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The influence of total pressure in the reactor and carrier gas on the chemical vapor deposition of Al from tri-isobutyl aluminum

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The influence of total pressure in the chamber and carrier gases on the chemical vapor deposition of aluminum using tri-isobutyl aluminum was studied. The superior penetrability of chemical vapor deposition is expected to make it effective for aluminum deposition onto complex-shaped materials such as turbo-charger rotors, fibrous preform, and multifilament. It may also be a suitable method for the development of fiber-reinforced composite materials. The apparatus was composed of a raw material gas supply system, a three-zone electric furnace, a reaction chamber, an auto pressure controller, and an exhaust system. Aluminum was deposited onto a graphite fiber in the quartz reactor. The results show that, in the diffusion rate-determining stage of aluminum thermal decomposition, the rate of deposition for aluminum shows a marked increase as the pressure increases; in contrast, in the reaction rate-determining stage, this tendency is limited. This can be explained by the fact that, as the total pressure decreases, the gas diffusion coefficient becomes larger, and there is an increase in the uniformity of film formation. On the other hand, as the carrier gas flow rate increases, the amount of raw material supplied increases; consequently, a higher rate of deposition is obtained. Moreover, in the diffusion rate-determining stage, there is a tendency for an increase in flow rate to elevate the probability of arrival of the raw material, and, in combination with high temperatures, for nucleus generation to be accelerated and the average diameter of aluminum granules to become smaller. In the reaction rate-determining stage, there appears to be hardly any dependency of granule diameter on the flow rate. When Ar or He is used as the carrier gas, under the same conditions argon, rather than helium, is seen to increase the rate of deposition.

I. INTRODUCTION

Almost all papers on aluminum metallizing using organic aluminum have focused either on chemical vapor deposition (CVD) in a system at normal pressure (1 atm), as represented by the studies of Pierson[1] and Malazgirt and Evans[2], or on low-pressure CVD in the range of less than 10^2 Pa (1 Torr), as found in the reports of Cooke *et al.*,[3] Levy *et al.*,[4] and Schmaderer *et al.*[5] There have been virtually no papers focusing on the intermediate region between these two, that is, CVD under reduced pressures, from the 10^2 Pa to the 10^2 KPa level. However, it can be thought that the conditions under reduced pressures are also worthy of research, from the perspectives of film formation unity[6] and the rates of film formation. Research into this area would make possible the systematization of aluminum deposition by means of CVD, especially the rates and film formation, it can be expected that the superior penetrability of CVD makes it effective for aluminum deposition onto complex shapes such as turbo-charger rotors, fibrous preform, and multifilament, and it may also be a suitable method for fundamental research on fiber-reinforced composite materials.

Conditions for the thermal decomposition of tri-isobutyl aluminum and the morphology of the deposited Al have been reported previously.[7–10] In this paper, the influence of total pressure in the chamber, and carrier gases on the thermal decomposition of aluminum under reduced pressure, using tri-isobutyl aluminum, is described.

II. EXPERIMENTAL PROCEDURE

A. CVD apparatus and materials

The apparatus provided for the experiments was composed of a raw material gas supply system, a three-zone electric furnace in which the uniformly heated zone was 300 mm, a thermal decomposition chamber, an auto pressure control (APC) system, and an exhaust system. Further details will be omitted here because they have been described in previous papers.[7–10,11] Figure 1 shows details of the reaction chamber and the holder. Ar

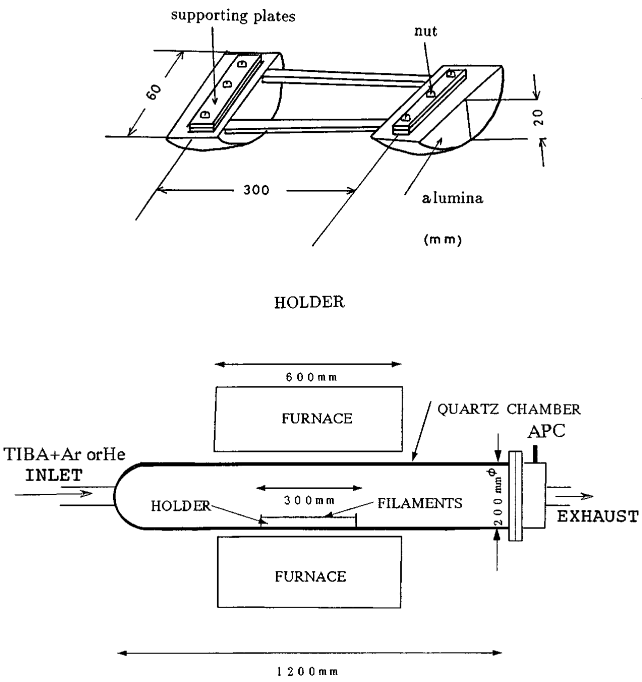

FIG. 1. Schematic diagrams of the reaction chamber and the holder for chemical vapor deposition.

