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Asymmetrical strain distribution in sputtered TiN layers

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Abstract

The strain and texture in magnetron sputtered TiN layers were investigated by means of X-ray diffraction. The results indicated either a fiber or a biaxial texture of the specimens. In a fiber texture, there is only a preference for the plane that grows parallel to the interface and for the biaxial texture, there is a preferential growth direction within this plane. The components of strain in the samples are determined and the measured strain shows that in the samples with a fiber texture there is no dependence on the angle ϕ . This is different for the biaxial texture samples, i.e. changing ϕ changes the strain. The strain in the fiber and biaxial textured samples are due to the same origin; thermal strain and a strain due to the atomic peening process. This results in a rotationally symmetric biaxial strain field (strain tensor in the sample system has only two relevant components, ε_{11} and ε_{22} , and these are equal). Consequently the difference in strain distribution can only be due to the difference in texture. Indeed there appears to be a relation between strain distribution and texture in these specimens via the high anisotropy in the elastic compliance of TiN. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Physical vapor deposition (PVD); Sputtering; Stress; Titanium nitride; X-Ray diffraction

1. Introduction

In this paper the texture and strain in different TiN layers are investigated with X-ray diffraction. The layers are magnetron sputtered TiN layers and the Ti concentration during sputtering, the bias voltage and the deposition time were taken as variables during the deposition process. X-ray diffraction is a commonly accepted method to determine the strain that is present in a material [1,2]. In general, however, one is interested in the actual stress state. Indeed, to obtain the values of the stress from the strain measurements the elastic compliance of the material should be known. In fact in the present case of TiN the values that can be found in literature for the XEC (X-ray elastic con-

stants) seem to vary over a wide range. That is to say the absolute values, from 350 to 600 GPa, and also the anisotropy factor calculated with the XEC [3–7]. In this paper the texture and strain in different TiN layers are investigated with the aid of X-ray diffraction. The layers are magnetron sputtered TiN layers and the Ti concentration during sputtering, the bias voltage and the deposition time were taken as variables during the deposition process.

The influence of the deposition time is such that the layers grow thicker and the strain decreases upon increasing thickness [8]. As a result there must be a strain gradient present in the layers, i.e. high at the interface and decreasing towards the outer surface [9,10]. A consequence of this gradient is that measurements performed by means of X-ray may show a non-linear behavior and measurements performed at different 2θ angles or with different X-ray tubes may differ considerably. So a comparison between results

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Table 1
Deposition conditions and sample numbers

Batch	Bias voltage (V)	Sample numbers					
1	–40	1	2			3	4
2	–65			5	6		
3	–80	7	8			9	10
Ti concentration during sputtering (%)		40	50	55	55	60	80
Deposition time (min)		60	60	30	60	60	60

obtained from different $\{hkl\}$ planes may lead to erroneous conclusions. Furthermore, the Ti concentration and the bias voltage affects the layer thickness, the texture and the stress state in the layers. The main difference in texture is that one class has a fiber texture, i.e. there is a preference in the plane that lies parallel to the interface but there is a rotational freedom around the axis perpendicular to this plane. In contrast, another group of samples has a biaxial texture, i.e. no rotational freedom but a preference in the direction the planes like to grow [11]. In this paper the strain distribution in the different samples are determined in relation to the texture that is present in the samples. With the measured strain distribution an anisotropy factor for TiN is calculated.

2. Experiment

The deposition chamber contained two titanium targets, which were aligned in opposite direction to each other and in the middle a rotating drum onto which the samples were mounted. The base pressure in the chamber is $6.65 \cdot 10^{-4}$ Pa. Next, the chamber is filled with Argon until the pressure is 0.4 Pa. The samples were cleaned by means of sputtering during 30 min at a bias voltage of –1000 V and a current of 0.2 A. Finally nitrogen was admitted into the chamber and the desired bias voltage was adjusted.

