Determination of Average X-ray Strain (AXS) on TiN Hard Coatings using $\cos^2\alpha\sin^2\psi$ X-ray Diffraction Method

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Abstract

For stress measurement on thin films and coatings using X-ray diffraction (XRD) methods, the uncertainty is commonly acknowledged to be from the elastic constants. However, the uncertainty can be due to the statistical fluctuation of strain measured by XRD. In this study, we proposed a method where the average X-ray strain (AXS) was determined using $\cos^2\alpha\sin^2\psi$ XRD technique at several rotational (ϕ) angles to improve the accuracy of the measurement of X-ray stress or X-ray elastic constants (XECs). The major concept was to increase sampling volume by measuring X-ray strain at multiple rotational angles. TiN hard coating on Si (100) substrate was selected as the model system, where the residual stress was determined by laser curvature technique and the accompanying lattice strain was measured by $\cos^2\alpha\sin^2\psi$ method. The average effective elastic constant (AEXEC) could be attained by substituting the residual stress into the slope of AXS vs. $\cos^2\alpha\sin^2\psi$ plot. The AEXEC was served as an indicator to validate the AXS measurement. By substituting AEXEC in conventional $\sin^2\psi$ XRD stress measurement, the deviation of the result from the stress obtained by laser curvature method was less than 7%, indicating that AXS effectively reduced the uncertainty in XECs and thus increased the accuracy of stress measurement. The concept of increasing sampling volume was also confirmed using synchrotron X-ray source, where the statistical fluctuation in X-ray strain could be further reduced by performing the

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measurement at all azimuthal direction. The experimental results showed that the uncertainty on XECs measurement by $\sin^2\psi$ method was less than 10%, if sufficient sampling volume was provided. Furthermore, using AXS and elastic constant measured by nanoindentation (E_{NIP}) to calculate X-ray stress, the stress deviation from that by laser curvature method could be substantially reduced even down to 3 % with sufficient sampling points. Therefore, AXS may serve as a convenient parameter, when combining with E_{NIP} , in X-ray stress measurement, by which residual stress of hard coatings comparable to that by laser curvature method can be obtained without using XECs.

Keywords: average X-ray strain (AXS), average effective X-ray elastic constant (AEXEC), $\cos^2\alpha\sin^2\psi$ method, high energy X-ray, laser curvature method, TiN hard coating

1. Introduction

X-ray diffraction (XRD) is one of the major nondestructive techniques for the measurement of residual stress in crystalline materials. The lattice distortion of a crystalline material is determined by XRD, and then the residual stress can be calculated from theory of elasticity if the X-ray elastic constants (XECs) are available, where XECs include Young's modulus (E), Poisson's ratio (ν) or the combination of E and ν . However, the stresses measured from optical curvature and XRD techniques are often not consistent, and the deviation can reach up to 30% [1]. The discrepancy could be due to the uncertainty in elastic constants or the strain measurement, and the issue is especially significant for thin films and coatings, where the determination of strain and elastic constants is usually problematic.

Various techniques on the measurement of elastic constants of thin films have been proposed, which can be divided into two categories: destructive and nondestructive methods. Destructive techniques generally involve design of test apparatus or applying load to execute

the measurement on thin films, such as tensile test [2-5], bulge test [6-8], bending test [9] and nanoindentation [10,11]. Among those techniques, nanoindentation is the most popular one that can simultaneously determine both hardness and elastic constant of a thin film. Following ISO 14577 standard procedures, the uncertainty of the nanoindentation measurement can be limited to $\pm 5\%$. For tensile or bending tests accompanied with XRD [2,9], XECs are determined from Hooke's law, by applying a controlled load and using interplanar distance as a strain gauge. Although the testing procedures are straightforward, the effectiveness of measurement depends on complicated factors, such as the alignment of external force, utilizing sophisticated XRD equipment, and detecting bi-axial stress during loading. Moreover, damage of the thin film specimen is difficult to be avoided, and thereby the resultant elastic constants may not be considered as intrinsic properties.

Thin films deposited by ion-assisted physical vapor deposition (PVD) methods commonly possess high residual stress, and hence nondestructive XRD techniques can be employed [12-14] to measure the elastic constants without externally applying force. The main concept is to measure strain of the film using XRD method and acquire residual stress by other techniques such as laser curvature method, from which E and ν can be obtained. Since the nondestructive measurement does not alter the film structure and properties, the resultant elastic constants can be considered as the intrinsic properties of the film. In our previous study [12], we proposed a method to simultaneously determined E and ν by combining $\sin^2\psi$ XRD and laser curvature techniques, where six strain components (ϵ_{11} , ϵ_{22} , ϵ_{33} , ϵ_{12} , ϵ_{13} and ϵ_{23}) could be obtained individually. However, the resultant E of a random-textured TiN film was 816 GPa, which was unreasonably high compared with other literature values measured by XRD methods, ranging from 250 GPa to 640 GPa [15-20]. For polycrystalline TiN coatings deposited on Si, the typical E value obtained from mechanical methods is ranged from 300 to 500 GPa [21,22], which is fairly consistent with the values

from density function theory (DFT) calculations [23,24]. Obviously, the variation range of the Young's modulus measured by XRD is larger than that obtained by destructive methods or theoretical calculation. Nevertheless, the discrepancy of the measurement on the elastic constants between XRD method and the other techniques has not been fully understood. Since XECs are generally calculated from strain measured by XRD with known applied stress, it is speculated that the large variation in XECs may be derived from statistical fluctuation in X-ray strain measurement due to limited sampling volume.

