Chemical Vapor Deposition of Al_2O_3 Thin Films under Reduced Pressures

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ABSTRACT

Al_2O_3 thin films were deposited by reduced-pressure CVD using aluminum tri-isopropoxide as a source. The dependence of the growth rate on the substrate temperature and the source gas supply was determined. The activation energy of the decomposition reactions was determined to be 18 kcal/mol. The electrical resistivity and the dielectric properties are characterized. The origin of the frequency dispersion in the sample prepared under the surface reaction limited conditions are discussed.

Chemical vapor deposition of amorphous thin films of Al_2O_3 for electron device applications has been reported by Aboaf (1). He obtained dense and etchable amorphous Al_2O_3 films using aluminum tri-isopropoxide [$Al(OC_3H_7)_3$, ATI in the following] as source material at the deposition temperature of 420°C. In his deposition system, the source gas with atmospheric pressure was heated in the quartz tube furnace, so that the deposition process included homogeneous reactions.

CVD-Al_2O_3 films were studied as insulator films for MIS structures of GaAs (2, 3) and InP (4, 5). In the case of Ref. (4), Al_2O_3 films are considered to be deposited through heterogeneous reactions on the substrates, although the authors did not refer to the situation explicitly. They did not report the systematic study of deposition conditions, however.

In this report, Al_2O_3 thin films were deposited through heterogeneous reactions on the substrate under reduced pressure at substrate temperatures below 420°C. The substrate temperature and the source gas supply were varied systematically as the deposition parameters. Their electric properties such as resistivity, dielectric constant, and dielectric loss factor are studied in relation to the deposition conditions.

Experimental

Figure 1 shows the deposition apparatus. The carrier gas is N_2 gas. The bubbler containing ATI is maintained at 120° ± 0.2°C, and the stainless steel pipes and the valves are heated to 130° ± 5°C to avoid the condensation of ATI vapor. The total flow of gases was kept 1000 ml/min throughout the study and the gas flow through the ATI bubbler (referred to as an ATI flow rate in the following) was varied mainly from 50 to 200 ml/min. The ATI bypass line was used in order to settle the bubbling condition before starting the deposition. The reaction chamber was stainless steel and vertical type. The diameter of the substrate holder was 5 cm. The gases blow down onto the heated substrates through a stainless steel mesh diffuser to obtain films with a uniform thickness. The gases were not heated to the cracking temperature before reaching the substrate surface. The reaction chamber was evacuated to a pressure of about 10 torr during deposition throughout the study. The homogeneous reactions can be minimized in the case of reduced-pressure CVD because of low concentration of gas molecules. Moreover, since the gas velocity is increased under the reduced pressure, the gas-phase heating by the substrate heater and gas convection can be largely avoided, which assures also the heterogeneous reactions and uniform gas flow as much as possible.

Silicon wafers and glass plates were used as substrates for the thickness measurement and the electrical properties measurement, respectively. Aluminum was evaporated as an electrode on the glass substrate prior to the Al_2O_3 deposition. The substrate temperature (T_{sub}) was controlled to an accuracy within 0.5°C.

ATI (Nakarai Chemicals Limited) is white, semitransparent, and brittle solid. But once melted, it does not solidify, even if the temperature is lowered to room temperature. The ATI melt is colorless and transparent. The liquid state is maintained for more than 10 days under N_2 atmosphere, but it begins to solidify in a few days if the melt is exposed to the air.

The film thickness was measured on the Si wafer sample by multi-interference microscopy. A part of Al_2O_3 films was etched off by HF, and Al was evaporated on it to obtain high reflectivity. The film thicknesses were usually 1000-2000Å.

Aluminum dots with the area of 0.025 cm² were evaporated on the Al_2O_3/Al/glass structure. The current-voltage

