Electron microscopic study of sputter-deposited Ir films

J. ECHIGOYA, K. MUMTAZ
Department of Materials Science and Engineering, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan
E-mail: echigoya@iwate-u.ac.jp

Y. HAYASAKA, E. AOYAGI
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The microstructural development of iridium (Ir) film deposited on isotropic graphite by a sputtering method was investigated using a transmission electron microscope. A columnar structure was developed in which the diameters of columnar grains were distributed from 3 to 50 nm at the substrate temperature of 330 K. Directions of grains were almost perpendicular to the substrate surface, and grain boundaries were wavy. Grains forming the columnar structure indicated different orientations of a growth direction, though growth orientations of grains showed the weak preferred orientation of a [111] direction. Non coincident related boundaries, as well as low angle grain boundaries and twin boundaries tend to be observed more frequently than coincidence lattice related boundaries.

1. Introduction

Iridium is the most promising material for the coating of structural carbon materials such as C—C composite and graphite, because its melting temperature is 2723 K, it has a very low oxygen permeability up to 2373 K, it is non reactive with carbon below 2553 K, and it is an effective barrier to carbon diffusion [1]. Coating with iridium films has been performed using methods such as physical vapor deposition and chemical vapor deposition [2]. Rf magnetron sputtering is a suitable method for deposition of iridium film because it achieves coating through low temperature processing. The structure of the film deposited by sputtering is characterized by the zone model proposed by Thornton [3]. He represented the structure of film as functions of the substrate temperature (T_s) and inert gas pressure by taking into account the effective processes of shadowing, surface diffusion, and bulk diffusion. If the inert gas pressure is constant during the sputtering experiments, the structure of the film depends only on the ratio of the substrate temperature to the melting temperature (T_m). The increase of the substrate temperature promotes diffusion and results in a structure consisting of large equiaxed grains. At temperatures of $T_s/T_m < 0.1$, significant adatom diffusion and grain boundary movement are not expected, and the grains extend in the direction of growth, i.e., the so-called columnar structure is developed. The shadowing effect is more dominant than the effects of other factors at low substrate temperatures. Shadowing is a phenomenon arising from the geometric constraint imposed by the roughness of the growing film and line-of-sight impingement of arriving atoms. The grain sizes of film are distributed in the range from 5 to 20 nm [4]. Grovenor *et al*. examined the structure of film deposited by an e-beam method, and observed that small equiaxed crystalline grains were present in film evaporated at low T_s. From their results, they suggested that the structure is produced by some kind of athermal process which occurs when the precursor phase reaches a critical thickness [4]. Ekinci and Valles investigated the early stages of zone I using *in situ* scanning tunneling microscopy and suggested that athermal crystallization from an amorphous phase takes place in stage I of the film growth [5].

Since iridium has a high melting temperature, the T_s/T_m is about 0.1 when the substrate temperature is room temperature. Investigation of the microstructure of iridium film sputtered on a graphite substrate at a temperature of 330 K using high resolution transmission electron microscopy (HRTEM) is of interest, because the zone model proposed by Thornton is based on optical and scanning electron microscope observation, which yields macroscopic information. The purpose of the present study was to further investigate the microstructural development of iridium film through the observation of grain boundaries and dislocations of as-sputtered films onto isotropic carbon structural materials at a low substrate temperature ($T_s/T_m = 0.11$). An electron diffraction pattern with a nano size beam was extensively used in an analysis of grain orientation, because of small grain size which was about 20 nm. Experimental results on the microstructure of iridium film were also obtained in the case of a substrate temperature of 1070 K ($T_s/T_m = 0.3$) and compared with results on the microstructure formed at a lower substrate temperature.

