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Determination of Thermal Expansion Coefficient of Titanium Thin Film
鈦薄膜的熱膨脹係數之萃取

Feng-Yuan Chen[1], Rwei-Ching Chang[2]
Ming-Jun Kuo[3] and Shih-Bin Wang [4]
陳峯元　張瑞慶　郭銘駿　王士賓

Department of Mechanical Engineering, Lee-Ming Institute of Technology[1,3,4]
黎明技術學院機械工程學系 [1,3,4]

Department of Mechanical and Computer-Aided Engineering,
St. John's University[2]
聖約翰科技大學機械與電腦輔助工程系 [2]

Abstract

The coefficient of thermal expansion (CTE) is an important factor of thermal stress for thin film materials since thermal stress arises from the mismatch of thermal expansion between the thin films and the underlying substrate. In this paper, the thermal expansion coefficient of titanium thin film with a thickness of 200nm between 23 and 300 ºC was determined by nanoindentation, X-ray diffraction (XRD), $\sin^2\psi$ technique and finite element method. The results show that the coefficient of thermal expansion between 23 and 300 ºC is a curve between 11 and 17 ppm/ºC, and the higher temperature the larger coefficient of thermal expansion. For the range between 23 and 100℃, the equivalent coefficient of thermal expansion (ECTE) is 19ppm/℃ as shifting the reference temperature to 68 ℃.

Key Words: coefficient of thermal expansion, X-ray diffraction, titanium thin film

摘　要

對於薄膜系統而言，熱應力係來自薄膜與母材受熱後產生不同的膨脹或收縮所致，因此薄膜與母材的膨脹係數是造成熱應力非常重要的影響因素。所以本文利用奈米壓痕機，X-ray 擾射法，$\sin^2\psi$ 法及有限元素法，分析在矽母材上鍍上 200nm 厚的鈦薄膜，求出在 23 到 300 ºC 時 200nm 厚的鈦薄膜的膨脹係數。得到介於 23 and 300 ºC 之間為一曲線，其膨脹係數介於 11 到 17 ppm/ºC 之間，且溫度愈高膨脹係數愈大，並求出當參考溫度移至 68 ℃時，其等效膨脹係數為 19ppm/℃。

關鍵詞：熱膨脹係、X-ray 擾射法、奈米鈦薄膜

1. Introduction

In recent year, the mechanical surface properties of many materials can be improved by depositing an appropriate thin film. But all the thin films have the residual stress in spite of various deposition processes or working environment. There are two kinds of residual stress components: intrinsic and thermal [1]. Such stresses can lead to various deleterious effects; for example, the mismatch of thermal expansion between the thin films and the underlying substrate may lead to thermal residual stresses and the deposition process, oxidation and incorporation of impurities may cause to intrinsic residual stresses [2, 6]. Therefore the study of residual stress is tremendous importance. Because the coefficient of thermal expansion plays a fundamental important role of thermal residual stress. This paper investigates the thermal expansion coefficient of titanium thin film about 200nm thick between 23 and 300 °C. At first, the titanium thin films, 200nm thick, are deposited on silicon wafers by a RF magnetron sputtering. Second, the Young's modules of titanium thin films and silicon substrate can be obtained by using nanoindentation and Oliver method [7]. Moreover, the specimens heated at XRD heating chamber from 23 to 300°C, the residual stresses versus temperature are presented by using $\sin^2\psi$ technique method. Finally, the thermal expansion coefficients versus temperature curve are extracted by FEM for reproducing the residual stresses versus temperature curve.

2. Experimental Procedure

2.1 Films Manufacture

The Titanium thin films are deposited on silicon wafer substrates by a RF magnetron sputter. At first, a silicon wafer (100) substrates, 500μm thick, were carefully cleaned by acetone and de-ionized water. Second, all substrates were subsequently dried in hot air at approximately 115 °C. Finally, the substrates are loaded into the sputter for deposition as the condition listed in Table 1. Before deposition, the vacuum chamber is evacuated to 3×10^{-6} torr and the working pressure is maintained at approximately 5.6×10^{-3} torr. The thickness of all films is 200 nm, which are also confirmed by a surface profiler after deposition. Five specimens are tested for each case and average data are presented in this work.