The objective of this study was to develop a nondestructive technique to measure the X-ray strain with which the statistical fluctuation could be reduced and therefore reliable effective X-ray elastic constant (EXEC), $\frac{E}{1+\nu}$, or X-ray stress for hard coatings could be acquired. TiN hard coating on Si(100) wafer was chosen as the model material due to the well-established mechanical properties. The average X-ray strain (AXS) was measured by $\cos^2\alpha\sin^2\psi$ XRD method [25] at several rotational ϕ -angles. The average effective X-ray elastic constant (AEXEC) was obtained by substituting the residual stress measured from laser curvature method into the slope of AXS vs. $\cos^2\alpha\sin^2\psi$ plot.

2. Theoretical Basis for Measuring Average X-ray Strain (AXS)

To reduce the uncertainty in measuring X-ray strain and EXEC for hard coatings, the systematic errors derived from the stress applying process can be avoided by using residual stress as an alternative stress source. Furthermore, the large fluctuation of XECs in thin film materials is conjectured to be due to limited sampling volume of XRD measurement, where the sampling volume means the volume of total amount of grains with which orientation fulfill the Bragg law. From the definitions of macro- and micro-strain proposed by Hauk [26], the strain fluctuation is the local response of mutual constraints between different domains. Since the local strain should compensate each other to reach an equilibrium state, the mean

deviation must be zero. If the sampling volume is sufficiently large, the statistical error can be minimized, and consequently the macroscopic strain will be nearly constant with limited statistical error. In addition, the macro-strain can lead to local alteration of constraint, depending on the microstructure and elastic characteristics. The relation between macro- and micro-strain is given by [26]

$$\langle \varepsilon^{II} \rangle = \bar{\varepsilon}_0 + [f_{mn}(\psi, \phi) - I] \varepsilon^I \quad (1)$$

where $\langle \varepsilon^{II} \rangle$ is the mean deviation between micro-strain measured by X-ray method and the macro-strain measured by optical curvature method, $\bar{\varepsilon}_0$ is the independent part due to grains interaction and ε^I is the macro-strain. The prefactor I is the identity matrix, and f_{mn} is the stress-transfer factors, where $f_{mn}(\psi, \phi) = \frac{\partial(\bar{\varepsilon})_m}{\partial(\varepsilon^I)_n}$ and $m, n = 1 \dots 6$. Since ε^I is caused by the biaxial stress, $f_{mn}(\psi, \phi)$ depends on the angle between in-plane and X-ray strain ($\bar{\varepsilon}_0$) measurement directions. For different tilting ψ -angles, f_{mn} is constantly changing and thus inducing statistical error. Although increasing the range and number of ψ -angle is commonly suggested to acquire reliable X-ray stress in $\sin^2\psi$ method, the sampling region is still limited in the thickness direction even with wider ψ range. In contrast, f_{mn} is fixed in the azimuthal direction (ϕ). Therefore, in addition to changing ψ angle, several ϕ angles may have to employ to effectively increase the sampling volume and thus reducing the statistical error in measuring strain.

Accordingly, we propose an average X-ray strain (AXS) defined as the average strain measured at several rotational ϕ angles with the same range of ψ -angle, which can be measured by $\cos^2\alpha\sin^2\psi$ method [25]. The method to determine AXS is outlined as follows. First, $\cos^2\alpha\sin^2\psi$ method is conducted to measure the strain of the thin film at different ψ tilt angle, where the X-ray incident angle is chosen to have a penetration depth covering the

entire film thickness [27,28]. The XRD measurement is performed at several ϕ angles, by which the strain $\frac{d_{\alpha\psi}(\phi) - d_o}{d_o}$ is determined. The bi-axial strain in $\cos^2\alpha\sin^2\psi$ method is independent of ϕ angles and is given by [25]

$$\frac{d_{\alpha\psi}(\phi) - d_o}{d_o} = \frac{1+\nu}{E}\sigma\cos^2\alpha\sin^2\psi + \frac{1+\nu}{E}\sigma\sin^2\alpha - \frac{2\nu}{E}\sigma \quad (2)$$

where $\frac{E}{1+\nu}$ is the effective X-ray elastic constant (EXEC), σ is the residual stress and

$\alpha = \gamma - \theta_o$, where γ is the X-ray incident angle and θ_o is the diffraction angle. The slope of

$\frac{d_{\alpha\psi}(\phi) - d_o}{d_o}$ vs. $\cos^2\alpha\sin^2\psi$ obtained from linear regression of all measured data at several ϕ

angles is the average X-ray strain (AXS); that is, $\text{AXS} = \left(\frac{1+\nu}{E}\right)\sigma = \frac{1}{\text{AEXEC}} \cdot \sigma$. If σ is

obtained by laser curvature method, AEXEC can be calculated by substituting σ into the slope of $\frac{d_{\alpha\psi}(\phi) - d_o}{d_o}$ vs. $\cos^2\alpha\sin^2\psi$ plot.