2. Experimental procedures

Isotropic graphite, provided by Toshiba Ceramics Company, was used as the substrate material in this study. The thermal expansion coefficient of the substrate is 5.8×10^{-6}/K at 298 K. The isotropic graphite was polished with 3000 grit emery paper. Iridium film was deposited by RF magnetron sputtering; details of the sputtering procedure can be found in [1]. The rate of sputter-deposition was 1 nm/s. This rate is relatively slow in comparison with that of the electron beam deposition (16 nm/s) conducted by Grovenor *et al*. The substrate temperatures were 330 and 1070 K. The thickness of the films was 1.5 μm. After the deposition of iridium, the samples were characterized using a high resolution transmission electron microscope (HRTEM). Transmission electron microscopic studies were carried out with a Jeol ARM 1250 operated at 1250 kV. A Jeol-3010 electron microscope operated at 300 kV was used to determine the orientation of grains through a nano-beam diffraction technique. Thin foils for TEM were prepared by ion milling. Since the samples were obtained by ion-milling of only one side of the substrate, the plan view of the observed area was close to the surface of the deposited film, i.e., the observed microstructure was obtained at about 1.5 μm thick. Cross-sectional specimens were prepared using the procedure outlined in a previous work [6].

3. Results and discussion

Fig. 1 shows a transmission electron micrograph of a boundary area between two columns of the iridium film deposited at the substrate temperature of 330 K. Since the boundaries between the columns had already been polished out during ion milling, the density of this area seems to be lower than that of the center of the column. The graphite substrate was sintered material including many pores, which were connected with each other and formed canals on the surface [1]. The irregularities of the surface of the substrates in addition to the restricted diffusion length of adatoms due to the low substrate temperature of 0.1 T_m resulted in the shadowing effect being the dominant process at this substrate temperature. The low density at the column boundaries may be coincident with the result that iridium-coated graphite was easily broken at the boundary between columns. Fig. 2 shows an electron micrograph of a cross-sectional view of iridium deposited on graphite at the substrate temperature of 330 K. The substrate indicated the two kinds of surface roughness, one was a small up and down of the order of 50 nm and an another of the order larger than 100 nm. It is of interest to point out that a film showed quite different growth morphology when a surface of the substrate had a deep valley. Since grains have a tendency to grow perpendicular to the substrate surface, the grains, growing from a deep valley, collided and this resulted in formation of the area with low density at the front of growing grains (marked V in Fig. 2), as shown in Fig. 2. Though the growth direction of grains was almost perpendicular to the substrate, grains elongated in a 20 degrees declined direction were observed in Fig. 2 (marked D). This means that the anisotropic growth of grains was taken place. Fig. 3 shows a high resolution electron micrograph of a cross-sectional view of the iridium film deposited on graphite at the substrate temperature of 330 K. This figure revealed that the size of grains being at the thickness less than 50 nm from the substrate was relatively small and an order of 20 nm or less. Chisholm and Smith have estimated characteristic lengths of grain boundary migration and surface diffusion during the growth of a film in zone I [7]. In our case, the length of grain boundary migration was determined by the length of the deposition time. If the surface diffusion is the dominant process during nucleation, grain size should be around 20 nm. This is almost coincident to the experimental value. Though nucleation of grains takes place in the early stage, some grain was elongated in the growth direction from the substrate. This means that athermal crystallization, which is the phenomenon of the amorphous to crystalline transformation of the initial growth layer after several atomic layers have been grown in thickness, did not take place in the present experiment, because successive and repeating athermal crystallization from an amorphous phase results in the equiaxial grain configuration [5]. After the nucleation stage of

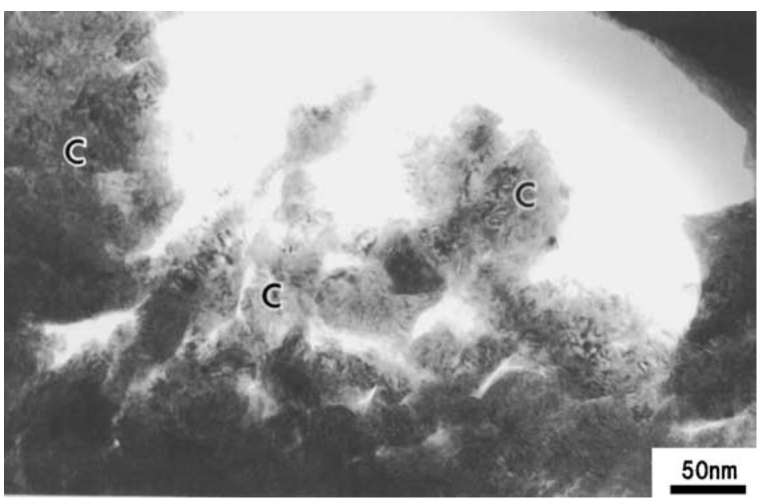

Figure 1 Electron micrograph of a boundary area between two columns of the iridium film deposited at the substrate temperature of 330 K. Mark C indicates a column.

