Short Communication

Phase transformation of single crystal β-tungsten nanorods at elevated temperatures

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Abstract

We report the phase transformation of single crystal β-phase W(100) nanorods that occurs at an elevated temperature of ~950 ºC. The β-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 ~450 nm and an average width of ~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 ºC 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 β-phase W(100) nanorods phase transformation temperature is higher than that of the polycrystalline simple-cubic β-phase (A15) W films. Depending on the deposition conditions, W films generally transform to thermodynamically stable bcc α-phase at temperatures ranging from room-temperature to ~650 ºC. The transformation is accompanied with the removal of oxygen atoms from the β-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.

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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 α-phase W, which has the equilibrium bcc structure, or the metastable β-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 α-W and β-W, respectively. These two phases may have very different properties, for example, the measured resistivity of β-W film is one order of magnitude higher than that of the α-W film [6]. It was suggested that oxygen incorporation might play a role in the formation of the metastable β-W. The polycrystalline β-phase W films, depending on the deposition conditions, have been observed to transform to thermodynamically stable bcc α-phase at annealing temperatures ranging from room-temperature to ~650 ºC [1,2,7,8]. The transformation has been observed to accompany the removal of oxygen atoms from the β-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 β-W film with larger grain sizes and less number of grain boundaries, the phase transformation from β to α is expected to occur at relatively higher temperatures.

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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 $\sim 950\,^\circ C$, 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 $\sim 5 \times 10^{-5}\, Torr$ was achieved by a turbomolecular pump backed by a mechanical pump. The depositions were performed on oxidized p-Si(100) (resistivity $12\sim25\, \Omega \cdot cm$) substrates ($\sim 2 \times 2\, cm^2$ 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 $85^\circ$. The substrate rotation speed was set to $0.5\, Hz$ ($30\, rpm$). In the normal incidence sputter deposition the tilt angle was set to $0^\circ$, 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 $\sim 85\, ^\circ C$ 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 ($T_\text{A}$) ranged from $700\sim1000\, ^\circ C$ and the annealing time was $30\, min$ for each annealing temperature. The uncertainty in the measured annealing temperature was about $\pm 15\, ^\circ C$. The samples were kept in the cold zone of the furnace until the vacuum was pumped down to the range of $2 \times 10^{-6}\, Torr$. 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 $0.5^\circ/min$ with $0.01^\circ$ 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 ($\sim 40\, nm$) W film before and after the annealing process at $T_\text{A}=700\, ^\circ C$. 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 $700\, ^\circ C$. In addition, the position of the XRD $\beta$(200) peak from as deposited W film in Fig. 1 shifted from the equilibrium position at $2\theta=35.525^\circ$ towards a smaller $2\theta$ angle at $\sim 35.26^\circ$. 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 ($\sim 35.26^\circ$) corresponds to a lattice spacing of $\sim 0.99\, Å$. This is about $\sim 0.79\%$ larger than the equilibrium lattice parameter of a $\beta$-W ($\sim 5.05\, Å$) film. However, after annealing at $\sim 700\, ^\circ C$, the W film that transformed to $\alpha$-phase has a $\alpha$(110) peak located at $\sim 40.32^\circ$ (Fig. 1), which is slightly larger than the equilibrium position $2\theta=40.26^\circ$. 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 ($\sim 3.164\, Å$) 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 $\sim 40\, nm$ thick tungsten film sputter deposited at normal incidence (bottom), and the $\theta$ vs. $2\theta$ profile of the same film after annealed at $T_\text{A}=700\, ^\circ C$ 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 $2\theta=35.26^\circ$ and $\beta$(210) at $2\theta=39.43^\circ$ and transforms to the thermodynamically stable $\alpha$-W phase (bcc, lattice constant is $3.164\, Å$) at $T_\text{A} \leq 700\, ^\circ C$ with $\alpha$(110) peak located at $2\theta=40.32^\circ$. The $\gamma$-axis intensity for the spectrum of the annealed film is offset for clarity.](image-url)
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 \( \approx 35.46\)° that corresponds to a lattice spacing of \( \approx 5.06 \) Å. This is about \( \approx 0.20\% \) larger than the equilibrium lattice parameter of a \( \beta \)-W (\( \approx 5.05 \) Å) film. This smaller change in the lattice spacing for \( \beta \)-W nanorods as compared to \( \beta \)-W film shown in Fig. 1 (\( \approx 0.79\% \)) 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 \( \approx 450 \) nm in average length and \( \approx 75 \) 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 (\( \approx 40 \) 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 (\( \approx 40 \) nm) and the nanorods (\( \approx 75 \) nm) before they escape outside. Fig. 2 compares the XRD