To verify the effectiveness of AXS, different elastic constants including EXEC, XECs and Young's modulus measured by nanoindentation (E_{NIP}) were used in different X-ray stress measurements, and the deviations of the resultant stresses from that obtained by laser curvature method were compared. XECs were determined by combining $\sin^2\psi$ with laser curvature techniques [12], and E_{NIP} was acquired following ISO 14577 standard procedures. Each elastic constant measured from different technique has its statistical significance which will be discussed in this paper. Finally, the average strain measured by high-energy synchrotron X-ray was used to evaluate the statistical influence on X-ray strain, AEXEC and macroscopic X-ray stress.

3. Experimental Procedures

TiN films with different thickness and residual stress were chosen as the model material. The substrate material was P-type Si (100) wafer with dimensions of $40 \times 35 \times 0.525 \text{ mm}^3$. The substrates were ultrasonically cleaned in acetone and methanol each for 5 min, and then immediately placed into the deposition chamber. Deposition of TiN film was carried out using a dc unbalanced magnetron sputtering (UBMS) system. The chamber was continuously pumped down to a base pressure of $8 \times 10^{-4} \text{ Pa}$ ($6 \times 10^{-6} \text{ torr}$) and the substrate material was heated to 400°C . Prior to deposition, the substrate surface was pre-sputtered by argon ions discharged at a bias of -1000V for 5 min to remove the oxide layer on the surface. During deposition, the pressure in the chamber was maintained at $1.7 \times 10^{-1} \text{ Pa}$ ($1.3 \times 10^{-3} \text{ torr}$), the flow rates of high purity argon and nitrogen gases (both of 99.9995% in purity) were maintained at 30 sccm and 1 sccm, respectively. The target material was pure Ti (99.995% in purity) and the target current was fixed at 0.4 A. Substrate bias voltages of -60 V and -70 V were applied to control the magnitude of residual stress.

X-ray photoelectron spectroscopy (XPS) was used to determine the N/Ti ratio of the coatings using an X-ray source of Mg $K\alpha$ (1253.6 eV). The microstructure of the TiN coatings was observed using a field-emission gun scanning electron microscope (FEG-SEM) and the film thickness of the specimen was measured from the cross-sectional SEM image. Residual stress of the TiN coatings was acquired optically using laser curvature method with Stoney's equation [29]. The measurements were performed at several azimuthal angles to insure the uniformity of the in-plane stress. The Young's modulus (E) was measured using a Hysitron TriboScope[®] nanoindenter equipped with a Berkovich diamond indenter head following ISO 14577 standard procedures, and the data were within an uncertainty of $\pm 5\%$. The Poisson's ratio (ν) of the TiN coatings was adopted to be 0.21 from previous literature [20].

Texture coefficient, degree of randomness and grain size of the TiN coatings were characterized by XRD, using a M18XHF-SRA diffractometer with Cu K α X-ray source ($\lambda = 1.5405\text{\AA}$). The (200) texture coefficient is defined as $I(200)/[I(200)+I(111)]$, where $I(hkl)$ is the integrated intensity of the corresponding (hkl) plane by conventional $\theta/2\theta$ scan, ranging from $2\theta = 20$ to 65° . The degree of randomness is defined as the ratio of the (200) texture coefficient to that calculated from JCPDS data (File No. 65-0565). The grain size of the thin films was estimated by the Scherrer equation [30]. In addition, grazing incident X-ray diffraction (GIXRD) was carried out with an incident angle of 2° and 2θ ranging from 20 to 100° . The diffraction pattern was used to calculate lattice parameter of the TiN coatings [31].

The $\cos^2\alpha\sin^2\psi$ method [25] was employed to measure the X-ray strain of all samples. The strain measurement was performed using a 4-circle diffractometer with psi-goniometer (Bruker D8 HRXRD) and Cu K α X-ray source ($\lambda=1.5405\text{\AA}$) was used. The diffractometer was under parallel-beam configuration with point focus for the X-ray strain measurement. Before XRD measurement, the film thickness was determined from the cross-sectional SEM images. The grazing incident angles were selected according to the film thickness, where the penetration depth should cover the film thickness. The X-ray penetration depth was calculated following X-ray penetration theory using the energy of Cu K α and the X-ray mass attenuation coefficient of TiN [27,28,32]. Accordingly, three X-ray incident angles, 9° , 16° and 25° , were selected corresponding to the three different sample thicknesses 1.55, 2.69 and $3.89\text{ }\mu\text{m}$, respectively. Nine ψ tilt angles, namely, $\pm 50^\circ$, $\pm 42^\circ$, $\pm 33^\circ$, $\pm 23^\circ$, and 0° , were used in one set of ψ scan, and TiN (220) peak was chosen for the strain measurement, where the (220) peak intensity was collected ranging from $2\theta = 55$ to 63° . Each set of ψ scan was performed at five ϕ angles, 0° , 30° , 45° , 60° and 90° , to explore the statistical variation of strain in the azimuthal direction. The position of each Bragg peak was determined by fitting the peak with Voigt function using Peakfit software. AEXEC was calculated by substituting

the residual stress into the slope of the AXS vs. $\cos^2\alpha\sin^2\psi$ plot.