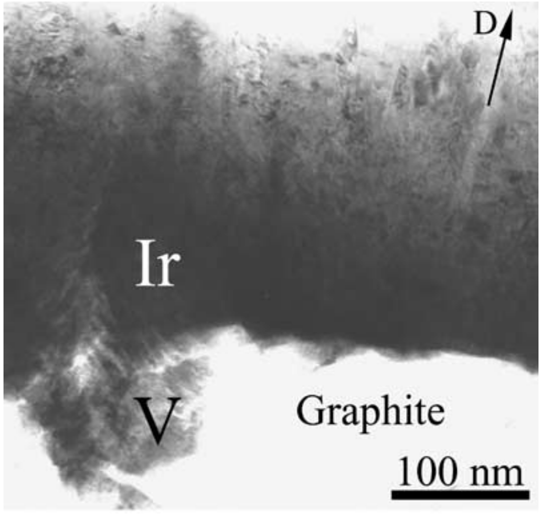

Figure 2 Electron micrograph of a cross-sectional view of iridium film deposited on graphite at the substrate temperature of 330 K.

Figure 3 High resolution electron micrograph of a cross-sectional view of the iridium film deposited on graphite at the substrate temperature of 330 K.

50 nm in thickness, grains growing from the substrate have been a tendency to elongate in the direction of film growth. The growth morphology is able to regard as the columnar structure in the film thicker than 50 nm. An aspect ratio of grains was larger than 5, which means that the grains elongated in the growth direction longer than 100 nm. Grain boundaries elongated in the growth direction were wavy as seen in Fig. 3. Twin boundaries can be observed frequently and their planes were almost perpendicular to the growth direction, though some of twin boundaries having their planes parallel to the growth direction was also observed. Because

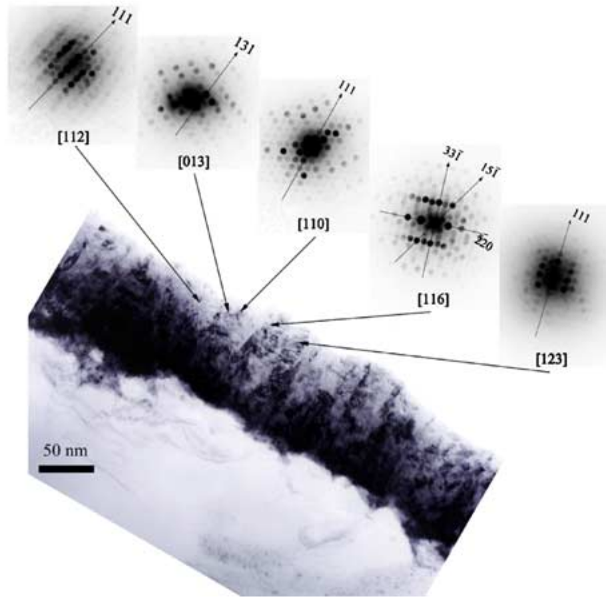

Figure 4 Electron micrograph of a cross-sectional view with electron diffraction patterns to indicate the orientation of each columnar grain.

images taken by a transmission electron microscopy give two-dimensional information, care must be taken to obtain the correct result through it. It has a possibility for the decrease of a grain width or shrinkage during growth observed in a cross sectional sample by the electron microscopy to be artificial effect shown in Fig. 3, because the direction of grains were not exactly perpendicular to the substrates as shown in Fig. 2. Electron diffraction patterns taken from each grain using a nano size beam revealed a direction of grain growth in an as deposited iridium film. Fig. 4 shows an electron micrograph of a cross-sectional view with electron diffraction patterns to indicate the orientation of each columnar grain. Several grains were oriented to [111] directions as the growth direction, but not all. The orientation relationship between adjoining grains was difficult to determine the exact relationship, because relation between adjoining grains had both tilt and twist components. Rough estimation of the relationship gave the results of few coincidence related boundaries between them. Though grains had a tendency of growing in [111] directions, the direction of growth of grains was distributed randomly.