(boiling point 87.1 K, specific gravity 1.783, 99.9995% pure, containing less than 0.5 ppm of O_2 and less than 5 ppm of H_2O) or He (boiling point 4.1 K, specific gravity 0.1785, 99.9999% pure, containing less than 0.05% O_2) was used as the carrier gas. The organic aluminum used as the raw material was tri-isobutyl aluminum [TIBA: Al $(i\text{-}C_4H_9)_3$] (95.7% pure, molecular weight 198.33, specific gravity 0.787) (Alpha Co.).

B. Method

After setting graphite filaments (10 μm in diameter each) on an alumina holder inside the reaction chamber, a vacuum pump was used to evacuate the chamber to approximately 0.1 Pa, and then the carrier gas was introduced. The temperature and total pressure in the chamber and the temperature of the evaporator were set for the individual conditions of each experiment. Because the vapor pressure for TIBA is approximately 1333 Pa at 363 K and 133 Pa at 323 K, the evaporation temperature (Tv) was set between 313 K and 373 K.[8] Also, because thermal decomposition of TIBA occurs at 530 K and higher,[9] the deposition temperature (Td) was made to vary between 523 K and 673 K. The temperature of the path between the evaporator and the reaction chamber was kept at 363 K. When it was determined that the conditions had reached equilibrium, TIBA evaporation was carried out for a unit of time, and Al was deposited onto the filaments.

The grain size and film thickness of the deposited aluminum were observed with a scanning electron microscope (Akashi MSM-6). For structural analysis, an x-ray diffraction apparatus (Rigaku Denki GRX-RAD3C) was used.

C. Preliminary study on deposition rate of Al and the Al structure

The deposition rate (Rd) as estimated from the mean thickness of Al films deposited in an area of uniform deposition (i.e., 300 mm in length at Tv = 373 K). As shown in Fig. 2, the length of the area of uniform deposition depends on the Tv and Td. Here, the evaporation rate of TIBA under 1330 Pa was 5 × 10^{-6} mol/s at Tv = 333 K, 1 × 10^{-5} mol/s at 353 K, and 2.2 × 10^{-5} mol/s at 373 K, respectively.[8,9] The length reached 300 mm at Tv = 373 K for a wide variety of Td. Figure 3 shows the x-ray diffraction spectrum of the deposited Al at Td = 673 K, Pd = 1330 Pa, and F =7 ml. It was clarified that a crystalline Al was deposited under these conditions.

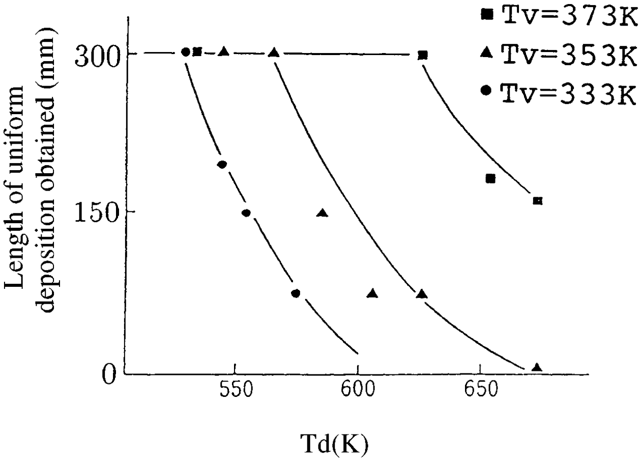

FIG. 2. Change in length of area of uniform deposition with deposition temperature (Td) and evaporation temperature (Tv).

