Electron Microscopic Study of Small Particles of Tungsten Oxide Formed by the Evaporation of Tungsten Trioxide*

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Abstract
The formation, composition and shapes of small particles of tungsten oxide, which are formed by the evaporation of tungsten trioxide (WO\textsubscript{3}) powder onto silicon monoxide substrate film at various air pressures, are investigated with a transmission electron microscope. WO\textsubscript{3} crystals of about 0.15 to 0.015 \textmu m in diameter are formed on the substrate film at air pressures of 101.3 to 1.3 kPa, and the size of the crystals becomes smaller with decreasing air pressure. If the air pressure is lower than 1.3 kPa, the evaporated tungsten oxide is liquid in the gas phase and condenses as amorphous particles of 50 Å diameter on the substrate films. At an air pressure of 1.3 to 0.13 Pa, tungsten oxide drops are formed on the substrate monoxide film and become hemispherical or flat truncated-sphere-shaped particles when the diameters are smaller or larger than about 700 Å respectively. The drops condensed on the substrate are heated in various vacua and it is noted that the drops contain much smaller amounts of oxygen than do WO\textsubscript{2} crystals.

1. Introduction
It has been reported by one of the present authors (Hashimoto, Naika, Mannami & Fujita, 1959; Hashimoto, Kumao, Etoh & Fujiwara, 1970; Hashimoto, Kumao, Etoh, Fujiwara & Maeda, 1970) that drops are often formed on the tips and surfaces of minute tungsten oxide whiskers while they are growing and play an important role in the crystal growth process. But the formation conditions and composition of the drops have not yet been studied in detail.

The formation of drops during crystal growth was studied also in molybdenum oxide (Yoda, 1960) and the chemical composition of the drops was found to be MoO\textsubscript{4} (Yano, 1975). The growth mechanism of a crystal by the aid of drops was named the DG (drop growth) mechanism. Takagi (1957) observed spheres attached to iron oxide whiskers, which seemed to be formed by the solidification of drops. Similar observations were reported by Webb & Forgeng (1957) and Edward & Happel (1962). Wagner & Ellis (1964, 1963) observed by the optical microscopic method that the drops at the tips of Si whiskers contributed to the growth of the whiskers and called this the VLS (vapor liquid solid) mechanism. This mechanism is essentially the same as the DG mechanism. Thereafter, many similar observations have been carried out (Nittono & Nagakura, 1969; Edward & Huang, 1966; Patrick, Hamilton & Choyke, 1966; Ryan, Berman, Marshall, Considine & Hawley, 1967; Derjaguin, Fedossev, Lukyanovich, Spitzin, Ryadov & Lavrentyev, 1968; Ellis, Farsch & Zetterstrom, 1968; Wagner & Doherty, 1968; Ishii & Hashimoto, 1969). In this report, using an electron microscope and the diffraction method, the present authors have studied the formation conditions and composition of drops of tungsten oxide, which seem to be rather important in clarifying the growth mechanism of tungsten oxide needle crystals grown from the drops.

2. Experimental procedures
Tungsten oxide powder of purity 99.99% was evaporated in various air pressures at various temperatures. The evaporation was carried out by using an alumina-coated tungsten basket in a conventional vacuum evaporation apparatus. The temperature of the basket was measured by a thermocouple attached to it and monitored by recording the temperature continuously. The evaporated tungsten oxide was collected on the silicon oxide films with supporting platinum grids which were set at 60 and 30 mm from the evaporation source by manipulating a shutter from outside the vacuum when the temperature of the basket reached 1370 K. It took about 80 s to reach this temperature, and 60 s to collect a suitable amount of sample on the substrate films after opening the shutter. The temperature of the substrate film went up to several tens of degrees higher than room temperature during the exposure to the evaporation source and decreased somewhat after closing the shutter; this was measured...
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by a thermocouple with a recorder which was attached to the platinum grid.

Six levels of air pressure were used in the work chamber, viz 101 \times 10^{3}, 13 \times 10^{2}, 13 \times 10^{2}, 1.3 \times 10^{2}, 1.3 and 0.13 Pa. A mercury manometer and MacLeod gauge were used to measure the air pressures. The variation of the pressure in the work chamber due to out-gassing during evaporation was negligible at pressures higher than 13.3 Pa, but the total pressure in the chamber became 2.7 and 1.1 Pa at air pressures of 1.3 and 0.13 Pa, respectively, in the final stages of evaporation. The temperature of the mesh was also changed in the final stage of evaporation by the heat radiation; the mesh reached 320 K at a pressure of 1.3 Pa. After removal from the work chamber, the samples were placed in a JEM-6A electron microscope and photographed at a magnification of 10,000 times at 100 kV.

