Reactive sputter deposition and characterization of TiN thin films

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Abstract. TiN films were deposited on Si<100> substrates by both RF and DC reactive magnetron sputtering under varying conditions of power, pressure, argon and nitrogen gas flow rates as well as temperature and characterized by SEM, AFM, RBS and resonant RBS. The films tend to getter oxygen. We found that introducing hydrogen together with the reactive gas (N_2) reduces oxygen contamination on the films. The films were found to adhere well to the substrates.

1. Introduction

Transition metal nitrides are of great technological importance. They are used as diffusion barriers in microelectronics, corrosion resistance barriers in a variety of optical and mechanical components as well as wear-resistant coatings on cutting tools [1]. Most of the different transition metal nitrides such as CrN, HfN, TaN, TiN are popular because of their good chemical and physical properties. However both TiN and ZrN suffer from easy oxidation, which happens mostly during deposition [2]. Various attempts have been made by several workers to reduce this problem of oxidation. To lower oxidation many elements (Y [3], Cu [4], Ni [5], Si [6], etc.) have been included within the metal nitride film.

We could not find any paper where hydrogen has been used to lower oxidation of TiN. In this work we synthesize TiN films using reactive magnetron sputter deposition in a mixture of N_2 and H_2 gases. We characterize the films by SEM, EDS, RBS, resonant RBS and AFM. The samples obtained from reacting nitrogen (with 10% hydrogen) then compared to those where pure nitrogen is used as a reactive gas.

2. Experimental procedure

Substrates used for the sputter deposition of TiN were silicon wafers and silicon wafers covered with Cu. Before any deposition substrates were chemically cleaned using methanol, followed by acetone, then trichloroethylene, then acetone, and finally methanol. High purity distilled water was then used to rinse the samples. The samples were then loaded in AJA's Orion 5 Sputtering System and the deposition chamber was evacuated to a pressure of better than $4x10^{-7}$ Torr. The sputtering target used to cover some of the Si wafers with Cu was a 2 inch diameter, 0.250 inch in thickness, high purity (99.995%) Cu target. DC magnetron was varied between 100 W to 200 W and time duration of varied from 1 hour to 2 hrs. A 2 inch Ti target was used for the deposition of Ti. Its purity was 99.995 %. All targets were obtained from AJA Inc of USA. The argon flow rate during depositions was varied between 4 – 8 sccm. Nitrogen was introduced to act as a reactive gas so as to form TiN. The target to sample distance was kept at 34 mm. It is clear that for relatively high magnetron power (a lot of Ti atoms will be produced from the target) and for a low N_2 flow rate, a metallic film will form. For relatively low magnetron power and higher flow rates of N_2, a reactive mode will be reached and a compound TiN_x ($x>0$) will form. It must be noted however that very low power means fewer Ti atoms sputtered and lower growth rates for the film. A downstream valve in the sputtering system allows for a variation of pressure during deposition. Running the sputtering

system in a throttling mode (partially closing the valve between chamber and pumps) allows for lower inflow rates of both process and reactive gases. It also saves the pumps from overworking (leads to longer pump lives).

3. Results and discussion

First we used Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) to characterize the samples. Whereas the SEM characterization helped us view the surface of the film, EDS was used to estimate the ratio between Ti:N and find out whether there were any impurities, like oxygen in the film.

3.1 SEM and EDX results

Figure 1 shows a high resolution image of a TiN sample where Ti was deposited using DC magnetron sputtering at a power of 200 W for a duration of 2 hrs. The chamber pressure during deposition was $3x10^{-3}$ Torr and the argon and nitrogen flow rates were 4 sccm and 8 sccm respectively. The deposition was done at room temperature. It is seen from the image shown in figure 1 that the film surface is relatively rough, even when viewed under high magnification.

