Nucleation of fcc Ta when heating thin films

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Abstract

Thin tantalum films have been studied during in-situ heating in the TEM. 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.

Keywords:

focused ion beam (FIB)

high-resolution electron microscopy (HREM)

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crystal structure

Tantalum

The metal Ta has many applications, in part because it has a very high melting point, and in part because it is the most corrosive-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 anti-corrosion 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.

Tantalum (Ta) is well known as a refractory metal with the bcc structure (space group Im3m; lattice parameter $a = 0.33058$ nm; density = $16.55\text{--}16.27$ g/cm³). A second phase, β -Ta, with a tetragonal unit cell is formed when thin films are grown on clean substrates. A third phase, tantalum 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 body-centered cubic 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 $\sim 420^\circ\text{C}$.

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 approximately 0.6 nm/s at room temperature (giving a nominal thickness of ~ 20 nm), with less than 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 300kV) for in-situ testing within 30 minutes following the deposition.

The ProtoChips heating grid consists of a 20 nm thick film of amorphous carbon with an array of $2\text{ }\mu\text{m}$ holes spaced $2\text{ }\mu\text{m}$ apart; the carbon film itself is supported on a thicker substrate of amorphous silicon nitride with lithographically positioned circular holes of $\sim 50\text{ }\mu\text{m}$ 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 , with 5-10 minute intervals between heating steps until it reached 400°C to allow the holder to equilibrate. At and above 400°C , 20-35 minute 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 hours and 45 minutes.

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 above 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 {111} family which gives a lattice constant of $a_{\text{fcc}} = 0.43$ nm. This measurement is completely consistent with the fcc Ta lattice constant measured in [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 demonstrates the prevalence of these small fcc grains, i.e., the crystallites in Figure 2 are not isolated or unique, they were simply oriented conveniently.

Figure 4 shows a similar crystallite in the stand-alone Ta film (i.e., there is no supporting carbon film) that was heated to approximately 420 °C in the Gatan heating holder. The 0.249 nm lattice spacing was measured in several different regions. The crystallites are presumed to be smaller in this case because the maximum heating temperature was 420°C.

Although, in the present study, the Ta films were deposited at ambient temperature (~20°C) and appeared to be amorphous from the diffraction patterns, the possibility that very small crystalline nuclei are present in such films cannot be discounted but the size would then be <1 nm diameter. Indeed, it is proposed that there is a close relationship between the present study and previous studies of thin-film growth that resulted in the formation of fcc Ta. In the 1966 study by Denbigh and Marcus [11], the substrates were heated to temperatures of up to 700°C during deposition. They found that when the substrate temperature was set to be 750°C radiation from the Ta source actually increased the substrate temperature by an additional 150°C. Even when the substrate heater was not turned on, the temperature of the film was reported to rise to 400°C to 500°C. Thus in all case it is likely that the film was essentially being heat-treated at a temperature of at least 400 °C—a temperature that is quite comparable to the annealing temperature used in the present study. A study [15, 16] of the effects of residual stresses in DC-magnetron- sputtered films used thicker films and did not heat the film; this study did not report the fcc phase. RF magnetron sputtering was also used to produce thick (~1 µm) films of nanocrystalline β-Ta, again with no indication of the fcc phase [17]. The temperature rise for magnetron sputtering is estimated to be less than 150°C [18].

In the later (1968) study by Marcus and Quigley (MQ) [12] the substrate temperature varied between ~100°C and 800°C. In the MQ study, fcc Ta was observed for growth on all substrates except single crystal MgO (on which β-Ta formed and remained); the substrate temperature is not given in the MQ study but their comment that the growth of β-Ta was frustrated by the transition to the bcc structure at 750 °C implies that the substrate temperature was usually quite high. MQ also commented that epitaxial β-Ta could be grown on MgO at a ‘relatively low substrate temperature’ implying that in the case of an MgO substrate, epitaxy was influencing the phase formed. The MQ fcc unit cell had a lattice parameter $a = 0.442$ nm. Other early studies have reported values for a_{fcc} , namely 0.442 nm [19], 0.439 nm and 0.447 nm [20] and 0.449 nm [21]. When the bcc Ta appeared the bcc unit cell had a lattice parameter $a = 0.35$ nm, which is significantly larger than the regular value of 0.331 nm and is referred by MQ to as the ‘expanded bcc’ [11, 12] structure. The study of Schrey et al [22] found that films deposited using RF sputtering between 13°C and 200°C were bcc with $a = 0.325$ nm, but that films deposited at a temperature of 325 °C had an fcc structure with a lattice parameter of 0.448 nm. Surprisingly, the study by Schrey et al [22] found that amorphous material was produced at the higher temperatures—a result that appears inconsistent with other studies including the present one.

The observation in Figure 4 that the 0.249 nm fringes are also present in the film heated without the supporting carbon film supports the conclusion that the fcc phase is not due to the uptake of carbon to form TaC. Additionally, no hexagonal phase was observed which would be expected in the formation of a carbide: Ta₂C has hexagonal symmetry and the 33 at% C phase should be observed before the 50 at%

C TaC phase if the Ta film was indeed taking up carbon. The lattice parameter of TaC (melting temperature 3985 °C) is very similar to that of fcc Ta and it has the same crystal symmetry (TaC has the fcc rocksalt structure). Fukunaga et al [23] produced a mixture of TaC and Ta₂C by heating Ta powder and carbon nanotubes at 780°C for 48h. As expected from the Ta-C phase diagram [24, 25], the hcp phase Ta₂C formed first. It is therefore very unlikely that the fcc TaC would form within 10 minutes at 500 °C. It is clear that the new crystalline phase observed here is fcc Ta metal and not the fcc carbide, which is consistent with earlier observations where carbon was not present.

Finally, it is interesting to consider why the lattice parameter of the fcc Ta is so large compared to that of the bcc phase since this implies that the density of the "cubic close-packed" phase is actually lower. It is proposed that the answer lies in the interatomic bonds. The bonding in bcc metals can be regarded as being partly covalent. Clearly the bonding in the fcc phase must be different (implying that atomistic calculations should really use a different interatomic potential); bonding in the fcc phase would be purely metallic, which is expected to be weaker than bonding with a partially covalent character. The very small size of the fcc crystallites means that the total reduction in energy resulting from forming those partially covalent bonds is too small to drive the phase transformation.

Grains consisting of the fcc phases of Ta can be produced by deformation or during deposition. It is suggested that the earlier studies of the growth of the fcc phase by deposition may actually have involved heating the sample at similar temperatures to those used in the present study so that the heat-treatment is actually the fundamental aspect of the development of the fcc grains during deposition. The grains are invariably small but they may grow to become large enough to contain twin boundaries or even microtwins.

The fact that the substrate for the initial Ta growth and for the subsequent crystallization was amorphous makes it clear that the presence of the fcc phase is not influenced by epitaxy contrary to the suggestion of Marcus and Quigley [12] although their paper only suggests that it 'may also be involved'.

As shown in the present study, these thin films of Ta provide a model system for studying the bcc to fcc phase transformation. One improvement to be made in future work on this process will be a more accurate calibration of the temperature of the specimen during in-situ heating.

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Figure Captions

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.

Figure(s)
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