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Fiber texture of sputter deposited molybdenum films and structural zone model

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HIGHLIGHTS

- Ultra thin (2.5 nm) to thin film (100 nm) of Mo was studied.
- Texture evolution was studied by TEM diffraction patterns with tilting film.
- Fiber texture was observed for ultra thin film at initial growth stage.
- Zone II growth mechanism was proposed without intentional substrate heating.

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ABSTRACT

The texture orientation of 2.5, 5, and 100 nm thick Mo films grown by sputter deposition on SiO_2 membranes at room temperature has been studied quantitatively using transmission electron microscopy. The sample tilt angle dependent diffraction patterns of these films revealed a fiber texture with the [110] out-of-plane direction for all film thicknesses. Films grown at different sputtering power and substrate–target distance showed a similar texture orientation. These results would imply that the growth was in zone II, according to the microstructure classification of the structural zone model. This is in contrast to the conventional assignment of zone I for Mo deposition at room temperature based on the low Mo homologous temperature of ~0.1. It was found that texture dispersion was reduced as the thickness of the film increased. Possible mechanisms, including energetic particles bombardment during growth, which could affect the surface mobility and texture of the films, were discussed.

1. Introduction

Structural zone model (SZM) has generally been used as a guide to understand microstructures including morphology and texture of films grown by physical vapor deposition, in particular, by sputter deposition. The model was originally suggested by Movchan and Demchishin [1]. Later, the model was modified and extended in more detail by a number of authors including Thornton [2], Messier et al. [3], Eckertova [4], and Mirica et al. [5]. Growth parameters that would affect the microstructure of films include growth temperature, Ar gas pressure, growth rate, target to substrate distance, adatom energy, neutral Ar energy, ion energy, and impurities [6–8]. The microstructures are divided into several zones that possess distinctly different features. For example, within a range of low deposition pressure, the microstructures can be divided into zone I, zone T (a transition regime between zone I and zone II), zone II, and zone III regimes as a function of a reduced homologous temperature $R = T_s/T_m$, where T_s and T_m are the substrate temperature and bulk melting temperature, respectively.

Typically in zone I ($R < 0.1$), because of the lack of surface mobility during growth, the texture is either amorphous or random polycrystalline with no preferred orientation. In zone T ($0.1 < R < 0.3$), an increase of surface diffusion leads to the competition between adjacent grains. The net result is that the out-of-plane direction is dominated by the crystallographic direction that grows the fastest [9] with faceted minimum energy planes. For example, for a Body-Centered-Cubic (BCC) structure, the fastest growth is in the [100] direction and the film would have a [100] out-of-plane crystal orientation [10]. If the film is deposited at normal incidence, there will be no preference in the in-plane orientation, that is, a fiber texture. At an even higher value of R (>0.3) surface atom mobility is sufficiently high that recrystallization among the grains occurs to minimize the surface energy. In this case, zone II, the plane parallel to the surface would be the

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minimum energy crystal plane and the out-of-plane orientation would be the [110] direction for a BCC structure. Again, there is no preferred orientation in the in-plane direction.

For Mo, room temperature deposition implies R ~ 0.1 and it falls within zone I regime, or at the very low end of zone T, according to the structural zone model. However, recent experiments on the sputter deposition of thin Mo films with no intentional substrate heating appeared to exhibit the minimum energy (110) plane parallel to the substrate surface [11–24]. In these experiments, a variety of substrates had been used, including glass [16], polymer [20], amorphous Si [22], and Si with native oxide [21]. So it appears that the [110] texture formation is independent of the substrate used. Other refractory metals including W [25–29], Ta [30–33], and Nb [34–36], all behave the same under similar deposition conditions, that is, they all give the (110) minimum energy plane texture. The deposition conditions were far from the condition that is required for a recrystallization ($R > 0.3$) to occur which would give a (110) minimum energy plane parallel to the surface. It is of great interest to know quantitatively how such texture is formed at the initial stages of growth. In this paper we report a transmission electron microscopy (TEM) study of the initial stages of ultrathin Mo films grown onto TEM grids with 40 nm thick SiO_2 membranes without intentional substrate heating under normal incidence DC magnetron sputter deposition. This method requires no elaborated sample preparation procedures and allows us to study how the texture evolves during Mo film growth. We selected the SiO_2 membranes because their surfaces mimic a glass surface [16] or a Si wafer substrate covered with native SiO_2 [21,23,24], which was used in the past. Here, we describe how to extract texture axis and its quantitative texture dispersion angle using a newly derived equation and compared it with the experimentally observed tilt angle dependent TEM diffraction patterns. The contributing factors to this fiber texture formation and the implications of the findings on the classification of the conventional structural zone model will be discussed.