By measuring the radial emission of the plasma it is possible to determine the particle density of a specific element in the plasma. Sputtering of pure titanium gives an intensity of 100%. By the admittance of nitrogen into the chamber the density of titanium in the plasma will decrease and as a result a lower intensity will be measured. The actual amount of nitrogen that is injected into the chamber will influence the stoichiometry of the coatings. A stoichiometric TiN coating was attained at a titanium concentration ranging between 55 and 60%.

In total, three different batches were prepared. In the first batch the bias voltage was kept to –40 V, and the titanium concentration was varied. For the second batch the Ti concentration was kept constant, 55%, but the deposition time was varied at a bias voltage of –65

V. The third set of samples was prepared at a bias voltage of –80 V and again the titanium concentration was varied. In the first and third batch the titanium concentration was varied from 40 to 80%. The deposition time was 60 min. The bias voltage was chosen in such a way that for the –80 V series the stresses would be high having a (111) orientation and that for the –40 V batch the stresses are low without a (111) texture. All the layers are deposited onto a WC based cermet cuboids of dimensions $20 \times 20 \times 3$ mm. The sample numbers and there deposition parameters are listed in Table 1.

The X-ray diffraction technique was employed to examine the texture and the strain state in the coating. The actual diffractometer was a Philips X'Pert PW3040 goniometer.

3. Results

First the thickness of the samples is determined from cross-sections inspected by scanning electron microscopy. The results are listed in Table 2 and it can be concluded that the actual layer is getting thinner upon decreasing the titanium concentration, i.e. upon adding more nitrogen. This is because the titanium target gets 'poisoned' with adsorbed nitrogen atoms. Obviously the sputter rate of Ti drops upon an increase of nitrogen because the ion bombardment sputters now both kind of atoms, Ti and adsorbed nitrogen. Consequently the coating will be thinner. A comparison of the layer thickness for the different bias voltages indicates that by increasing the bias voltage the layer thickness will decrease. This is due to the increase in the (re)sputter rate accompanying the increase in bias voltage.

Table 2
Influence of the deposition conditions on the layer thickness

Batch	Bias voltage (V)	Layer thickness (μm)				
1	–40	1.9	3.0	3.2	4.2	
3	–80	1.8	2.4	2.6	3.5	
Ti concentration during sputtering (%)		40	50	60	80

Fig. 1. Laboratory system L and the coordinate system S of the specimen, together with the angles ϕ and ψ .

3.1. Texture

The crystallographic texture in the samples is determined with a ψ -goniometer. The intensity of a specific diffraction peak is measured as a function of the polar and azimuthal angles ψ and ϕ , respectively (Fig. 1). There is, however, still a rotational freedom around the axis perpendicular to this specific plane. Therefore, to get a clear picture of the orientation of the crystallites it is necessary to perform measurements on different lattice planes. Next to this it is also necessary to perform a background correction and a correction for the defocus effect to obtain the correct intensity which gives information about the amount of crystallites with a specific orientation. For the texture measurements the $\{200\}$ and the $\{220\}$ planes are used.

The first three samples from batch 1 — 1, 2 and 3 — and the samples from batch 2 — 5 and 6 — all have a clear biaxial texture, i.e. a preference in the plane and in the direction. The intensity of the measured $\{200\}$ and the $\{220\}$ planes of sample 3 are shown in Fig. 2a,b. For the $\{200\}$ plane the maximum is found for $\psi = 45^\circ$. This is the case when the $\{220\}$ planes are parallel to the interface. This is in agreement with the intensity plot of the $\{220\}$ planes, the maximum is found in the center of the plot. Therefore, most crystallites have their $\{220\}$ planes perpendicular to the surface and their $\{200\}$ planes at ϕ angles of 45° and 225° . The only difference between these samples is the intensity and the intensity distribution.

The first three samples from batch 3 — 7, 8 and 9 — all have a fiber texture ($\{200\}$ and $\{220\}$ planes of sample 9 are shown in Fig. 3). The intensity only varies as a function of the ψ angle and there is no ϕ dependence. The $\{200\}$ and the $\{220\}$ planes have a maximum intensity at $\psi = 55^\circ$ and $\psi = 35^\circ$, respectively, and this

corresponds with the $\{111\}$ planes being parallel to the interface. The remaining samples, 4 and 10, have a texture with no clear features, as can be deduced from Figs. 4 and 5.

