Reactive DC magnetron sputter deposition and characterization of ZrN thin films

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Abstract. ZrN films were deposited on Si<100> substrates, Al and brass strips by DC magnetron sputtering under varying conditions of power, pressure, argon and nitrogen gas flow rates as well as temperature and characterized by SEM, RBS and resonant RBS. The films are transparent and semiconducting. They tend to absorb oxygen. The films were found to adhere well to the substrates. The colour of the films varied depending on deposition conditions and have been expressed in the Lab* colour system. Potential uses of such films are as protective hard coatings as well as decorative layers.

1. Introduction

The interest in the nitrides and carbides of the transition metal elements such as titanium, hafnium and zirconium is due to their extreme physical and chemical properties. Some of these desirable properties are a high melting point, hardness and good corrosion resistance [1]. ZrN has been named as a possible inert nitride matrix material to burn plutonium or transmute long-lived actinides in accelerator driven submicron nuclear systems or fast nuclear reactors [2]. Because of the properties of some transition metal nitrides they also have been used as field emitters [3]. Required properties for an emitter material are chemical stability, a high melting point, low vapour pressure, low work function, no deformation by ion bombardment and relative ease for making the material into needle-like arrays [3]. It has been suggested that ZrN films may be used as barrier layers for oxygen [4]. ZrN has been found by industry to make good decorative films [6]. Due to their extreme wear resistance they have been used as hard-coatings to expand the lifetimes of mechanical compounds in cutting tools and dies. Their gold-like colour makes them excellent replacements for gold coatings [6].

The most common method of depositing ZrN films is by DC magnetron sputtering. However other methods have also been used. Some of these are: plasma nitridation, vacuum arc deposition, ion-beam assisted deposition, ion plating, pulsed laser deposition, cathodic arc evaporation and high vacuum sputtering [7].

It has been reported that ZrN has higher contamination susceptibility when compared for example to other nitrides such as TiN. There have therefore been fewer studies of ZrN when compared to other transition metal nitrides. In this paper we report on the growth and characterization of ZrN films on silicon, aluminum and brass strips as well as on Cu on Si, Al and brass. We also study the uptake of oxygen by ZrN films using resonant Rutherford Backscattering Spectrometry (RBS), a technique that has not been applied to ZrN before.

2. Experimental procedure

Silicon wafers, brass or aluminum strips were chemically cleaned using methanol, followed by acetone, then trichloroethylene, then acetone, and finally methanol. These were then rinsed in ionized water and then dried in air. The samples were then loaded in AJA's Orion 5 Sputtering System where a thin layer of ZrN was deposited on the substrate. The chamber was evacuated to a base pressure of better than 8×10^{-7} Torr. The sputtering target used was a 2" Zr metal. Argon was used as a process (sputtering) gas. Nitrogen was introduced to act as a reactive gas so as to form ZrN. It is clear that for relatively high magnetron power (a lot of Zr atoms will be produced from the target) and 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 ZrN_x ($x>0$) will form. It must be noted however that very low power means fewer Zr atoms sputtered and lower growth rates for the film. The design of the sputtering system is such that there is a valve between the chamber and the evacuation pumps (turbo pump and rotary pump). 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 Rutherford Backscattering Spectrometry (RBS) in order to find layer thicknesses as well as to check whether the correct stoichiometry between Zr and N had been achieved.

The films were deposited either at room temperature or higher temperatures (~ 200 ^{o}C) on a rotating Si wafer to ensure uniformity of the film. DC magnetron power applied to the Zr target was varied between 100 W and 200 W and the argon flow rate used was varied between 2 sccm and 8 sccm. Nitrogen was introduced next to the sample at values varying from 2 sccm to 20 sccm. The duration of deposition varied from 30 minutes to 2 hrs. After deposition samples were kept in air under dry conditions.