3. Experimental results

Fig. 1(a), (b), (c) and (d) shows the electron microscopic images of the samples evaporated at a temperature of 1370 K at pressures of 101 \times 10^{3}, 13 \times 10^{2}, 13 \times 10^{2}, and 1.3 \times 10^{2} Pa respectively and (a'), (b'), (c') and (d') are the corresponding electron diffraction patterns. As can be seen in Figs. 1(a) and (b), the mean diameters of the particles produced at air pressures of 101 and 13 kPa are about 0.15 and 0.06 \mu m respectively and have a regular crystal habit, which is much more pronounced at 101 kPa than at 13 kPa. As shown in the corresponding diffraction patterns in Fig. 1(a') and (b'), the particles are found to be crystals of \( \alpha \)-tungsten oxide (monoclinic, WO\(_{3}\)). Some diffraction spots are enlarged in Fig. 1(a'') to show the fine structures due to the refraction effect of the electrons in the wedge-shaped crystals. As can be seen in Fig. 1(c) and (d), the particle sizes at 13 \times 10^{2} and 1.3 \times 10^{2} Pa are about 150 and 50 \AA respectively and corresponding diffraction patterns in (c') and (d') show continuous rings and halos respectively. The halo pattern suggests that the small particles are amorphous or consist of very small crystals. The micrographs (Fig. 1) indicate that the size of the evaporated particles becomes smaller as the air pressure decreases.

When the basket was heated in an air pressure of 1.3 Pa, circular particles were formed on the substrate, and denuded areas occurred around these particles (Fig. 2). As can be seen in Fig. 2, around a large particle A, a large denuded area B is formed, and around a small particle C, a small denuded area occurs. Some particles 0.2 \mu m in diameter are uniformly transparent to the electron beam, suggesting that the particles are amorphous, others are not homogeneous, but contain minute black spots (Fig. 3). Fig. 3(a), (b) and (c) shows, respectively, the bright-field and dark-field images; and the corresponding electron diffraction pattern of a large particle containing minute spots. Since the dark-field image corresponding to a part of the diffraction rings in (c) shows that the dark spots appear bright, it is seen that the dark spots in the particles are small crystals. It may be concluded that the transparent regions in the bright-field image of the particles are amorphous. The amorphous region seems to be formed by the rapid cooling of liquid particles. This supposition is not contradicted by the easy migration of small particles in Fig. 2, i.e. the small drops form in the gas phase, deposit onto the substrate film and then coagulate to various

![Fig. 1. Electron micrographs and the corresponding electron diffraction pattern of tungsten oxide particles produced at various air pressures: (a), (a') at 101 kPa; (b), (b') at 13.3 kPa; (c), (c') at 1.3 kPa; and (d), (d') at 0.13 kPa. Evaporation temperature and collecting position were 1370 K and 60 mm, respectively. (a') shows the split spots which are enlarged from a part of the diffraction pattern in (a').]
sizes of droplets of liquid by rapid migration. These liquid droplets are cooled rapidly and then become amorphous. The lattice spacings of the small crystals and relative intensities of the diffraction rings in Fig. 3(c) are given in Table 1. Some spacings in Table 1 are the same as those observed previously (Hashimoto, Kumao, Etoh & Fujiwara, 1970) in the drops at the tips of \( \gamma \)-tungsten oxide needles. Therefore, it can be concluded that the small crystals in the drops are the same as those at the tips of needles. Although there are twice as many diffraction rings as observed previously, it is still difficult to estimate the atomic structure of the small crystals. At the present moment, no known tungsten oxide crystal structures can explain the diffraction rings satisfactorily. Fig. 4 is the image of the specimens formed at a distance of 30 mm in a vacuum of 0.13 Pa. Here, most of the particles have distorted spherical shapes with some tails, as if they were liquid.

**Table 1. Lattice spacings (Å) measured from the diffraction pattern in Fig. 3(c)**

<table>
<thead>
<tr>
<th>Lattice spacing</th>
<th>Relative intensity</th>
</tr>
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<tbody>
<tr>
<td>2.97 ± 0.03</td>
<td>v.s.</td>
</tr>
<tr>
<td>2.03 ± 0.02</td>
<td>w</td>
</tr>
<tr>
<td>1.64 ± 0.02</td>
<td>s</td>
</tr>
<tr>
<td>1.45 ± 0.01</td>
<td>w</td>
</tr>
<tr>
<td>1.29 ± 0.02</td>
<td>w</td>
</tr>
<tr>
<td>1.17 ± 0.01</td>
<td>w</td>
</tr>
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**4. Discussion**

4.1 *The formation mechanism of small crystals and drop-shaped particles*

As shown in Fig. 1, if the air pressure is higher than...
13.3 kPa, the evaporated particles of tungsten oxide become large perfect crystals of about 0.1 μm in diameter, but at an air pressure lower than 1.3 kPa small crystals of about 100 Å diameter are formed. The difference in size of formed particles can be explained as follows. In the gas with high air pressure, evaporated oxide particles (ions and neutral molecules) remain for a relatively long time in the gas as a result of collisions with molecules of residual air, and therefore have many chances to collide and combine with oxygen gas and oxide particles. The length of time a particle remains in the gas phase and the degree of oxidation seem to be proportional to the air pressure and therefore large crystals which are completely oxidized are formed at higher air pressures. But at low air pressure, the time particles remain in the gas phase becomes small and therefore the particle size and degree of oxidation are small. As shown and discussed already, these spherical particles with low oxygen content are liquid in the gas phase and become amorphous on the substrate film.

