Stress Reduction in Sputter Deposited Thin Films Using Physically Self-Assembled Nanostructures as Compliant Layers

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ABSTRACT
The stress in thin films has been a major limiting factor for obtaining high quality films. We will present a new strategy of stress reduction in sputter deposited films by a nano-compliant layer at the substrate using physically self-assembled nanostructures obtained either by an oblique angle deposition technique or by a high working-gas pressure process prior to the deposition of the continuous film. The technique is all in-situ, does not require any lithography steps, and the nanostructures are made of the same material as the deposited thin film. The nanostructures have a lower material density and can act as a compliant layer to reduce the stress of the later deposited continuous film. By using this approach we were able to reduce stress values by approximately one order of magnitude in sputter deposited tungsten films. Our experimental results agree well with the predictions of a theoretical model that we developed to explain the stress relief through the nanostructured compliant layer. This strategy leads to the growth of much thicker films with high structural reliability.

INTRODUCTION
The control of stress in physical vapor deposited thin films is of continued interest due to its close relationship to technologically important material properties. Further, thin film stress often determines its adhesive strength to the substrate [1-3], the limit of film thickness without cracking, buckling, or delamination [4-9], electrical properties [10-12], and optical properties such as distortions in x-ray masks [13].

It has been shown [14,15] that the intrinsic stress in sputtered tungsten films is correlated to Thornton’s structure zone model (SZM) [16]. The SZM relates the microstructures of sputtered thin films to the most prominent deposition parameters such as working-gas pressure and substrate temperature. The studies by Haghiri-Gosnet et al. [14] and Windischmann [15] have revealed that the transition from zone-1 of a porous and columnar structure to zone-T of a denser film, e.g. by passing from high to lower working-gas pressures, corresponded to a dramatic change of stress from high tensile to high compressive values (i.e. from a few GPa tensile to a few GPa compressive for tungsten). The rapid change of stress with pressure allows only a narrow window of pressures that yields reasonably low stress values (i.e. ≤ a few hundred MPa for tungsten). Therefore, obtaining low-stress films by controlling the working-gas pressure (at a fixed pressure during deposition) has been difficult and is not a robust method [14]. In the high-pressure part of zone-1 it is possible to produce low stress films. However, these films exhibit poor electrical properties due to the columnar microstructure.

Similarly, the stress is a sensitive function of dc bias voltage [11] and substrate temperature [14,17] near the transition between tensile and compressive values, which makes the stress control difficult. A rf-substrate biasing technique has been shown to improve the stress control over an optimum regime of cathode current, pressure, and the rf-substrate bias values [11]. On the other hand, the method is sensitive to the type of materials to be deposited, and finding the optimum parameter space can be challenging. In addition, Maier et al. studied the effect of plasma-etch surface treatment of graphite substrates before a deposition on the adhesion properties of tungsten films sputter deposited at various temperatures [9]. Their plasma treatment is a chemical method that suffers limitations of the type of substrate materials and the material to be deposited. Also, the deposition may need high substrate temperatures. Recently, Windt [18] was able to reduce the stress in sputter deposited W films using a bilayer structure of W/Cr. He adjusted the deposition conditions to give compressive and tensile stress in W and Cr layers, respectively. His results suggest that with a suitable choice of layer thicknesses for W and
Cr, the net stress in the bilayer can be made to balance each other.

In the present work, it will be shown that a nanostructured compliant layer (NCL) obtained by a self-assembled growth mechanism can effectively relieve the stress of a continuous sputter deposited film. The self-assembled nanostructures will provide the single processing step of low-stress films and will avoid the lithographic steps. The compliant layer can make the stress reduction independent of the deposition parameters like pressure, temperature, and substrate biasing.

We will study two in-situ methods of producing physically self-assembled NCL: 1) Oblique angle sputter deposition (OASD), and 2) processing at higher working-gas pressures. OASD has been recently shown to be an effective method of fabricating nanostructures of various shapes (i.e., nanorods, nanosprings, and etc.) and sizes (i.e., from a few nanometers up to a few hundred nanometers) by a physical self-assembly mechanism [19-21]. The method is simple, easy to implement, all in-situ, and can be applied to any materials that can be vaporized. Basically, in the OASD the incident flux of sputtered material impinges on a tilted substrate. The preferential growth of incident particles on the taller surface features results in the formation of slanted nanocolumns. Also, if the substrate is set to rotate with the rotational axis perpendicular to the substrate, vertical nanocolumns can be formed.

