable than the ones deposited at low nitrogen content. Such films would be more suitable when they are used as diffusion barrier, gate electrode of MOSFETs, adhesion layer or as capacitor electrodes in integrated circuits.

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