Topologically Close-Packed Phases:

Deposition and Formation Mechanism of Metastable β -W in Thin Films

Jiaxing Liu,* Katayun Barmak

Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027

USA

Abstract – β -W is a metastable, topologically close-packed phase with the A15 structure. The deposition of β -W, using N_2 as the impurity gas introduced into the sputtering chamber, is reported and a mechanism for its formation is proposed. Molecules of the impurity gas in the chamber are adsorbed onto the surface during the deposition process and act as nucleation sites for the formation of β -W. The proposed mechanism is supported by the dependence of β -W phase fraction in sputter deposited films on pressure of N_2 and on substrate temperature.

Keywords: β -W; Nucleation; Adsorption; Thin Films; Metastable Phases

1. Introduction

β -W is a metallic phase frequently encountered in tungsten thin films [1-5]. In contrast to α -W with the body-centered cubic (A2) structure, β -W has the A15 structure and will transform to α -W by thermal annealing [6]. β -W has an electrical resistivity of 5 to 10 times that of α -W at room temperature [2] and becomes a superconductor at around 3 K [5]. The giant spin Hall effect, wherein the applied charge current generates a transverse spin current due to spin-flip scattering [7-9], has also recently been discovered in β -W films and has sparked renewed interest in this phase [10].

However, despite both the long-standing and the renewed interest, the nature of β -W has remained unclear. Although β -W is a metastable phase, the origin of its stability cannot be explained by the theories commonly applied to other metastable phases, such as those obtained by epitaxial deposition onto single crystal underlayers that provide suitable templates for the formation of the metastable phases [11], or higher entropy metastable phases favored by higher formation probabilities of their local atomic configurations as atoms deposit onto a surface and are then buried under the subsequently arriving atoms [12]. Instead, β -W is stabilized by the presence of impurity gases during the deposition process [2, 13-15]. Since oxygen is commonly found to promote the formation of β -W, some have suggested that it is a non-stoichiometric oxide such as W_3O [13, 14], while others have shown that the oxygen in β -W films is **in a zero valence state**, and hence β -W should be an allotrope of W [2, 15]. The role of oxygen as a gaseous impurity has not been fully clarified. One major difficulty in elucidating the role of oxygen is the high reactivity between tungsten and oxygen and additional complication caused by the ready formation of oxides. In the work presented here, nitrogen is shown to also have the ability to facilitate the formation of β -W. Since the strength of the interaction between nitrogen

and tungsten atoms is in the right range to allow reproducible β -W formation, the adoption of nitrogen as the impurity gas allows the mechanism of formation of β -W to be investigated by quantifying the dependence of the volume fraction of β -W on the deposition parameters.

2. Experiments

Tungsten thin films were prepared by DC magnetron sputtering from 99.95% 3" diameter W targets onto Corning PyrexTM glass substrates. The substrates were cleaned in acetone and isopropyl alcohol and dried using nitrogen gas prior to deposition. The base pressure of the sputtering chamber was better than 2×10^{-8} Torr. Since the amount of gas impurities is critical to the formation of β -W, the pressure of O₂ was monitored by the residual gas analyzer prior to the deposition, and was below the detection limit of 10^{-10} torr. Therefore, the effect of O₂ on β -W formation can reasonably be neglected. Then ultra-high purity N₂ gas at the pressure range of 10^{-6} to 10^{-5} torr was introduced as the impurity gas along with 3×10^{-3} torr of Ar as sputtering gas. The target-to-substrate distance was 50 cm, and the deposition rate was kept at 0.02 nm/s with 50 W of power in order to minimize the heating effect caused by adatom condensation, which was likely to have a negative effect on the formation of β -W. All tungsten films were deposited at room temperature except for those used to investigate the impact of substrate temperature.