The second, and maybe a simpler way of obtaining a NCL is using the SZM of sputter deposited films themselves. A “revised SZM” study by Messier et al. [22] has shown that zone-1 of classical SZM in fact consists of five different sub-zones of columnar “nanostructures” with typical sizes varying from 1-3 nm to 200-400 nm. At high working-gas pressures, enhanced collision and scattering events result in particles that obliquely incident on the substrate surface. Therefore, the shadowing effects give rise to the formation of columnar structures. The reduced ion bombardment at high pressures slows down the adatom mobility and therefore results in less dense films. The nanocolumns are typically separated from each other by voids that are lower density regions [23]. This indicates that the low-density regions can be as small as atomic scales, and also at the same time be as large as a few tens of nanometers in size.

Hence, once the nanostructured compliant layer by either one of the methods described above is formed, we can simply change the angle of incidence to normal incidence (for the method of using OASD) or decrease the working gas pressure (for the method of using higher working-gas pressures) in-situ to deposit the usual continuous dense layer of material. Then we can expect that the compliant layer will relieve the stress in the continuous thin film, which then results in better adhesion, larger critical thickness, and better quality films. The process can be repeated to form thick multilayer films.

**EXPERIMENTAL**

In our experiment, a dc magnetron sputtering system was used to deposit W films. The films were deposited on oxidized p-Si(100) (resistivity 12-25 Ω-cm) wafers (diameter ~7.6 cm) using a 99.95 % pure W cathode (diameter ~7.6 cm). The substrates were mounted on the sample holder located at a distance of about 15 cm from the cathode. In the OASD, the substrate is tilted so that the angle θ between the surface normal of the target and the surface normal of the substrate can be large. In our present case, the angle was either 85° (for nanorods) or 50° (for continuous films). In the normal incidence sputter deposition (NISD) the tilt angle was set to 0°. The base pressure of ~2 × 10⁻⁶ Torr was achieved by a turbo-molecular pump backed by a mechanical pump. In all the deposition experiments, the power was 200 Watts at an ultra pure Ar pressure of 2.0 mTorr (for dense films at normal incidence or nanorods at oblique angle incidence) or 15 mTorr (for columnar films at normal incidence). The deposition rates were measured to be ~12 nm/min for normal incidence deposition, ~11 nm/min at θ = 50°, and ~5 nm/min at θ = 85° for oblique angle depositions all at 2 mTorr Ar pressure. At 15 mTorr, normal incidence growth gave ~16.5 nm/min deposition rates. The thickness of a film was determined by a step-profilometer and also verified by scanning electron microscopy (SEM) cross-sectional images. In this study, we will label the very first NCL layer on the silicon substrate as n = 1, the second denser W layer as n = 2, the following NCL as n = 3, and so on.

The surface topography was investigated using optical microscopy and atomic force microscopy (AFM). We used a contact-mode AFM (Park Scientific Auto CP) where the radius of the silicon tip used was about 10 nm, and the side angle was about 12°. The scan sizes were 2×2 μm² with 512×512 pixels. The root mean square (RMS) roughness values were extracted from the quantitative surface height values. The crystal structure information was studied by X-ray diffraction (XRD) measurements using a Scintag diffractometer with a Cu target (λ = 1.5405 nm) operated at 50 kV and 30 mA. The diffractometer was calibrated with respect to the peak positions of a Si calibration standard.

The measurements of intrinsic thin film stress were performed by using a dual wavelength (λ₁ = 670 nm and λ₂ = 750 nm) Flexus 2320 system, which uses a wafer
The film stress $\sigma$ then was calculated using Stoney's equation [24]

$$\sigma = \frac{1 - \nu^2}{2} \frac{E}{R} \frac{d}{d_{\text{sub}}}$$  \hspace{1cm} (1)

where $E$, $\nu$, and $d_{\text{sub}}$ are Young's modulus, Poisson's ratio, and thickness of the substrate, respectively, and $d$ is the film thickness (assuming $d \ll d_{\text{sub}}$). Before a deposition, the $R$ is the radius of curvature of the reference wafer ($R_1$). After a deposition, the $R$ becomes the relative substrate radius of curvature and is calculated as $R = R_1 R_2 / (R_1 - R_2)$, where $R_1$ and $R_2$ are the radii of curvatures before and after depositions, respectively. In conventional notations, positive signs of film stress correspond to tensile and negative signs to compressive stress values. However, since all the tungsten films we investigated were in compressive stress state, in this paper positive signs will be used to represent the compressive stress. The maximum temperature of the substrate during the deposition was measured to be $\sim 85^\circ$C. It has been previously shown that a $-50^\circ$C increase in substrate temperature during sputter deposition of tungsten corresponded to a negligible “thermally induced” stress value of $\sim 50$ MPa [10]. Therefore, in our work the reported stress values are mostly incorporated during film growth or “growth induced” stress.

