Synthesis of Metastable or Non-Equilibrium-Phased Oxides by the Mist CVD method

by

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This paper reviews a previously reported paper published in the Journal of the Society of Materials Science, Japan (Vol. 68, No.10, pp.733-738(2019)). The original paper describes the specific growth mechanism of metastable oxides using the mist CVD technique, and is of great usefulness for growing them with this technique, which requires relatively low growth temperatures and normal pressures. Metastable oxides have been gaining increasing attention for their unique and excellent physical characteristics. The Mist CVD technique is a key to synthesizing a wide variety of metastable materials efficiently.

Key words: Metastable, Non-equilibrium, High-entropy, Oxide, Artificial mineral, Mist CVD, Corundum

1 Introduction

The synthesis of metastable or non-equilibrium crystals that do not exist easily in nature and the development of their physical properties are greatly significant because they often have the power to develop technology drastically. Many of the compounds that exist in the metastable phase and non-equilibrium state have attractive physical properties, and many of them have not been evaluated for their physical properties in detail. On the other hand, high-pressure and high-temperature conditions are often indispensable for synthesizing these compounds, and it takes a lot of energy and time to prepare samples. In the conventional crystal growth method, mass synthesis of samples is extremely difficult. Developing new synthetic routes for these metastable materials under lower energy conditions is an important key to discovering their unrevealed physical properties. The mist chemical vapor deposition (CVD) method is one of the great candidates for a new synthetic route.

2 Properties of the mist CVD method

In the mist CVD method1) the whole process is performed under normal pressure with open air conditions. It does not require gas replacement or evacuation in the equipment (Figure 1) and yet it can realize dense crystal growth. Fig. 2(a) is the surface SEM image of a three-dimensional structure with nanometer-order pores3). It can be confirmed that the three-dimensional structure has an average pore diameter of about 300 nm and a relatively uniform distribution of pore diameters. Gallium oxide (Ga2O3) was fabricated on the structure using the mist CVD method. In Fig. 2(b), the Ga2O3 thin film is uniformly formed around the pores of the structure, the average pore size is reduced to about 150 nm, and the pore size distribution is as uniform as before the film formation. Ga2O3 grew with excellent wraparound and as a result, crystals were fabricated in three-dimensional parts including the back side of the structure. In this way, mist CVD method can realize high step-coverage growth not only on a flat surface but also on a complicated structure: for example, a porous three-dimensional structure with nanometer-order pores, a flat body with a complicated uneven shape such as a stainless separator used for polymer electrolyte fuel cells4), and for an indwelling stent (Fig. 3).

3 Growth of metastable oxides by mist CVD

The synthesis of metastable α-Ga2O3 had been hard work. For example, α-Ga2O3 microcrystal is obtained by exposing β-Ga2O3, which is stable phase of Ga2O3 powder, to 44 kbars (= 4.4 GPa), 1000 °C under high pressure and high temperature6). In 2008, our laboratory synthesized α-Ga2O3 thin films on sapphire substrates under lower temperature conditions of 470 °C at normal pressure using the mist CVD technique5). This is the first time that a metastable phase of α-Ga2O3 has been obtained by a small thermal energy of 470 °C at normal pressure.

Then using mist CVD, metastable phases of α-In2O37), α-V2O38), α-Rh2O39), and their alloy crystals with α-Ga2O38)-10) and α-Ir2O311),12) were obtained. In addition, it has become possible to prepare oxides with different valences under these conditions, for example, Fe2O3 and Fe3O413), SnO214), and SnO15).

In the growth of metastable phased compounds by the mist CVD method, the choice of crystal shape of substrates is crucial. For example, metastable phased corundum-structured oxides (α-M2O3 M=Ga, In, V, Rh, Ir) were fabricated on sapphire (α-Al2O3) substrates having the same crystal structure of corundum.

Fig.1 Schematic image of hot-wall-type mist CVD equipment.