3.2. Strain

The strain distribution in the different samples is determined and this is done in relation to the present texture. With the use of a ψ -goniometer the position of the $\{220\}$ peak is measured as a function of the angle ψ and this is done in three different ϕ directions; 45° , 90° and 135° . The reason that the $\{220\}$ lattice plane is chosen is that the other diffraction peaks gave either an oscillating $d - \sin^2\psi$ behavior or the intensity was too low to obtain a proper diffraction peak.

Fig. 2. Schmidt projection of the intensity as a function of the ψ and ϕ angles for sample 3: (a) $\{200\}$ plane and (b) $\{220\}$ plane. Ti concentration during sputtering 60%; deposition time, 60 min; bias voltage, -40 V.

Fig. 3. Schmidt projection of the intensity as a function of the ψ and ϕ angles for sample 9: (a) (200) plane and (b) (220) plane. Ti concentration during sputtering 60%; deposition time, 60 min; bias voltage, -80 V.

Fig. 4. Schmidt projection of the intensity as a function of the ψ and ϕ angles for sample 4, (200) plane. Ti concentration during sputtering 80%; deposition time, 60 min; bias voltage, -40 V.

Fig. 5. Schmidt projection of the intensity as a function of the ψ and ϕ angles for sample 10, (200) plane. Ti concentration during sputtering 80%; deposition time, 60 min; bias voltage, -80 V.

Assuming a biaxial stress state then the measured strain in the laboratory system is given by:

$$(\varepsilon'_{33})_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0} = \left[\varepsilon_{11} \cos^2 \phi + \varepsilon_{12} \sin 2\phi + \varepsilon_{22} \sin^2 \phi - \varepsilon_{33} \right] \sin^2 \psi + \varepsilon_{33} \quad (1)$$

By measuring the d spacing as a function of the ψ , the term $(\varepsilon_{11} \cos^2 \phi + \varepsilon_{12} \sin 2\phi + \varepsilon_{22} \sin^2 \phi - \varepsilon_{33})$ can be determined for different ϕ angles.

First the samples from batch 1 are investigated. The results are plotted in Fig. 6. The results show that for

Fig. 6. Experimental values of the strain for the samples in the three batches at different ϕ angles.

the samples with a biaxial texture, samples 1, 2 and 3, the value for the 135° direction is higher than for the 90° direction, which is again higher than the 45° direction (not clearly visible for sample 2 as the strain is almost equal to zero). There is only one sample from the first batch for which this relation is not present and that is sample 4. This is the sample, which does not have a biaxial texture.

The samples from the second batch, both having a biaxial texture, show the same relation between the strain term and the ϕ angles as the samples with a biaxial texture from the first batch. That is the values $|\phi_{135}| > |\phi_{90}| > |\phi_{45}|$.

Finally for the samples from the third batch the strain term is determined and here there appears to be no relation between the strain and the ϕ direction. This is the case for all the samples, i.e. independent of the fiber texture like sample 10.

From these measurements two conclusions can be drawn; first whether or not there is a relation between the strain term and the ϕ angle is determined by the kind of texture present in the layers, when the texture depends on the ϕ angle then the strain term does as well. Secondly, there is a relation between this asymmetrical distribution and the strain generating mechanism, e.g. for the sample with no strain, sample 2, the absolute difference is also very small.