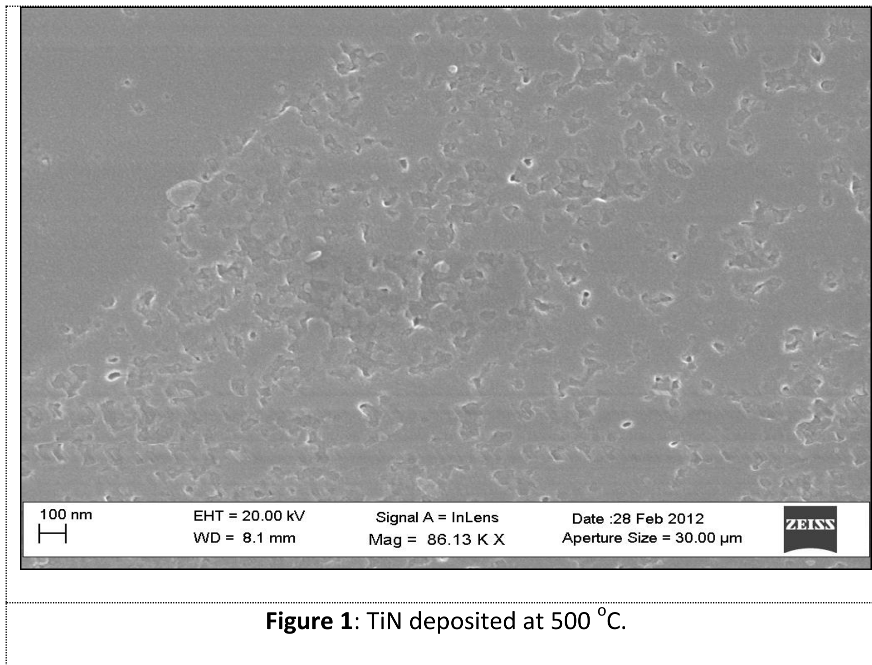

Figure 1: TiN deposited at 500 ^{o}C.

3.2 Normal RBS

In order to compare RF sputtering to DC sputtering we deposited several samples at an RF power of 200 W for a period of 2 hrs using the same argon flow rate of 4 sccm but different nitrogen flow rates as shown in figure 2. We noticed that the sample thicknesses were almost equal at the different flow rates. The thicknesses were also too small to measure the ratios of Ti to N (since we were not sure that the Ti signal had reached its natural height –was not flat-topped).

