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# Investigation of magnetron-sputtered titanium nitride films using positron annihilation spectroscopy

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**Abstract.** Positron annihilation spectroscopy in conjunction with a variable-energy beam has been used to investigate the variation of the vacancy-type defect density of titanium nitride films with varying nitrogen concentrations. Decreases in the Doppler-broadened lineshape parameter were observed as the nitrogen partial pressure used in the manufacture of the samples was increased from 0.01 Pa to 0.1 Pa indicating a decrease in the positron trapping at vacancy defects in this range. It is suggested that the positrons are trapped in Ti vacancies with the variation in trapping being due to increasing N-atom migration onto Ti sublattice vacancy sites as the nitrogen partial pressure is increased.

## 1. Introduction

Titanium nitride films display many valuable properties, such as high wear resistance, a high melting point and chemical inertness [1]. One important and popular method used to deposit TiN films is magnetron sputtering. Certain substrates require that the deposition temperature is limited to a few hundred degrees Celsius—for instance glass and integrated circuits where TiN is used as a diffusion barrier [2]. The use of TiN coatings on plastics to protect the surface against abrasive wear is also expected to become increasingly important in the near future. In this case, the substrate temperature during deposition should not exceed 200 °C. Only a few investigations have dealt with magnetron sputtering of TiN below 300 °C [3–5]; hence little information is known regarding the exact structural, mechanical, and corrosion resistance properties resulting from low-temperature magnetron sputtering of films as well as the concentration of defects such as vacancies or impurities. A recent study by Elstner *et al* [6] investigated TiN films deposited on silicon substrates at a constant temperature of 200 °C for different nitrogen partial pressures ($pN_2$). They found a distinct dependence of hardness, and therefore defect concentration, on $pN_2$.

Positron annihilation spectroscopy (PAS) has proved to be an excellent non-destructive probe of materials containing a distribution of vacancy-type defects [7], and previously has been used to investigate TiN films [8, 9]. Most recently Rice-Evans *et al* [10] studied

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the effect of substrate bias on the defect concentration of magnetron-sputtered TiN films deposited on steel and found that an optimum voltage of −60 V produced fewest defects in the film.

In this study, we have used PAS to investigate the effect of nitrogen partial pressure ($pN_2$) on the vacancy-type defect density for TiN films deposited on a silicon substrate at 200 °C by magnetron sputtering using samples identical to those of Elstner *et al* [6]. The results are compared to values of hardness obtained for similar samples.

## 2. Experimental details

The TiN films were deposited using reactive dc magnetron sputtering performed using a high-vacuum assembly with a base pressure of $1 \times 10^{-3}$ Pa. A circular magnetron with a diameter of 95 mm was used. The target plate consisted of vacuum-melted high-purity titanium. For the sputtering process, a mixture of nitrogen (purity 99.99%) and argon (purity 99.999%) was used. In all cases, the total pressure of the gas mixture during the sputter deposition was 0.36 Pa. The discharge power was 520 W, and the discharge current was ∼1.3 A. The deposition time was kept constant at 20 minutes for all samples. Prior to deposition, the substrates were etched using argon-ion bombardment at a discharge current of 50 mA.

The substrates were polished single-crystal Si(111) with a resistivity of ∼10 Ω cm. They were placed on a substrate holder 30 mm from the magnetron cathode. During sputtering, the substrate temperature was held constant at 200 °C during all film depositions. The substrate holder was electrically isolated and held at a potential of −100 V. An adhesion layer of titanium was initially deposited to a thickness of ∼100 nm.

An optical microscope (EPIVAL) equipped with a microhardness tester (mhp 160) was used to measure the hardness of the layers according to the Knoop method [11].

