Residual Stresses of Sputtering Titanium Thin Films at Various Substrate Temperatures

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This work seeks to characterize the residual stresses of titanium thin films as they are affected by various substrate temperatures during the sputtering process. The titanium thin films are deposited on silicon wafers by a RF magnetron sputter while different substrate temperatures are considered. The residual stresses are measured by both X-ray diffraction and a substrate curvature method, and consistent results are obtained by both methods. The results show that the residual stress decreases as the substrate temperature increases, in which the stress changes from tensile to compressive when the substrate temperature increases from 25 to 50 °C. Furthermore, the elastic modulus and hardness of the titanium thin films are tested with a nanoindenter using a standard Berkovich probe. Correlations between the residual stresses and mechanical properties measured by nanoindentation are also discussed.

Keywords: Residual Stresses, Thin Films, Sputtering, Mechanical Properties.

1. INTRODUCTION

Residual stresses can be either beneficial or detrimental to the mechanical properties of a thin film, which may improve the film stiffness or distort its structures, resulting in cracking in the case of tensile stresses or buckling in compressive stresses. Many studies reported that residual stresses of thin films strongly depend on the deposition conditions and elaboration methods. Satomi et al.¹ found the stress in thin films varies sufficiently from compressive to tensile, depending on the deposition rate and substrate temperature. Therefore, a nearly zero stress is possible in the case of suitable evaporation conditions. Kuratani et al.² found the residual stress changes from compressive to tensile with increasing ion beam energy. They also found that it is possible to control the residual stress in multilayer films by using a suitable combination of films or by changing the ion beam energy.

On the methods of residual stress measurement of thin films, Pienkos et al.³ studied the stress in thin silver and copper films by means of an optical system for measuring the sample’s curvature. They observed that, as the film thickness above 30 nm, the stress changes to compressive for Ag films but to tensile for Cu films. They concluded the difference that silver is less sensitive than copper to adsorption of impurities. Ryu et al.⁴ utilized this method to obtain the stress state of different thickness films deposited by vacuum thermal evaporation. Similarly, Mani et al.⁵ studied the residual stresses of thin films with various sputtering pressures. They also found the compressive stress and hardness increases when the pressure decreases, and the compressive stress is directly related to the hardness rather than the grain size. Taylor et al.⁶ developed a non-destructive and non-intrusive method to measure the residual stress in thin films by using Raman spectroscopy. Furthermore, Karlsson et al.⁷ used X-ray diffraction (XRD) to measure the residual stress of thin films deposited by arc evaporation, and found the stress state was altered through variations in the negative substrate bias. Recently, Savaloni et al.⁸ presented a comprehensive study on the residual stress of Ti sputtered films at various substrate temperatures by means of XRD.

In this work, how the residual stress of a thin film is affected by the substrate temperature during sputtering deposition and also affects the results of mechanical properties measurement by using nanoindentation are presented. A titanium thin film has been deposited on a silicon wafer substrate with a RF magnetron sputter. The residual stress in the thin film is measured by means of XRD and the substrate curvature method. In addition, the elastic...
modulus and hardness of the thin film is determined by using nanoindentation. The correlation between the internal stress and modulus as well as the hardness is discussed in the conclusion.

2. RESIDUAL STRESS MEASUREMENTS OF THIN FILMS

Two non-destructive techniques have been commonly used for residual stress measurements, one of which utilizes XRD and the other measures the bending radius of the substrate. The basic concept of the former XRD analysis is that the lattice spacing varies with the orientation of the lattice planes with respect to the loading direction. As shown in Figure 1, assume a polycrystalline specimen is subjected to a stress parallel to its surface, where \( \theta \) denotes the diffraction angle, \( \varphi \) is the rotation angle of the specimen about the surface normal, \( \psi \) is the inclined angle of the specimen surface normal with respect to the diffraction direction, and \( d \) denotes the lattice spacing. In XRD analysis, Bragg’s law gives

\[
n\lambda = 2d \sin \theta \tag{1}
\]

where \( n = 1, 2, 3, \ldots, \lambda \) is the wavelength, \( d \) denotes the lattice spacing, and \( \theta \) is the diffraction angle. According to the variation of the lattice spacing, the elastic strain can be defined as