The $\sin^2\psi$ combining with laser curvature method [12] was employed to determine the XECs (E and ν). The $\sin^2\psi$ strain measurement was performed using the X-ray scattering station at beamline 17B1 of National Synchrotron Radiation Research Center (NSRRC) at Hsinchu, Taiwan. Again, TiN (220) peak was chosen for the strain measurement. Three ϕ angles, 0° , 45° and 90° and eleven ψ angles, 0° , $\pm 25^\circ$, $\pm 37^\circ$, $\pm 47^\circ$, $\pm 57^\circ$, $\pm 70^\circ$, were applied.

High energy XRD experiments were conducted at the 11-ID-C beamline of Advanced Photon Source (APS) in Argonne National Laboratory (ANL). Scattering geometry of the synchrotron high energy XRD experiment is depicted in Fig. 1, where incident X-ray is in in-plane and out-of plan direction. 1.5-mm wide slides were prepared by a diamond glass cutter and examined by 115 keV synchrotron X-ray. The incident X-ray hit the specimen from the lateral edge and diffracted in forward direction. This scattering geometry allows us to compare in-plane and out-of-plane lattice strain and texture preference in single exposure, where the $\chi = 90^\circ$ is the out-of-plane (film normal) direction while $\chi = 0^\circ$ and 180° are the in-plane direction. The diffracted signal was collected by a two dimensional area detector with a pixel size of $200 \times 200 \mu\text{m}^2$. For each measurement, multiple exposures, with a maximum of ~50k counts in a single pixel, were collected. The high counting improves the statistics of the data, which allows the reliable data analyses. The diffraction intensity, $I(\theta)$, versus the Bragg angle was obtained by integrating the 2D diffraction rings azimuthally using the software package FIT2D [33]. The 2D pattern was sliced azimuthally with 2° per slice and each slice was integrated to obtain diffraction curve, $I(\theta)$. A Matlab[®] program was used to perform the single-peak fitting using Voigt function [34]. The high-energy synchrotron X-ray has the advantage that the beam penetrates the entire sample and covers the entire azimuthal direction in a single exposure as shown in Fig.1. Using the average strain calculated from

(220) peaks, the relation between strain and biaxial stress is $\sigma_m = \frac{E}{1-\nu} \bar{\varepsilon}_m$ following simple Hook's law, where σ_m is the biaxial stress, $\bar{\varepsilon}_m$ is the AXS from all azimuthal angles and $\frac{E}{1-\nu}$ is the combination constant of Young's modulus (E) and Poisson's ratio (ν). By substituting optically measured stress and average strain into the aforementioned relation, the combination constant, $\frac{E}{1-\nu}$, can be determined.

4. Results and Discussion

The experimental results are summarized in Table 1. By adjusting the substrate bias from -70 to -60V, the compressive residual stresses of the specimens are reduced from -3.04 to -1.9 GPa. The designation of the samples follows the stress level, where H denoting the highest stress, L the lowest stress and M the stress in between, as listed in Table 1. The film thicknesses for samples H, M and L are 1.55, 2.69 and 3.89 μm , respectively. N/Ti ratio varies in a narrow range from 1.1 to 1.2. The grain size and lattice parameter are calculated from XRD and GIXRD patterns shown in Fig. 2 (a,b), respectively. For all samples, the grain sizes are about 24 nm, and the lattice parameters are around 4.236 Å in average, which are comparable to the data reported for slightly off-stoichiometric TiN, ranging from 4.228 to 4.238 Å [35]. The results of XRD pattern, N/Ti ratio, grain size and lattice parameter indicate that the specimens are typical TiN coatings.

TiN (220) plane was selected for the strain measurements in both $\sin^2\psi$ and $\cos^2\alpha\sin^2\psi$ methods. For $\sin^2\psi$ method, the diffraction volume in thin film under Bragg-Brentano (B-B) geometry is proportional to the film thickness, and thus the thickest sample L with a thickness of 3.89 μm was measured using synchrotron X-ray to further increase the intensity. The (200) texture coefficient and degree of randomness for the samples are tabulated in Table 1. Sample

H is deviated 57% from the random texture showing (111) preferred orientation. For samples M and L, smaller deviations from randomness about 17~18% were observed, indicating that the coatings are with nearly random texture.

The slopes of strain vs. $\cos^2\alpha\sin^2\psi$ plot calculated at different ϕ angles and AXS are listed in Table 2, where the deviations of slopes at different ϕ angles from AXS are also shown. The correlation coefficients (R^2) of linear regression for all measurements are higher than 0.7. For sample H with the highest residual stress, the deviations of the slopes from AXS are within 7%. By contrast, slope values of samples L and M fluctuate up to 35% and 24% compared with AXS values for the respective samples. The significant variation of the slope of strain at different ϕ angle indicates that the grain groups sampling by XRD are not fully isotropic along azimuthal direction. The fluctuation in strain measurement further leads to the deviation of EXEC that is calculated by substituting the optically measured residual stress (ORS) into the slope of strain, as shown in Fig. 3. Since the sampling volume of ORS covers the whole specimen, the resultant stress is the bulk average stress of the coating, which is less sensitive to the anisotropy of grains. Therefore, EXEC can serve as an indicator for verifying the statistical influence on X-ray measured strain.