Fig. 5 shows a plan view of the iridium film deposited at the substrate temperature of 330 K, which was obtained from the area close to the surface of the film (1.5 μm apart from the substrate). It consists of fine and coarse grains. The distribution of grain sizes ranged from 5 to 50 nm in diameter as shown in Fig. 5. Voids less than 1 nm in size were observed in grains and grain boundaries. These were already observed in a cross sectional sample as shown in Fig. 3. Fig. 6 shows a high resolution micrograph of an as sputtered iridium film deposited at the substrate temperature of 330 K. It revealed few isolated dislocations. The boundaries included in the film were non-coincidence high angle (marked H in Fig. 6),low angle (L) grain boundaries and twin boundaries (t). The grain boundaries did not have a thermal equilibrium configuration, i.e., they were neither straight nor of regular shape at the triple point,

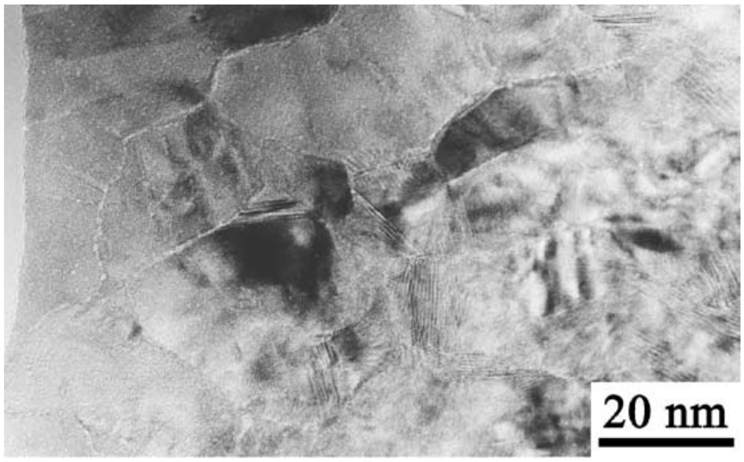

Figure 5 Plan view of the iridium film deposited at the substrate temperature of 330 K, which was obtained from the area close to the surface of the film (1.5 μm apart from the substrate).

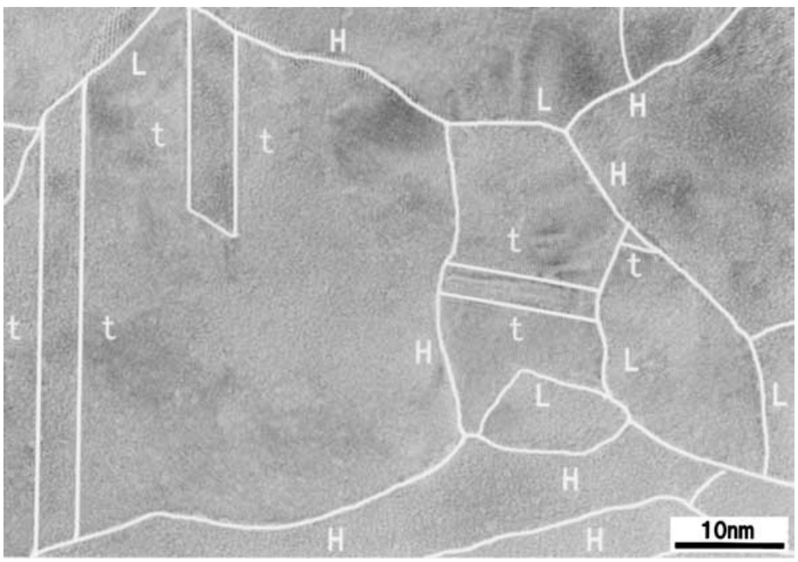

Figure 6 Plan view of iridium film deposited at the substrate temperature of 330 K, showing the grain boundary configuration. H, L, and t indicate high angle, low angle and twin boundaries, respectively.

though the configuration of grains at the early stage is more complicated than that observed near the end surface of the deposit. Even though the twin boundaries were straight and formed by the (111) planes of iridium, microscopically, they seemed to be curved and include large steps. It should be noted that the grains observed in Fig. 6 indicated mostly [110] directions, though some grains with different orientations were embedded in the grains with the [110] orientation. This means that the area having common orientations of grains was formed during film growth.