\[
\varepsilon = \frac{d - d_0}{d_0} \tag{2}
\]

where \( d_0 \) is the strain-free lattice spacing. Note that the lattice spacing is measured in the direction of the scattering vector, which decreases as the lattice spacing plane parallel to a tensile stress and increases as its planes are normal to a tensile loading direction. For elastically isotropic crystallites, Hooke’s law relating the mechanical strain tensor \( \varepsilon_{ij} \) to the mechanical stress tensor \( \sigma_{ij} \) is given as

\[
\varepsilon_{ij} = S_{ijkl}\sigma_{kl} = \left[ S_{ij} \delta_{ij} + \frac{1}{4} S_2 (\delta_{ij} \delta_{jk} + \delta_{ik} \delta_{jk}) \right] \sigma_{kl} \tag{3}
\]

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

\[
S_1 = -\frac{\nu}{E}, \quad S_2 = \frac{2(1 + \nu)}{E} \tag{4}
\]

which relate to the elastic modulus \( E \) and Poisson’s ratio \( \nu \). Consequently, the strain tensor in the diffraction direction can be expressed as

\[
\varepsilon_{\varphi\varphi} = \frac{1}{2} S_1 \sin^2 \varphi [\sigma_{11} \cos^2 \varphi + \sigma_{12} \sin 2\varphi + \sigma_{22} \sin^2 \varphi] + \frac{1}{2} S_2 [\sigma_{13} \cos \varphi \sin 2\varphi + \sigma_{23} \sin \varphi \sin 2\varphi + \sigma_{33} \cos^2 \varphi] + S_1 (\sigma_{11} + \sigma_{22} + \sigma_{33}) \tag{5}
\]

For a rotationally symmetric biaxial stress state, it gives

\[
\sigma_{11} = \sigma_{22} = \sigma, \quad \sigma_{12} = \sigma_{13} = \sigma_{23} = \sigma_{33} = 0, \quad \varphi = 0
\]

Then, the strain in Eq. (5) can be reduced to

\[
\varepsilon_{\varphi} = (2 S_1 + S_2 \sin^2 \varphi) \sigma \tag{6}
\]

Therefore, from Eq. (6), the biaxial stress or the residual stress \( \sigma \) can be obtained from the slope of the straight line in the plot of \( \varepsilon_{\varphi} \) versus \( \sin^2 \varphi \). This method is also called the sin\(^2\) \( \varphi \) method and will be used in the following discussion.

The latter residual stress measurement is the substrate curvature method, which is the most commonly used technique in thin film stress measurement. In this method, the residual stresses are determined by measuring the change of substrate curvature induced by the deposited thin film. Thus, the specimen’s surface becomes concave when the thin film is under a tensile stress, whereas the surface becomes convex under a compressive stress. By using Stoney’s formula, the residual stress in thin films can be determined as

\[
\sigma_f = \frac{E_s t_s^2}{6(1 - \nu_s)} \left( \frac{1}{R} - \frac{1}{R_0} \right) \tag{7}
\]

where \( \sigma_f \) is the internal stress in the thin film, \( E_s \) and \( \nu_s \) are the Young’s modulus and Poisson’s ratio of the substrate. \( t_f \) and \( t_s \) indicate the film and substrate thicknesses. \( R \) is the radius of curvature of the specimen after deposition, and \( R_0 \) stands for the radius of curvature before deposition. The curvature method will be utilized in the following discussion and the results will be confirmed with the XRD method.