Compared with the conventional $\sin^2\psi$ method, the grazing incident geometry of X-ray in the $\cos^2\alpha\sin^2\psi$ method can increase the sampling volume of thin film specimens. However, since the strains are measured in the in-plane direction through a few tilting angles, the effective sampling volume is still influenced by the texture at those tilting angles. Fig. 4 (a) shows a 2D diffraction pattern of sample L with in-plane scattering geometry, where different diffraction rings correspond to different (hkl) planes of TiN thin film as labeled and the diffraction spots are from the Si substrate. If the sample is texture free, the intensity distribution of a selected (hkl) along azimuthal direction should be uniform, which means the projection of such diffraction cone on a 2D detector plane should be a continuous ring. In Fig.

4(a), it is observed that the diffraction rings of both (111) and (200) are discontinuous, indicating that the orientation distribution of the grains is not uniform along azimuthal direction, which implies that sample L has moderate texture, even though the degree of randomness (Table 1) suggests sample L with a nearly random texture. The intensity distributions of in-plane and out-of-plane X-ray pattern are shown in Figs. 4 (b) and (c), respectively. Since the intensity is proportional to the number of grains in the sampling volume, the intensity fluctuation shown in Fig. 4(b,c) indicates the orientation distribution of the grains in both in-plane and out-of-plane direction, which can lead to fluctuation of the resultant strain (Table 2). To reduce the strain fluctuation due to texture, AXS is calculated by using the strains at all azimuthal angles to increase the sampling volume, which is used to calculate the AEXEC and the results are listed in Table 3.

Table 3 presents elastic constants of the TiN coatings measured by three different methods. The Young's moduli from AEXEC (E_{AEXEC}), assuming $\nu = 0.21$, are ranged from 377.5 to 457.5 GPa using AXS from $\cos^2\alpha\sin^2\psi$ method. The Young's moduli from nanoindentation (E_{NIP}), with $\nu = 0.21$, are quite close, ranging from 417.8 to 473.0 GPa. Both E_{NIP} and E_{AEXEC} are within a reasonable range compared with the literature XECs data and the results from *ab initio* calculations (Table 4). However, both E_{NIP} and E_{AEXEC} are derived from combination values of E and ν , with ν assuming to be 0.21. To individually acquire XECs, $\sin^2\psi$ method accompanied with laser curvature technique was adopted for the measurement [12], and the resultant E and ν for sample L are 395.4 GPa and 0.21, respectively, where the ν value is consistent with the assuming value. In addition, by substituting the XECs into the definition of EXEC ($= \frac{E}{1+\nu}$), the resultant EXEC is equal to 326.7 GPa which is only 5% deviation from the AEXEC of sample L, suggesting that the AXS measurement can obtain the correct combination value of E and ν .

To further validate the elastic constants obtained from AXS measurement, the AEXEC and EXEC are employed in $\sin^2\psi$ XRD stress measurement, and the residual stresses are compared with ORS. The deviation from ORS can indicate the effectiveness of AXS measurement, as tabulated in Table. 5. It can be seen that X-ray residual stress (XRS) shows a large deviation ranging from 3% to 49% by using EXEC. By contrast, the stress deviation is narrowed down to 0% to 7% by using AEXEC obtained from AXS of $\cos^2\alpha\sin^2\psi$ measurement. The results indicate that the AXS measurement can increase the accuracy of X-ray strain and thus reduce the stress deviation.

If AXS measurement can obtain a strain close to the macro-strain, the accurate stress can be attained using elastic constants (E and ν) determined by mechanical methods. Nanoindentation is the most common technique to measure Young's modulus of thin films and hard coatings, and thus is often adopted in XRS calculation. In this study, E_{NIP} was applied to calculate XRS using the strain measured by $\sin^2\psi$ XRD or AXS methods, where the stress deviation from ORS is taken as an indicator to verify the effectiveness of elastic constants, and the results are listed in Table 5. The stress deviations for samples H and M are respectively 8% and 5%, which are the same using both $\sin^2\psi$ XRD and AXS methods, suggesting that E_{NIP} is a suitable elastic constant for XRS measurement. However, the stress deviations of sample L are significantly high, 41% and 26% for $\sin^2\psi$ XRD and AXS methods, respectively. Since the uncertainty of E_{NIP} is less than 10% (Table 3), the stress deviation is considered to be resulted from the uncertainty of X-ray strain measured by in-house X-ray diffractometer.

As shown in Table 2, sample L has large fluctuation in strain measured at different ϕ angle. Fig. 4 (c) also depicts an asymmetrical out-of-plane intensity distribution for (220) peak. The diffraction intensity is proportional to the number of (hkl) planes, and therefore the asymmetrical intensity distribution may affect the sampling volume when the measurement

was conducted using in-house X-ray at only five ϕ angles in the first quadrant. The influence of insufficient sampling volume can be revealed by calculating AXS with the data selected from different number of ϕ angle in Fig. 4(c). The resultant AXS is shown in Fig. 5 which indicates that as the number of ϕ angle is less than 20, the fluctuation of average strain is quite large, until the number of ϕ angle is larger than 80, close to 160° , the fluctuation of average strain shrinks to a narrow range. In other words, to reduce the statistical fluctuation the sampling region should cover about 180° in the azimuthal direction to properly collect the biaxial strain of the TiN film. Using AXS measured from all azimuthal angles and E_{NIP} , the residual stress is computed again and the results are tabulated in Table 6. It can be seen that the stress deviations are reduced to 3% and 8% for samples M and L, respectively, suggesting that E_{NIP} is the correct elastic constant and the major error of XRS is due to insufficient X-ray sampling volume.