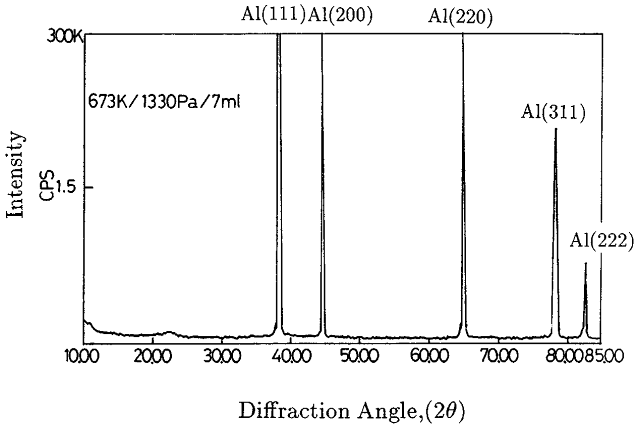

FIG. 3. X-ray spectrum and assignment of Al thermally decomposed from tri-isobutyl aluminum onto a substrate at Td = 673 K, Pd = 1330 Pa, and F = 7 ml.

III. RESULTS AND DISCUSSION

A. Rate-determining steps for the chemical vapor deposition of Al from TIBA

An approximate value for the activation energy for the decomposition of TIBA onto graphite fiber has been deduced from a plot of the deposition rate (*Rd*) of aluminum against reciprocal temperature ($1/Td$) in an Arrhenius plot, Fig. 4. The deposition rate is limited by the transport of TIBA to the surface at temperatures higher than 580 K. The activation energy obtained from this experiment was 95 kJ/mol, which is close to the range 100–130 kJ/mol given by Cooke *et al.*[3] However, this is somewhat higher than the figure of 53 kJ/mol given by Malazgirt and Evans.[2] However, according to Smith and Wartik, the activation of energy for the breaking of aluminum-ethyl bonds in TEA is 120 kJ/mol.[12] Moreover, Bent *et al.* have explained that the chemical vapor deposition of aluminum from tri-isobutyl aluminum is limited by beta-hydride elimination.[13] Figure 4 suggests that the range from 580 K t 630 K is the diffusion rate-determining step, and at more than 630 K gas decomposition will occur.

B. Influence of the total pressure

Figure 5 indicates the relationship between the total pressure in the reaction chamber (*Pd*) and the deposition rate (*Rd*) of aluminum, when the deposition temperature ($Td = 553$ K or $Td = 623$ K) and the carrier gas flow rate ($F = 7$ ml/s STP) were both fixed. These results indicate that, in the diffusion rate-determining stage, the rate of deposition for aluminum shows a marked increase as the pressure increases; in contrast, in the reaction rate-determining stage, this tendency is limited. From this it can be inferred that, to carry out aluminum deposition at a high *Rd*, the *Pd* should be increased in the diffusion rate-determining stage. However, with an increase in *Rd*, coarsening of the crystalline granules occurs,[7,8] and it becomes difficult to obtain the fine polycrystalline layer that would be regarded as favorable film structure for deposition. Figure 6 shows the morphology of Al for the cases of *Pd* of 133 Pa (=1 Torr) and 66.5 KPa (=500 Torr) (in both cases, $Td = 623$ K, $F = 7.0$ ml/s). It is evident that, with a Pd of 133 Pa, deposition is comparatively smooth, with deposited aluminum crystalline granules of approximately 1 μm; in contrast, at 66.5 KPa, deposition occurs in nodule-shaped granules with a diameter of approximately 5 μm.

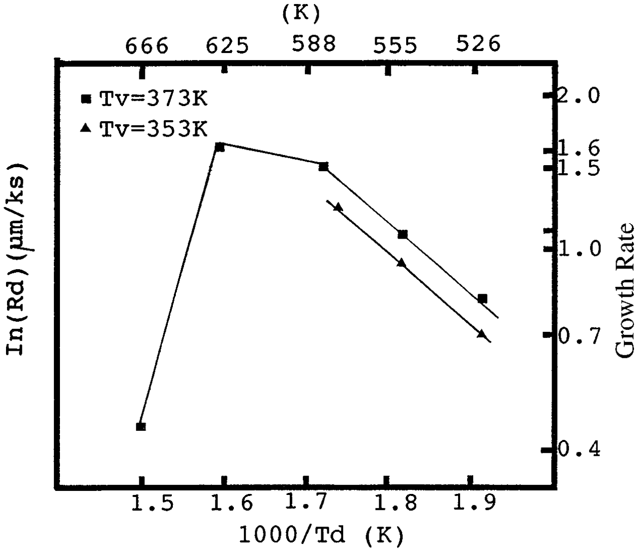

FIG. 4. Deposition rate variation with reciprocal growth temperature ($1/Td$), the evaporation temperature (Tv) of Al from tri-isobutyl aluminum.