The strain in the magnetron sputtered layers might have two causes; a thermal strain [12] due to the difference between linear expansion coefficient of the coating and the substrate and a strain component generated by the atomic peening process [13–15]. The thermal strain is determined by the difference in expansion coefficients between the substrate and the coating, $\alpha_{\text{TiN}} \approx 8.6 \times 10^{-6} \text{ [K}^{-1}]$ and $\alpha_{\text{wc}} = 4.6\text{--}8.9 \times 10^{-6} \text{ [K}^{-1}]$ [16,17] and the temperature difference. The thermal strain is given by $\varepsilon = \Delta\alpha\Delta T$. Assuming that the expansion coefficients of the substrate and the coating are isotropic and that the coating is a polycrystalline material without a texture, then this will lead to a rotationally symmetric strain distribution, $\varepsilon_{11} = \varepsilon_{22}$ and the $\varepsilon_{12} = 0$. The same is true for the atomic peening process, the peening will result in an expansion of the unit cell, which will be independent on the orientation of the cell. This increase in volume is restricted by the substrate and a strain is introduced in the coating. For a polycrystalline material without a texture this will result in a uniform strain.

The question that can be addressed is what happens in a material with a specific texture and anisotropic XEC? Consider a square single crystal, which is oriented with the (200) and the (220) planes perpendicular to the substrate. (The $\langle 200 \rangle$ direction is defined as the x -direction and the $\langle 220 \rangle$ as the y -direction.) To match the expanded crystal onto the substrate it is necessary

to apply a force. For a material with isotropic elastic compliances the forces in the x and y directions are the same and so the stresses are the same. However, when the material is anisotropic then the stress fields in the x - and y -directions are not the same.

For cubic materials there are only three independent elastic compliances; s_{11} , s_{12} and s_{44} and with $2(s_{11} - s_{12})/s_{44} \times (s_{11} - s_{12})/s_{44}$ it is possible to calculate the anisotropy factor of a material [1]. These three compliances also define the E modulus and the Poisson ratio of a specific $\{hkl\}$ plane,

$$E_{\{hkl\}} = \frac{1}{s_{11} - 2 \cdot \Gamma_{\{hkl\}}(s_{11} - s_{12} - 1/2s_{44})} \quad (2)$$

$$\nu_{\{hkl\}} = -\frac{s_{12} + \Gamma_{\{hkl\}}(s_{11} - s_{12} - 1/2s_{44})}{s_{11} - 2 \cdot \Gamma_{\{hkl\}}(s_{11} - s_{12} - 1/2s_{44})} \quad (3)$$

using Reuss's approximation.

With the gamma defined by:

$$\Gamma_{\{hkl\}} = \frac{(h^2k^2 + h^2l^2 + l^2k^2)}{(h^2 + k^2 + l^2)^2} \quad (4)$$

The relation between the strain of a specific $\{hkl\}$ plane in the laboratory system and the stresses in the sample system reads:

$$\begin{aligned} (\varepsilon'_{33})_{\phi\psi} &= \frac{d_{\phi\psi} - d_0}{d_0} = \left(\frac{1 + \nu}{E} \right)_{\{hkl\}} \\ &\quad \times [\sigma_{11} \cos^2 \phi + \sigma_{22} \sin^2 \phi] \sin^2 \psi \\ &\quad - \left(\frac{\nu}{E} \right)_{\{hkl\}} [\sigma_{11} + \sigma_{22}] \end{aligned} \quad (5)$$

It is now possible to calculate the ratio between the stresses in the $\langle 200 \rangle$ and the $\langle 220 \rangle$ direction for the square single crystal mentioned above [(200) and the (220) planes perpendicular to the substrate and the $\langle 200 \rangle$ direction is defined as the x and the $\langle 220 \rangle$ as the y -direction]. The strain components in the x and y directions, ε_{11} and ε_{22} , must be equal and this will result in a ratio between the stresses in the $\langle 200 \rangle$ and the $\langle 220 \rangle$ direction given by;

$$\frac{\sigma_{11}}{\sigma_{22}} = \left(\frac{E}{1 + \nu} \right)_{\langle 200 \rangle} \cdot \left(\frac{1 + \nu}{E} \right)_{\langle 220 \rangle} \cdot \frac{\varepsilon_{11} - \varepsilon_{33}}{\varepsilon_{22} - \varepsilon_{33}} \quad (6)$$

For a coating with a fiber texture and also for a layer without a texture, the average E modulus in a plane parallel to the interface is independent of the ϕ angle. However, this is not necessarily the case for a material with a biaxial texture and then it is possible that the stresses σ_{11} and σ_{22} are different.