In addition, qualitative adhesion tests were made by using a scotch-tape peel test. However, in cases where the film was already peeling off or flaking itself we did not perform the peel test and considered this film as failed in adhesion.

**RESULTS AND DISCUSSION**

We first studied the evolution of stress and adhesion properties of W films deposited on silicon wafers at normal incidence with no compliant layer present. W film was observed to delaminate and peel off after a thickness of $\sim 240$ nm. Figures 1 shows optical microscopy topographies of the delaminated W film at various thicknesses. The delamination patterns are in the form of randomly oriented wrinkles at thickness $\sim 240$ nm (Fig. 1(a)), parallel periodic wrinkles at $\sim 600$ nm (Fig. 1(b)), and irregular-shaped flakes at $\sim 1,440$ nm (Fig. 1(c)). Similar decohesion patterns for W films were observed before [5,6] and explained by the high compressive stress values in the film and followed by relaxation in the form of wrinkles. As a driving force of the wrinkle formation, the elastic energy that originates from the film stress stored in the layer/substrate system is considered [6,25].

**Figure 1.** Optical microscopy images of tungsten morphologies: (a) $\sim 240$ nm, (b) $\sim 600$ nm, (c) $\sim 1,440$ nm thick W films deposited on bare Si substrates. Film delaminations can be seen clearly. Black color regions in (b) are the W film that delaminated and completely peeled off. Light-gray parts in (b) and (c) are delaminated W films that still barely stick to the Si surface, and dark-gray regions are exposed Si surface areas. The scale bars are 100 $\mu$m.

Then, we investigated two in-situ techniques in order to obtain the physically self-assembled NCL.

1) **Nanostructured Compliant Layers by Oblique Angle Sputter Deposition**

To relieve the stress, we fabricated the NCL using the OASD technique. We deposited W films on Si wafers tilted at a high oblique angle of $\theta = 85^\circ$ with no substrate rotation. Due to the shadowing and physical-self assembly mechanisms we were able to obtain the slanted tungsten nanorods structure. The inset in Fig. 2 shows an example of nanorods structure ($\sim 650$ nm thick) obtained this way. The actual NCL structures for our present study were fabricated at a much smaller thickness of $\sim 50$ nm. The stress measurements on the NCL samples ($\sim 50$ nm W nanorods) revealed that the compliant layer had only a negligible stress value of $\sim 3.8 \pm 5.2$ MPa. Then, W films were deposited on the NCL substrate at normal incidence and at various thicknesses. W films did not delaminate up to a thickness of $\sim 500$ nm (almost twice the critical thickness compared to that without NCL), and started to display delamination features in parts of the wafer. In addition, these W films with NCL were smooth (e.g RMS $= 0.87 \pm 0.05$ nm for $\sim 240$ nm thick film).

**Figure 2.** Measured stress values of tungsten films are plotted as a function film thickness in log-log scale. The open circles are from the depositions with no NCL. Filled squares represent the stress data for W films deposited on Nano-Compliant Layer (NCL) of slanted W nanorods ($\sim 50$ nm thick). The inset shows a SEM image of slanted W nanorods fabricated by oblique angle sputter deposition (OASD). The thickness is $\sim 650$ nm. The actual Nano-Compliant Layer (NCL) that we used for our study is only $\sim 50$ nm thick. The scale bar is 100 nm.

