Short Communication

Phase transformation of single crystal $\beta$-tungsten nanorods at elevated temperatures

Tansel Karabacak *, Pei-I Wang, Gwo-Ching Wang, Toh-Ming Lu

Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

Received 15 March 2005; received in revised form 23 June 2005; accepted 29 June 2005

Abstract

We report the phase transformation of single crystal $\beta$-phase W(100) nanorods that occurs at an elevated temperature of $\sim 950 \degree$C. The $\beta$-W nanorods oriented perpendicular to the flat silicon substrate were grown by an oblique angle sputter deposition technique with substrate rotation. The nanorods typically have an average length of $\sim 450$ nm and an average width of $\sim 75$ nm. The phase transformation was investigated by X-ray diffraction measurements of the nanorods vacuum-annealed at various temperatures in the range 700–1000 $\degree$C for 30 min at each annealing temperature. As deposited individual nanorods are found to be single crystal, as evidenced from the analysis of transmission electron microscopy diffraction patterns. Our single crystal $\beta$-phase W(100) nanorods phase transformation temperature is higher than that of the polycrystalline simple-cubic $\beta$-phase (A15) W films. Depending on the deposition conditions, W films generally transform to thermodynamically stable bcc $\alpha$-phase at temperatures ranging from room-temperature to $\sim 650 \degree$C. The transformation is accompanied with the removal of oxygen atoms from the $\beta$-matrix. However, our results of W rods suggest that the removal of oxygen atoms from the single crystal W nanorods is more difficult due to the absence of grain boundaries that leads to the requirement of higher annealing temperatures for the phase transformation.

$© 2005$ Elsevier B.V. All rights reserved.

Keywords: Tungsten; $\beta$-tungsten; A15; Phase transformation; Oblique angle deposition; Glancing angle deposition; Nanorods; Nanocolumns

In recent decades, tungsten films have attracted significant scientific and technological interest. Some technological applications of W films include field emitters, photonic crystals, diffusion barriers in semiconductor interconnect structures, absorbing layers in X-ray masks, and X-ray mirrors. W film is often deposited by sputter deposition technique due to the high melting temperature of W and robustness of the sputter technique. Depending on the growth conditions and thickness of the films, normal incidence sputter deposition of tungsten films can give rise to either the $\alpha$-phase W, which has the equilibrium bcc structure, or the metastable $\beta$-phase W, which has an A15 (cubic) structure, or a mixture of both phases [1–5]. The lattice constants are 3.164 and 5.05 Å for $\alpha$-W and $\beta$-W, respectively. These two phases may have very different properties, for example, the measured resistivity of $\beta$-W film is one order of magnitude higher than that of the $\alpha$-W film [6]. It was suggested that oxygen incorporation might play a role in the formation of the metastable $\beta$-W. The polycrystalline $\beta$-phase W films, depending on the deposition conditions, have been observed to transform to thermodynamically stable bcc $\alpha$-phase at annealing temperatures ranging from room-temperature to $\sim 650 \degree$C [1,2,7,8]. The transformation has been observed to accompany the removal of oxygen atoms from the $\beta$-matrix [1]. One of the factors that affect the removal rate of oxygen from the film is the availability of grain boundaries where they can act as lower energy diffusion paths for oxygen. In addition, the energy stored at grain boundaries can enhance the phase transformation. These prior observations suggest that for a $\beta$-W film with larger grain sizes and less number of grain boundaries, the phase transformation from $\beta$ to $\alpha$ is expected to occur at relatively higher temperatures.

* Corresponding author.

E-mail address: karabt@rpi.edu (T. Karabacak).
In this letter, we report that the novel $\beta$-W nanorods obtained by oblique angle sputter deposition technique [9,10] transform to the $\alpha$-phase only after annealing temperature reaches $\sim$950 °C, which is much higher than the previously reported values. We explain the retardation of phase transformation by the lack of the grain boundaries in our single crystal W nanorods that makes the oxygen removal difficult and requires higher annealing temperatures.

In our experiment, a dc magnetron sputtering system was used to deposit tungsten films and nanorods. The base pressure of $\sim$5 x 10^{-5} Torr was achieved by a turbomolecular pump backed by a mechanical pump. The depositions were performed on oxidized p-Si(100) (resis-
tivity 12–25 $\Omega$-cm) substrates ($\sim$2 x 2 cm²) size using a 99.95% pure W cathode (diameter $\approx$7.6 cm). The substrates were mounted on the sample holder located at a distance of $\sim$15 cm from the cathode. In the oblique angle deposition, the substrate is tilted so that the angle between the surface normal of the target and the surface normal of the substrate was 85°. The substrate rotation speed was set to 0.5 Hz (30 rpm). In the normal incidence sputter deposition the tilt angle was set to 0°, with no sample rotation. In all the deposition experiments, the power was 200 W at an ultra pure Ar pressure of 1.5 m Torr. The maximum temperature of the substrate during the deposition was measured to be $\sim$85 °C by a thermocouple. The thickness of the films was determined by a step-profilometer and also verified by scanning electron microscopy (SEM) cross-sectional images. The deposition rates were measured to be $\sim$8 nm/

min for the normal incidence and $\sim$4 nm/min for the oblique angle depositions.