3. EXPERIMENTAL PROCEDURE

Titanium thin films have been deposited on silicon wafer substrates by a RF magnetron sputter, where the sputtering parameters are listed in Table I. The 500 \( \mu \)m thickness silicon wafer (100) substrates are carefully cleaned
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Table I. Sputtering parameters of Ti thin films.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Si wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature (°C)</td>
<td>25, 50, 75, 100, 125, 150</td>
</tr>
<tr>
<td>Pre-sputtering pressure (torr)</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Sputtering pressure (torr)</td>
<td>$5.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>Sputtering Ar gas flow (sccm)</td>
<td>50</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>100</td>
</tr>
<tr>
<td>Pre-sputtering time (min)</td>
<td>5</td>
</tr>
<tr>
<td>Sputtering time (min)</td>
<td>55</td>
</tr>
<tr>
<td>Film thickness (nm)</td>
<td>200</td>
</tr>
</tbody>
</table>

with acetone and de-ionized water. All substrates were subsequently dried in hot air at approximately 115 °C, and then loaded into the sputter chamber for deposition. Before deposition, the vacuum chamber is evacuated to $3 \times 10^{-6}$ torr and the working pressure is maintained at approximately $5.6 \times 10^{-3}$ torr. In order to study the variation of the residual stresses in thin films, the substrate temperature during the deposition process is controlled. Six different temperatures are considered, ranging from 25 to 150 °C in increments of 25 °C. All film thicknesses are 200 nm, which are also confirmed by a surface profiler after deposition. Five specimens are tested for each case and the average data are presented in this work.

A grazing-incidence XRD machine (PANalytical X'Pert PRO MPD) with a copper anode ($\lambda = 0.154$ nm) is utilized. The $\sin^2 \psi$ method is used to measure the residual stresses of the thin film, of which the basic theory has been previously discussed. In addition, the residual stresses of the specimens are also tested by the substrate curvature method with a surface profiler (Kosaka ET4000). The substrate curvature is measured before and after deposition, and then the residual stresses of the thin film are achieved by using Eq. (7). Note that both the $\sin^2 \psi$ method and the curvature method are conducted at the room temperature.

Typical nanoindentation experiments are performed by using a Hysitron Triboindenter fitted with a standard Berkovich indenter. The loading time, holding time, and unloading time of the indentation tests are all 5 sec. But for this work, the peak load is carefully controlled so that the indentation depth is always less than 20% of the film thickness for each specimen. A standard analysis to determine the hardness and elastic modulus from the unloading load-depth curve is conducted according to the Oliver and Pharr method.

4. RESULTS AND DISCUSSION

In the XRD analysis, Figure 2 shows the typical diffraction patterns of the Ti thin films at various sputtering substrate temperatures. It illustrates similar patterns for all different temperatures, where a strong (002) texture at $2\theta = 38.4^\circ$ is presented. The results show that the XRD intensity increases as the sputtering substrate temperature increases. Besides, the peaks slightly shift to the left as the temperature increases, because compressive stresses appear at higher substrate temperatures. The substrate peaks (Si) are scarcely observed since a grazing angle of $0.5^\circ$ has been adopted. The full width at half maximum (FWHM) of (002) is shown in Figure 3, illustrating that the FWHM decreases with the sputtering substrate temperature. For example, the FWHM is 0.60° at 25 °C and then decreases to 0.50° at 150 °C. The decreasing FWHM reveals larger grains with better crystallinity at higher temperature, agreeing well with the increasing intensity shown in Figure 2. However, the peak broadening depends on not only the grain size but also the stress state of the thin films.
The results of residual stresses using the $\varepsilon - \sin^2 \psi$ method are shown in Figure 4. The $\varepsilon - \sin^2 \psi$ plot of the Ti thin film sputtered on the substrate at 25 °C is shown in Figure 4(a). Seven peaks, except (110) as shown in Figure 2, are identified to measure the lattice strain, and the residual stress is calculated from a linear regression. A tensile stress of 243.1 ± 34.8 MPa is found since the slope of $\varepsilon - \sin^2 \psi$ is positive. Figures 4(b) and (c) show the results of 75 and 125 °C sputtering substrate temperatures, where compressive stresses $-181.5 \pm 27.9$ and $-430.1 \pm 35.3$ MPa are found because of the negative slope.