**Table 1.** A summary of the results obtained from positron annihilation spectroscopy and hardness testing. The thicknesses are from Auger measurements made by Elstner *et al* [6].

| Sample | $pN_2$ (Pa) | Thickness (nm) | Mean $S$ | Microhardness (GPa) |
|---|---|---|---|---|
| a | 0.01 | 3600 | 0.4518 | 27 |
| b | 0.0015 | 3160 | 0.4468 | 25 |
| c | 0.0017 | 3160 | 0.4510 | 27 |
| d | 0.0027 | 2200 | 0.4306 | 22 |
| e | 0.005 | 1400 | 0.4230 | 18 |
| f | 0.1 | 1400 | 0.4265 | 18 |

Six samples corresponding to nitrogen partial pressures ranging from 0.01 Pa to 0.1 Pa (see table 1) were mounted one at a time in the sample holder of the Tacitus variable-energy positron beam. Positrons from a $^{22}$Na positron source are moderated by a tungsten mesh and guided magnetically towards the sample chamber, then focused by an electrostatic lens onto the target. By varying the target voltages it is possible to vary the positron energies and hence the penetration depths. The annihilation photons were recorded for one hour for each positron energy using a germanium detector placed behind the target.

The Doppler-broadening $S$-parameter which is sensitive to the material composition and the concentration of vacancy-type defects was measured as a function of incident energy.

It is defined as the counts in a central region of the 511 keV annihilation peak divided by the total counts in the peak [7]. In this study, Doppler curves for incident energies ranging from 0.1 to 25 keV were recorded.

## 3. Positron implantation and diffusion in thin films

Positrons implanted into a multilayered sample of $i$ layers thermalize very rapidly in comparison to their mean lifetime, ending with a stopping profile $P(z, E)$ given by [12]

$$P(z, E) = -\frac{\mathrm{d}}{\mathrm{d}z} \exp\left[-\left(\frac{z - \delta_i}{z_{0i}}\right)^m\right] \tag{1}$$

(for the case of a film on a substrate one has values of $i = 1, 2$) where $\delta_i$ is a constant determined by assuming the positron transmission to be continuous, and has the values $\delta_1 = 0$ and $\delta_2 = x[1 - (\rho_1/\rho_2)]$, where $x$ is the film thickness, and $\rho_1$ and $\rho_2$ are the film and substrate densities. The term $z_{0i}$ is given by [12]

$$z_{0i} = \left(\frac{A}{\rho_i}\right) E^n / \Gamma\left[1 + (1/m)\right] \tag{2}$$

where $\Gamma$ is the gamma function, and $A, n$ and $m$ are constants. If $m = 2$, $\Gamma\left[3/2\right] = 0.88$.

After thermalization the positrons diffuse in the sample with diffusion constants governed by the nature and quality of the material layer until eventually they annihilate with electrons. In this study, it is assumed that the annihilations occur either in the TiN film, in the Si substrate, at the surface of the TiN or as epithermal positrons. Each annihilation state has a distinct $S$-parameter value. The total measured $S$-parameter value is then given by

$$S(E) = J_E(E)S_E + J_S(E)S_S + J_F(E)S_F + J_B(E)S_B \tag{3}$$

where the subscripts E, S, F and B refer to epithermal, surface, film and bulk substrate respectively, and $J$ represents the fraction of positrons annihilating in each state.

## 4. Results

Figure 1 shows the measured $S$-parameter variation with positron injection energy for the six samples under study. The values of $S$ at the lowest energies (1500 eV) may be ignored as they include a contribution from positrons forming positronium near the surface of the sample. Figure 2 shows plots of the mean $S$-parameter for each sample, averaged for incident energy values from 3.5 keV to 13.5 keV, and also the hardness of similar TiN films, as a function of nitrogen partial pressure when the samples were created (see table 1). Figure 3 shows the $S$-curves for samples e and f and these have been fitted with a positron diffusion model by using the program VEPFIT [13].

## 5. Discussion

The $S$-curves in figure 1 show a clear variation of the mean $S$-parameter value for the TiN film with the nitrogen partial pressure ($p\mathrm{N}_2$). For samples a, b and c the positrons probe only the TiN film itself and have no interaction with the Si substrate. In the cases of the thinner samples d, e and f, however, a steady increase in the value of $S$ at incident energies above 15 keV is consistent with positrons annihilating in the Si which is known to have a value of 0.493 in this experimental system [14]. This conclusion is confirmed by the