To investigate the critical temperature of phase transformation, W samples were annealed in a Lindberg quartz-tube annealing furnace under vacuum. The annealing temperatures ($T_A$) ranged from 700–1000 °C and the annealing time was 30 min for each annealing temperature. The uncertainty in the measured annealing temperature was about $\pm$15 °C. The samples were kept in the cold zone of the furnace until the vacuum was pumped down to the range of 2 x 10^{-6} Torr. After the temperature of the hot zone reached the set point, the hot zone was moved towards the sample until the sample was positioned in the middle of the hot zone and annealed for 30 min. The samples were kept inside the furnace during the cooling period. The texture information of W films and W nanorods was studied by a series of X-ray diffraction (XRD) $\theta$ vs. $2\theta$ measurements using a Scintag diffractometer with a Cu target operated at 50 kV and 30 mA. The diffractometer was calibrated with respect to a calibration standard from Si peak position. The scans have been performed at a rate of 0.5°/min with 0.01° steps. In addition, W nanorods were removed from the Si substrate and then dispersed onto the lacy carbon film on a Cu grid (from Ernest F. Fullam, Co) for the transmission electron microscopy (TEM) investigation. The microstructure was studied using a Philips CM-12 microscope operating at 120 kV. In addition, selective area electron diffraction (SAED) was employed to characterize the crystal structure.

From the XRD analysis, W-films deposited at normal incidence were observed to be in the $\beta$-phase at the initial times of growth. However, as the thickness increased, the $\alpha$-W became the dominant phase similar to the observations by previous studies [7,9–11]. Fig. 1 shows the XRD results of a thin (~40 nm) W film before and after the annealing process at $T_A$=700 °C. As can be seen, as deposited $\beta$-W film transformed to the stable $\alpha$-phase after the annealing. From the results of previous studies, it is expected that the transformation occurred at temperatures much lower than 700 °C. In addition, the position of the XRD $\beta$(200) peak from as deposited W film in Fig. 1 shifted from the equilibrium position at 2$\theta$=35.525° towards a smaller $\theta$ angle at $\sim$35.26°. This type of shift indicates the existence of a larger atomic plane spacing, and has been explained to originate from a compressive stress in the film [11–13]. The location of the $\beta$(200) peak for the as deposited W film ($\sim$35.26°) corresponds to a lattice spacing of $\sim$0.9 Å. This is about $\sim$0.79% larger than the equilibrium lattice parameter of a $\beta$-W (~5.05 Å) film. However, after annealing at $\sim$700 °C, the W film that transformed to $\alpha$-phase has a $\alpha$(110) peak located at $\sim$40.32° (Fig. 1), which is slightly larger than the equilibrium position 2$\theta$=40.26°. This corresponds to a lattice spacing of $\sim$3.161 Å that is about $\sim$0.09% smaller than the equilibrium lattice parameter of an $\alpha$-W (~3.164 Å) film. This small decrease in the lattice spacing is believed to originate from a tensile stress that may have formed after the phase transformation. Similar stress relaxation followed by the development of a

![Fig. 1. X-ray diffraction (XRD) $\theta$ vs. $2\theta$ profile of an as deposited ~40 nm thick tungsten film sputter deposited at normal incidence (bottom), and the $\theta$ vs. $2\theta$ profile of the same film after annealed at 700 °C for 30 min in a vacuum (top). The as deposited polycrystalline W film has a $\beta$-phase (simple cubic, lattice constant is 5.05 Å) with peaks $\beta$(200) at 2$\theta$ = 35.26° and $\beta$(210) at 2$\theta$ = 39.43° and transforms to the thermodynamically stable $\alpha$-W phase (bcc, lattice constant is 3.164 Å) at $T_A$=700 °C with $\alpha$(110) peak located at 2$\theta$ = 40.32°. The $\gamma$-axis intensity for the spectrum of the annealed film is offset for clarity.]
small tensile stress has been observed previously for tantalum films (initially under compressive stress) associated with a phase transformation from tetragonal $\beta$-Ta to cubic $\alpha$-Ta [14].