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4 Control of crystal structures in the mist CVD method

Fig. 2 Surface SEM images of nanoporous structures (a) before fabrication of α-Ga2O3 thin film and (b) after fabrication.1

(a) Stable phase

(b) Metastable phase

Fig. 4 XRD profiles of stable phase In2O3 on YSZ (111) substrate and metastable phase α-In2O3 on α-Fe2O3 buffer layer and α-Al2O3 (0001) substrate.8

4.1 Control of the thin film crystal structure by crystal shape of the substrate

Indium oxide (In2O3) has two structures, a cubic bixbyite structure that is a thermally stable phase (c-In2O3) and a trigonal corundum structure that is a metastable phase (α-In2O3). In the mist CVD method, c-In2O3 and α-In2O3 can be obtained on a YSZ (111) substrate at 450 °C and a hematite (α-Fe2O3) buffer thin film can be grown on a c-plane sapphire (α-Al2O3) substrate at 600 °C, respectively. The α-Fe2O3 buffer layer was introduced for reducing the lattice mismatch in the a-axis direction from 15% (α-In2O3 / α-Al2O3) to 9% (α-In2O3 / α-Fe2O3) at the interfaces. Fig. 4 shows the X-ray profile of each thin film on YSZ (111)(a) and α-Fe2O3/α-Al2O3(b) substrates, respectively. In2O3, which is a stable phase with the same cubic bixbyite structure, grew on the cubic YSZ substrate, and metastable phase α-In2O3, which has the same crystal structure, grew on α-Fe2O3, which has a corundum structure. The crystal shape of thin films was strongly affected by the shape of underlying crystal and growth temperature.

Similarly, in Ga2O3, the α-type and β-type crystal forms can be controlled by selecting the growth substrate.16 When growing a stable phase β-Ga2O3 thin film on hetero-structured crystal, a c-plane α-Al2O3 substrate is often used because the arrangement of O atoms is similar on the β-Ga2O3 (201) plane and the α-Al2O3 (0001) plane. However, in the mist CVD method, the α-Ga2O3 thin film grows on c-plane α-Al2O3 substrate preferentially below the phase transition temperature (600 °C).16 Therefore, a cubic yttria-stabilized zirconia (YSZ) substrate is used. In YSZ, the arrangement of O atoms on the (111) plane and the β-Ga2O3 (201) plane is close, and the crystal growth of the β-Ga2O3 thin film using the YSZ (111) substrate has been reported in previous studies17. Fig. 5 shows the X-ray profile of the thin film prepared on each substrate of YSZ(a) and α-Al2O3(b). On the YSZ substrate, at a growth temperature of 500 °C it became amorphous and no peak was confirmed, but at
of crystal structures in the mist CVD method

Fig. 2 Surface SEM images of nanoporous structures (a) before and (b) after fabrication.

Fig. 3 A photograph of a stent covered with oxide thin film fabricated using an 

Fig. 4 XRD profiles of stable phase In_2O_3 on YSZ (111) substrate and metastable phase 

600 °C, an orthorhombic β-Ga_2O_3 grew. On the other hand, it was shown that a metastable phase α-Ga_2O_3 was fabricated on the α-Al_2O_3 substrate at 500 °C. By the mist CVD method, β-Ga_2O_3 grows on the β-Ga_2O_3 substrate at a growth temperature of 700 °C or higher, which is due to the effect of homoepitaxial growth, and β-Ga_2O_3 is a stable phase at 700 °C or higher.