Following deposition, X-ray diffraction (XRD) experiments for quantification of β -W volume fraction were conducted using a PANalytical X-ray diffractometer with Cu K α radiation. The microstructure of the films was characterized using a JEOL 2100F transmission electron microscope (TEM) operating at 200 kV. Electrical resistivity of the films was measured using a Signatone CM-170 probe station. The TEM characterization and the electrical measurements

were conducted at the Center for Functional Nanomaterials at the Brookhaven National Laboratory.

3. Results

The XRD pattern of a 112 nm-thick W film deposited at 1.2×10^{-5} torr N_2 is shown in Fig. 1. The film consists primarily of β -W with a lattice constant of 0.506 ± 0.001 nm, in close agreement with the values given in references [16-19]. The film also contains a small amount ($<5\%$) of α -W as indicated by its weak (211) peak. Since prior studies of deposited W films have found single phase β -W only in ultra-thin films with thicknesses of the order of 10 nm and a decrease in the volume fraction of β -W at higher film thicknesses [10, 20, 21], the predominance of β -W in the relatively thick films in the current study (such as the 112 nm-thick film of Fig. 1) confirms that using N_2 as the impurity gas during sputtering facilitates the formation of β -W.

To quantify the dependence of the volume fraction of β -W, f_β , on the pressure of nitrogen, 14-nm-thick films were used. The XRD patterns of these films deposited at different pressures of N_2 are shown in Fig. 2. It can be seen that the (211) and (200) peaks from β -W grow stronger relative to the central (210) peak as the pressure of N_2 increases. The increase in the intensity of the outer two peaks relative to the (210) peak again confirms that the introduction of N_2 into the deposition chamber promotes the formation of β -W.

For the quantification of f_β , some complications caused by the crystallographic structure and texture of α - and β -W have to be addressed. As shown in Fig. 1 for the 112 nm-thick film, the (110) peak from α -W and the (210) peak from β -W coincide. Additionally, the (200) peak from α -W is absent as a result of crystallographic texture of this phase in the films. Therefore,

the presence of α -W can only be detected through the appearance of its (211) peak. This peak is extremely weak and cannot be observed for thinner films or films that contain smaller volume fractions of α -W. In light of these difficulties, f_β is calculated using Klug's equation [22] under the assumption that the preferred crystallographic texture in the film is independent of f_β , and that the X-ray absorption factors of α and β phases of W are equal. The overlapping peak at about 40° from the (110) α -W and (210) β -W reflections is used for the calculation, because it is the most sensitive of the reflections to the change of f_β as shown in Fig. 2. Furthermore, this peak has the highest intensity among all the diffraction peaks and thus allows the most precise calculation of the α - and β -W phase fractions. Klug's equation for these peaks can thus be written as:

$$I = f_\alpha I_{\alpha,110} + f_\beta I_{\beta,210} \quad (1)$$

where f_α, f_β are the volume fraction of α - and β -W, I is the measured peak intensity at around $2\theta = 40^\circ$, $I_{\alpha,110}$ and $I_{\beta,210}$ are respectively the intensity of (110) α -W and (210) β -W peaks of reference samples containing only one phase, and are taken from the XRD spectra of films deposited with no N_2 and 1.2×10^{-5} torr of N_2 introduced into the chamber, respectively. The calculation procedure and the adoption of reference samples will be discussed in detail below.

The dependence of f_β upon the pressure of nitrogen calculated using Eq. 1 is shown in Fig. 3. There is no appreciable amount of β -W formation below 10^{-6} torr N_2 . As pressure of nitrogen is increased above this value, f_β increases sharply and saturates at a value of approximately one (100%) at a pressure of approximately 6×10^{-6} torr N_2 .

The dependence of f_β on substrate temperature during deposition at a fixed pressure of N_2 of 1.2×10^{-5} torr is shown in Fig. 4. As seen in the figure, f_β decreases at higher substrate temperatures as a result of reduced stability of β -W against α -W. As will be shown below, by modeling the dependence of f_β upon the deposition parameters of N_2 pressure and substrate temperature insight into the mechanism of formation of β -W can be gained.