To further explore the influence of elastic constants on stress measurement, the EXEC, AEXEC and XECs are employed with AXS from high energy X-ray to calculate XRS, and the results are listed in Table 6. The stress deviation from ORS by using EXEC shows a large variation from 2 to 37%, which is evidently due to the asymmetrical X-ray strains (Table 2). By contrast, the stress deviations are only 5% and 10% by using AEXEC and XECs, respectively. The result shows that the uncertainty of XECs is around 10% with sufficient sampling volume.

Since E_{NIP} was from nanoindentation, the error propagation due to the measurement of reduced Young's modulus (E_r) and the choice of Poisson's ratio should be examined. The relationship for calculating E_{NIP} in Oliver-Pharr analysis is given by [36]

$$\frac{1}{E_r} = \frac{(1-\nu^2)}{E_{NIP}} + \frac{(1-\nu_i^2)}{E_i} \quad (3)$$

where ν_i ($= 0.07$ [10]) and ν are Poisson's ratios of the diamond indenter tip and the coating,

and E_i ($= 1141\text{GPa}$ [10]) and E_r are the Young's modulus of the indenter and the reduced modulus from nanoindentation, respectively. From Eq. (3), the effective elastic constant

A ($= \frac{E_{NIP}}{1+\nu}$) is given by

$$A = \left(\frac{1}{E_r} - C_{tip} \right)^{-1} \cdot (1 - \nu) \quad (4)$$

where $C_{tip} = \frac{(1 - \nu_i^2)}{E_i}$. Hence, the absolute error propagation from E_r and ν can be estimated by

$$\frac{dA}{A} = \left| \frac{dA}{A \cdot dE_r} \right| dE_r + \left| \frac{dA}{A \cdot d\nu} \right| d\nu. \quad (5)$$

Substituting Eq. (4) into (5), the absolute error becomes

$$\frac{dA}{A} = \left(\frac{1}{1 - C_{tip} E_r} \right) \frac{dE_r}{E_r} + \left(\frac{\nu}{1 + \nu} \right) \frac{d\nu}{\nu}, \quad (6)$$

where $\frac{dE_r}{E_r}$ is the uncertainty from nanoindentation test and $\frac{d\nu}{\nu}$ is due to the choice of

inaccurate Poisson's ratio. Eq.(6) indicates that the two pre-factors $\frac{1}{1 - C_{tip} E_r}$ and $\frac{\nu}{1 + \nu}$

contribute to the uncertainty in the effective elastic constant ($\frac{E}{1 + \nu}$). Closely examining the

two factors, it is found that the former factor is 1.4 for $E_r \cong 340\text{ GPa}$, and the latter factor is

much smaller ($\frac{\nu}{1 + \nu} = 0.17$, when $\nu = 0.21$) and can be neglected. Thus, the uncertainty of the

effective elastic constant is mainly from the uncertainty of E_r . Since $\frac{dE_r}{E_r}$ is within 10%

when following ISO 14577 standard procedures, the maximum error propagation from E_r ,

according to Eq.(6), is 14%. Compared E_{NIP} with E_{AEXEC} from high energy XRD for samples

M and L (Table 3), it is found that both E_{NIP} with E_{AEXEC} are within the same range if

considering the uncertainty of the respective technique. Therefore, elastic constant measured by nanoindentation should be comparable to XEC if X-ray sampling volume is sufficient.

Again, the difference in sampling volume could be the reason that leads to deviation in different measurements. The sampling volume of nanoindentation is the plastic zone size under the indenter. Previous studies [37,38] reported that the plastic zone size under nanoindentation can be estimated as follows

$$r_p = \sqrt{\frac{3P}{2\pi\sigma_{ys}}} \quad (7)$$

where r_p is the plastic zone size, P is the applied load, and the σ_{ys} is the yield strength of the material. Since the indentation depth is less than 1/10 of the film thickness, the stress state can be assumed to be plane strain condition. σ_{ys} is about 7 GPa for TiN thin films from tensile test [39] or one-third of the hardness [40]. The smallest applied load P in this study was 3500 μ N. Inserting the values of P and σ_{ys} into Eq. (7), the smallest $r_p = 489$ nm. Hence, the sampling volume should be about 4.90×10^8 nm³, which can contain about 36800 grains for the grain size listed in Table 1. Since E_{NIP} is directly measured from the elastic-plastic deformation on the film, it is an average mechanical performance of the entire sample, and therefore E_{NIP} is a reliable measurement of Young's modulus.

On the other hand, the sampling volume for X-ray strain measurement is associated with crystal orientation, incident beam size, penetration depth, and tilting and rotational angles (ψ, ϕ). The diffraction volume under the X-ray beam can be estimated from the product of the **X-ray footprint size** and the **film thickness**. Taking sample L for example, the diffraction volume under B-B geometry is **about 1.1×10^{16} nm³**, which is much larger than that of nanoindentation. However, only (220) plane is measured in XRD method, and thus the actual sampling volume is a small portion of total grains. As shown in Fig. 2(b), the integrated intensity of (220) at $\psi = 0^\circ$ is about 30% to 35% of the total intensity of all diffraction peaks.

