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# In situ TEM observations of irradiation-induced phase change in tungsten

**C. L. Chen · T. Nagase · H. Mori**

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**Abstract** Electron irradiation-induced phase change in tungsten was examined by in situ high resolution electron microscopy. In samples prepared by a chemical polishing technique using a NaOH aqueous solution, an α to β phase change was induced under 200 keV electron irradiation at 773 K. It is suggested that sodium atoms deposited on the tungsten sample from the solution, rather than oxygen atoms, may play an essential catalytic role in inducing the phase change.

## Introduction

Tungsten is an important material widely used not only in refractory applications but also in semiconductor interconnect structures [1, 2]. Although the most thermodynamically stable phase of tungsten at temperatures below 3,680 K at 1 atm is the α-W phase with the body-centered-cubic (bcc) structure, it is reported that a β-W metastable phase with the A15 primitive cubic crystal structure often appears [3–6]. An early report for the formation of β-W can be found in the study of dendritic metallic deposits (including β-W) on cathodes prepared by electrolysis of phosphate melts below 923 K [3]. It is also known that β-W can be produced by sputtering, evaporation, gas condensation, and hydrogen reduction of tungsten-oxides [4–6]. The phase change from metastable β-W to stable α-W has been widely observed [7–10], while that from α-W to β-W has been scarcely observed. To the authors' knowledge, there is only one report describing the change from α-W to β-W. Namely, Hegedus et al. [11] reported that α-W first changes to tungsten-oxides after oxidation and then the oxides change to β-W by reduction with hydrogen. Strictly speaking, however, this is not the direct phase change from α-W to β-W but the phase change associated with an oxidation–reduction cycle. A direct phase change from α-W to β-W without introducing any intermediate product has never been reported.

It is well known that the electron irradiation technique can achieve phase transformation in alloys and compounds through unique non-thermal processes [12–15]. This kind of irradiation technique can also be used in tungsten. In this article, a direct phase change from α-W to β-W induced under 200 keV electron irradiation is described.

## Experimental procedures

High purity tungsten (>99.9999 wt%), supplied by Nippon Mining & Metals Co. Ltd, was used in this study. Tungsten foils for transmission electron microscopy (TEM) were prepared by the twin-jet polishing technique using a 20 wt% NaOH aqueous solution kept at 273 K (sample CHEM). For comparison, other two types of samples were prepared. One type is samples prepared in the same twin-jet polishing technique but annealed at 1,223 K in vacuum (in the same TEM) for 300 s prior to the irradiation experiment (hereafter designated as sample ANN), and the other is samples prepared solely by the standard ion-milling technique (hereafter designated as sample ION). Electron microscopy studies on irradiation-induced phase change were carried out in a Hitachi HF-2000 type 200 kV high resolution electron microscopy (HREM) under a high

C. L. Chen (✉) · T. Nagase · H. Mori
Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
e-mail: chen@uhvem.osaka-u.ac.jp

vacuum condition better than $10^{-6}$ Pa. A Gatan heating holder (Model 628) was used for heating the foil specimen. Specimen temperature was kept at 773 K. During irradiation, electron beam was condensed to a small disk with a diameter about 50 nm. The dose rate measured by means of a Faraday cup was of the order $10^{23}$ e/m$^2$ s. Occurrence of a phase change during electron irradiation was monitored in situ using a supersensitive CCD camera (AMT, XR-60BFE) and a digital video recorder system.

## Results and discussions

Figure 1 shows two typical examples of a phase (a region appearing in dark, arrowed in Fig. 1a, c) produced by 200 keV electron irradiation at 773 K and the corresponding microdiffraction patterns taken from the phase (Fig. 1b, d). Electron irradiations were done for about 10 s at a dose rate of the order $10^{23}$ e/m$^2$ s. During irradiation, crystalline grains of the phase first appeared at the center of irradiated area and then they grew in size. Analysis of the diffraction patterns reveals that patterns in Fig. 1b and d can be consistently indexed as the [100] and [1$\bar{2}$0] net patterns of a crystal with the A-15 crystal structure, respectively. This fact suggests that the phase produced is the $\beta$-W phase.