Table 1. Sputtering parameters of Ti thin films

Substrate temperature (°C)	25
Pre-sputtering pressure (torr)	3×10^{-6}
Sputtering pressure (torr)	5.6×10^{-3}
Sputtering Ar gas flow (sccm)	50
RF power (W)	100
Pre-sputtering time (min)	5
Sputtering time (min)	55
Film thickness (nm)	200

2.2Nanoindentation and Oliver Method

The Ti film on Si substrate were studied with a high-resolution nanomechanical test instrument which is a nanoindenter (Triboscope, Hysitron) assembled on an atomic force microscope

(Autoprobe, CP-Research), and a three side pyramidal Berkovich probe tip is used in the test. Five indentations were made in each sample at the same maximum loads. Nanoindentation is performed under a precisely continuous measurement of the load and the depth during the test. Figure 1 shows a schematic drawing of an indentation load via depth curve.

In the Oliver and Pharr [7] method, the hardness H and the reduced modulus E_r are derived from

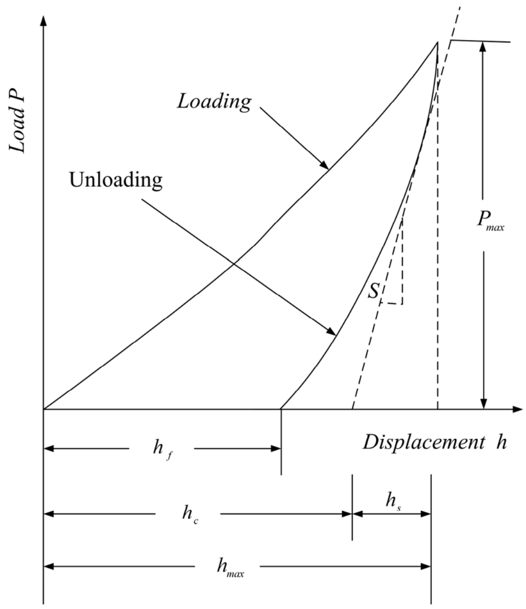

Fig. 1 schematic representation for load-depth data for a nanoindentation experiment

$$H = \frac{P_{\max}}{A} \quad (1)$$

and

$$\left(\frac{dP}{dh}\right)_{unload} = S = 2\beta E_r \sqrt{\frac{A}{\pi}} \quad (2)$$

where $P_{\max}$ is the maximum indentation load, A is the projected contact area, S is the unloading stiffness measured at maximum depth of penetration h, β is a constant that depends on the geometry of the indenter, for Berkovich indenter $\beta = 1.034$. The reduced modulus is used in the analysis to take into account that elastic deformation occurs in both the indenter and the specimen and it is given by

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

where E, E_i, ν and ν_i are the elastic modulus and Poisson's ratio of the indenter and the specimen material, respectively. For evaluating the elastic modulus E_r, the slope $\left(\frac{dP}{dh}\right)_{unload}$ and the contact area A should be determined precisely. A least mean square fit to 90% of the unloading curve is made according to the hypothesis that the unloading data will be expressed by a power law

$$P = P_{\max}\left(\frac{h-h_f}{h_{\max}-h_f}\right)^m \quad (4)$$

For an indenter with a known geometry, the projected contact area is a function of the contact depth. The area function for a perfect Berkovich indenter is given by

$$A = f(h_c) = 24.56h_c^2 \quad (5)$$

Indenters used in practical nanoindentation testing are not ideally sharp. Therefore, tip geometry calibration or area function calibration is needed. A series of indentations is made on fused quartz at depths of interest. A plot of A versus h_c can be curve fit according to the following functional form

$$A = f(h_c) = 24.56h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + \ldots + C_8h_c^{1/128} \quad (6)$$

where C_1 through C_8 are constants. The lead term describes a perfect Berkovich indenter.

From Eqs 1-6, the Young's module of titanium thin films and silicon substrate can be obtained by using nanoindentation and Oliver and Pharr method.

2.3 XRD Experiments

In order to study the variation of the temperature in thin films, the specimen temperature during the XRD measurements process is controlled from 23 to 300 ºC. The XRD chamber is designed to enable the heating and cooling of the specimen from room temperature to 300ºC. A grazing-incidence XRD heating machine (PANalytical X'Pert PRO MPD) with copper anode (λ =0.154 nm) is utilized.