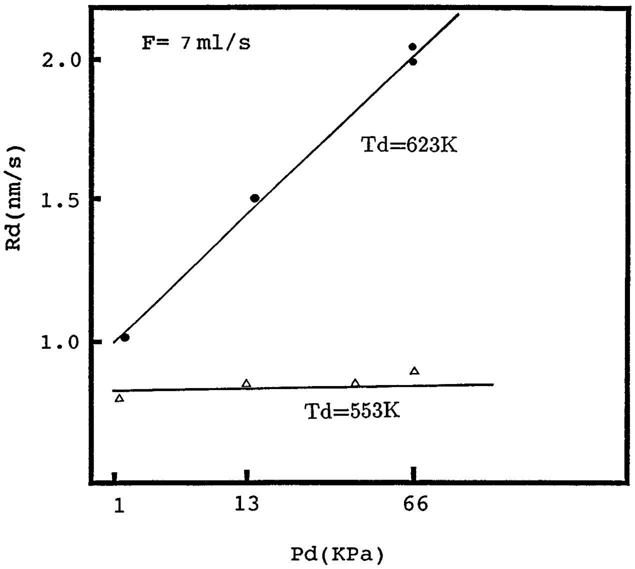

FIG. 5. Change in the deposition rate (*Rd*) of Al with the total pressure (*Pd*) at $Td = 553$ K or $Td = 623$ K under *F* 7 ml/s.

In the diffusion rate-determining stage, with an increase in pressure, the average diameter of the aluminum granules becomes greater, and along with this, irregularities in the surface of the deposition layer become more acute. In the reaction rate-determining stage, granule diameter shows almost no dependency on the pressure. With a reduction in pressure, the deposited aluminum layer becomes flat and smooth, and deposition uniformity also improves. It can be said that the total pressure (*Pd*) should be low to obtain uniform micropolycrystalline aluminum.

This tendency can be explained with a quasi-experimental formula[15,16] for the temperature and pressure dependency of the diffusion coefficient *D* for group III materials, as follows:

$$D = D_0\left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)^b . \qquad (1)$$