The microstructure of W films is shown in Fig. 5. The film deposited at 2×10^{-8} torr contains only α -W at a grain size of about 70 nm as seen in Fig. 5(a). With increasing pressure of N_2 , an increasing number of β -W grains appear. The grain size of β -W is determined to be about 4 nm using high resolution lattice images such as that seen in Fig. 5(e). At the pressure of 1.2×10^{-5} torr N_2 , no α -W grains are visible, from which it is concluded that the film contains only the β -W phase.

The conductivity of 14 nm-thick W films is plotted as a function of the volume fraction of β -W phase in Fig. 6. From the measured conductivities, the resistivity of the single phase α -W film is calculated as $24 \mu\Omega\cdot\text{cm}$. This value is in good agreement with the values of 19 to $30 \mu\Omega\cdot\text{cm}$ for 10 nm-thick films reported previously [20, 21]. For the single-phase β -W film, the resistivity is calculated as $160 \mu\Omega\cdot\text{cm}$. This value is approximately seven times the value of the resistivity single phase α -W film, and is consistent with prior studies that found that the resistivity of β -W films to be 5 to 10 times those for α -W films [2]. In the intermediate region where the films are a mixture of α - and β -W, the conductivity shows a linear dependence upon the volume fraction of β -W. This dependence will be discussed below.

4. Discussion

In the calculation of β -W phase fraction using Eq. 1, the intensity of $I_{\alpha,110}$ and $I_{\beta,210}$ are taken from tungsten films deposited with no N_2 and 1.2×10^{-5} torr N_2 as reference samples respectively, as was noted above. Therefore, these films must only contain one of the two phases. Phase purity is demonstrated by the microstructures shown in Fig. 5 (a) and (d), respectively, in which grain size is relatively uniform at 70 nm for α -W and 4 nm for β -W. Phase purity of the chosen reference films is also demonstrated by the close agreement between the measured resistivity of the films and the resistivity values reported in the literature for α - and β -W [2, 20, 21]. Thus, the choice of tungsten films deposited with no N_2 and 1.2×10^{-5} torr N_2 as reference samples in Eq. 1 is justified. In addition, as shown in Fig. 6, the conductivity exhibits a linear relationship with the volume fraction of β -W calculated using Eq. 1. Since a linear relationship for conductivity is commonly found for two-phase mixtures containing spherical particles with conductivity values that are of the same order of magnitude [23], the use of Eq. 1 is seen to be self-consistently justified.

The dependence of f_β on N_2 pressure, P_{N_2} , in Fig. 3 shows a sigmoidal shaped curve. Given that in the deposition of W films only the competition between α and β -W need be considered, the function describing the dependence of f_β upon P_{N_2} has to satisfy the following requirements: (i) it must be a monotonically increasing function of P_{N_2} , (ii) it must approach zero as P_{N_2} approaches zero, and, 3) it must approach one (100%) as P_{N_2} goes to infinity. One function that fulfills the above requirements has the following form:

$$f_{\beta} = \frac{\left(P_{N_2} / P_o\right)^n}{1 + \left(P_{N_2} / P_o\right)^n} \quad (2)$$

where P_{N_2} is the pressure of N_2 , P_o is a coefficient that incorporates the influence of all other deposition parameters such as substrate temperature and choice of substrate material and is thus constant when these parameters are kept fixed. Using the above function, the best fit to the experimental data in Fig. 3 gives the values of $P_o = 2.63 \times 10^{-6}$ torr and $n = 3.97 \approx 4$.

Eq. 2 has the form of the Langmuir-Freundlich (LF) adsorption isotherm, where f_{β} is equivalent to the adsorbed fraction, and P_o is equivalent to $1/K_{LF}$, where K_{LF} is the equilibrium constant [25]. Given the systematic dependence of f_{β} on the pressure of nitrogen in the deposition chamber and the similarity of the form of Eq. 1 for f_{β} to the form of this isotherm, it is reasonable to conclude that the adsorption of N_2 onto the glass substrates is integral to the formation of β -W in the deposited film.