The $\sin^2\psi$ method is used to measure the residual stresses of thin films. As shown in Figure 2, assume a polycrystalline specimen is subjected to a stress parallel to its surface, where φ is the rotation angle of the specimen about the surface normal and ψ is the inclined angle of the specimen surface normal with respect to the diffraction direction. In XRD analysis, Bragg's law gives

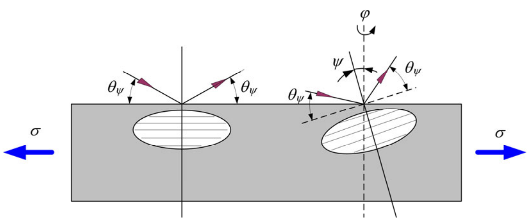

Fig. 2 XRD directions and angles.

$$n\lambda = 2d\sin\theta \tag{7}$$

where n=1, 2, 3,…, λ is the wavelength, d denotes the lattice spacing, and θ is the diffraction angle. According to the variation of the lattice spacing, the elastic strain can be defined as

$$\varepsilon = \frac{d - d_0}{d_0} \tag{8}$$

where d_0 is the strain-free lattice spacing. Note that the lattice spacing is measured in the direction of the diffraction direction. For an elastically isotropic crystallites, Hooke's law relating the mechanical strain tensor ε_{ij} to the mechanical stress tensor σ_{ij} is given as

$$\varepsilon_{ij} = S_{ijkl}\sigma_{kl} = \left[S_1\delta_{ij}\delta_{kl} + \frac{1}{4}S_2\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right)\right]\sigma_{ij} \tag{9}$$

where S_{ijkl} is the compliance tensor. Summation convention over the dummy indices is adopted throughout the paper. The only two independent components S_1 and S_2 are defined as

$$S_1 = \frac{-\nu}{E}\ , \qquad S_2 = \frac{2(1+\nu)}{E} \tag{10}$$

which relate to the elastic modulus E and Poisson's ratio ν . Consequently, the strain tensor in the diffraction direction can be expressed as

$$\begin{aligned}\varepsilon_{\varphi\psi} &= \frac{1}{2}S_2\sin^2\psi\left[\sigma_{11}\cos^2\varphi + \sigma_{12}\sin 2\varphi\right.\\ &\left.+\sigma_{22}\sin^2\varphi\right] + \frac{1}{2}S_2\left[\sigma_{13}\cos\varphi\sin 2\psi\right.\\ &\left.+\sigma_{23}\sin\varphi\sin 2\psi + \sigma_{33}\cos^2\psi\right]\\ &+S_1\left(\sigma_{11} + \sigma_{22} + \sigma_{33}\right)\end{aligned} \tag{11}$$

For a rotationally symmetric biaxial stress state, it gives $\sigma_{11} = \sigma_{22} = \sigma$, $\sigma_{12} = \sigma_{13} = \sigma_{23} = \sigma_{33} = 0$, $\varphi = 0$ then, the strain in Eq. (11) can be reduces to

$$\varepsilon_{\psi} = \left(2S_1 + \frac{1}{2}S_2\sin^2\psi\right)\sigma \tag{12}$$

Therefore, from Eq. (12), the biaxial stress or the residual stress σ can be obtained from the slop of the straight line in the plot of ε_{ψ} versus $\sin^2\psi$. This method is also called $\sin^2\psi$ method and will be used. Moreover, the specimens heated at XRD heating chamber from 23 to 300°C, the residual stresses versus temperature can be presented.

3. Numerical Approach

In this study, a commercial finite element code ANSYS was used to simulate the residual stresses versus temperature curves of the Ti film on Si substrate in heating process. An axisymmetric condition was used in this study and the Plan42 elements were adopted. Figure 3 shows the axisymmetric and boundary conditions. The titanium thin film and silicon substrate were modeled as elastic material and both elastic modulus can be obtained by using nanoindentation and equations (1)-(6). While the heat loading was employed at FEM, the CTE must be changed for reproducing the residual stresses versus temperature curves by XRD.

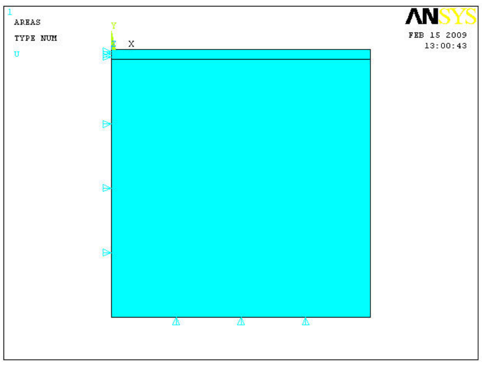

Fig. 3 the axisymmetric mesh

4. Result and discussion

In this work, CTE of titanium thin film, 200nm thick, between 23 and 300 °C was determined. The titanium thin films are deposited on silicon wafers by a RF magnetron sputter at room temperatureThe Young's module of titanium thin films and silicon substrate can be obtained by using nanoindentation and Oliver and Pharr method also the young's modulus of titanium thin films and silicon substrate are 117 and 177 GPa and Poisson' ratio of titanium thin films and silicon substrate are 0.34 and 0.25, respectively. Moreover, the specimens heated at XRD heating chamber from 23 to 300°C, the residual stresses versus temperature are presented by using $\sin^2\psi$ technique method.