Figure 2 compares the stress values of W films as a function of film thickness deposited on bare Si wafers and NCL. The stress of the W-film was calculated by defining the NCL/Si-wafer structure as the reference substrate ($E$, $\nu$; and $d_{\text{sub}}$ were approximated to be the Si-wafer’s values due to the negligible NCL stress.) All the stress data presented are compressive type. It is realized from Fig. 2 that W films with no compliant layer quickly develop a high compressive stress value. On the other hand, the stress values for W films deposited on NCL are approximately one order of magnitude lower than the ones at similar thicknesses without NCL. This shows the effectiveness of NCL in stress reduction. We should also note that a continuous W film on NCL nanorods only
develops after a film reaches a thickness of ~10 nm as observed from SEM images (not shown here). Before that the W film is in the form of isolated islands due to the underlying nanorods surface. In addition, all the W films deposited on NCL in Fig. 2 passed the Scotch tape peel test that indicates the enhancement in adhesion.

To explain the stress reduction effect of NCL we developed [26] a simple model that was inspired from the previous calculations by Luryi et al. [27] and Zubia et al. [28,29] who studied the effects of patterned surfaces on heteroepitaxial film stress. We obtained the following representation for the final stress of a film with NCL

\[ \sigma = \frac{E}{c d + K c} \]

where \( d \) (or \( d_c \)) is the thickness of the film (or NCL) and \( c \) is a material specific constant. \( D \) is the average nanorod diameter in NCL. \( K \) in Eq. (2) is defined as

\[ K = \frac{E c}{c (1-\nu^2)} \]

where \( E \) (or \( E_c \)) and \( \nu \) (or \( \nu_c \)) are the Young’s modulus and Poisson’s ratio of the film (or nano-compliant layer), respectively. Figure 3 shows the best-fit predicted by Eq. (2) to the experimental stress values of the W films deposited on NCL (from Fig. 2). The model agrees well with the experimental results and it is shown that the stress will be saturated after a critical thickness. In addition, Eq. (2) also predicts that for a given film thickness the stress should decrease with the increase of NCL thickness. In fact, we performed a series of experiments where we prepared NCL for various thicknesses. As shown in Fig. 4, we observed that the high stress values for ~120 nm W films decreased to negligible amounts as we increased the thickness of NCL.

Figure 3. The evolution of stress with thickness for W films deposited on Nano-Compliant Layer (NCL) of W nanorods (~50 nm thick) is predicted with the model from Eq. (2). The solid line is a best-fit using this model. \( d \) is the thickness of the NCL and \( D \) is the average diameter of nanorods that form NCL. \( c \) and \( K \) are the material specific constants.

Figure 4. The reduction in the stress values for ~120 nm W films as a function of the thickness of the NCL.

In addition, we also investigated the possibility of growing very thick tungsten films successively by repeating the multilayer structure steps of NCL/W-film. For this, we used an in-situ controller to change the tilt angle \( \theta \) of substrate such that at high \( \theta \) we got the nanorods for NCL and at low \( \theta \) we obtained the continuous film. However, the angle values that were allowed by the geometry of the current setup were limited to 50°-90°. Fortunately, 50° was small enough to give continuous W films (which have similar stress and delamination behavior as the films deposited at \( \theta = 0° \)) as evidenced from SEM measurements. Figure 5(a) shows the optical microscopy image of a continuous ~550 nm thick W film deposited at \( \theta = 50° \). The film had an extreme delamination. Then we deposited a multilayer W film obtained by successively depositing the W film in-situ with the first ~50 nm at 85° (layer number n = 1), the second ~550 nm at 50° (n = 2) and so on (up to total number of layers n = 6). As can be seen from Figs. 5(b) and 5(c), the multilayer film was ~1,850 nm thick, and was relatively smooth (RMS ~ 14.0±0.5 nm). There was no delamination at all. In addition, the film passed the peel test and had a very low stress value of \( \sigma \sim 384.1 \) MPa.

Figure 5. (a) Optical microscopy image of a continuous ~550 nm thick W film deposited on a bare Si substrate at \( \theta = 50° \). Extreme peeling exists in the film. (b) Optical microscopy image and (c) cross sectional SEM image of a multilayer (number of layers n = 6) W film grown by successively depositing the W film in-situ with the first ~50 nm film at 85° (n = 1), the second ~550 nm film at 50° (n = 2), and so on. The multilayer film is ~1,850 nm thick and there was no delamination. The surface RMS roughness was ~14.0±0.5 nm. The scale bar is 100 nm.

