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To cite this article: Jing Shi et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 220 012010

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IOP Conf. Series: Materials Science and Engineering 220 (2017) 012010 doi:10.1088/1757-899X/220/1/012010

The crystal morphology effect of Iridium tris-acetylacetonate on MOCVD iridium coatings

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Abstract. Iridium tris-acetylacetonate is the most commonly used precursor for the metal organic chemical vapour deposition (MOCVD) of iridium coating. In this paper, the crystal morphology effect of iridium tris-acetylacetonate on iridium coatings prepared by MOCVD was studied. Two kinds of Ir(acac)₃ crystalline powder were prepared. A precursor sublimation experiment in a fixed bed reactor and an iridium deposition experiment in a cold-wall atmospheric CVD reactor were designed. It is found that the volatility of the hexagonal columnar crystals is better than that of the tetragonal flake crystals under the experimental conditions. It's due to the hexagonal columnar crystals exposed more crystal faces than the tetragonal flake crystals, increasing its contact area with the transport gas. An adequate supply of iridium tris-acetylacetonate during the pre-deposition period contributed to obtain an iridium coating with a smooth and uniform continuity surface.

1. Introduction

The refractory metal iridium (Ir) is well-known for its superior high-temperature strength and remarkable resistance against different types of corrosions, especially oxidation [1]. This combination of properties makes Ir a potential material for use as protective coatings in high-temperature anaerobic environments [2-5]. Several methods are available in fabricating Ir, such as physical vapour deposition (PVD), plasma spraying (PS) and metal organic chemical vapour deposition (MOCVD). Among these methods, MOCVD is an effective method to prepare high-purity Ir of particular shapes with high density [6].

Several Ir organic molecular compounds have been investigated as precursors for Ir MOCVD process [7-9], among which, iridium tris-acetylacetonate is the most commonly used in Ir deposition studies and preparations. Iridium tris-acetylacetonate (Ir(acac)₃) is an air-stable crystalline powder with a melting point of 265 $^{\circ}$ C and a decomposition temperature of 290 $^{\circ}$ C. The decomposition products of Ir(acac)₃ are CO₂, H₂O and other non-toxic gas, which will not corrode metal substrate and operating equipment. These characteristics of this Ir complexes effectively lower the demands for apparatus and increase the ease of operation during the MOCVD process.

Although there are some seemingly advantages of $Ir(acac)_3$ as being the precursor for Ir MOCVD process, yet only several studies have been reported, much less on the effect of crystal morphology of $Ir(acac)_3$ crystals on iridium coatings prepared by MOCVD. In this work, two kinds of $Ir(acac)_3$ crystalline powder were prepared. A precursor sublimation experiment in a fixed bed reactor and an iridium deposition experiment in a cold-wall atmospheric CVD reactor were designed to find out the relationship between the deposition and precursor.

2. Experimental

Ir(acac)₃ crystalline powder in different shapes were prepared in anhydrous ethanol and methylene chloride, respectively. The anhydrous ethanol solution with the concentration of 2g/100mL was prepared at the boiling point of anhydrous ethanol, and crystallized at 0°C, 10°C, 20°C, 30°C for 30min, adding magneton with a speed of 200r/min, 400r/min, 600r/min, 800r/min or ultrasound with a frequency of 40Hz, 60Hz, 80Hz, 100Hz. The methylene chloride solution with the concentration of 1g/8mL was prepared at 20°C and crystallized at 20°C by volatilization method or -60°C by low temperature cooling method for 30min, respectively. The Ir(acac)₃ crystalline powder was collected from the solution by filtering, and dried in a vacuum oven at 80°C for 4 hours. The morphology of the Ir(acac)₃ crystalline powder was observed via scanning electron microscopy (SEM) (Hitachi S-4800), accelerating voltage of 20 keV.

The evaporation of $Ir(acac)_3$ crystalline powder in different shapes was tested prior to deposition in a fixed bed reactor. Defined amount of $Ir(acac)_3$ crystalline powder and SiC sand was weighed via electronic balance (Hengzheng, FA2004N) and mixed uniformly, put into the fixed bed reactor, which was heated at 255°C. Stopped heating every 10min to weigh the mass of the mixture, draw the curve of the loss of the $Ir(acac)_3$ and time.