On the other hand, W nanorods deposited by oblique angle sputter deposition showed a prominent $\beta$-W(100) phase independent of their thickness, see Fig. 2. The position of the XRD $\beta$(200) peak from the as deposited W nanorods was measured to be at a 2$\theta$ angle $\sim$35.46° that corresponds to a lattice spacing of $\sim$5.06 Å. This is about $\sim$0.20% larger than the equilibrium lattice parameter of a $\beta$-W ($\sim$5.05 Å) film. This smaller change in the lattice spacing for $\beta$-W nanorods as compared to $\beta$-W film shown in Fig. 1 ($\sim$0.79%) is consistent with the lower compressive stress values expected for the nanorods structure [12].

The mechanism that leads to the formation of $\beta$-W nanorods during oblique angle deposition is believed to originate from a competitive growth that includes the shadowing effect and different vertical growth rates and adatom mobilities on $\alpha$- and $\beta$-islands [9,10]. The nanorods were $\sim$450 nm in average length and $\sim$75 nm in average width as observed from SEM images (not shown here, see Ref. [9]). Therefore, the lateral size of nanorods was comparable to the thickness of the flat W film ($\sim$40 nm). In addition, the nanorods were isolated from each other by gaps of tens of nanometers. Hence, during an annealing, oxygen atoms are subject to diffuse at similar length scales in both the flat W-film ($\sim$40 nm) and the nanorods ($\sim$75 nm) before they escape outside. Fig. 2 compares the XRD

---

**Fig. 2.** X-ray diffraction (XRD) $\theta$ vs. 2$\theta$ lines of $\sim$450 nm length tungsten nanorods obtained by oblique angle sputter deposition are shown at various annealing temperatures ($T_A$). The as deposited rods have the XRD peaks $\alpha$(200) and $\beta$(210) located at 2$\theta$ $\approx$ 35.46° and 39.69°, respectively. Each annealing experiment was performed for 30 min in vacuum. The $\beta$-W nanorods were able to transform to the $\alpha$-W phase (the $\alpha$(110) peak is located at 2$\theta$ $\approx$ 40.37°) only after $T_A$ $\approx$ 950 °C unlike the low temperature transformation of $\beta$-W film by normal incidence deposition. A small peak starts to appear at 2$\theta$ $\approx$ 36.64° for $T_A$ $\approx$ 900 °C and shifts to $\approx$ 36.90° after the rods was annealed at 950 °C (indicated by arrows). The y-axis intensity for each spectrum is offset for clarity.
profiles obtained from the nanorods annealed at various temperatures. Interestingly, the W nanorods did not transform to the α-phase until temperatures \( T_A \approx 950 \degree \text{C} \). This is much higher than the maximum transformation temperature of \( \sim 650 \degree \text{C} \) for polycrystalline β-W films reported in the literature [2]. At \( T_A \approx 950 \degree \text{C} \), the W nanorods were able to transform to the thermodynamically favorable α-W(110) phase. The \( \alpha(110) \) peak of the transformed W rods shown in Fig. 2 is located at \( \sim 40.37\degree \) (Fig. 1). This corresponds to a lattice spacing of \( \sim 3.157 \text{Å} \) that is about \( \sim 0.22\% \) smaller than the equilibrium lattice parameter of an α-W (\( \sim 3.164 \text{Å} \)) film.

In addition, it can be realized from Fig. 2 that at the annealing temperature 900 \degree \text{C}, a small peak starts to appear at \( 2\theta \approx 36.64\degree \) and shifts to \( \sim 36.90\degree \) when the rods annealed at 950 \degree \text{C} (indicated by arrows in Fig. 2). This peak does not correspond to any known α- or β-W texture and is believed to originate from the transient lattice planes that may occur during the β-to α-phase transformation. One possible transient is the partial formation of WO\(_2\) that can lead to 2 \( \alpha \)-W, as evidenced from the TEM diffraction pattern shown in Fig. 2. This is much higher than the maximum transformation temperature of \( \sim 650 \degree \text{C} \) for polycrystalline β-W films ever reported in the literature. We explain our results based on the single crystal structure of β-W nanorods, as evidenced from the TEM diffraction pattern. In addition, the sizes of our nanorods are much larger than the typical grains in a polycrystalline W-film. The removal of oxygen atoms may be more difficult from an individual single crystal rod due to the absence of grain boundaries that may require higher annealing temperatures for the phase transformation. We expect that the resilient nature of β-W nanorods against high temperatures can enhance their robustness in their field emission [16] and gas ionization applications [17].

**Acknowledgments**

This work was supported in part by the NSF.

**References**