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Nucleation of fcc Ta when heating thin films

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Thin tantalum films have been studied during in situ heating in a transmission electron microscope. Diffraction patterns from the as-deposited films were typical of amorphous materials. Crystalline grains were observed to form when the specimen was annealed in situ at 450 °C. Particular attention was addressed to the formation and growth of grains with the face-centered cubic (fcc) crystal structure. These observations are discussed in relation to prior work on the formation of fcc Ta by deformation and during thin film deposition.
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The metal Ta has many applications, in part because it has a very high melting point, and in part because it is the most corrosion-resistant metal. In both cases, these properties apply to the body-centered cubic (bcc) α-phase. Thin films, including those with ultrafine grains [1–3], also have many applications. In the case of Ta these include electronic devices such as resistors [4] and capacitors [5], bioactive coatings, especially in orthopedics [6], and protective coatings on steel [7]. In fact, Ta films are a key material of choice to replace chromium coatings across the board in anticorrosion applications, due to the toxicity of hexavalent Cr [8]. It is clearly important to know which phase is being produced when such thin films are used.

Ta is well known as a refractory metal with the bcc structure (space group *Im3m*; lattice parameter $a = 0.33058$ nm; density = 16.55–16.27 g cm^{-3}). A second phase, β-Ta, with a tetragonal unit cell is formed when thin films are grown on clean substrates. A third phase, Ta with the face-centered cubic (fcc) structure, can be formed under certain special conditions. For example, it has been demonstrated previously that the fcc phase of Ta can form when the bcc phase is deformed [9] or when Ta is deposited as a thin film onto a heated substrate [10–12]. In the present paper it is shown, using in situ heating in the transmission electron microscope (TEM) [13], that grains with the fcc phase grow from the amorphous phase during heat treatment of thin Ta films at temperatures as low as ~420 °C.

The deposition of Ta was conducted via DC magnetron sputtering using a Kurt J. Lesker PVD 75 thin-film deposition system. The base pressure in the system was 7.6×10^{-7} Torr while the deposition pressure was 3 mTorr with a working gas of Ar. The target was 99.95% Ta with an operating power of 60 W. Prior to deposition, the target was pre-sputtered for 60 s with the shutter closed. The total deposition time was 35 s with a deposition rate of ~0.6 nm s^{-1} at room temperature (giving a nominal thickness of ~20 nm), with <1 °C self-heating of the substrate. The Ta was deposited as a thin film directly onto a Protochips heating grid (type E-AHA21) that was masked with Kapton tape such that only the electron-transparent window was accessible for Ta deposition. The heating grid was then mounted in a Protochips Aduro holder and then was loaded into the TEM (FEI Tecnai F30 G2 operating at 300 kV) for in situ testing within 30 min following the deposition.

The ProtoChips heating grid consists of a 20 nm thick film of amorphous carbon with an array of 2 μm holes spaced 2 μm apart; the carbon film itself is supported on a thicker substrate of amorphous silicon nitride with

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lithographically positioned circular holes of ~50 μm diameter. This silicon nitride substrate is then resistively heated in the TEM. During the in situ heat treatment, the temperature of the specimen is determined by measuring the heater current and using the calibration provided by the manufacturer for that particular chip, i.e. the relationship between the heater current and the temperature of the supporting film is calibrated for each heating chip by the supplier. The specimen was heated in 100 °C increments at a rate of 10 °C s^{-1}, with 5–10 min intervals between heating steps until it reached 400 °C to allow the holder to equilibrate. At and above 400 °C, 20–35 min intervals were used between heating steps to allow for imaging. The specimen was heated to a maximum temperature of 1000 °C. The total time of the heating was approximately 2 h and 45 min.

A second film was deposited using the same deposition conditions but with a substrate consisting of a thin film of PMMA that had been deposited onto single-crystal Si. In this case, the film was cut into squares and floated off the substrate by dissolving the PMMA in acetone. The Ta film was then caught on a Mo grid which could then be loaded directly into a single-tilt Gatan model 620 heating holder.

An image of the as-deposited film (in the Protochips holder) and its associated diffraction pattern are shown in Figure 1. There is no diffraction contrast in the image (the darker contrast near the edge of the hole is attributed to the holey carbon film folding back on itself). The uniform, light gray contrast is typical of amorphous material and the diffraction pattern, with no sharp spots or rings, supports this interpretation.