\[ \text{Fig. 2. X-ray diffraction (XRD) } \theta \text{ vs. } 2\theta \text{ lines of } \approx 450 \text{ nm length tungsten nanorods obtained by oblique angle sputter deposition are shown at various annealing temperatures } (T_A). \text{ The as deposited rods have the XRD peaks } \alpha(200) \text{ and } \beta(210) \text{ located at } 2\theta = 35.46\text{° and } 39.69\text{°, respectively. Each annealing experiment was performed for 30 min in vacuum. The } \beta \text{-W nanorods were able to transform to the } \alpha \text{-W phase (the } \alpha(110) \text{ peak is located at } 2\theta = 40.37\text{°) only after } T_A = 950 \text{ °C unlike the low temperature transformation of } \beta \text{-W film by normal incidence deposition. A small peak starts to appear at } 2\theta = 36.64\text{° for } T_A = 900 \text{ °C and shifts to } \approx 36.90\text{° after the rods was annealed at } 950 \text{ °C (indicated by arrows). The y-axis intensity for each spectrum is offset for clarity.} \]

\[ \text{Fig. 3. (a) Bright field transmission electron microscopy (TEM) image of an individual W nanorod before annealing and (b) its corresponding SAED pattern (selective area electron diffraction). (c) As illustrated, a single set of diffraction spots denoted by open circles in the SAED pattern indicates that the W nanorod is a single crystal. The electron diffraction pattern consists of a single set of spots originated from the (001) planes of the } \beta \text{-phase W nanorod. The diffused rings at the background originate from the underlying amorphous carbon substrate.} \]
profiles obtained from the nanorods annealed at various temperatures. Interestingly, the W nanorods did not transform to the α-phase until temperatures \( T_A \approx 950 \) °C. This is much higher than the maximum transformation temperature of \( \sim 650 \) °C for polycrystalline β-W films reported in the literature [2]. At \( T_A \approx 950 \) °C, the W nanorods were able to transform to the thermodynamically favorable α-W(110) phase. The α(110) peak of the transformed W rods shown in Fig. 2 is located at \( \sim 40.37^\circ \) (Fig. 1). This corresponds to a lattice spacing of \( \sim 3.157 \) Å that is about \( \sim 0.22\% \) smaller than the equilibrium lattice parameter of an \( \alpha\)-W (\( \sim 3.164 \) Å) film.

In addition, it can be realized from Fig. 2 that at the annealing temperature 900 °C, a small peak starts to appear at \( 2\theta \approx 36.64^\circ \) and shifts to \( \sim 36.90^\circ \) when the rods annealed at 950 °C (indicated by arrows in Fig. 2). This peak does not correspond to any known \( \alpha\)- or \( \beta\)-W texture and is believed to originate from the transient lattice planes that may occur during the \( \beta\)-to-\( \alpha\)-phase transformation. One possible transient is the partial formation of \( \mathrm{WO}_3 \) that can lead to \( 2\theta \) peaks of (020) at 36.666° and (002) at 36.853°, which are close to the measured peak positions at \( T_A = 900 \) and 950 °C, respectively. We also note that after 950 °C annealing, no morphological change has been observed in \( \alpha\)-W nanorods as analyzed from the SEM images (not shown here).

The mechanism behind the delayed phase transformation of W nanorods at higher temperatures can be better understood from the TEM investigation. Fig. 3(a) shows the bright field TEM image of an individual W nanorod of length \( \sim 325 \) nm and width \( \sim 60 \) nm and its corresponding SAED pattern shown in Fig. 3(b). Note that the sizes of the nanorods produced in the same sample are not uniform and the W rod shown in Fig. 3(a) has dimensions smaller than the average values (\( \sim 450 \) nm in length and \( \sim 75 \) nm in width). As illustrated in Fig. 3(c), the existence of a single set of diffraction spots in the SAED pattern indicates the W nanorod is single crystal (i.e. no grain boundaries within an individual rod). To the best of our knowledge, this is the first time that a single crystal \( \beta\)-phase W structure has ever been reported. The electron beam in Fig. 3 was incident at a direction perpendicular to the rod axis. The electron diffraction pattern consists of a single set of spots originated from the (001) planes of the \( \beta\)-phase W nanorod. The diffused rings come from the amorphous carbon substrate. The oxygen atoms incorporated in the W nanorod essentially arranged themselves to increase the lattice parameter and therefore gave rise to closely spaced spots in diffraction pattern. Thus, the large lattice spacing of the \( \beta\)-phase W nanorod in real space results in very small spacing among the diffraction spots in the reciprocal space. In addition, the sizes of these single crystal rods are much larger than the typical grain sizes expected in a polycrystalline W-film that is in the range of a few to tens of nanometers [15]. This novel property of W nanorods suggests that the oxygen atoms can not easily leave the crystal matrix of \( \beta\)-phase due to the lack of grain boundaries in the nanorods. Therefore, the phase transformation may require much higher temperatures as evident from our experiments.

In conclusion, we have observed that \( \beta\)-phase W nanorods made by oblique angle sputter deposition transforms to the thermodynamically favorable α-W at annealing temperatures \( \sim 950 \) °C. This is much higher than the maximum transformation temperature of \( \sim 650 \) °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 \( \beta\)-W nanorods against high temperatures can enhance their robustness in their field emission [16] and gas ionization applications [17].

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References