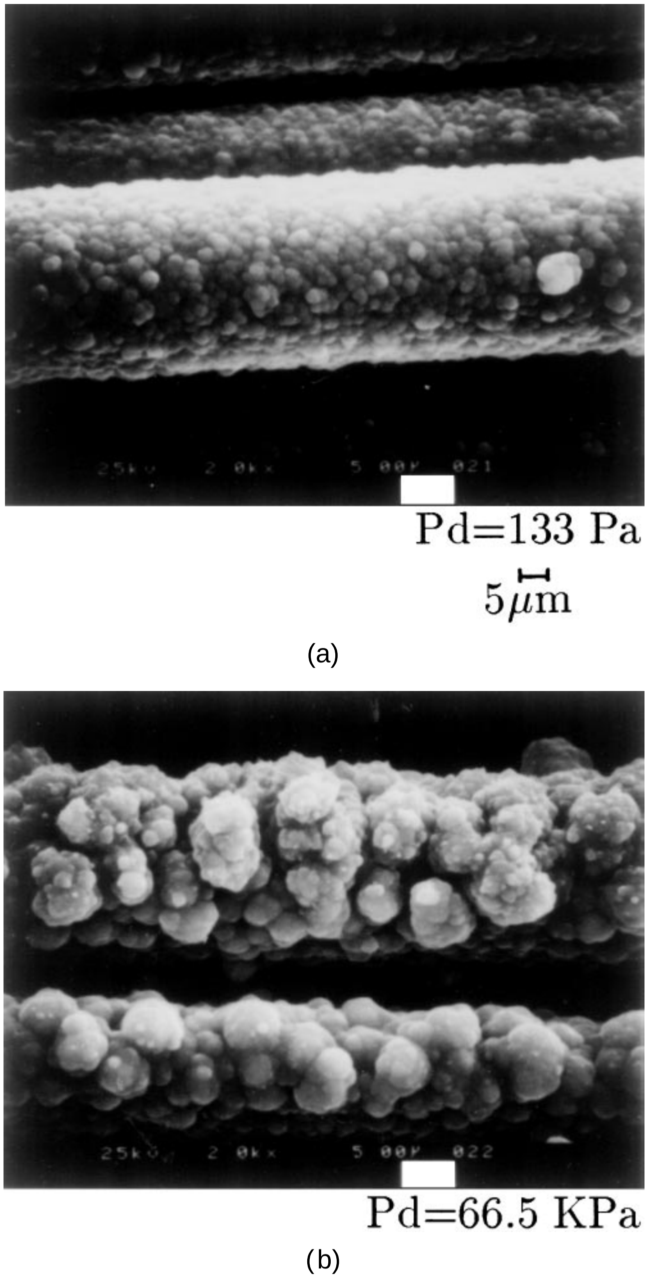

FIG. 6. Scanning electron micrographs of Al deposition on graphite fiber. (a) $Pd = 133$ Pa, $Td = 623$ K, $F = 7$ ml/s; (b) $Pd = 66.5$ KPa, $Td = 623$ K, $F = 7$ ml/s.

Here b is 1.82–1.88 in the case of a nonpolar gas, and the diffusion coefficient D_0, deposition reaction pressure P_0, and deposition temperature T_0 are fixed. That is, as the deposition reaction pressure decreases, the gas diffusion coefficient becomes larger, and there is an increase in the uniformity of film formation.

C. Flow rate of carrier gas

From the preceding section, it is clear that a low total pressure (Pd) incurs a decrease n the aluminum deposition rate (Rd). Accordingly, an experiment was carried out on increasing the carrier gas flow rate as a means to elevate the Rd. Figure 7 shows the relationship between deposition rates (Rd) and flow rates (F). In the diffusion rate-determining stage, at $Pd = 1330$ Pa and $Td = 623$ K, an increase in the flow rate (F) of the carrier gas causes an increase in the Rd. At a fixed rate of carrier gas flow, an increase in the total pressure results in an increase in the amount of raw material conveyed to the reaction chamber. The increase in raw material density elevates the degree of saturation inside the reaction chamber, resulting in an elevation in the rate of deposition. The same tendency is also apparent at other pressures. Regarding the effect of the gas velocity and density on the deposition, Ghandi and Field[14] have shown that the growth rate of films in diffusion rate-determination is proportionate to the stream velocity of the gas which traverses the boundary layer[15] and diffuses over the surface. The growth rate also depends on the thickness of the boundary layer which is formed on the substrate surface. The thickness of the boundary layer formed on the substrate surface is determined by the free stream velocity. However, with respect to the conditions for these experiments, flow rate controls that are sufficient to cause significant change in the thickness of the so-called boundary layer were not exercised.

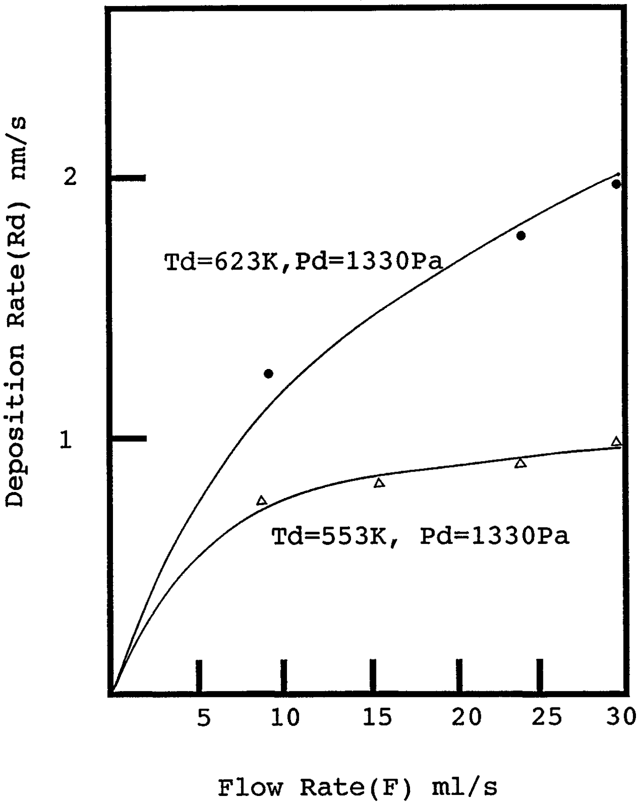

FIG. 7. Change in the deposition rate (Rd) of Al with Ar flow rate (F) at $Td = 553$ K, $Pd = 1330$ Pa or $Td = 623$ K, $Pd = 1330$ Pa.