2. Experimental

The Mo samples were grown on TEM grids made of ~40 nm thick SiO_2 membranes (Ted Pella 21530-10). The individual SiO_2 membrane has a root mean square roughness of ~0.65 nm. The TEM grid was mounted on a sample holder using double-sided Scotch tape in a DC magnetron sputtering system before pumping down. The Mo target was a 3″ (76.2 mm) round disk of ¼″ (6.35 mm) thickness and 99.95% purity. The distance from the Mo target surface to the center of the substrate holder was ~15 cm. The base pressure of the system was $\sim 6.5 \times 10^{-7}$ Torr (8.67×10^{-5} Pa). The Ar gas flow rate was controlled at 2.01 sccm (3.35×10^{-7} m^3 sec^{-1}). The working pressure of Ar was set to 2.3 mTorr (0.307 Pa) and the power was 200 W with a voltage of 370 ± 2 V. The Mo target was facing at the normal direction to the SiO_2 membrane. Three samples of 2.5, 5, and 100 nm thick were prepared. The calibrated Mo deposition rate using scanning electron microscopy was ~0.25 nm s^{-1}. To further study the effect of deposition parameters on the texture formation, a different sputtering power (50 W), and different substrate–target distances (1.5 cm, 3 cm and 4.5 cm) were also used. No intentional heating was used in all the depositions and also for our ultra-thin film, the deposition time is very short (as low as 10 s), the substrate temperature should not be too high. According to Thornton's structural zone assignment, zone II for Mo should occur at a homologous temperature $R > 0.4$. The substrate temperature corresponding to $R \sim 0.4$ should be 1158 K for Mo. At this temperature the Scotch tape which were used to mount the grid on the sample holder would be burnt. The fact that the tape was perfectly intact after the deposition indicated that the temperature of the grid is well below 400 K. Also, at 1158 K, the amorphous SiO_2 membranes would not be stable and we would not be able to image the films.

TEM (Tecnai T12, 120 keV) was used to study the morphology and diffraction patterns of the Mo films at various thicknesses. The diffraction patterns were recorded for various sample tilt angles up to 45° with respect to the incident electron beam direction. The sample tilt axis is in parallel to the sample plane. The purpose of tilting the sample is to differentiate between a randomly oriented polycrystalline film and a fiber texture film. It also allows us to determine quantitatively the dispersion angle around the texture axis [37,38].

3. Results

3.1. Diffraction patterns vs. film thickness

TEM bright field image, diffraction pattern, and the radial intensity distribution for each Mo film thickness are shown in Fig. 1 for electron beam incident normally to the samples. The bright field image of 2.5 nm thick sample in Fig. 1(a) is almost featureless. More contrast develops when film thickness increases to 5 nm (Fig. 1(d)) and grains of a few nm size can be seen from the uniform brightness regions. When the film is 100 nm thick (Fig. 1(g)) the grain size distribution widens but the dominant ones are less than 10 nm. These sizes are also cross-checked from dark field images (not shown here). It is clear from the diffraction patterns shown in Fig. 1(b), (e) and (h) that even for the 2.5 nm thick film, the Mo(110) diffraction ring was already well developed and the intensity along each ring is uniform. The halo ring next to the transmitted electron beam is from the amorphous SiO_2 membrane. The reciprocal radii $|\mathbf{G}(hkl)|$ (where h, k, and l are Miller indices) measured from the transmitted electron beam to the next three rings beyond the halo amorphous SiO_2 ring for the 5 nm sample are 4.65, 6.62 and 8.08 nm^{-1}. The inverse of these values are 0.215, 0.151 and 0.124 nm, respectively. These values are within 5% of the theoretical interlayer spacing values of Mo, i.e., $d_{110} = 0.222$ nm, $d_{200} = 0.157$ nm and $d_{211} = 0.128$ nm, calculated from $d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}$, where $a = 0.315$ nm is the lattice constant of BCC Mo. The condition $h + k + l =$ even is satisfied for a BCC structure. The first three continuous rings are identified as 110, 200 and 211. This identification is also cross checked by the measured ratio 1.42 of the reciprocal distance of the 2nd ring to the first ring and the measured ratio 1.74 from the 3rd ring to the 1st ring. These measured ratios are consistent with the theoretical ratios of 1.414 and 1.732 from $\mathbf{G}(211)/\mathbf{G}(110)$ and $\mathbf{G}(200)/\mathbf{G}(110)$, respectively. Similar calculations from the diffraction pattern of the 100 nm thick film yield $d_{110} = 0.233$ nm, $d_{200} = 0.164$ nm and $d_{211} = 0.134$ nm. For the 2.5 nm thick film, only the (110) ring is clearly visible, with $d_{110} = 0.215$ nm.

While the normal incident TEM diffraction rings shown in Fig. 1 implies that the films are polycrystalline in nature, they do not reveal the existence of possible preferential orientation of the crystals normal to the surface of the films. In order to probe such possibility, we collected the diffraction patterns of the samples with the TEM electron beam tilted with an angle β with respect to the surface normal (Fig. 2). The sample tilt axis is defined as OT in the sample plane and is along a line approximately going through the azimuthal angles at $\phi = 90°$ and 270° (See the dashed line labeled OT in Fig. 2(c), (f) and (i)). The $\phi = 0°$ is defined as at the three o'clock position and the increasing azimuthal angle circles in the counter-clockwise direction.

Fig. 2 shows the diffraction patterns for the three samples when the TEM electron beam was tilted with an angle β of 15°, 35°, and 45° for the 2.5 nm sample and 15°, 30°, and 45° for the 5 nm and 100 nm samples with respect to the surface normal. Qualitatively