2) Nanostructured Compliant Layers by Processing at Higher Working-Gas Pressures

As described in the introduction, another and even simpler method of producing nanostructures is by working in the deposition conditions of zone-1 of SZM. Especially at high working gas pressures, the film structure is formed by the closely packed nanocolumns. Therefore, we studied the possibility of using zone-1 films as NCL. In a previous study by Shen et al., who used a similar W deposition system, it has been shown that the film stress gets close to zero at around ~15 mTorr [30]. Therefore, we set the Ar pressure to 15.0 mTorr to obtain the low stress NCL of columnar W. For the low-pressure value, we used 2.0 mTorr, which would give dense but stressed films. We performed normal incidence depositions on silicon wafers starting from the high-pressure step and successively changing the pressure between high and low at the end of each layer. We set the thicknesses of the NCL and the denser film to 165 nm and 120 nm, respectively.

The multilayer NCL/dense W films of high/low Ar pressure (e.g. 15 mTorr/2 mTorr) did not delaminate for any of the thicknesses we investigated (e.g. up to ~2,300 nm formed by n = 16 individual layers). The films were smooth (e.g. RMS = 1.3±0.1 nm for ~570 nm thick multilayer W film with n = 4). In addition, all these W
films deposited with NCL passed the scotch tape peel test that indicates the enhancement in adhesion.

Figure 6 shows the measured stress values of multilayer (high/low Ar pressure) tungsten films as a function of total film thickness. As shown in Fig. 2, single layer W films made under low Ar pressure quickly develop very high compressive stress values (~2.35 GPa even at ~120 nm thickness). On the other hand, a single layer of high-pressure W film made by using an NCL step (~165 nm thick) has a low stress value ~50 MPa (off scale and is not shown on Fig. 6). This is consistent with the previous studies on the change of stress with the working-gas pressure [14,15].

In conclusion, it has been shown that a nano-compliant layer formed by the oblique angle sputter deposition or high working-gas pressure processing technique can provide stress reduction, adhesion improvement, and a high critical thickness for thin films. The technique is all in-situ and the nanostructures are made of the same material as the deposited thin film. This method does not require any lithography steps. The nanostructures have a lower material density and can act as a compliant layer to
reduce the stress of the subsequent deposited continuous film. By using this approach we were able to significantly reduce stress values in sputter deposited tungsten films on Si surfaces. Our experimental results agree well with the predictions of a theoretical model that explains the stress relief through the nanostructured compliant layer. These lower stress thin films exhibit stronger adhesions to the substrates thereby avoiding delamination. In addition, by using a multilayer structure made under alternating nanostructured compliant layer and dense continuous film, we obtained very thick W with high structural integrity.

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REFERENCES


EQUATIONS

\[ \sigma = \frac{1}{6R (1-\nu)} \frac{E}{d} \frac{d_{sub}^2}{d}, \quad (1) \]

\[ \sigma = c \, D \left( 1 - e^{-\frac{\pi d}{D}} \right) \left[ 1 + K \left( \frac{1-e^{-\frac{\pi d}{D}}}{1-e^{-\frac{\pi d_{sub}}{D}}} \right)^{-1} \right], \quad (2) \]

\[ K = -\frac{E}{(1-\nu)} \frac{(1-\nu_e)}{E_e}, \quad (3) \]
Figure 1  Karabacak et al.
Figure 2  Karabacak et al.
Figure 3  Karabacak et al.

$\sigma$ (MPa) vs. Tungsten film thickness $d$ (nm)

- $d_c = 50$ nm (fixed)
- $K = -0.92 \pm 0.04$
- $D = 53.9 \pm 7.6$ nm
- $c = 1.29 \pm 0.56$ MPa/nm
- Chi$^2 = 9896.1$

Stress model fit
Figure 4 Karabacak et al.

Stress $\sigma$ (MPa) vs. Slanted tungsten nanorods layer (NCL) thickness $d_c$ (nm)

~120 nm W film on slanted W nanorods (NCL)
Figure 5    Karabacak et al.
Figure 6 Karabacak et al.

Multilayer high/low pressure W film

High-pressure step (NCL) : 165 nm @ 15 mTorr Ar
Low-pressure step (dense film): 120 nm @ 2 mTorr Ar

Stress $\sigma$ (MPa) vs. Total tungsten film thickness $d$ (nm)

- $n = 1$ (with no NCL)
- $n = 2$
- $n = 4$
- $n = 8$
- $n = 16$
Counts/sec

$\theta (^\circ)$

Figure 7  Karabacak et al.