Consequently, it can be thought that the amount of raw material supply increased because of the increase in carrier gas flow rate, and the result was a higher rate of deposition.

Figure 8 shows the relationship between flow rate and the granule diameter of deposited aluminum. In the diffusion rate-determining stage, there is a tendency for an increase in flow rate to elevate the probability of arrival of the raw material, and, in combination with high temperatures, for nucleus generation to be accelerated and the average diameter of aluminum granules to become smaller. On the other hand, in the reaction rate-determining stage, there appears to be hardly any dependency of granule diameter on flow rate.

D. Difference in the types of carrier gas

It can be expected that changing the type of carrier gas will cause a change in the diffusion rate of the raw material gas onto the substrate, and affect deposition rates and deposition forms. The use of argon and helium as carrier gases was compared for the reaction rate-determining stage at $Td = 570$ K and the diffusion rate-determining stage at $Td = 623$ K, $Pd = 1330$ Pa, 13.3 KPa, $F = 7$ ml/s. Figure 9 shows the aluminum deposition rates against the flow rates for each gas.

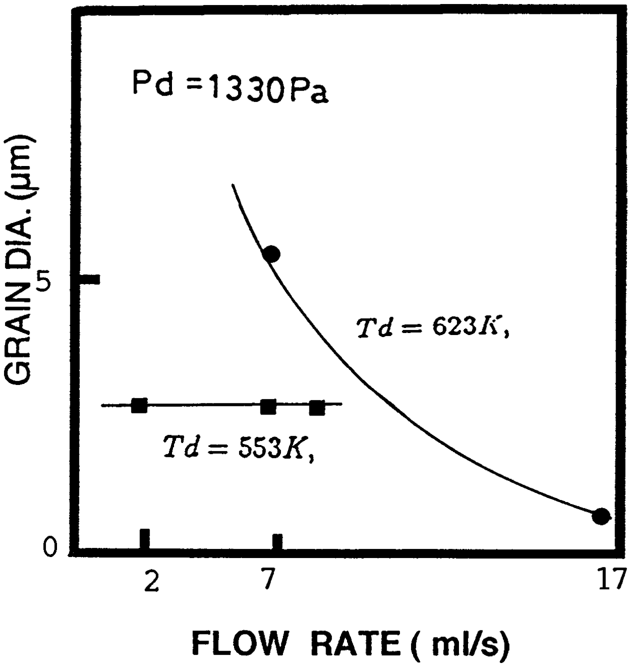

FIG. 8. Change in the grain diameter of deposited Al with Ar flow rate at $Td = 553$ K, $Pd = 1330$ Pa or $Td = 623$ K, $Pd = 1330$ Pa.

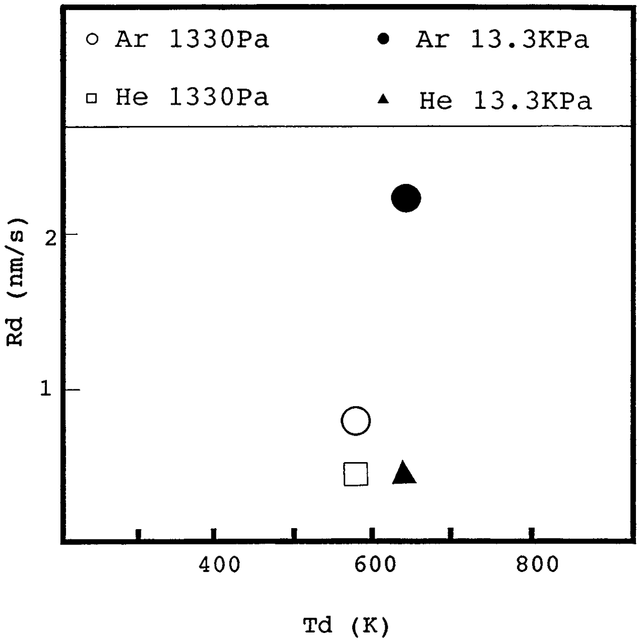

FIG. 9. Change in the deposition rate (Rd) of Al with Ar flow or He flow at $Pd = 1330$ Pa or $Pd = 13.3$ KPa.