4.2 Growth mechanism and morphology of drops on the substrate film

As can be seen in Fig. 2, large denuded areas are formed around the large drops on the substrate film and small denuded areas occur around the small drops. From this observation the three-dimensional shape and the mechanism of growth of drops on the surface of the substrate film can be inferred as follows. Let $R$ and $r$ be the radii of the denuded area and of the drop respectively as shown in Fig. 5(a). If it is assumed that the material which is uniformly accumulated on the substrate becomes drops of volume $V$ by leaving equivalent denuded areas around them,

$$V = Sd = k\pi r^n,$$

where $S$ is the area of the denuded area and is given by $S = \pi R^2$, $d$ is the thickness of uniformly accumulated material and $n$ is an integer, which takes the values 2 and 3 when the drops become circular plates and hemispheres or truncated spheres respectively. $k$ is the shape constant and corresponds to the thickness for plate-shaped drops and to $\frac{2}{3}$ for perfect hemispherical drops. Since (1) can be written

$$\log S = n \log r + \log k\pi/d,$$

$n$ can be determined from the gradient of double logarithmic plots of $S$ versus $r$. The denuded area $S$ and
the radius of drops \( r \) have been measured from Fig. 2 and plotted in Fig. 5(b). In Fig. 5(b), two straight lines whose gradients are 2 and 3 are superimposed. It seems to be reasonable to conclude that the measured values appear on a slightly bent line with gradients between 2 and 3. These values suggest that the small drops have the shapes of hemispheres or truncated spheres with nearly round tops and the large drops have those with slightly flat tops as shown in Fig. 5(c). The shapes of hemispheres and truncated spheres of the drops are dependent on the wetting angle on the substrate and the temperatures of the substrate and the drops. An example of the distorted shapes of the drops is seen in Fig. 4, which was obtained at a high drop temperature.

If it is assumed that the measured values are close to the two lines indicated in Fig. 5(b), \( k \) can be deduced to be 619 Å for \( n=2 \) and 0.6 (=1.8/3) Å, for \( n=3 \) respectively by substituting \( d = 30 \) Å and the measured values \( S \) and \( r \) in the \( n=2 \) and \( n=3 \) regions into equation (2). If it is assumed further that the small drops are hemispheres and large drops are plates, the radius of the drop \( r \) at the transition point from \( n=2 \) to \( n=3 \) is equal to the thickness of the circular plate \( k \). The measured radius \( r \) in Fig. 5(b) of the drops at the transition point is about 700 Å, which corresponds to the calculated value 619 Å. Consequently the shapes of the drops are considered to be as shown schematically in Fig. 5(c).

4.3 Composition of drops

As discussed already the oxygen content of the specimen formed in an air pressure lower than 1.3 Pa seems to be small. In order to confirm the low content of oxygen in the drops, the drops formed on the silicon oxide substrate films were heated by an electric furnace after being sealed off into glass tubes at various air pressures. After heat treatment, the specimens were taken out from the glass tube, and observed in an electron microscope. When the drops were heated in a vacuum lower than 0.13 Pa, the drops did not change at all (Fig. 6), but in air pressure above 1.3 kPa, the drops become oxide crystals of \( \gamma \)-type (WO\(_3\)) and \( \alpha \)-type (WO\(_3\)), and in very few cases \( \delta \)-type (WO\(_2\)) crystals were formed (Fig. 7). The above observations suggest that the drops contain very small amounts of oxygen, less than WO\(_2\) crystals.

5. Conclusions

The growth process, composition and shapes of small particles of tungsten oxide formed on the silicon oxide substrate by the evaporation of tungsten trioxide powder in various air pressures have been studied in a JEM-6A transmission electron microscope. In air pressures of 101.3 to 1.3 kPa, tungsten trioxide crystals of about 0.15 to 0.015 \( \mu \)m have been formed. In air pressures of 1.3 \times 10^4 to 1.3 Pa, coagulated amorphous particles of 50 Å diameter have been formed. In 1-3 to 0.13 Pa, hemispherical and circular-plate-shaped particles of 100 to 2000 Å diameter have been formed. In air pressure lower than 1.3 kPa, evaporated tungsten oxide is considered to be liquid in the gas phase and becomes solid on the surface of the substrate.

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References


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