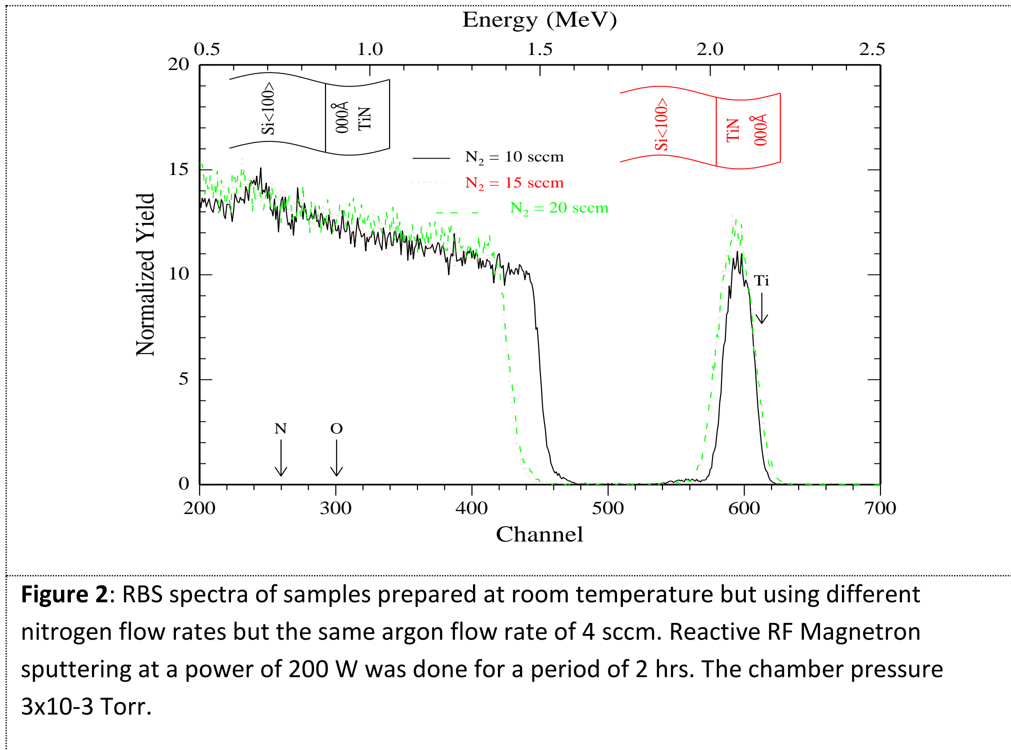

Figure 2: RBS spectra of samples prepared at room temperature but using different nitrogen flow rates but the same argon flow rate of 4 sccm. Reactive RF Magnetron sputtering at a power of 200 W was done for a period of 2 hrs. The chamber pressure 3x10-3 Torr.

In order to have ratios of Ti almost equal to N we increased the deposition rate by using DC magnetron sputtering at a power of 200 W. We also wanted a thicker sample and we achieved such a sample by depositing for a longer time period (2 hrs in this case). To characterize the samples we used Rutherford Backscattering Spectrometry (RBS) by charged alpha particles at an incident energy of 2 MeV. RBS results are shown in figure 3.

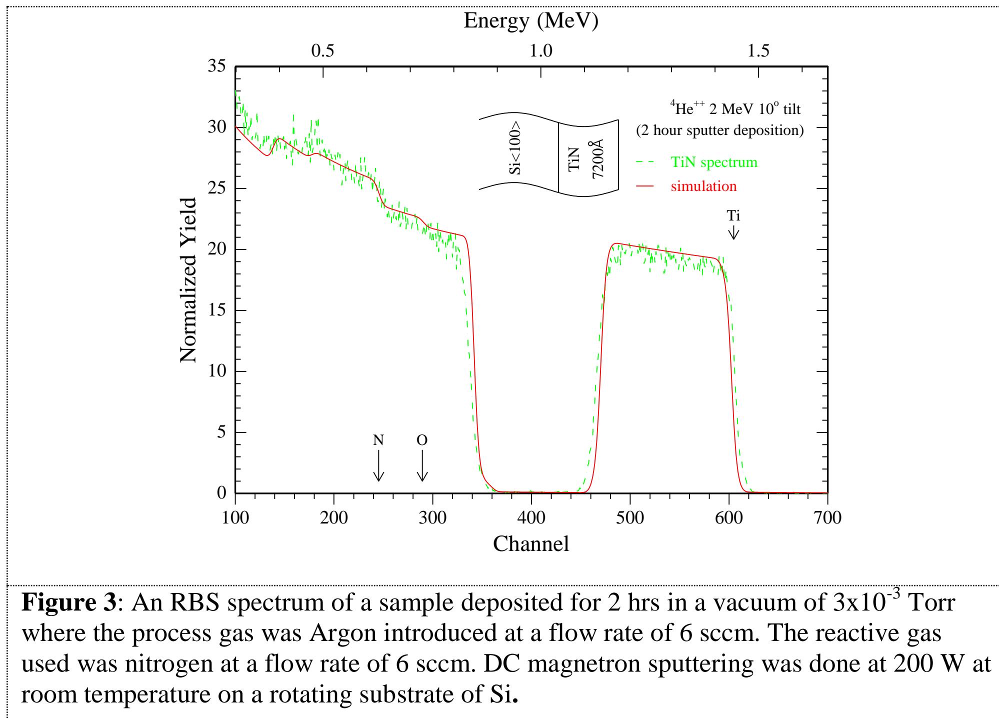

Figure 3: An RBS spectrum of a sample deposited for 2 hrs in a vacuum of $3x10^{-3}$ Torr where the process gas was Argon introduced at a flow rate of 6 sccm. The reactive gas used was nitrogen at a flow rate of 6 sccm. DC magnetron sputtering was done at 200 W at room temperature on a rotating substrate of Si**.**

