The Effect of Nitrogen on the Stability of the β Phase in W Thin Films

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Principal Investigator(s): Shefford P. Baker
User(s): Yue Zhao, Jiayi Cao, Samantha Wang, Hannah Morgan-Smith Myers

Affiliation(s): Department of Materials Science and Engineering, Cornell University

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Contact: shefford.baker@cornell.edu, yz2722@cornell.edu,
jc2732@cornell.edu, mw842@cornell.edu, hem66@cornell.edu

Primary CNF Tools Used: AJA Sputter Deposition, FleXus Film Stress Measurement, P7 Profilometer, Dektak XT Profilometer, CDE ResMap Resistivity 4-pt Probe, Panalytical X-ray Diffractometer, Veeco Icon Atomic Force Microscope, Zeiss Supra Scanning Electron

Abstract:

The body centered cubic (BCC) phase (α-W) is the only known stable structure in tungsten. However, a metastable phase (β-W) having A15 structure can be produced using atom-by-atom deposition methods. Interest in the metastable phase recently spiked it has been shown to exhibit a giant spin Hall effect (GSHE) [1], which is expected to enable significant miniaturization in next-generation magnetoresistive random access memory (MRAM). To be useful in technology, it must be possible to reliably produce β-W and to retain it during production and use. It is known that inclusion of small amounts of nitrogen facilitates production of the β-phase [2] {Liu, 2016 #3025}. However, little is known about the stability of this metastable phase or how and why it forms. In this work we explore the effects of N on the formation and thermal stability of β-W. We deposit W films with different N contents in CNF and use x-ray diffraction to determine the fractions of α- and β-W before and after thermal cycling. Results are modeled to examine the kinetics and mechanisms of the β-α phase transformation.

Summary of Research:

Tungsten thin films were deposited onto 4" Si <100> wafers with native oxide using the AJA DC magnetron sputtering system in CNF and a 99.95% 3" W target. The Si wafers were plasma cleaned for 60 seconds before deposition. The base pressure was better than 2×10^{-8} Torr. Each film was sputtered at a power of 400 W in a working gas pressure of 3 mTorr for 1000 s. A total flow rate of 30 sccm of Ar and N was maintained with N flow rates of 0, 0.5, 1, 1.5, and 2 sccm. A temperature indicator was affixed to the back of the Si wafer to determine the maximum temperature the wafer reached during deposition. A "witness sample" of Si with a photoresist pattern was also attached to the substrate carrier. After deposition, the photoresist was lifted-off using acetone, and the thicknesses of the remaining W was measured using the Dektak® XT profilometer at CNF. The stresses in the as-deposited films were determined using the FleXus® film stress measurement instrument at CNF.

The as-deposited films were cleaved into 1 cm × 1 cm samples. Individual pieces were then heated at 10°C/min in a high vacuum furnace to temperatures of 300, 400, 500, 600 and 700°C, under a base pressure better than 10^{-7} Torr. No thermal oxidation was detected after the annealing.

The textures and phase fractions of α- and β-W were determined using x-ray diffraction on the as-deposited and the annealed samples. Symmetric 2θ scans were performed from 20° to 90° with a step size of 0.02°. Rocking curve scans using the ω geometry were obtained for all α and β peaks visible on the 2θ scans.

The deposited films had thicknesses of 190 ± 5 nm, the maximum temperature during the depositions was 66-71°C, and the stress in the as-deposited films was -2.3 to -2.1 GPa. Nitrogen concentrations in the as-deposited films were estimated from the flow rates to be 2.53, 4.95, 7.27, and 9.49 at% for films deposited in 0.5, 1.0, 1.5, and 2.0 sccm N_2, respectively.

For the as-deposited samples, all the 2θ diffraction peaks were identified as β, except for a small $\alpha(211)$ peak at $2\theta = 73.193°$. After thermal annealing, $\alpha(110)$ peaks emerged, indicating the initiation of the β to α transformation. With increasing annealing temperature, the intensities of the α peaks increase while those of the β peaks decrease. Eventually, all the β peaks vanished, indicating complete transformation to the α phase.

The rocking curves were analyzed to estimate the phase fractions in the samples. The phase fractions as a function of annealing temperature are shown in Figure 1. A Johnson-Mehl-Avrami-Kolmagorov type model (similar to [3]) was developed to describe the phase transformation as a function of temperature in terms of the different activation energies involved. The results of the model are also shown in Figure 1.

Conclusions and Future Steps:

The model suggests that nitrogen stabilizes the β phase by accumulating in phase boundaries, slowing their motion. In the future, we will use CNF equipment to attempt to make N-free β-W films and to measure their properties (e.g., resistivity) as a function of N content.

References:

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[2] Liu, J. and K. Barmak, Topologically close-packed phases: Deposition and formation mechanism of metastable β-W in thin films. Acta Mater 104, 223-227 (2016).

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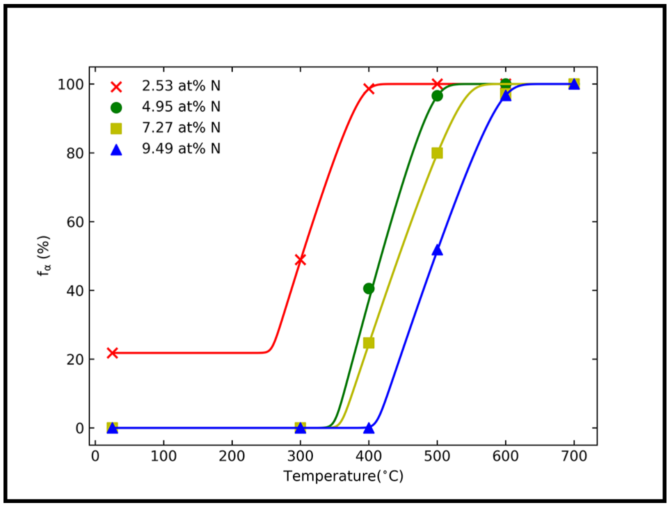

Figure 1: Volume fraction of α-W as a function of annealing temperature for films of varying N content. Points indicate experimental measurements, lines indicate results of a model.