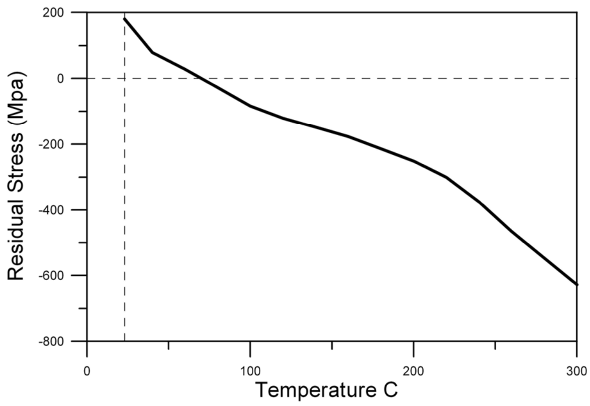

Fig. 4 schematic representation for the residual stresses versus temperature by XRD

Figure 4 showed the residual stresses versus temperature curve of titanium thin films deposited on silicon substrate between 23 and 300°C. There are two kinds of residual stress components: intrinsic and extrinsic. The intrinsic stress is due to the deposition process film on the substrate between 23 and 100°C. The extrinsic stress is thermal stress which is arised from the mismatch in the CTE between the film and the substrate material in the range from 100 to 300°C. In the room temperature 23°C, the residual is tension stress but heating to about 68° the residual stress changes to compression stress. Because the titanium thin films deposited on silicon substrate at room temperature, there is no thermal stress exists at room temperature. Therefore, the residual stress of temperature from 23 to near 100°C is intrinsic stress.

The thermal expansion coefficient is very important in thermal stress analysis and can be changed to extract the residual stress versus temperature curve by FEM for reproducing the residual stresses versus temperature curve by XRD. Figure 5 showed that the linear CTE is considered, CTE of silicon substrate is 2.5 ppm/°C and CTE of titanium thin film, α, are changed from 9 to 11 ppm/°C by FEM. The residual stresses versus temperature curves by FEM are straight lines with different slops. While CTE α = 10 ppm/°C the straight line of simulation by FEM is more close to the experimental XRD curve between 100 and 200 °C. The range from 23 to 100°C, the intrinsic stress dominated but the temperature larger than 200 °C may be nonlinear CTE effect.

In nonlinear analysis, the CTE of silicon substrate and titanium thin films are showed in Figures 6 and 7. Figure 6 is CTE versus temperature curve of silicon at microscopic situation by Okada et al. [8]. Figure 8 is the appropriate nonlinear CTE versus temperature curve of titanium thin films to make the residual stresses versus temperature curve by FEM very close of the curve by XRD in Fig. 8. If ignore the intrinsic stress effect from 23 to 100 °C, the coefficient of thermal expansion between 23 and 300 °C is a curve and vary from 11 to 17 ppm/°C, and the higher temperature, the larger coefficient of thermal expansion.

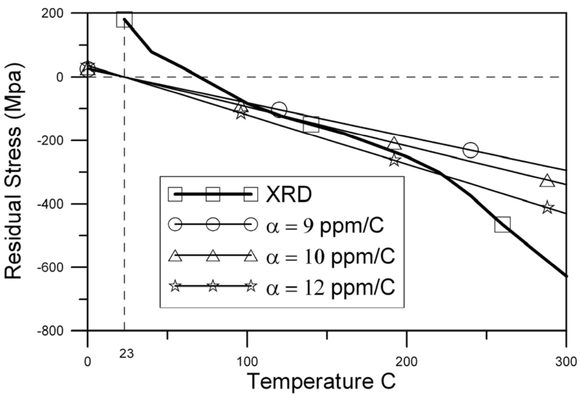

Fig. 5 the residual stresses versus temperature curve of linear CTE by FEM and of XRD