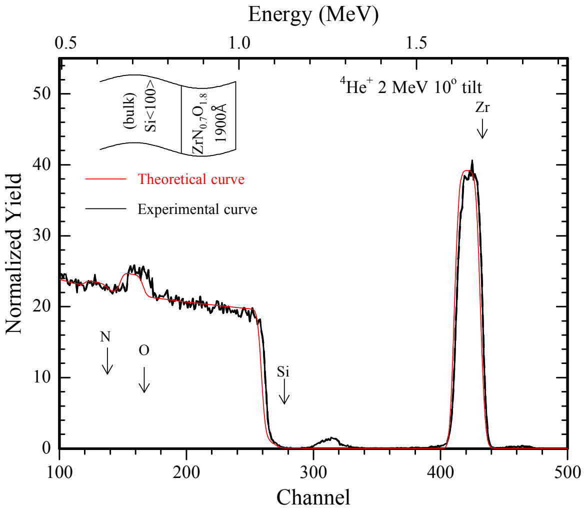

Figure 1A spectrum of a sample having configuration Si<100>/ZrN. According to the results of RBS analysis the atomic percentages are Zr = 28.6%, N = 20% and O = 51.4%. A simulation curve is also shown.

Figure 1 shows RBS spectrum of a sample O made of Si<100>(bulk)/ZrN. The deposition conditions for sample O were a DC magnetron power of 200 W, argon flow rate of 4 sccm and nitrogen flow of 8 sccm. Deposition duration was 45 minutes. The ZrN layer was found by means of RBS characterization to be 1 900 Å. Surface positions of Zr, Si, O and N are shown on the figure. The peak shown at channel 315 corresponds to that of Ar (Argon was used as a process gas to sputter a Zr target in a nitrogen rich environment). The sample was found to have 28.6% zirconium, 20% nitrogen and 51.4% oxygen. Checking the literature we found that it is normal for sputtered ZrN films to have that much oxygen. The film was found to be well adherent to the silicon wafer. This was deduced from strip test measurements.

We also looked at the film under a scanning electron microscope (SEM). The surface of the film appeared smooth and featureless. SEM results not shown here. The colour of the film appeared uniform to the eye –also implying a uniform thickness. We also used Energy Dispersive X-rays (EDX) to analyze the sample. Composition found agreed with that obtained from RBS measurements.

RUMP simulation showed that there was a significant amount of oxygen on all the samples. We decided to measure the amount of oxygen incorporated in ZrN much more accurately. The presence of oxygen had been mentioned in the literature but it had not been measured accurately.

The two samples A and B, shown in figure 2, were prepared under almost similar conditions. They were both deposited by magnetron sputtering from a Zr target using power of 200 W for a period of 45 minutes. They differ only in gas flow rates during deposition. The flow rate of argon during the deposition of sample A was 2 sccm while that of nitrogen was 8 sccm. The flow rate of argon was 2 sccm during the deposition of sample B, while that of nitrogen was 20 sccm. The chamber pressure during deposition was maintained at 3×10^{-3} torr in both cases. One expects the amount of Zr deposited in the two cases to be the same since the same magnetron power of 200 W was used.

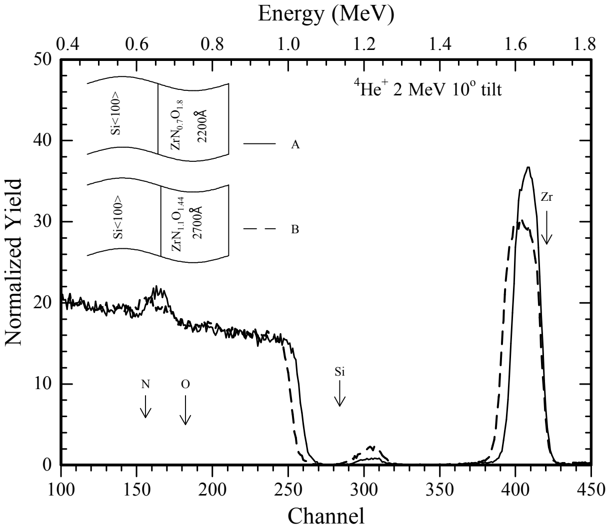

Figure 2 RBS spectra of sample A and B that were prepared under almost similar conditions. The only difference is the nitrogen flow rates (8 sccm for sample A and 20 sccm for sample B). The samples differed markedly in colour.