For both Ar and He, there was seen to be a tendency for deposition rates to increase when there was an increase in flow rate, and, at the same flow rate, for deposition rates to increase with higher total pressure. On the other hand, if the change in deposition rates caused by a difference in the carrier gas is compared, evidently deposition rates for Ar are higher than those for He. Here let us compare the values for the physical properties of Ar and He.[16] The values for viscosity are analogous, with 38.4 m poise (at 623 K) for Ar and 30.9 m poise (at 623 K) for He; however, the specific gravity of Ar is 1.78, whereas that of He is only 0.178. The thickness (μm) of the boundary layer of the laminar flow, which is located parallel to the stream of gas inside a level reaction chamber which is 1200 mm long and 600 mm in diameter, is represented by the following formula.[10] At the same flow rate, Ar with its greater density has a thinner laminar flow boundary layer than He.

$$\delta = \sqrt{\frac{x}{Re}}\,, \tag{2}$$

$$Re = VL/\nu\,, \tag{3}$$

$$\mu/\rho = \nu\,. \tag{4}$$

In this case, μ = viscosity, ρ = density, V = free stream velocity, Re = Reynold's number, ν = kinetic viscosity, L = shape factor, and x = distance from leading edge.

Here, if the rate of mass transfer toward the substrate is determined to be J, J can be expressed as the following formula[17]:

$$J = \frac{D(p^* - p^i)}{\mathrm{R}T\delta}\,. \tag{5}$$

In this case, D is diffusion coefficient of the constituent, p^* is vapor phase density of the constituent, and p^i is density at the gas-solid interface.

Based on the results of calculations for δ, if the rate of mass transfer is said to be J_{Ar} is used as the carrier gas and J_{He} when He is used, then the value of $J_{\mathrm{Ar}}/J_{\mathrm{He}}$ is approximately three. Here, if the aluminum deposition rate is thought to be proportionate to J (that is, at diffusion rate-determination), it should be possible, under the same conditions, to deposit aluminum three times as fast by using Ar. The results of these experiments, which are at diffusion rate-determination, also indicate the same thing.

In the case of Ar, the conditions to obtain a 1–2 μm fine micropolycrystalline aluminum layer at a deposition temperature of 583 K included $Pd = 1.3$ KPa; in contrast, with the same flow rate, the figure for He was ten times greater, i.e., 13 KPa. To investigate the reason for this, the Re values for both were sought, and it was found that the values were roughly equivalent. From this it can be inferred that, for stream forms with equivalent Reynold's number, even if the type of gas varies, an approximately similar deposition form will be obtained.

IV. CONCLUSION

The influence of the total pressure in the reaction chamber and the carrier gas on the chemical vapor deposition of aluminum from Tri-isobutyl aluminum was studied. The deposition rates were determined by the transport of TIBA to the substrate surface at temperatures higher than 580 K. In the diffusion rate-determining stage, the rate of deposition for aluminum shows a marked increase as the pressure increases. In contrast, in the reaction rate-determining stage ($<$580 K), this tendency is limited. Also, with an increase in total pressure, the average granule diameter of the deposited aluminum becomes greater. This can be explained by the fact that, as the deposition reaction pressure decreases, the gas diffusion coefficient becomes larger, and there is an increase in the uniformity of film formation.

On the other hand, as the carrier gas flow rate increases, the amount of raw material supplied increases, and consequently a higher rate of deposition is obtained. Moreover, in the diffusion rate-determining stage, there is a tendency for an increase in flow rate to elevate the probability of arrival of the raw material, and, in combination with high temperatures, for nucleus generation to be accelerated and the average diameter of aluminum granules to become smaller. In the reaction rate-determining stage, there appeared to be hardly any dependency of granule diameter on flow rate.

When argon or helium is used as the carrier gas, under the same conditions argon, rather than helium, is seen to increase the rate of deposition. If the aluminum deposition rate is thought to be proportional to the rate of mass transfer toward the substrate J (that is, at diffusion rate-determination), it should be possible, under the same conditions, to deposit aluminum three times as fast by using Ar.

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