Examples of small fcc Ta grains that were observed after the specimen was heated to a temperature >400 °C are collected in Figure 2. These crystalline grains were detected as soon as the sample had stopped drifting at 500 °C. The ABC stacking sequence characteristic of the fcc crystal structure is clearly evident in each grain, with the average [14] plane spacing measuring 0.249 nm. Because these are the close-packed planes, they must be in the {1 1 1} family which gives a lattice constant of a_{fcc} = 0.43 nm. This measurement is completely consistent with the fcc Ta lattice constant measured in Ref. [9]. It is significant that the fcc Ta formed by heat treatment of amorphous films has the same lattice constant as fcc Ta formed by deformation of bcc Ta, and furthermore that the interatomic separation of the atoms in fcc Ta is 6.1% larger than the equilibrium separation distance in the bcc phase. Figure 3 shows an overview of the film recorded after the in situ heat treatment. The large field of view image in this image

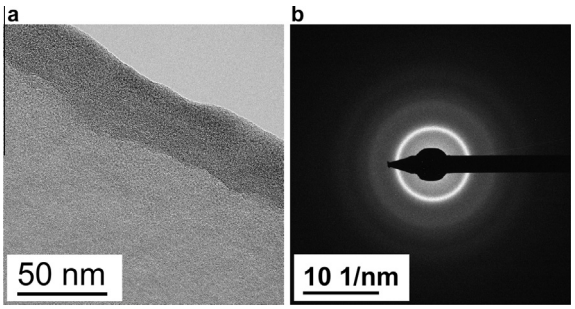

Figure 1. (a) BF-TEM image of the as-deposited Ta film. The dark contrast near the hole is due to the carbon film folding back on itself. (b) The corresponding selected-area diffraction pattern. Both the image and the diffraction pattern are characteristic of amorphous material.

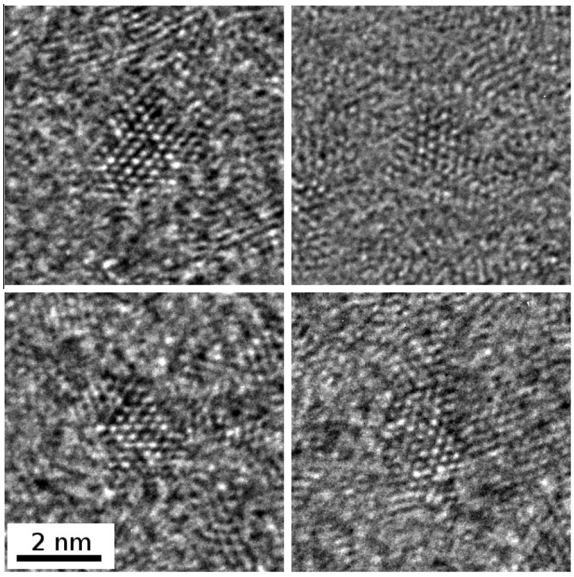

Figure 2. Four high-resolution TEM images demonstrating the fcc structure of the nucleating crystallites during heat treatment. The ABC stacking sequence characteristic of the fcc structure is clearly visible in each crystallite.

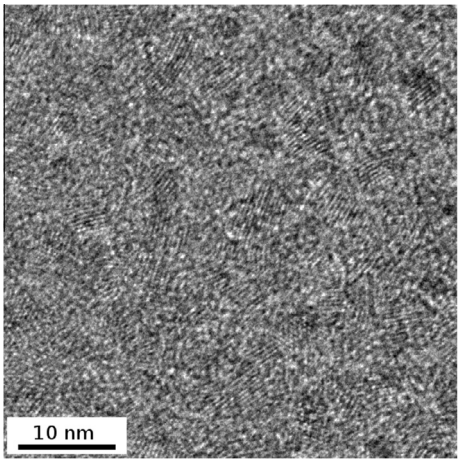

Figure 3. Lower-magnification view of the Ta film after the heating experiment showing the distribution of the crystallites in the film.

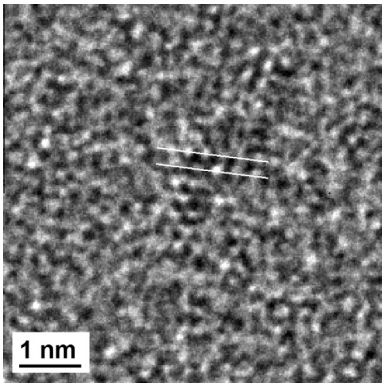

Figure 4. High-resolution TEM image showing the fcc structure's ABC stacking and 0.249 nm fringe periodicity of the nucleating crystallites as a result of heat treating an amorphous stand-alone Ta film.

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