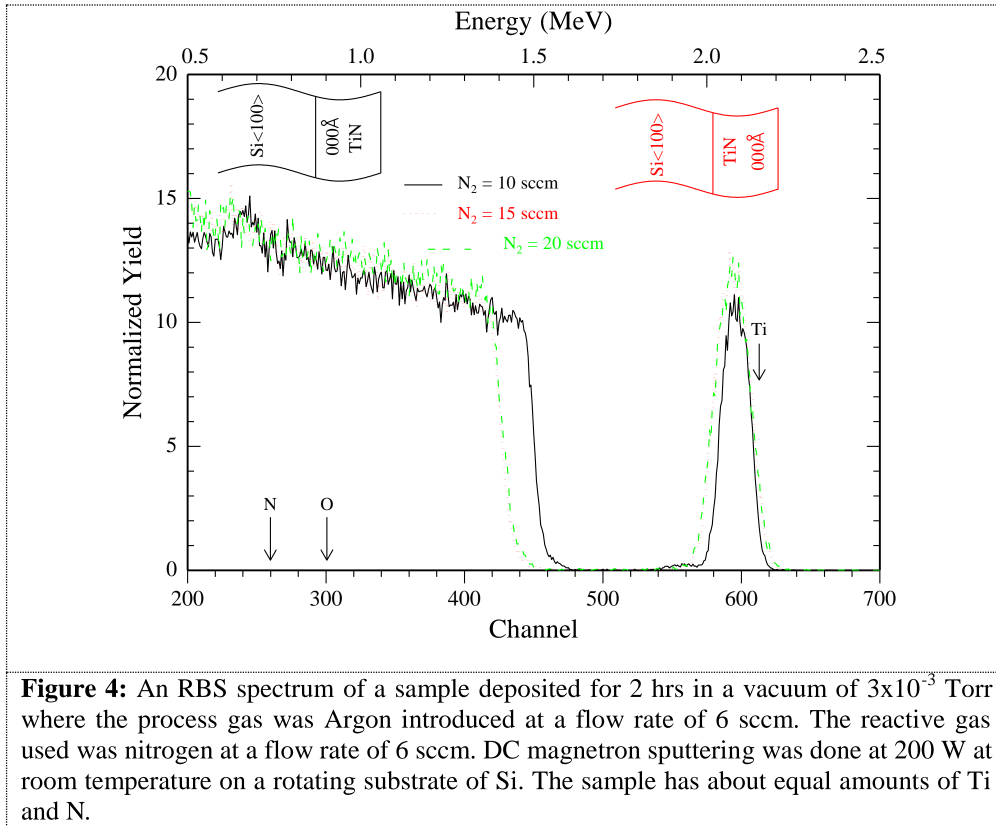

Figure 4: An RBS spectrum of a sample deposited for 2 hrs in a vacuum of $3x10^{-3}$ Torr where the process gas was Argon introduced at a flow rate of 6 sccm. The reactive gas used was nitrogen at a flow rate of 6 sccm. DC magnetron sputtering was done at 200 W at room temperature on a rotating substrate of Si. The sample has about equal amounts of Ti and N.

Figure 4 is an RBS spectrum obtained by backscattering 2 MeV α-particles on the surface of the TiN sputter deposited sample. During α-bombardment the sample was tilted at an angle of 10° with respect to the direction of the oncoming beam. The surface barrier detector used in the measurement was placed at an angle of 165°. RBS data shows that the thickness of the deposited film is about 7 200 Å. The surface positions of the elements Ti, O and N are clearly marked by means of arrows on the graph. These are positions where we expect to see the beginning of a spectrum belonging to these elements (e.g. Ti) if they lie on the surface of the sample. We see that both Ti and N are found throughout the deposited film. Rump simulation (shown as a solid red line) indicates that the sample has oxygen of about 11.5 atomic %.