Figure 2 is a series of HREM images showing successive stages of an $\alpha$ to $\beta$ phase change. The number inserted in each micrograph shows time in seconds elapsed relative to Fig. 2a. The *double-arrows* in micrographs indicate a fix position. The $0.22_3$ nm-spaced fringes in Fig. 2a correspond to the (110) lattice fringes of pure $\alpha$-W before phase change. After irradiation for 8 s (Fig. 2b), a region appearing in dark, indicated by a *white arrow*, is formed. It is noted lattice fringes different from those of $\alpha$-W can be already recognized in the dark region. With continued irradiation, the dark region expanded in area, as seen from Fig. 2c–e, until the whole field under observation was covered (Fig. 2f). The lattice image shown in Fig. 2e can be consistently explained as the one taken from the [1$\bar{2}$0] direction of $\beta$-W, based upon the analysis of the fringe spacing and geometry; namely, the two sets of crossing

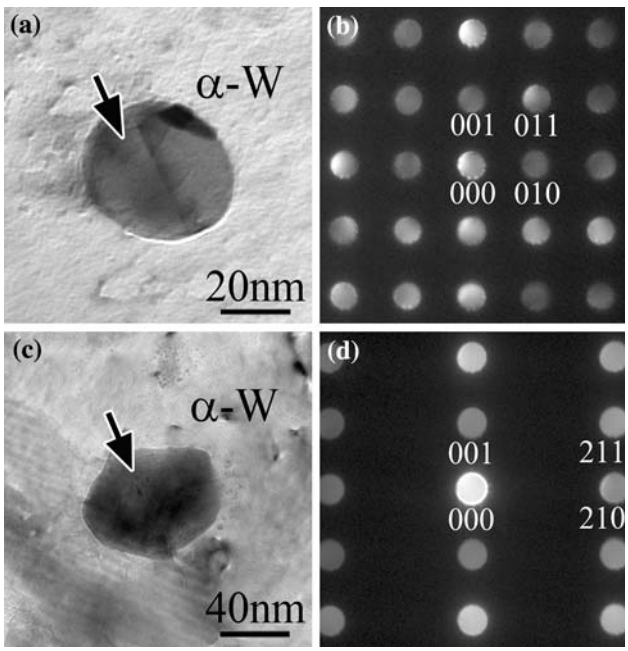


**Fig. 1** Typical examples of an $\alpha$ to $\beta$ phase change in W induced by 200 keV electron irradiation at 773 K. **a** A phase formed after irradiation for about 10 s (*arrowed*), being embedded in the $\alpha$ phase; **b** microdiffraction pattern taken from the phase formed in (**a**), being consistently indexed as the [100] net patterns of the $\beta$ phase; **c** a phase formed after irradiation for about 20 s (*arrowed*), being embedded in the $\alpha$ phase; and **d** microdiffraction pattern taken from the phase formed in (**c**), being consistently indexed as the [1$\bar{2}$0] net patterns of the $\beta$ phase