In the LF isotherm, the exponent n is the index of heterogeneity describing the non-uniform distribution of adsorption enthalpies and affinities over the substrate surface. This exponent is usually between 0 and 1, for the case of non-interacting adsorbates [25]. Exponents $n > 1$ indicate adsorbate-adsorbate interactions, as found, for example, for the adsorption of hydrogen on the (110) surface of a Ni film [26], where the exponent is $n = 1.5$ [25]. Therefore, the experimentally-determined exponent in the current study of $n = 3.97 \approx 4$ implies that the adsorbed nitrogen species are interacting, rather than acting as non-interacting species. The interacting nitrogen molecules then likely act as adsorbate clusters promoting the nucleation of

β -W. In areas free of nitrogen species, α -W nucleates. Thus, as surface coverage of nitrogen increases, so does the fraction of β -W relative to α -W.

In order to show that the similarity between Eq. 2 and the LF isotherm is not a mere coincidence, the above conclusion can be further supported by modeling the variation of f_β with substrate temperature at a fixed P_{N_2} shown in Fig. 4. Assuming thermally-activated adsorption, P_o is then given by

$$P_o = P_{oe} e^{-\frac{E}{RT}} \quad (3)$$

where E is the activation energy and P_{oe} is the pre-exponential term. P_{oe} incorporates the dependence on deposition parameters other than pressure of nitrogen and substrate temperature, and is taken as a constant in the experiments conducted here where all other deposition parameters have been kept fixed. By fitting the data in Fig. 4 for f_β obtained at a fixed nitrogen pressure of $P_{N_2} = 1.2 \times 10^{-5}$ torr, the values of P_{oe} and E are calculated as 4.0×10^{-5} torr and 6.8 kJ/mol, respectively. The value of the activation energy thus determined is in close agreement with the activation energy of 7 kJ/mol [27] reported for the physisorption of N_2 molecules onto glass substrates, and therefore provides independent support for the conclusion that the adsorption of nitrogen onto the glass is a necessary step in the formation of β -W.

The nucleation of β -W assisted by adsorbed N_2 molecules is difficult to observe directly in the sputtering deposition process by *in-situ* experiments, because the presence of Ar in the mtorr range precludes the use surface analysis instruments that require ultra-high vacuum conditions. On the other hand, when the deposition process is complete, the adsorbed N_2

molecules playing a role in the formation of β -W have been buried within the deposited films and become invisible to surface analysis techniques. Therefore, given the inability to make direct observations of the interaction between the β -W phase and the N_2 molecules, modeling provides a useful, though indirect, method for investigating the mechanism of β -W formation. Additional clues about the role of N_2 molecules in nucleation of α -W and β -W can be obtained by examining the microstructures seen in the TEM images. As seen in Fig. 5 (a), α -W has a relatively large grain size of about 70 nm, from which it is concluded that the nucleation of α -W is difficult since it is reported that post-deposition annealing even at temperatures as high as 850 °C does not result in any observable grain growth [21], and thus the grain size of α -W is determined by its nucleation density at the time of deposition. By contrast, the grain size of ~4 nm for β -W evidences a large density of nucleation sites, which are here hypothesized to be provided by small clusters of interacting nitrogen adsorbates. In other words, the nitrogen adsorbates on the surface of the glass substrate provide the requisite heterogeneous nucleation sites for β -W, allowing it to nucleate more readily than α -W, and, for the case when many nucleation sites are provided by the adsorbates, β -W can become the majority phase.

To address why β -W can more readily nucleate on the adsorbed nitrogen clusters, it is useful to consider that the A15 structure is a topologically close-packed Frank-Kasper structure [28]. Topologically close-packed structures have exclusively tetrahedral interstices by contrast to other simple metal structures (fcc, hcp, bcc) that have a mixture of tetrahedral and octahedral interstices. It is speculated that the nitrogen adsorbate clusters provide suitable templates for the formation of the W tetrahedra, which then pack as edge-sharing tetrahedra to form the icosahedral triangulated coordination polyhedra (CN12 Kasper polyhedra) that in turn form the

crystalline grains of the A15 structure [28]. The formation of every new edge-sharing tetrahedron requires the addition of only a single W atom to an existing triangular face.