Resonant RBS.

Resonant $^{16}O(^{4}He; ^{4}He)^{16}O$ was performed in a van De Graaf accelerator using He^{2+} ions with a kinetic energy of 3.05 MeV at a scattering angle of 165° and a sample tilt of 10° (to avoid channeling effects). The results are shown in figure 5 as well as in figure 6.

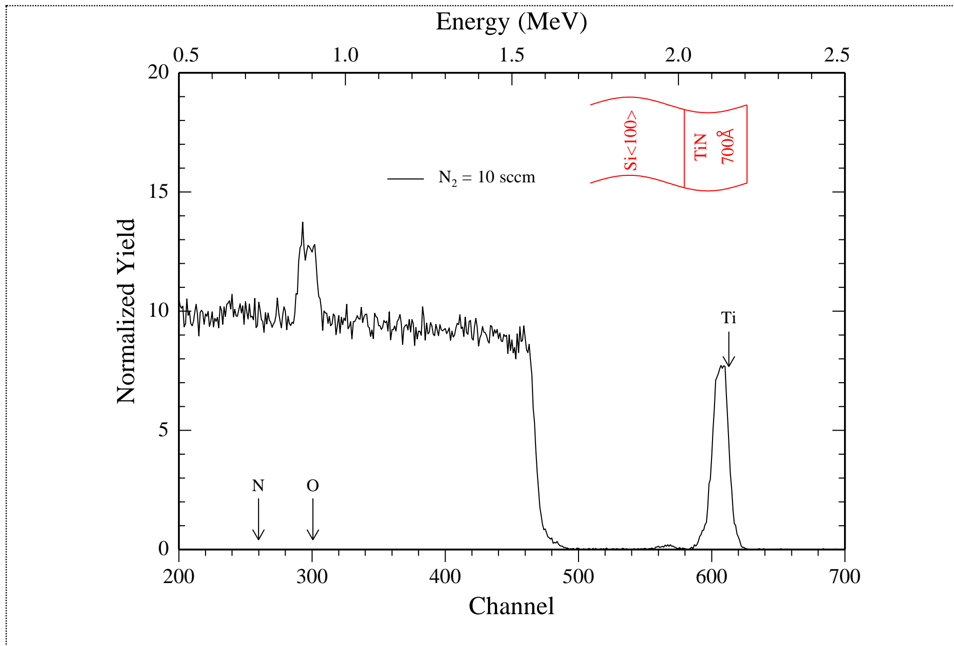

Figure 5: Resonant $^{16}O(^{4}He;\ ^{4}He)^{16}O$ was performed in a van De Graaf accelerator using He^{2+} ions with a kinetic energy of 3.05 MeV at a scattering angle of 165° and a sample tilt of 10° (to avoid channeling effects).