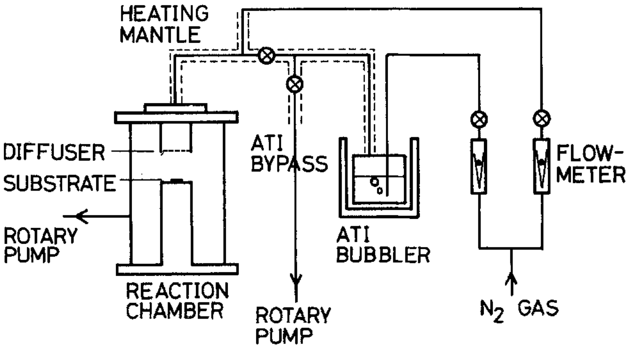

Fig. 1. Deposition apparatus

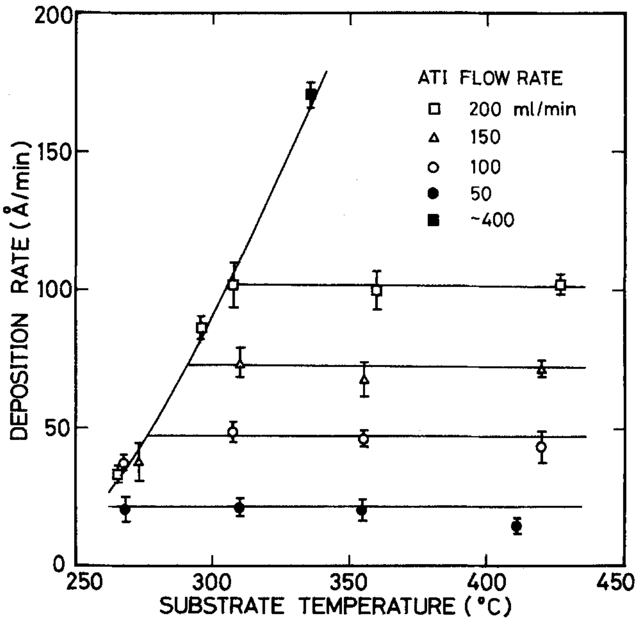

Fig. 2. Dependence of the deposition rate on the substrate temperature and the ATI flow rate. The total gas flow rate is 1000 ml/min and the pressure during deposition is about 10 torr.

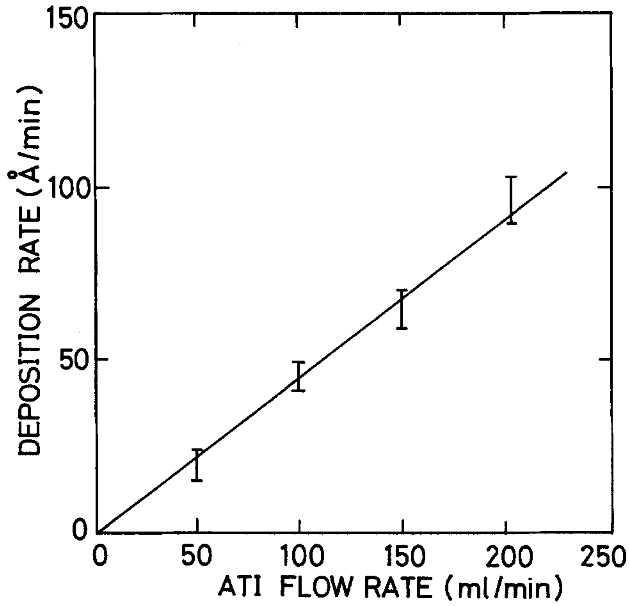

Fig. 3. ATI flow-rate dependence of the deposition rate in the mass-transfer limited region.

characteristics were measured step by step using picoammeter (Toa PM-18R), and the electrical resistivity was calculated from the slope between −0.5 and +0.5V. The current was measured 1 min after applying a voltage. The dielectric properties were measured as a function of the frequency by a universal bridge (120 Hz-10 kHz, Delica 12K) and a capacitance meter (1 MHz, Boonton 72D).

Results and Discussion

Surfaces of the deposited films are mirror smooth on both thin (1000-2000Å) and thick (~1 μm) films, and interference colors are observed clearly on the Si wafer substrates. Thickness was slightly larger at the periphery of the samples. The uniformity of the thickness was within 10% in the sample with dimensions of 20 × 20 mm^2. X-ray diffraction experiments on the thick samples show that all the films deposited in this study are amorphous.

Figure 2 shows the dependence of the deposition rate on the substrate temperature and the ATI flow rate. The deposition rate increases and then saturates as T_{sub} increases at the same ATI flow rate. The saturation values increase with increasing the ATI flow rate. This tendency is similar to the case of usual chemical vapor deposition, that is, the deposition rate is limited by surface reaction at low T_{sub} and is limited by mass transfer (source gas supply) at high T_{sub}. The total gas flow rate and the ATI flow rate are about one order of magnitude smaller than those in the case of Aboaf (1). The lowest T_{sub} for Al_2O_3 deposition is found to be about 250°C. This critical temperature coincides with the results of Aboaf (1) and Tanaka *et al.* (3), but is higher than that after Kobayashi *et al.* (5).