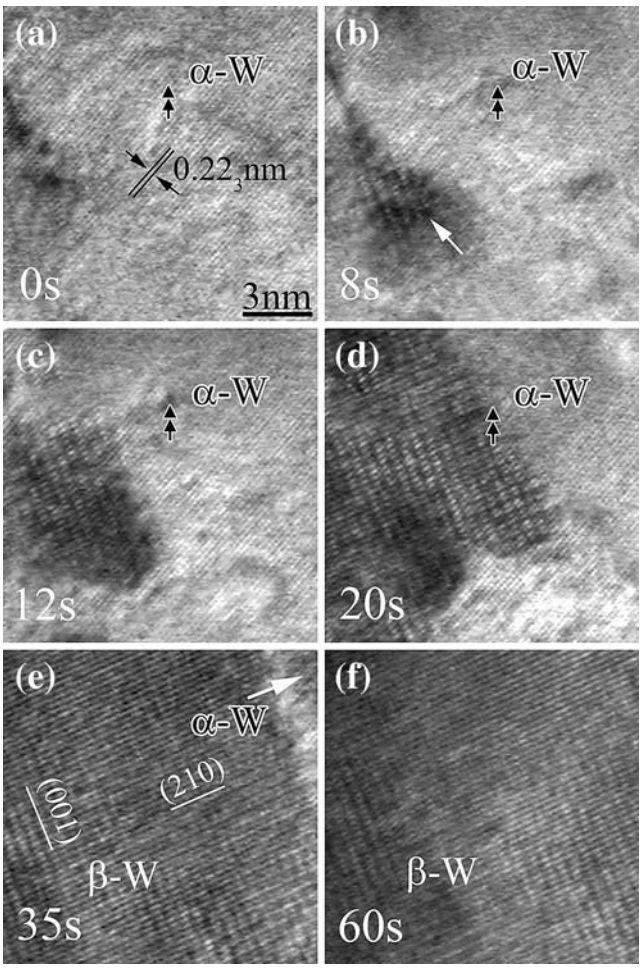


**Fig. 2** A series of HREM images showing successive stages of an $\alpha$ to $\beta$ phase change at 773 K. The *number* inserted in each micrograph shows time in seconds elapsed relative to **a**. The *double-arrows* in micrographs indicate a fixed position. See text for details

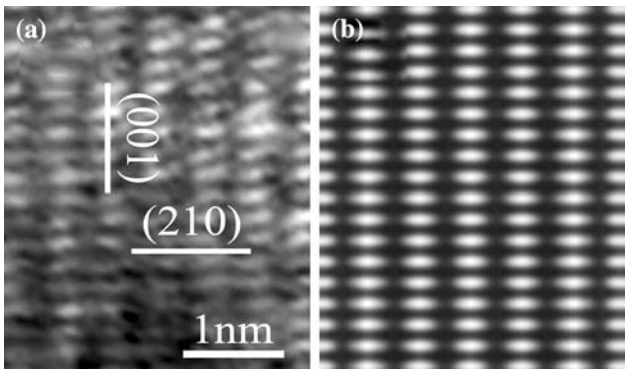


**Fig. 3** Comparison of a simulated HREM image of $\beta$-W (A15) with its experimental image. **a** Experimental HREM image of $\beta$-W along [1$\bar{2}$0] and **b** simulated HREM of $\beta$-W along [1$\bar{2}$0], defocus 30 nm and thickness 10 nm

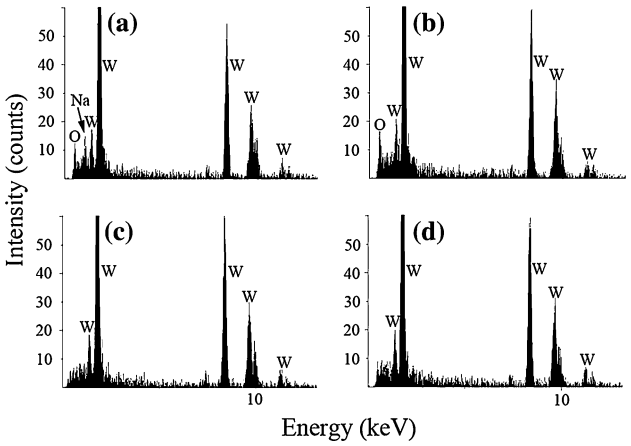


**Fig. 4** EDX spectra taken from samples prepared in different ways. **a** Spectrum from a sample prepared by chemical polishing with a NaOH aqueous solution (sample CHEM (before irradiation)), **b** from a sample prepared by ion-milling (sample ION), **c** from a sample prepared in the same way as (**a**) but additionally baked at 1,223 K in vacuum prior to irradiation experiment (sample ANN), and **d** from the $\beta$ phase formed by an $\alpha$ to $\beta$ phase change during electron irradiation of a sample that was prepared in the same way as (**a**) (sample CHEM (after irradiation)). An $\alpha$ to $\beta$ phase change was observed only in sample CHEM (**a**), while samples ION (**b**) and ANN (**c**) did not undergo such a phase change under electron irradiation

fringes can be identified as the (210) and (001) fringes of $\beta$-W. These two sets of fringes are consistent with a result of image simulation (see Fig. 3). Results shown in Figs. 2 and 3 suggest that an $\alpha$ to $\beta$ phase change in W was induced at 773 K under 200 keV electron irradiation across the whole thickness of the foil sample. The lattice fringes of $\beta$ replaced those of $\alpha$ matrix.