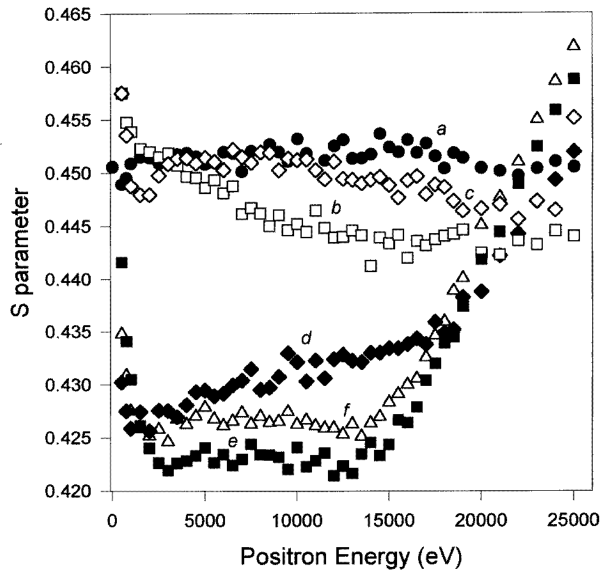


**Figure 1.** The *S*-parameter versus incident energy; closed circles: sample a; open squares: sample b; open diamonds: sample c; closed diamonds: sample d; closed squares: sample e; open triangles: sample f.

estimated values of film thickness given in table 1. At low incident energies (<1 keV) the *S*-values are strongly influenced by epithermal effects [15], but these have no significance here.

Measurements for samples a, e and f result in *S*-values that remain approximately constant, within statistical variation, for the TiN film suggesting that the distribution of defects is constant throughout. For samples b and c the *S*-value falls with increasing positron energy, and hence implantation depth, which suggests a declining density of defects beneath the surface. Sample d is unique in this set due to its increasing *S*-value with increasing positron energy, suggesting a rising concentration of defects beneath the film.

The plot of the mean *S*-parameter value versus nitrogen partial pressure ($pN_2$) shows a clear decrease in $S$ with increasing $pN_2$ for values of $pN_2$ ranging from 0.01 Pa to 0.1 Pa. It is therefore concluded that the concentration of open vacancies within the TiN film is at a minimum at nitrogen partial pressures ranging from 0.05 Pa to 0.1 Pa. This is in agreement with the results of hardness testing also shown in figure 2 which match the trend of $S$ versus $pN_2$ with marked consistency. In general the hardness of the substoichiometric TiN increases as stoichiometry is approached and decreases as the nitrogen content increases in superstoichiometric films [20]. Thus stoichiometric TiN is expected to be the hardest material. However, some substoichiometric TiN films have been reported with much higher hardness values than the stoichiometric maximum. These are generally produced by processes using energetic ion bombardment such as the magnetron sputtering used in this study. These high hardnesses have been attributed to microstructural factors such as small grain sizes or increased defect densities in the film.

The hardness of a ceramic coating such as TiN will thus depend on the material properties and microstructure of the coating. The deformation mechanism will depend on both microfracture and plasticity since dislocation mobility in the coating is limited at