In the plan view of the sample, orientation relationships between grains were observed in the electron diffraction pattern of each grain. Fig. 7 shows an example when the substrate temperature was 330 K. The electron diffraction patterns revealed that the grains had different growth orientations and were distributed around the [111] direction within 20 degrees. Even when the directions of grains were the same, rotation and tilt of the grains were observed. Low angle boundaries and twin boundaries were frequently observed. It should be reiterated that the orientations of grains tended to gather into one direction, the [112] direction in the present case, though some scattering of orientations was observed.

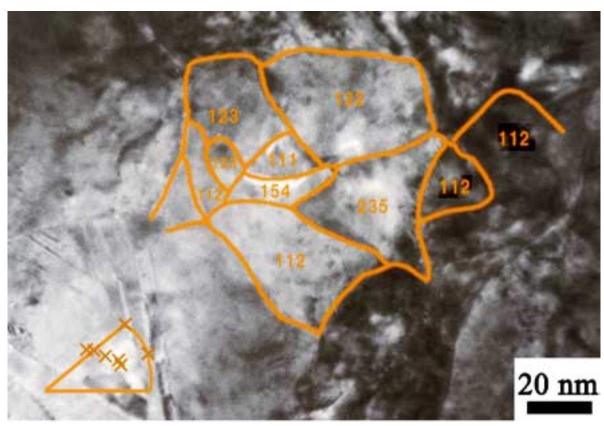

Figure 7 Growth direction of grains in films deposited at the substrate temperature of 330 K.

When the substrate temperature was increased up to 1070 K, the grain growth orientations were randomly distributed, and the fine grain structure of 20 nm in average size was no longer observed. Instead,

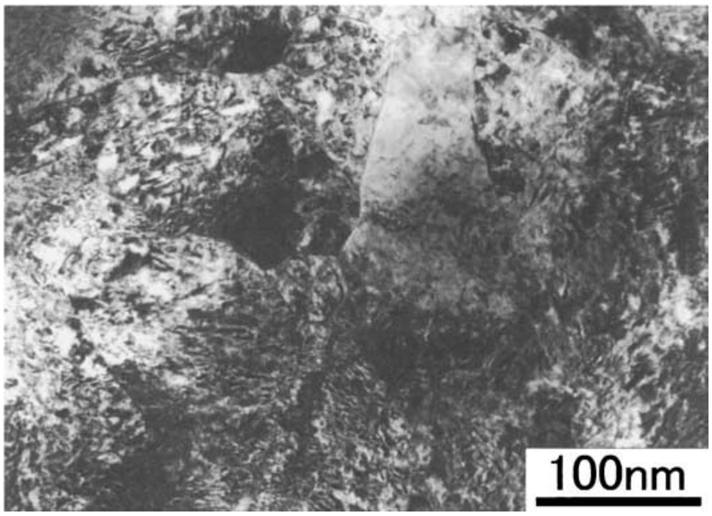

Figure 8 Electron micrograph of Ir film deposited at 1070 K ($T_s/T_m = 0.3$).

large grains of 250 nm in average size were revealed to be embedded with some small grains, as shown in Fig. 8. These results showed that substrate heating during deposition increased the grain size of the iridium film, but that the columnar structure still remained though the density between columns was high. The average grain size of 250 nm observed in the present experiment. The deposited film contained grain boundaries, twin boundaries, voids and dislocations. Grain boundaries were straight and the triple point of grains seemed to have a thermal equilibrium configuration.

4. Conclusions

Iridium films were deposited on isotropic graphite by the rf magnetron sputtering method and examined by transmission electron microscopy.

1. At low substrate temperature ($T_s/T_m = 0.11$), iridium grains were distributed between 5 to 50 nm in size. A columnar structure was developed just above the substrate and an average aspect ratio of a grain was larger than 5.

2. Grain boundaries were wavy in the growth direction and included voids. Growth direction of grains was almost perpendicular to the substrate, but grains elongated in a 20 degrees declined direction from the perpendicular direction to the substrate were observed. Grains forming the columnar structure have different orientations of growth direction, though growth orientations of grains are distributed around the [111] direction, which is the preferred orientation. The orientation relationship between adjoining grains possessed the relationship with few special orientation, except twin boundaries.

3. Low angle grain boundaries and twin boundaries were frequently observed, but there were few dislocations at the substrate temperature of 330 K.

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