Iridium coatings were deposited onto the $\Phi6\times25$ polycrystalline molybdenum substrates, in a coldwall CVD reactor under atmospheric pressure. The set-up is illustrated in Figure 1. Ir(acac)₃ was evenly heated and controlled using a high-temperature quartz valve. The substrate was vertically suspended in the reactor and heated via a high-frequency induction heating (Xi'anTianfeng, IGPS-30KW-200KHz). The temperature of the substrate was measured using an infrared thermometer (Xi'an Innocent, ATS). The flow rate of Ar (99.999 wt.%) was determined using an electronic massflow meter (Beijing Sevenstar, D07). Iridium coatings were deposited using Ir(acac)₃ as the precursor at 480 °C to 520 °C under 1.96×103 Pa Ir(acac)₃ partial pressure. The morphology of the coatings was observed via scanning electron microscopy (SEM) mentioned above.



3. Results and discussion

*3.1. Shape of the Ir(acac)*₃ *crystalline powder*

Figure 2 shows SEM image of morphology of $Ir(acac)_3$ crystalline powder at different temperatures in anhydrous ethanol system. The average size of particles in this experimental group was 300µm-500µm. The particles crystallized at 0°C, 10°C, 20°C were coarse and broken, with poor crystal development integrity and obvious layered growth morphology, hardly to see the complete crystalline face, while the particles crystallized at 30°C had better crystal development integrity and clear crystalline face.

According to previous study [10], the disperse coarse and broken $Ir(acac)_3$ particles can not be evenly heated in the fixed bed reactor, which has great effect on the evaporation of the precursor. A lack supply of the precursor resulted in coating cracks, shedding and other defects in Ir coatings. The

IOP Conf. Series: Materials Science and Engineering 220 (2017) 012010 doi:10.1088/1757-899X/220/1/012010

experiment results demonstrated that the temperature of 30°C is more favorable for the crystallization of the $Ir(acac)_3$ particles in this experimental group.



Figure 2. SEM image of morphology of $Ir(acac)_3$ crystalline powder at different temperatures in anhydrous ethanol system: (a) 0° C, (b) 10° C, (c) 20° C, (d) 30° C.



Figure 3. SEM image of morphology of Ir(acac)₃ crystalline powder at different magneton speeds in anhydrous ethanol system: (a) 200r/min, (b) 400r/min. (c) 600r/min. (d) 800r/min.

Figure 3 shows SEM image of morphology of Ir(acac)₃ crystalline powder at different magneton speeds in anhydrous ethanol system. The average size of particles in this experimental group was 30µm-40µm. The particle size decreases as the magneton speed increases. Most of the particles crystallized at 200r/min were hexagonal columnar crystals, which had good crystal development integrity and complete crystalline face. Some crystals in irregular shape such as rhombus were crystallized at 400r/min, 600r/min and 800r/min. For the consistency of the crystal development integrity and morphology of particles, only when the magnetic speed was 200r/min can obtain most hexagonal columnar crystals.



(b) 300µn

different crystalline powder at ultrasonic frequencies in anhydrous ethanol system: (a) 40Hz, (b) 60Hz, (c) 80Hz, (d) 100Hz.



Figure 4 shows SEM image of morphology of Ir(acac)₃ crystalline powder at different ultrasonic frequencies in anhydrous ethanol system. The average size of particles in this experimental group was 20µm-30µm. The particles in this experimental group were in good crystal development integrity, except the particles crystallized at 100Hz, which had some unformed small particles adhering on the crystals. The addition of ultrasound enhanced the collision of Ir(acac)₃ molecules, which accelerated the nucleation of the $Ir(acac)_3$ crystals, but made it difficult for the particles to grow in a stable environment, causing the crystalline powder finally obtained was very fine. This fine crystalline powder was easy to adhere to the wall of the MOCVD equipment, which was not conducive to the evaporation of precursor.

Above all, the anhydrous ethanol solution with the concentration of 2g/100mL prepared at the boiling point of anhydrous ethanol and crystallized at 30°C for 30min at 200r/min, was chosen to obtain the hexagonal columnar crystals with good crystal development integrity and regular shape.