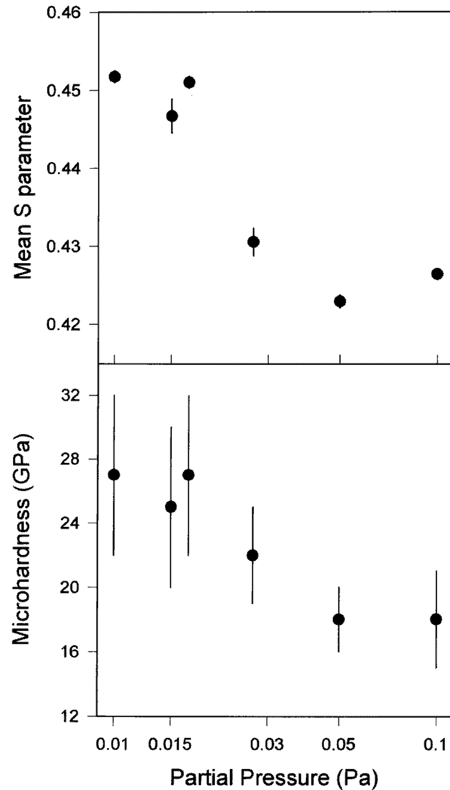


**Figure 2.** The mean $S$-parameter value (top) and microhardness (bottom) versus nitrogen partial pressure.

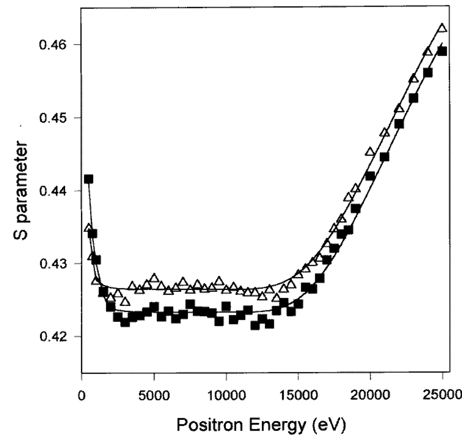


**Figure 3.** The $S$-parameter versus incident energy for samples e (closed squares) and f (open triangle). The curves have been fitted using the program VEPFIT [13].

temperatures less than 1000 °C. If the grain boundaries are weak, low hardness values are obtained; this is often the case in superstoichiometric films where voids and nitrogen bubbles can be found at the grain boundaries. However, these effects are not significant for the films investigated in this study. For large grain sizes where the dislocation density is low the hardness is determined by the Peierls stress and hence the bond strength between atoms in the structure. The bond strength will depend on stoichiometry, vacancies and impurities and it is thus stoichiometric material which should have the highest hardness. Hence one might expect the hardness to be reduced as the nitrogen content decreases.

Deposition of TiN at high rates and low temperatures will generally lead to high defect densities and small grain sizes which can dominate behaviour. The mobility of dislocations is reduced as the grain size is reduced and the hardness of fine-grained material is greater than that of material with a large grain size. This effect can be very significant and contributes a significant percentage ($\gtrsim$30%) to the measured hardness of TiN films [21]. Defects introduced during growth, such as impurity atoms, vacancies and dislocations, will also reduce dislocation mobility and increase hardness (so-called radiation hardening). In fact, at the very high dislocation densities present in magnetron-sputtered films it is difficult to distinguish between the effects of a fine grain size and damage, as the defects will produce an effective grain size (as evident from x-ray diffraction measurements) which is much smaller than the apparent grain size measured by electron microscopy. In this case the

effective grain size measured by the x-ray technique represents the size of a domain of crystalline perfection over which it is less likely that a moving dislocation will be impeded by damage.

For the films investigated here, Elstner *et al* [6] report a rather complex variation in grain size determinated by x-ray diffraction with a maximum at 0.16 Pa nitrogen. This would predict that the softest films would be produced at this pressure which is opposite to what is observed.

The reduction in hardness with increasing nitrogen partial pressure observed in this study is certainly significant, even if there is some scatter in the measurements on a single sample. The scatter is consistent with that obtained from tests on a range of ceramic materials. That the positron annihilation data closely follow the trend in hardness data is very apparent. Whether this is due to the fact that the open defects probed by positrons are responsible for restricting dislocation mobility themselves, or, as seems more likely, these open defects are associated with extended defects such as dislocations and grain boundaries which are known to have a significant blocking effect on dislocation motion, cannot be determined from the results obtained here.

Elstner *et al* [6] detected no further decrease in hardness for $pN_2$ above 0.05 Pa, and so it is reasonable to assume that the minimum concentration of defects is in fact attainable for $pN_2 = 0.05$ Pa. An interesting note is the relatively small error for the mean $S$-values compared to microhardness, which here are equal to the standard deviation of the measured $S$-parameter for the incident positron energy range 3.5 keV to 13.5 keV.