Figure 2 shows the spectra of both samples (A and B). Surface positions for elements Zr, Si, O and N are marked clearly by means of arrows on the figure. These are channels (or energy values) at which one expects the alpha particle energy when it has been backscattered from those elements, if the elements are on the surface of the sample. We integrated the area under the curve of the Zr signal in both cases (A & B) and found that the two areas are equal. This confirms that the same amount of Zr was deposited in each case. The thickness of the film in sample A was found from RUMP simulation to be 2 200 Å while that in sample B was 2 700 Å. The difference in the samples therefore in is in their composition. RBS analysis shows the composition of sample A to be Zr = 28.6%, N =20% and O = 51.4%. Sample B has be found to be made up of Zr = 28.2%, N = 31.1% and O = 40.7 %. Sample B had a goldish colour while A looked greenish.

We decided to measure the oxygen content of the samples much more accurately. To solve this problem resonant RBS at 3.05 MeV was done.

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^{o} and a sample tilt of 10^{o} (to avoid channeling effects). The spectra collected from samples A and B are shown in figure 3.

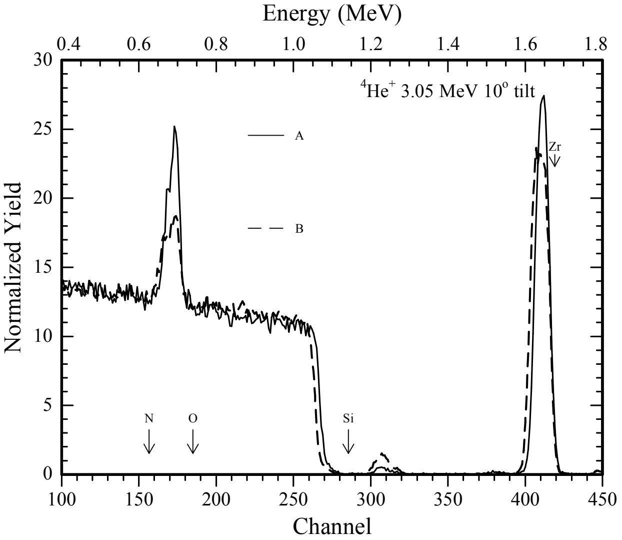

Figure 3 scattering at the resonant energy for oxygen enhances the peak corresponding to oxygen. The amount of oxygen is sample B is 38% less than that in sample A. Sample B appears golden in colour.

It will be noticed that the spectra has shifted to higher energies (i.e. the energies of the backscattered α particles are higher since higher beam energy has now been used). The heights of the spectra are generally lower than in figure 2. This is due to the fact that the surface barrier detectors used are less efficient at higher energies. Note however that the peaks corresponding to oxygen have grown larger. At energy of 3.05 MeV the scattering cross section for alpha particles scattering on oxygen is larger resulting in a higher yield, thus giving rise to a larger peak. Unfortunately one cannot use RUMP for the analysis of the spectra as it has no inbuilt ability for analysis a resonance at this energy. We can however compare the amounts of oxygen in the two samples by integrating the area under the curve of oxygen. The area under the oxygen curve for sample B is 62% that of sample A (i.e. sample B has 38% less oxygen when compared to sample A).

4. ZrN as a protective and decorative coating

The ZrN film looked flat and featureless under the Scanning Electron Microscope (SEM results not shown here). There were no bumps or voids on the film that could have indicated failure of the film to adhere or bond to the silicon. Adhesion was further tested by means of a tape stripping. This also showed that the film had bonded well to the substrate.

We also deposited Cu on two Al metal strips. We then deposited ZrN on top of the Cu film on Al. We wanted to find out whether the ZrN film will protect the Cu film from corrosion. Within two hours corrosion spots appeared on the Cu film not covered with ZrN. The film covered with ZrN showed no corrosion even after exposing it to air for three months.