Figure 5 shows SEM image of morphology of Ir(acac)₃ crystalline powder at different temperatures in methylene chloride system. The particles crystallized in this experimental group were all tetragonal flake crystals, but the particles crystallized at 20°C by volatilization method was much bigger than those crystallized at -60°C by low temperature cooling method. The size of the particles crystallized at 20° C were not in the same order of magnitude with that of the particles obtained in anhydrous ethanol system, so we chose the particles crystallized at -60° C as precursor in Ir MOCVD process.

3.2. Volatility of the $Ir(acac)_3$ crystalline powder

Figure 6 shows a curve of volatility of the Ir(acac)₃ crystalline powder in different shapes. The loss of Ir(acac)₃ and time were in a good linear relationship for both of the hexagonal columnar crystals and the tetragonal flake crystals, the sublimation rate of hexagonal columnar crystals was 0.0342g/min, the sublimation rate of tetragonal flake crystals was 0.0265g/min. It is found that the volatility of the hexagonal columnar crystals is better than that of the tetragonal flake crystals under the experimental conditions. The volatility of $Ir(acac)_3$ is related to its properties, sublimation temperature and mass transfer area. In this experimental condition, the properties and sublimation temperature was consistent for both samples. It's due to the hexagonal columnar crystals exposed more crystal faces than the tetragonal flake crystals, increasing its contact area with the transport gas.



Figure 6. A curve of volatility of the $Ir(acac)_3$ shapes: crystalline powder in different (a) hexagonal columnar crystals, (b) tetragonal flake crystals.



70

80

90

3.3. Surface morphology of the Ir coatings

Figure 7 shows XRD spectrum of iridium coating prepared of Ir(acac)₃ crystalline powder in different shapes. The Ir coatings both showed (111) preferred growth.

Figure 8 shows SEM image of surface morphology of Ir coating prepared of Ir(acac)₃ crystalline powder in different shapes. The surface of the Ir coating was consisted of many cellular protrusions, whose diameter was 10µm-40µm measured by intercept method. There was no crack or hole in the Ir coating prepared of hexagonal columnar crystals, with a smooth and uniform continuity surface. While there was obvious cracks between the cellular protrusions in the Ir coating prepared of tetragonal flake crystals.

IOP Conf. Series: Materials Science and Engineering 220 (2017) 012010 doi:10.1088/1757-899X/220/1/012010



Figure 8. SEM image of surface morphology of Ir coating prepared of $Ir(acac)_3$ crystalline powder in different shapes: (a) hexagonal columnar crystals (b) tetragonal flake crystals.

The growth of the Ir coating in MOCVD progress followed the island growth mechanism. The lateral spreading of the islands allowed continuous growth of the iridium coating, and the vertical spreading of the islands increased the thickness of the iridium coating. The sublimation rate of the tetragonal flake crystals was smaller than that of hexagonal columnar crystals in the first 20 min of heating in Figure 6, which lead to the insufficient supply of precursor during the pre-deposition period. The Ir coating deposited in initial period was uneven and the stress presented in the Ir coating grew subsequently resulted in the crack on the surface of Ir coating eventually. Thus, it's better to use hexagonal columnar crystals of $Ir(acac)_3$, which has a better volatility as precursor in Ir MOCVD process.

4. Conclusions

1. The anhydrous ethanol solution with the concentration of 2g/100mL was prepared at the boiling point of anhydrous ethanol, and crystallized at 30 °C for 30min at 200r/min to obtain the hexagonal columnar crystals. The methylene chloride solution with the concentration of 1g/8mL was prepared at 20 °C and crystallized at -60 °C for 30min to obtain the tetragonal flake crystals.

2. The sublimation rate of hexagonal columnar crystals was 0.0342g/min, and the sublimation rate of tetragonal flake crystals was 0.0265g/min. The volatility of the hexagonal columnar crystals is better than that of the tetragonal flake crystals under the experimental conditions. It's due to the hexagonal columnar crystals exposed more crystal faces than the tetragonal flake crystals, increasing its contact area with the transport gas.

3. The Ir coating prepared from the hexagonal columnar crystals of $Ir(acac)_3$ had a smooth and uniform continuity surface, while the Ir coating prepared from the tetragonal flake crystals of $Ir(acac)_3$ had more obvious cracks. Associated with the volatility of the precursor, it's better to use hexagonal columnar crystals of $Ir(acac)_3$ as precursor in Ir MOCVD process.

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