Furthermore, the fraction of (220) plane varies at different ψ angle as indicated in the 2D diffraction pattern (Fig. 4), where the intensity changes with in-plane direction. As mentioned, sampling volume is also changed in the azimuthal direction (ϕ). In other words, the X-ray strain measured using a specific grain group at one ϕ direction is a micro-strain value and may not represent the macro-strain of the overall specimen. It is not surprising that the small sampling size could cause large statistical fluctuation as shown in Table 2 and Fig. 3. Therefore, increasing sampling volume is crucial to obtain a reliable X-ray strain that is close to macro-strain of the entire specimen.

In this study, the concept of increasing sampling volume was carried out by conducting the X-ray strain measurement at several azimuthal angles, which effectively reduced the statistical fluctuation in the resultant AXS. Since sufficient diffraction volume was included in the measurement, AXS was equivalent to macro-strain. Therefore, E_{NIP} or mechanically determined elastic constants can be used accompanied with AXS to calculate stress without large uncertainty. The concept that difference in sampling volume could lead to statistical fluctuation in the measurement result may also explain the unreasonably large XEC for TiN, $E=816$ GPa, in our previous study [12] (Table 4). For XECs measurement using $\sin^2\psi$ method, the diffraction volume depends on the film thickness. The film thicknesses were $0.95\ \mu\text{m}$ in the previous study, which is only $\frac{1}{4}$ of that of the present study, $3.89\ \mu\text{m}$. Thus, insufficient diffraction volume could be the reason that caused large statistical fluctuation in X-ray strain and consequently very large Young's modulus.

5. Summary

In this study, we proposed a method to determine the average X-ray strain (AXS) using $\cos^2\alpha\sin^2\psi$ XRD technique at several rotational (ϕ) angles, by which the accuracy of the measurement of X-ray stress or X-ray elastic constants (XECs) could be improved. The major

concept was to increase sampling volume by measuring X-ray strain at multiple rotational angles. The average effective elastic constant (AEXEC) could be attained from AXS and the residual stress measured by laser curvature method. Using AEXEC in conventional $\sin^2\psi$ XRD stress measurement, the deviation from the stress obtained by laser curvature method was less than 7%, indicating that AXS effectively reduced the uncertainty in XECs and thus increased the accuracy of stress measurement. The concept of increasing sampling volume was verified using synchrotron X-ray source, where the statistical fluctuation in X-ray strain could be further reduced by performing the measurement at all azimuthal direction. The experimental results showed that the uncertainty on XECs measurement by $\sin^2\psi$ method was less than 10%, if sufficient sampling volume was provided. Furthermore, using AXS and E_{NIP} to calculate X-ray stress, the stress deviation from that by optical method could be reduced to 3 % when sampling volume was sufficient. Therefore, AXS is a convenient parameter, when combining with E_{NIP} , in X-ray stress measurement, by which residual stress of hard coatings comparable to that by laser curvature method can be obtained without using XECs.

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Tables and Figures Captions

Table 1 Summary of experimental results of the TiN coatings.

Table 2 The AXS and slopes ($\times 10^{-3}$) of strain vs. $\cos^2\alpha\sin^2\psi$ at five rotational angle (ϕ) for the TiN coatings. The deviation of the slope from AXS at each rotational angle were also shown in parentheses.

Table 3 Elastic constants of the TiN coatings derived from different methods.

Table 4 Comparison of X-ray elastic constants (XECs) of TiN with literature values.

Table 5 The X-ray residual stresses (GPa) for the three specimens calculated using different elastic constants. The strains were measured by $\sin^2\psi$ and $\cos^2\alpha \sin^2\psi$ methods. The deviations of the stress from that measured by laser curvature method are shown in parentheses.

Table 6 The X-ray residual stresses (GPa) calculated using different elastic constants and AXS of high energy XRD with out-of-plane incident geometry. The deviations of the stress from that measured by laser curvature method are shown in parentheses.

Fig. 1 Scattering geometry of the synchrotron high energy X-ray diffraction experiment, where X-ray incident in both (a) in-plane and (b) out-of-plane direction.

Fig.2 (a) The XRD patterns and (b) GIXRD patterns with incident angle of 2° for the three TiN specimens.

Fig.3 EXECs at different rotational angles (ϕ).

Fig. 4 (a) A typical 2D diffraction pattern of the specimen. The pattern shown here is from sample L with in-plane scattering geometry. The x-axis is defined as $\chi = 0^\circ$ (azimuthal angle) and y-axis as $\chi = 90^\circ$. Different diffraction rings correspond to different (hkl) planes of TiN thin film as labeled in figure. The spots are from the Si substrate. (b) The in-plane intensity distribution and (c) the out-of-plane intensity distribution of TiN (hkl) planes.

Fig. 5 The average strain calculated with randomly selected ϕ angles measured from

high-energy synchrotron X-ray with out-of-plane incident geometry.

Table 1 Summary of experimental results of the TiN coatings.

Sample No.	Film thickness (μm)	Residual stress (GPa)	N/Ti	Lattice parameter (Å)	Grain Size (nm)	(200) texture coefficient	Degree of randomness
H	1.55	-3.04	1.1	4.234	23.8	0.25	0.43
M	2.69	-2.40	1.1	4.237	23.6	0.69	1.18
L	3.89	-1.90	1.2	4.238	23.7	0.68	1.17

Table 2 The AXS and slopes ($\times 10^{-3}$) of strain vs. $\cos^2\alpha\sin^2\psi$ at five rotational angle (ϕ) for the TiN coatings. The deviation of the slope from AXS at each rotational angle were also shown in parentheses.