4.2 Mechanical stress from the substrate

In a fabrication of α-Ga_2O_3 on α-Al_2O_3, there is a large lattice mismatch in the a-axis direction of 4.8%. It is expected that α-Ga_2O_3 crystal continues to be stressed from the substrate. A cross-section observation was performed at the α-Ga_2O_3/α-Al_2O_3 interface with a transmission electron microscope (TEM). Fig. 7 (a) is the observation image. When observed from the [1120] direction, a clear periodic structure is confirmed along the [1100] direction at the α-Ga_2O_3/α-Al_2O_3 interface. This is due to the compressive and tensile stresses received by the α-Ga_2O_3 thin film and the α-Al_2O_3 substrate due to a large lattice mismatch. The length of this periodic structure per cycle is 8.6 nm, which is the length of 20 pieces of α-Ga_2O_3 crystal lattices in the [1100] direction (1 piece = 0.43 nm) and 21 pieces of α-Al_2O_3 crystal lattice (1 piece = 0.41 nm). It is almost the least common multiple of both numbers of 0.43 and 0.41. Fig. 7 (b) shows the observation image when the crystal zone axis is set to [1120] which is the vertical direction of Fig. 7 (a). At the α-Ga_2O_3/α-Al_2O_3 interface, a periodic structure is confirmed along the [1120] direction. The length per cycle is 5.0 nm, which is the length of 20 α-Ga_2O_3 crystal lattices (1 piece = 0.249 nm) and 21 α-Al_2O_3 crystal lattices in the [1120] direction. (1 piece = 0.238 nm), which is also the least common multiple of both numbers. In the two-beam condition observations, edge dislocation lines are mainly confirmed in α-Ga_2O_3 crystal and it is expected that an extra half-plane of α-Al_2O_3 is introduced at the interface. These cross-sectional TEM images are very similar to the domain epitaxy proposed by Narayan et al. In ZnO / α-Al_2O_3, etc. 20.

In the system of α-Ga_2O_3/α-Al_2O_3 with large lattice mismatches, one of the reasons the metastable α-Ga_2O_3 thin film occurs is the continuous mechanical stress during crystal growth from the α-Al_2O_3 substrate. On the other hand, α-Ga_2O_3 and α-Fe_2O_3, which grow on the c-plane α-Al_2O_3 substrate, contain a few percent of the rotational domain in the in-plane direction. This is because the mechanical binding force from the substrate works strongly, the crystal grows dominantly in the three-dimensional direction or the c-axis direction, and many columnar crystals with a trigonal corundum structure grow like columnar nodes in petrology. Further, it is suggested that the crystals may be bonded in the two-dimensional direction during the growth process. From the cross-section TEM images of the α-(Ga_0.56Fe_0.44)O alloy crystal grown on the α-Al_2O_3 substrate, columnar structures were observed along the c-axis. This suggests that crystal growth along the c-axis direction is dominant. On the other hand, in the planar TEM image of the sample, a structure like the surface of a columnar structure is observed, but the interface between the structures is unclear. This indicates that crystal growth also occurs in the two-dimensional (planar) direction.

4.3 Growth characteristic of the mist CVD method.

The dense crystal growth is possible in mist CVD; it is inferred that the interaction between atoms is more likely to occur between the thin film and the substrate than with other
crystal growth methods. During crystal growth, the crystals of the base substrate and that of the thin film form atomic bonds, but their binding energy is very small compared to the driving energy in crystal growth. However, mist CVD growth requires lower growth energy than the conventional ones, and the energy of the atomic bond, that is the mechanical stress acting on both layers, play an important role. In conventional crystal growth equipment, the crystal phase of the thin film was determined by the growth temperature and pressure, but in the case of the mist CVD method, the crystal structure of the substrate has a great influence on the crystal shape of the thin film.

As described above, the mist CVD method has many differences from the conventional crystal growth method, and it is presumed that it includes a mechanism that makes it easy to synthesize a metastable phase qualitatively. However, the quantitative evaluation and elucidation of the mechanism are insufficient, and its growth process should be quantitatively elucidated by in-situ crystal growth observation and evaluation, and time-resolved structural evaluation during crystal growth.

5 Conclusion

The mist CVD method is a powerful way to synthesize metastable phase or non-equilibrium oxides easily. Since it is non-vacuum and uses relatively low temperatures, the mechanical stress from the substrate works strongly on the thin film and its crystal structure is fixed in the similar or same shape as the substrate. In the future, it is highly expected that this mechanism will be applied to produce compounds that can only otherwise exist through synthesis at high temperature and high pressure.

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