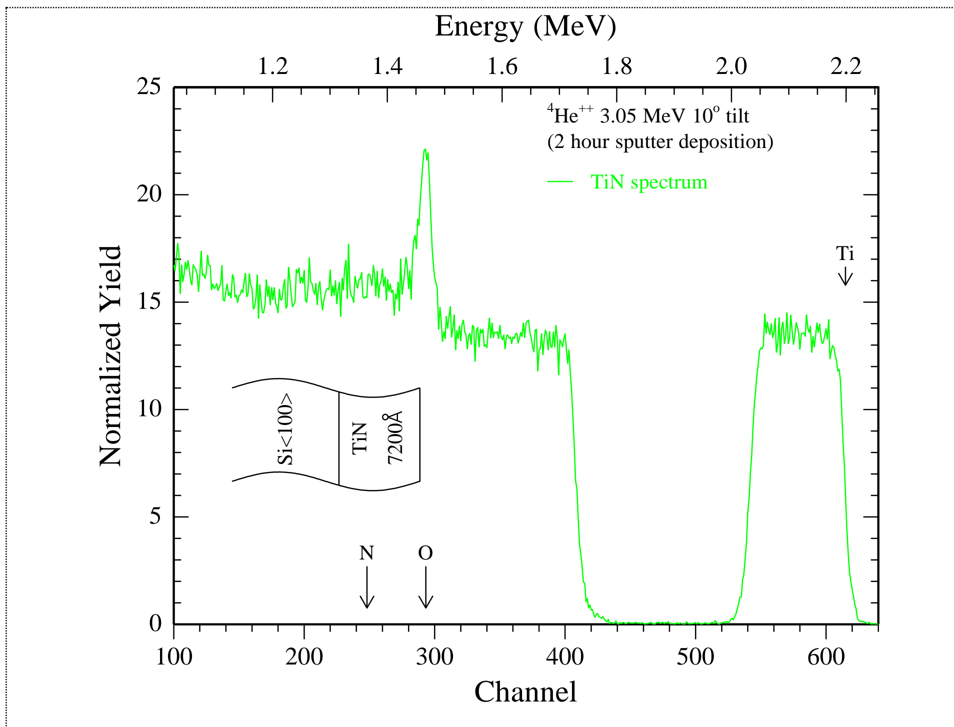

Figure 6: The RBS spectrum of the same sample shown in figure 5**.** In this case however the energy of the bombarding particles was increased to 3.05 MeV. The surface positions of the elements (such as Ti) have moved to higher energies. Note also the enhanced peak of oxygen. At this energy oxygen is said to be at resonance and its scattering cross-section is larger (for the energy of 3.05 MeV) when compared to other energies (e.g. 2 MeV for figure 4), leading to a higher yield.

Samples prepared by depositing Ti in a nitrogen environment so as to react Ti with N to form TiN were prepared. The RBS spectrum of such a sample is shown in figure 6. It is the same sample whose RBS is shown in figure 6. The difference between the spectrum shown in figure 6 from that given in figure 5 is that more energetic particles were used to obtain figure 6. The energies of the α-particles used in this case was 3.05 MeV. At this energy the scattering cross-section on oxygen for these particles is larger. There will therefore be larger numbers of α-particles backscattered. This happens only for oxygen at this energy and is called its resonance scattering. The oxygen peak is therefore enhanced as can be seen in figure 6. It is however a narrow resonance. The part of the oxygen spectrum that is larger is near the surface of the film since it is a thick film. The beam loses energy as it penetrates the film. Alpha particles whose energy is much less than 3.05 MeV will not scatter resonantly.

4. Conclusion.

We have deposited TiN films using DC magnetron sputtering at a chamber pressure of $3x10^{-3}$ Torr at various DC magnetron power (100 W → 200 W) and different rates of flow of both argon and nitrogen. The deposition temperature was varied from room temperature to 500 ^{o}C. Investigation by SEM showed that the samples deposited at room temperature had smooth and even surfaces with no visible cracks. Those deposited at higher temperature showed rougher cracked surfaces. Such features seen were however very small and were seen only at high magnification. Adhesive tape test measurements showed that the films adhered well to the silicon substrate. EDS investigation helped to show that the atomic ration between Ti and N were not equal. This information was used to change deposition parameters (power up to 200 W) such that the atomic ratio is Ti:N = 1:1. EDS also showed that the samples were oxidized.

We noticed that RF sputtering is less efficient in depositing samples compared to DC sputtering. Sample thicknesses were measured by RBS at an energy of 2 MeV and for the sample deposited at a magnetron power of 200 W and for 2 hrs was 7 200 Å. RUMP simulation showed that the samples had about 11.5 atomic percent of oxygen.

Acknowledgements:

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5. References:

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