5. Conclusions

β -W films can be deposited by introducing N_2 gas in the pressure range of 10^{-6} to 10^{-5} torr into the chamber. Based on the dependence of volume fraction of β -W on deposition parameters, a model has been proposed in order to gain insight into the formation mechanism of β -W. The model shows that the nucleation of β -W is mediated by adsorbed N_2 molecules, and this model is able to quantitatively describe the relationship between volume fraction of β -W and the deposition parameters, including nitrogen pressure and substrate temperature, which, in turn, provides the basis for understanding the film microstructure.

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References

- [1] H. H. Busta, C. H. Tang, Film thickness dependence of silicon reduced LPCVD tungsten on native oxide thickness, J. Electrochem. Soc. 133 (1986) 1195-1200.
- [2] P. Petroff, T. T. Sheng, A. K. Sinha, G. A. Rozgonyi, F. B. Alexander, Microstructure, growth, resistivity, and stresses in thin tungsten films deposited by rf sputtering, J. Appl. Phys. 44 (1973) 2545-2554.
- [3] C. C. Tang, D. W. Hess, Plasma-enhanced chemical vapor deposition of β -tungsten, a metastable phase, Appl. Phys. Lett. 45 (1984) 633-635.
- [4] A. Miller, G. D. Barnet, Chemical vapor deposition of tungsten at low pressure, J. Electrochem. Soc. 109 (1962) 973-976.
- [5] S. Basavaiah, S. R. Pollick, Superconductivity in β -Tungsten films, J. Appl. Phys. 39 (1968) 5548-5556.
- [6] W. R. Morcom, W. L. Worrell, H. G. Sell, H. I. Kaplan, The preparation and characterization of beta-tungsten, a metastable tungsten phase, Metall. Trans. 5 (1974) 155-161.
- [7] J. E. Hirsch, Spin Hall effect, Phys. Rev. Lett. 83 (1999) 1834-1837.
- [8] S. Zhang, Spin Hall effect in the presence of spin diffusion, Phys. Rev. Lett. 85 (2000) 393-396.
- [9] M. I. Kyakonov, V. I. Perel, Current-induced spin orientation of electrons in semiconductors, Phys. Lett. A 35 (1971) 459-460.
- [10] C. Pai, L. Liu, Y. Li, H. W. Tseng, D. C. Ralph, R. A. Buhrman, Spin transfer torque devices utilizing the giant spin Hall effect of tungsten, Appl. Phys. Lett. 101 (2012) 122404-1 – 122404-4.
- [11] K. L. Chopra, Metastable thin film epitaxial structures, Phys. Stat. Sol. 32 (1969) 489-507.