In the samples with a biaxial texture most crystals are oriented with the $\{220\}$ planes parallel to the inter-

face and their $\langle 220 \rangle$ axis in the $\phi = 45^\circ$ and their $\langle 200 \rangle$ axis in the $\phi = 135^\circ$ direction. The anisotropy factor for TiN is smaller than 1, $E_{\langle 200 \rangle} > E_{\langle 220 \rangle}$, so the average elastic modulus in the $\phi = 135^\circ$ direction is higher than in the 45° direction. Consequently the force being applied in the 135° direction must also be larger than in the 45° direction. So this will result in a difference in lattice spacing between the (220) planes measured in the 135° and the 45° direction.

The strain distribution is a result of the anisotropy of the elastic compliances and the biaxial texture and it must be possible to make an estimate of this value. First the ratios between the measured strain in the 135° and in the 45° direction are calculated (Fig. 7), which gives an average value of 1.47. Because the layer is polycrystalline with a specific texture and not a perfect single crystal the measured ratio must be smaller than the ratio calculated using Eq. (6). This is due to the averaging of different oriented grains. Taking the upper values from Kim and Achenbach [6]; $s_{11} = 1.8 \times 10^{-12}$, $s_{12} = -3.76 \times 10^{-13}$ and $s_{44} = 6.2 \times 10^{-12}$ [18,19], gives an anisotropy factor of 0.7 and calculating the ratio between the $\langle 200 \rangle$ and the $\langle 220 \rangle$ direction results in a ratio of 1.32. As mentioned before this value must be larger than the measured one, but instead it is smaller than the measured ratio of 1.47. Assuming that $s_{11} = 1.8 \times 10^{-12}$, $s_{12} = -3.2 \times 10^{-13}$ and $s_{44} = 8 \times 10^{-12}$, and using Eq. (6) again to calculate the ratio between the $\langle 200 \rangle$ and $\langle 220 \rangle$ direction results in a value of 1.67. This value is indeed larger than the measured ratio of 1.47. Using these compliances to calculate the anisotropy factor gives a value of 0.53, so the anisotropy is larger.

When the anisotropy is really as large as calculated, then this should also be visible in the samples with a symmetrical strain distribution. Diffraction measurements at the same ϕ angle but using different diffraction peaks should give a difference in strain between the different planes. This is a consequence of the stress equilibrium, which must exist in the same direction between differently oriented adjoining grains (Reuss's

Fig. 7. Ratio between the measured strains, $\varepsilon_{\phi} = 135$ and $\varepsilon_{\phi} = 45$.

Fig. 8. Measurements on the (200) and (220) planes for sample 9: (a) intensity of the planes and (b) the measured d -spacing as a function of the $\sin^2\psi$.

approximation). Using Eq. (5) to calculate the stresses from the measured strain should give the same value for the different diffraction planes (this is called the quasi-isotropic approach [18]). The ratio between the strain term of the different diffraction planes is then again given by Eq. (6). The lattice spacing for the (200) and the (220) planes of sample 9 are plotted in Fig. 8 (d spacing normalized to d_0). The slope of the (200) planes is considerably lower than the slope of the (220) planes. This is in agreement with the assumption of a higher anisotropy. The difference between the (200) and (220) plane is 1.76, and this is a little larger than the value calculated using Eq. (6), which is 1.67.

The difference can be a consequence of the fact that the data are obtained at different 2θ -values. When the 2θ value increases the penetration depth increases as well. Due to strain gradient [9,10], this will automatically result in a difference between different planes even when correct XEC are being used.

4. Conclusions

Due to different deposition conditions TiN layers with different textures were produced. A result of the texture was that samples with a fiber texture had a symmetrical strain distribution and samples with a biaxial texture a non-uniform distribution. The difference may be explained by assuming that TiN is elastic very

anisotropic and has an anisotropy factor of approximately 0.5. Quasi-isotropic stress calculations have confirmed this value.

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