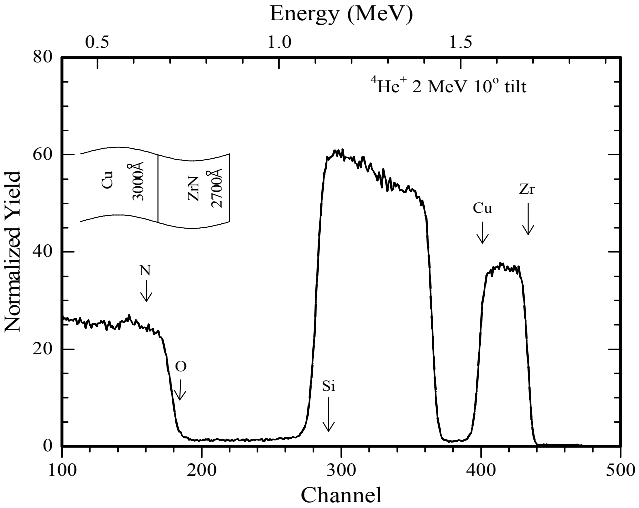

Figure 4 shows the RBS results of ZrN on Cu on Si. The thickness of the ZrN film was found to be 2700 Å, while the thickness of Cu was 3000 Å ZrN can therefore be used as a protective coating against corrosion. Even though ZrN films absorb oxygen, they however do not pass that oxygen to the under layer film.

The colour of the ZrN films changed depending on the deposition conditions. We have measured the colour in the Lab* colour system.

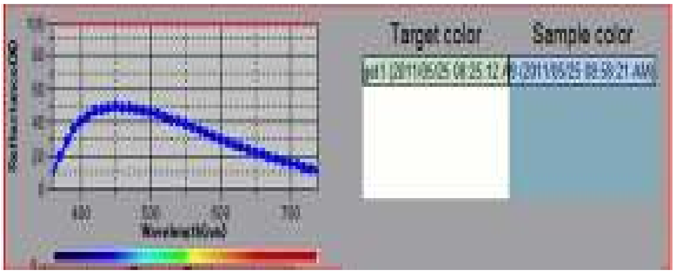

Figure 4 the colour of sample A appeared bluish. We have compared this to a white colour standard. The graph shows a reflectance spectrum in the visible region. The maximum reflectance for this film is at about 450 nm wavelength.

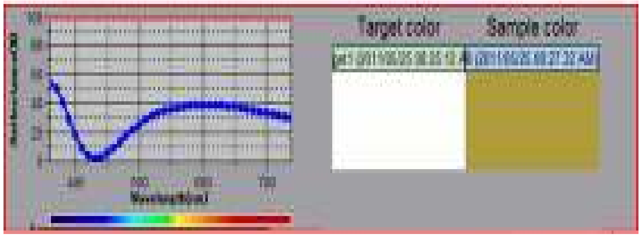

Figure 5 Reflectance colour spectrum on sample B. It is noted that the maximum of the reflectance is at about 600 nm and the greatest absorption occurs at 450 nm wavelength. Sample B appears golden in colour.

5. Conclusion.

Films of ZrN we deposited on various substrates (S_i, AZ, bras, glass and characterized from a Zr target in a argon nitrogen atmosphere at a pressure of $3\text{x}10^{-3}$ torr. The samples were characterized by means of SEM, RBS, and resonant RBS colour spectrometer as well as by strip test (for adhesion). The surfaces of the films appeared smooth under SEM investigation and no bubble or peeling was observed. It was found therefore that the ZrN films adhere well on all substrates tested. We also found that the ZrN films take up oxygen. To better characterize the oxygen uptake under different process conditions resonant RBS was carried out at 3.05 MeV. This helped to enhance the oxygen signal and allowed us to compare amounts of oxygen in different samples. Samples with less oxygen and ratio of Zr to N of close to 50% appeared golden in colour. We analyzed the colour using a colour spectrometer in the ab* system. We also found that ZrN forms a very good barrier to oxygen and may therefore be used to prevent corrosion by oxidation.

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