- [12] F. Z. cui, A. M. Vredenberg, R. de Reus, F. W. Saris, H. J. G. Draaisma, Structure and magnetism of metastable Bi-Fe alloy films, in: K. W. Samwer, M. Von Allmen, J. Bottinger, B. Stritzker (Eds.), *Metastable Alloys: Preparation and Properties*, Elsevier, New York, 1984, pp. 621-628.
- [13] G. Hägg, N. Schönberg, 'β-Tungsten' as a tungsten oxide, *Acta Cryst.* 7 (1954) 351-352.
- [14] A. K. Sinha, Topologically close-packed structures of transition metal alloys, *Prog. Mater. Sci.* 15 (1972) 81-185.
- [15] G. Mannella, J. O. Hougen, "β-Tungsten" as a product of oxide reduction, *J. Phys. Chem.* 60 (1956) 1148-1149.
- [16] V. An, Features of $\beta \rightarrow \alpha$ transformation in electroexplosive tungsten nanopowders, 9th Russian-Korean International Symposium on Science and Technology, (2005) 110-111.
- [17] M. J. O'Keefe, J. T. Grant, J. S. Solomon, Magnetron sputter deposition of A-15 and bcc crystal structure tungsten thin films, *J. Electron. Mater.* 24 (1995) 961-967.
- [18] T. Kizuka, T. Sakamoto, N. Tanaka, Growth of fine crystals with A-15 type structure in vacuum-deposited tungsten films studied by high-resolution electron microscopy, *J. Cryst. Growth* 131 (1993) 439-447.
- [19] T. Karabacak, P. I. Wang, G. C. Wang, T. M. Lu, Growth of fine crystals with A-15 type structure in vacuum-deposited tungsten films studied by high-resolution electron microscopy, *Thin Solid Films* 493 (2005) 293-296.
- [20] D. Choi, B. Wang, S. Chung, X. Liu, A. Darbal, A. Wise, N. T. Nuhfer, K. Barmak, A. P. Warren, K. R. Coffey, M. F. Toney, Phase, grain structure, stress, and resistivity of sputter-deposited tungsten films, *J. Vac. Sci. Technol. A* 29 (2012) 051512-1 – 051512-8.
- [21] S. M. Rossmagel, I. C. Noyan, C. Cabral Jr., Phase transformation of thin sputter-deposited tungsten films at room temperature, *J. Vac. Sci. Technol. B* 20 (2002) 2047-2051.

- [22] V. Perchinsky, P. Zavalij, *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, second ed., Springer, New York, 2009.
- [23] S. Kasap, C. Koughia, H. Ruda, R. Johanson, Electrical conduction in metals and semiconductors, in: S. Kasap, P. Capper (Eds.), *Springer Handbook of Electronic and Photonic Materials*, Springer, New York, 2007, pp. 30-35.
- [24] D. Choi, M. Moneck, X. Liu, S. J. Oh, C. R. Kagan, K. R. Coffey, K. Barmak, Crystallographic anisotropy of the resistivity size effect in single crystal tungsten nanowires, *Sci. Rep.* 3 (2013) 2591-1 – 2591-4.
- [25] R. I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, first ed., Wiley, New Jersey, 1996.
- [26] K. Christmann, O. Schober, G. Ertl, M. Neumann, Adsorption of hydrogen on nickel single crystal surfaces, *J. Chem. Phys.* 60 (1974) 4528-4540.
- [27] H. A. Wittcoff, B. G. Reuben, J. S. Plotkin, *Industrial Organic Chemicals*, third ed., Wiley, New Jersey, 2012.
- [28] M. D. Graef, M. E. McHenry, *Structure of Materials: An Introduction to Crystallography, Diffraction and Symmetry*, second ed., Cambridge University Press, UK, 2012.

Figure Captions

FIG. 1. The XRD pattern of a 112 nm-thick W film deposited at a N_2 pressure of 1.2×10^{-5} torr.

FIG. 2. The XRD pattern of a 14 nm-thick W film deposited at different N_2 pressures.

FIG. 3. Fraction of β -W in 14 nm-thick films as a function of N_2 pressure.

FIG. 4. Fraction of β -W in 14 nm-thick films deposited at a nitrogen pressure of 1.2×10^{-5} torr as a function of substrate temperature. The data is fitted to Eq. 1 with the assumption of thermally-activated nitrogen adsorption.

FIG. 5. Bright-field transmission electron micrographs of 10 nm-thick W films deposited at N_2 pressures of 2.0×10^{-8} (a), 2.2×10^{-6} (b), 3.9×10^{-6} (c) and 1.2×10^{-5} torr (d). The selected area diffraction patterns are shown as insets in the lower right. Figure (e) is a high-resolution transmission electron micrograph of β -W, which shows it to be ultrafine-grained, in contrast to α -W, which much coarser grained. The white circle in (b) is used to mark a region of β -W.

FIG. 6. Electrical conductivity is plotted as a function of the percentage of β -W for 14 nm-thick films.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6