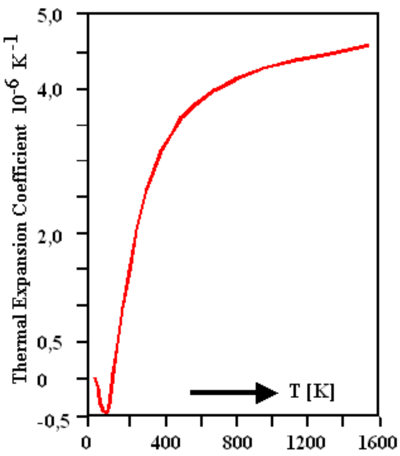

Fig. 6 CTE versus temperature curve of silicon [8]

Finally, we considered the intrinsic stress dominated region, the temperature between 23 and 100 °C. If shifted the reference temperature to 68 ℃ and CTE of silicon substrate is 2.5 ppm/°C and CTE of titanium thin film is 19ppm/℃. It showed in Figure 9, the curve of residual stresses versus temperature by FEM is very close of the curve by XRD between 23 and 100 °C. We called this special CTE is the equivalent coefficient of thermal expansion (ECTE) α*.

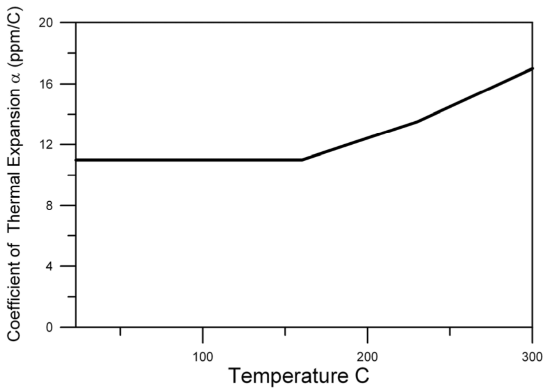

Fig. 7 CTE versus temperature curve of titanium thin films, 200nm thick.

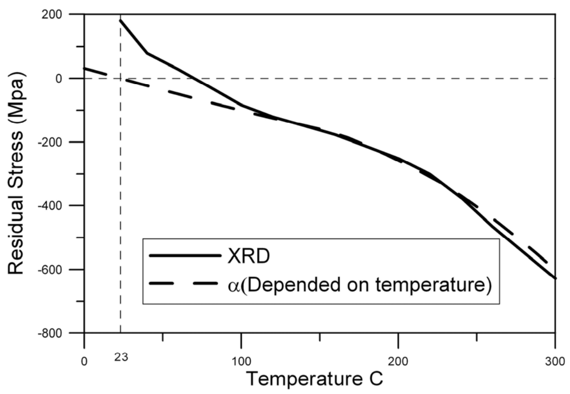

Fig. 8 the residual stresses versus temperature curve of nonlinear CTE by FEM and of XRD

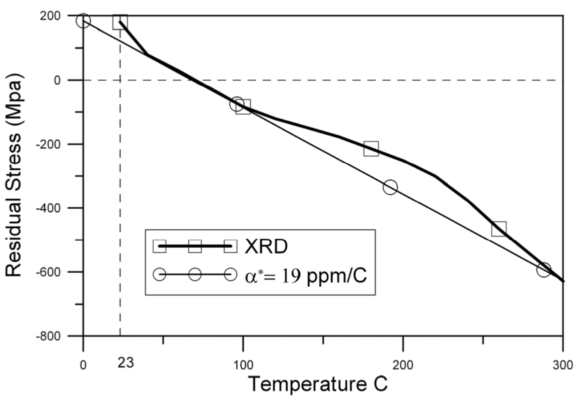

Fig. 9 the residual stresses versus temperature curve of linear ECTE by FEM and of XRD.

5. Conclusion

The thermal expansion coefficient of titanium thin film with a thickness of 200nm between 23 and 300 °C was determined by nanoindentation, X-ray diffraction (XRD), $\sin^2\psi$ technique and finite element method. The results show that the intrinsic stresses dominates from room temperature to 100 ℃ and the thermal stress dominates from 100°C to 300°C. If ignore the intrinsic stress effect, the coefficient of thermal expansion between 23 and 300 °C is a curve between 11 and 17 ppm/°C, and the higher temperature the larger coefficient of thermal expansion. For the range of intrinsic stresses between 23 and 100℃, the equivalent coefficient of thermal expansion (ECTE) is 19ppm/℃ as shifting the reference temperature to 68 ℃.

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