Sample No.	slopes ($\times 10^{-3}$) of strain at rotational angle (ϕ)					AXS
	0°	30°	45°	60°	90°	
H	-8.49 (5%)	-8.18 (2%)	-7.81 (3%)	-7.83 (3%)	-7.45 (7%)	-8.04
M	-7.5 (12%)	-7.74 (15%)	-7.09 (6%)	-5.09 (24%)	-6.30 (6%)	-6.72
L	-4.28 (30%)	-6.39 (5%)	-7.24 (19%)	-8.24 (35%)	-6.00 (1%)	-6.09

Table 3 Elastic constants of the TiN coatings derived from different methods.

Sample No.	Nanoindentation	Average effective X-ray elastic constant (AEXEC) using $\cos^2\alpha\sin^2\psi$ method		X-ray elastic constants (XECs)			Average effective X-ray elastic constant using high energy X-ray	
	E_{NIP} ($\nu = 0.21$) (GPa)	$\frac{E}{1+\nu}$ (GPa)	E_{AEXEC} ($\nu = 0.21$) (GPa)	$\frac{E}{1+\nu}$ (GPa)	E_{XEC} (GPa)	ν	$\frac{E}{1-\nu}$ (GPa)	E ($\nu = 0.21$) (GPa)
H	417.8 ± 16.1	378.1 ± 18.9	457.5 ± 22.9	-	-	-	-	-
M	450.7 ± 37.0	357.1 ± 17.9	432.1 ± 21.6	-	-	-	523.5 ± 45	418.8 ± 36
L	473.0 ± 25.4	312.0 ± 15.6	377.5 ± 18.9	326.7 ± 16.3	395.4 ± 18.7	0.21 ± 0.01	552.3 ± 52	441.8 ± 41

Table 4 Comparison of X-ray elastic constants (XECs) of TiN with literature values.

Experiment		
E (GPa)	ν	Reference
395	0.21	This study
816	0.184	[12]
250	-	[15]
427	0.23	[16]
594	-	[17]
600	0.25	[18]
640	0.3	[14]
<i>ab initio</i> calculation		
E (GPa)	Reference	
417 for (111)	[23]	
424 for (220)		
451 for (200)		
400 for (111)	[24]	
420 for (220)		
530 for (200)		
459	[41]	

Table 5 The X-ray residual stresses (GPa) for the three specimens calculated using different elastic constants. The strains were measured by $\sin^2\psi$ and $\cos^2\alpha \sin^2\psi$ methods. The deviations of the stress from that measured by laser curvature method are shown in parentheses.

Sample No.	H		M		L	
<div>Strain</div> <div>Elastic constant</div>	$\sin^2\psi$ method	AXS from $\cos^2\alpha \sin^2\psi$ method	$\sin^2\psi$ method	AXS from $\cos^2\alpha \sin^2\psi$ method	$\sin^2\psi$ method	AXS from $\cos^2\alpha \sin^2\psi$ method
	Stress (GPa)					
E_{NIP}	- 2.80 (8%)	*-2.80 (8%)	-2.53 (5%)	*-2.53 (5%)	- 2.68 (41%)	*-2.4 (26%)
EXEC from $\cos^2\alpha \sin^2\psi$ method	-3.19(5%) to -2.90 (5%)	-	- 2.94 (23%) to -1.93 (19%)	-	- 1.84 (3%) to -0.96 (49%)	-
AEXEC from $\cos^2\alpha \sin^2\psi$ method	-3.10 (2%)	-	-2.23 (7%)	-	-1.90 (0%)	-

* $\nu = 0.21$ was assumed in the calculation of X-ray residual stress using E_{NIP} and AXS from $\cos^2\alpha \sin^2\psi$ method.

Table 6 The X-ray residual stresses (GPa) calculated using different elastic constants and AXS of high energy XRD with out-of-plane incident geometry. The deviations of the stress from that measured by laser curvature method are shown in parentheses.

Sample No.	E_{NIP}	EXEC					AEXEC	XECs
		0°	30°	45°	60°	90°		
M	-2.47±0.20 (3%)	-2.22±0.19 (8%)	-2.15±0.18 (11%)	-2.34±0.20 (2%)	-2.63±0.22 (10%)	-2.47±0.21 (3%)	-2.60±0.17 (5%)	-
L	-2.05±0.20 (8%)	-2.30±0.22 (21%)	-1.68±0.16 (12%)	-1.37±0.13 (28%)	-1.20±0.11 (37%)	-1.62±0.15 (15%)	-1.80±0.17 (5%)	-1.72±0.16 (10%)

(a) In-plane incident X-ray

(b) Out-of-plane incident X-ray

Fig. 1 Scattering geometry of the synchrotron high energy X-ray diffraction experiment, where X-ray incident in both (a) in-plane and (b) out-of-plane direction.

(a)

(b)

Fig.2 (a) The XRD patterns and (b) GIXRD patterns with incident angle of 2° for the three TiN specimens.

Fig.3 EXECs at different rotational angles (ϕ).

(a)

(b)

(c)

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