In view of getting an insight into the origin of such an $\alpha$ to $\beta$ phase change, it is of significance to mention about samples (prepared in different ways) with which the $\alpha$ to $\beta$ phase change was *not* observed in the same electron irradiation condition. There are two types of samples where the phase change was absent. One type is samples prepared in the same twin-jet polishing technique described in the present paper but annealed at 1,223 K in vacuum (in the same TEM) for 300 s prior to the irradiation experiment (hereafter designated as sample ANN), and the other is samples prepared solely by the ion-milling technique (hereafter designated as sample ION). With these two types of samples, such an electron irradiation-induced phase change as shown in Fig. 2 did not take place. In an attempt to make clear a factor(s) that determines the occurrence (or the absence) of the $\alpha$ to $\beta$ phase change, chemical analyses by EDX were carried out with these two types of samples as well as the sample the phase change behavior in which is illustrated in Fig. 2 (hereafter designated as sample CHEM). With regard to sample CHEM, EDX analysis was made on samples both before and after irradiation experiment. In the latter case, an EDX spectrum was taken from the $\beta$ phase formed. The results obtained are presented in Fig. 4. Figures 4a–d show EDX spectra taken from sample CHEM (before irradiation), sample ION, sample ANN, and sample CHEM (after irradiation), respectively. A sodium peak and an oxygen peak can be seen in the spectrum from sample CHEM (before irradiation) (Fig. 4a), while no sodium peak and only an oxygen peak will be seen in the spectrum from sample ION (Fig. 4b). Neither a sodium nor an oxygen peak can be seen in the spectrum from sample ANN (Fig. 4c). Both the sodium and oxygen peaks that were present in sample CHEM (before irradiation) (Fig. 4a) seems to be reduced in intensity after phase change to the $\beta$ phase (see Fig. 4d for sample CHEM (after irradiation)), suggesting some unknown depletion process for these impurities operating in the phase change. It is noted that both sample CHEM (before irradiation) and sample ION exhibit an oxygen peak (i.e., Fig. 4a, b) but the $\alpha$ to $\beta$ phase change was induced only in sample CHEM and not in sample ION. This fact indicates the presence of oxygen does not play a key role in the electron irradiation-induced phase change reported here.

In the literature, there are two different sorts of claims on the effect of oxygen on the formation of the $\beta$ phase with the A15 structure. One sort of claim is that the presence of oxygen is absolutely necessary to form the $\beta$ phase. In this case, the $\beta$ phase is considered to be either a sub-oxide of tungsten such as $W_3O$ and $W_{20}O$ [16, 17] or a phase with the tungsten-tungstide [$W_3$*W] structure containing tungsten ions of different oxide state in the lattice [18, 19]. The other sort of claim is that the $\beta$ phase can exist in vacuum or in a reducing atmosphere without oxygen in the lattice [20]. The present indication that the presence of oxygen does not play a key role in the phase change observed here, resulting from the comparison between Fig. 4a and b mentioned above, as well as the absence of an oxygen peak in the spectrum taken from the $\beta$ phase (i.e. Fig. 4d) provides further support to the latter claim.

On the other hand, it is evident that a Na peak appears only in sample CHEM (before irradiation) (Fig. 4a) that undergoes the α to β phase change under electron irradiation, while no Na peak can be seen in sample ION (Fig. 4b) and sample ANN (Fig. 4c) that remain α under the same irradiation condition. This fact strongly suggests sodium atom contamination from the 20 wt% NaOH aqueous solution may play an essential, key catalytic role in activating the α to β phase change induced by 200 keV electron irradiation. One point that should be discussed here is whether or not the phase formed under electron irradiation is a kind of sodium tungsten bronze. The following two experimental results suggest that the phase formed should not be a kind of sodium tungsten bronze. First, comparison of Fig. 4a and d reveals that the concentration of sodium and oxygen decreased rapidly during the phase change. If the phase formed is a kind of sodium tungsten bronze, the concentration of sodium and oxygen would not decrease after the phase change. This fact suggests the phase is not a kind of sodium tungsten bronze. The second but more important result is that the diffraction patterns (Fig. 1b, d) obtained from the phase cannot be consistently indexed as those of any kind of sodium tungsten bronze known to date. Therefore, it is considered that the phase change observed here is the change from α-W to β-W, not the change that from α-W to sodium tungsten bronze.

Further work to make clear the atomistic mechanism behind the electron irradiation-induced α to β phase change is in progress in our laboratory.

## Conclusions

Conclusions from the present study are as follows: (1) an α-W to β-W phase change was induced by 200 keV electron irradiation at 773 K. (2) No evidence for the effects of oxygen in inducing the phase change was obtained. It is strongly suggested that the presence of sodium may play an essential catalytic role in inducing the α to β phase change.

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