The summary of the residual stresses of the Ti thin films which are found by using XRD at various sputtering temperatures is shown in Figure 5. It exhibits that the residual stress decreases from 0.220 to $-0.468$ GPa as the substrate temperature increases from 25 to 150 °C. The residual stress is the sum of the intrinsic stress, the thermal stress, and the external stress.$^{8,15,16}$ The intrinsic stress is due to the deposition defects and lattice mismatch between the thin film and the substrate. The thermal stress is caused by the thermal mismatch between the thin film and the substrate, and the temperature difference between the deposition and the ambient during stress measurement. The external stress denotes the stress resulting from an external mechanical load. However, the total stress state attracts the most attention in engineering applications. Note that a zero stress appears between 25 and 50 °C, where the stress changes from tensile to compressive. Two decreasing stages are observed in Figure 5. At the first stage, the residual stress decreases quickly as the substrate temperature increases from 25 to 100 °C. At the second stage, the slope of the residual stress in relation to the change in sputtering temperature decreasing when the substrate temperature is higher than 100 °C. In our observation, the first stage is dominated by the intrinsic stress induced by the lattice mismatch between the deposited film and the substrate, and the thermal stress induced by thermal mismatch will influences the second stage.

In addition, the results of the residual stress measured by using the substrate curvature method are shown in Figure 5.
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Figure 6. Residual stresses of Ti thin films with various sputtering substrate temperatures by curvature method.

Figure 7. Elastic moduli of Ti thin films with various sputtering substrate temperatures.

Figure 8. Hardness of Ti thin films with various sputtering substrate temperatures.

Figure 9. Correlation between residual stresses and measured mechanical properties.

Figure 6. It shows the residual stress decreases from 0.205 to −0.474 GPa as the substrate temperature increases from 25 to 150 °C. Comparing to Figure 5, the difference between the curvature method and XRD method is 0.02~0.04 GPa or less than 10%, which indicates this two methods agree well with each other.

In the nanoindentation analysis, Figure 7 shows the elastic modulus of Ti thin films with various sputtering substrate temperatures. It illustrates how the elastic modulus increases from 102 to 127 GPa as the substrate temperature increases from 25 to 150 °C. Meanwhile, the hardness increases from 2.52 to 3.34 GPa, as shown in Figure 8. Note that, to avoid effects from the substrate, the indentation load has been carefully controlled such that the indentation depth has not exceeded 20% of the film thickness. The indentation results reveal that both the elastic modulus and the hardness increase with the decreasing residual stress of the thin film. This phenomenon can be interpreted by the fundamental theory of nanoindentation based on the Oliver-Pharr method. That is, a tensile stress in a thin film will increase the indent depth and shift the load-depth curve toward the right, which results in a smaller measured elastic modulus and hardness. On the contrary, a compressive stress shifts the load-depth curve to the left, resulting in a larger elastic modulus and hardness.

The residual stress relating to the elastic modulus and hardness measured by nanoindentation is shown in Figure 9. An obviously linear correlation is found for both the elastic modulus and the hardness. It shows the elastic modulus decreases 3.33% and the hardness decreases 4.15% as the residual stress increases 0.1 GPa. The results emphasize that the elastic modulus and hardness of thin films, measured by nanoindentation, may be
underestimated or overestimated when the thin film is subjected to tensile or compressive residual stresses.

5. CONCLUSIONS

Residual stresses of titanium thin films deposited on silicon wafer substrates at various sputtering substrate temperatures are presented. Both the $\sin^{2}\psi$ method of XRD and the substrate curvature method of surface profiling are utilized to measure the residual stresses of the thin films. The two different methods reveal a consistent result that the residual stress decreases 300% when the substrate temperature increases from 25 to 100 °C, then decreases 25% as the temperature increases from 100 to 150 °C. The stress changes from tensile to compressive when the substrate temperature increases from 25 to 50 °C, which indicates that it is possible to produce a zero stress thin film through controlling the substrate temperature during sputtering. Furthermore, the effects of the residual stresses on the mechanical properties of thin films measured by nanoindentation are discussed. The results illustrate linear correlations with negative slopes, where the elastic modulus decreases 3.33% and the hardness decreases 4.15% as the residual stress increases 0.1 GPa.

Acknowledgments: The support of the National Science Council through Grant NSC 95-2221-E-129-008-MY2 is gratefully acknowledged.

References and Notes


Received: 20 July 2008. Accepted: 20 January 2009.