Titanium nitride films contain two possible types of vacancy—those on the titanium sublattice and those on the nitrogen sublattice. The existence of vacancies in the Ti sublattice even in stoichiometric TiN is in accordance with the experience of others. Ehrlich [16] has found the fraction of vacancies in stoichiometric bulk TiN to be of the order of some at.% in both sublattices (up to 4 at.%). It is evident that in sputtered films this fraction will be even greater. Schaffer *et al* [8] suggested that the Ti atoms surrounding a N vacancy are positively charged and thus screen the vacancy, and so it is no longer an efficient positron trap. A Ti vacancy is a strong trap, however, because it is surrounded by a net negative charge. They extended this idea to explain trapping in Ti-rich films as a result of the diffusion of Ti atoms onto N sublattice sites, thus creating Ti sublattice vacancies. We believe, however, that the movement of Ti atoms into N sites is unlikely because of the large amount of energy required. Since the structure of TiN is effectively nearly close-packed titanium with nitrogen occupying the octahedral interstices, the maximum radius of an atom which will fit on the nitrogen site without distorting the structure significantly is about $0.414\,r_{Ti}$ where $r_{Ti}$ is the radius of the Ti atom in the TiN structure ($\sim$1.5 Å). Clearly considerable distortion would be necessary to move a Ti atom onto this site so it is unlikely to be occurring in the films investigated here.

The samples in this study were N-deficient $TiN_y$, with $y$ ranging from 0.43 for $pN_2 = 0.01$ Pa to 0.92 for $pN_2 = 0.1$ Pa [6]. Unlike Schaffer *et al* who found for their bulk titanium-rich samples that $S$ did not vary with $y$ for $y < 1.00$, we find large differences in $S$ as $y$ varies between 0.43 and 0.92. The discrepancy maybe due to the greater sensitivity of the present study with a monoenergetic beam, as compared to the bulk technique. Ti vacancies depend, in the main, on the levels of ion bombardment used during deposition. Since the bias voltage was the same for all samples the density of Ti vacancies is thought also to be the same. The number of empty sites on the N sublattice depends directly on the N partial pressure. However, it is unlikely that the variations in the mean $S$-parameter values observed here are due to variable trapping of positrons in N sublattice vacancies, as it is known that typically for metals and semiconductors the

trapping of positrons saturates above vacancy concentrations $\sim 10^{-4}$ [17]. We therefore suggest that the different trapping fractions observed in this study are the result of N atoms partially filling Ti sublattice vacancies. Greater partial pressures of N would result in more Ti vacancies being filled.

It seems to be plausible that for a great fraction of vacancies in the N sublattice, additional N atoms tend to fill these vacant sites (samples a–c). Then, when the fractions of vacancies in the two sublattices become roughly equal (samples d–f), which corresponds to stoichiometry (cf. figure 2 in [6]; the stoichiometry begins at a nitrogen partial pressure of 0.027 Pa (sample d)), additional nitrogen atoms fill with comparable probability the Ti vacancies and the N vacancies, thus yielding the observed decrease of vacant titanium sites. In addition to this a non-negligible fraction of nitrogen atoms will occupy interstitial places. The latter effect—which is not detectable by positron annihilation—is clearly shown by annealing experiments done by Elstner *et al* [18].

The spectra in figure 3 for samples e and f have been fitted using the diffusion model program VEPFIT [13]. In these cases the thickness of the film is only 1400 nm and so a significant proportion of the positrons incident at high energies annihilate in the substrate, as discussed above. The thickness measurements were made using Auger depth profiles and it is assumed that they are accurate to within $\sim$15%. These relatively thin films allow the $S$-curves to be fitted with a model allowing for the different densities of the film and substrate assuming a known film thickness, and allowing the parameters $A$ and $n$ in (2) to vary [19]. The positron diffusion length in the TiN film was assumed to be $<$20 nm, limited by the positrons being trapped at defects, and for the Si crystalline substrate it was taken to be 220 nm [7]. Taking the nominal thickness of the sample (f) to be 1400 nm as measured by the Auger method, we find that the diffusion equation can be fitted, but the derived parameters, $A$ and $n$, have no real physical meaning because of the different layer densities.

## 6. Conclusion

Positron annihilation spectroscopy has been shown to be a sensitive non-destructive probe of low-temperature magnetron-sputtered titanium nitride films. The mean Doppler $S$-parameters measured for the films indicate a decrease in the concentration of vacancy-type defects as the partial pressure of the nitrogen used in the manufacture of the samples is increased from 0.01 Pa to 0.1 Pa. This is in agreement with the relatively crude hardness measurements carried out on the same samples.

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