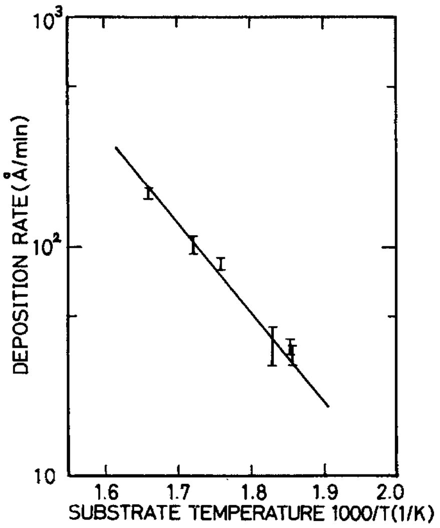

Fig. 4. Arrhenius plot of the deposition rate

Figure 3 shows the ATI flow rate dependence of the deposition rate in the mass-transfer limited region. The deposition rate increases linearly with the ATI flow rate, which is reasonable in the mass-transfer limited region.

Figure 4 shows the Arrhenius plot of the deposition rate in the surface-reaction limited region. The activation energy of the Al_2O_3 deposition was calculated from the slope to be 18.2 kcal/mol.

Figure 5 shows the dc electrical resistivity. The resistivity is in the range between 10^{13} and 10^{15} Ω cm and increases gradually with T_{sub}. The ATI flow-rate dependence was not so clear. These values are sufficiently high for electron device applications such as MIS structures. The time constant of the absorption current increases with decreasing T_{sub}. This fact shows that the samples prepared at low T_{sub} include slowly polarizing centers. The resistivity of these samples shown in Fig. 5 may be estimated slightly lower because the current was measured for all the samples 1 min after the application of voltages.

Figure 6 shows a typical example of the dielectric constant ϵ and the loss factor tan δ as a function of the frequency for the samples prepared in the mass-transfer limited region. The dielectric constant is 8-9 and similar to the data of Aboaf (1). The value of tan δ is 1-2% at low frequencies and increases to 10 kHz. These values are larger than that reported by Aboaf (1). The loss factor tends to decrease at higher T_{sub} and at a lower ATI flow rate, that is, at a slower deposition rate.

Figure 7 shows ϵ and tan δ for the samples prepared at T_{sub} of 265°C and at the ATI flow rate of 100 ml/min, that is, prepared in the surface reaction limited region. Both ϵ

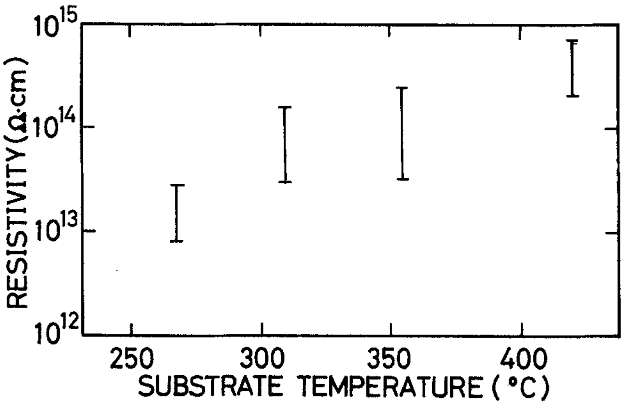

Fig. 5. DC electrical resistivity *vs.* the substrate temperature. The data include samples prepared at different ATI flow rates. The ATI flow rate does not affect the resistivity so much.

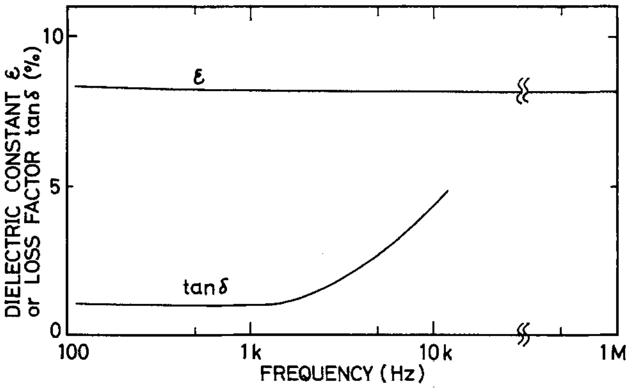

Fig. 6. Frequency dependence of the dielectric constant and the loss factor. The sample was prepared at T_{sub} of 420°C and at the ATI flow rate of 150 ml/min.

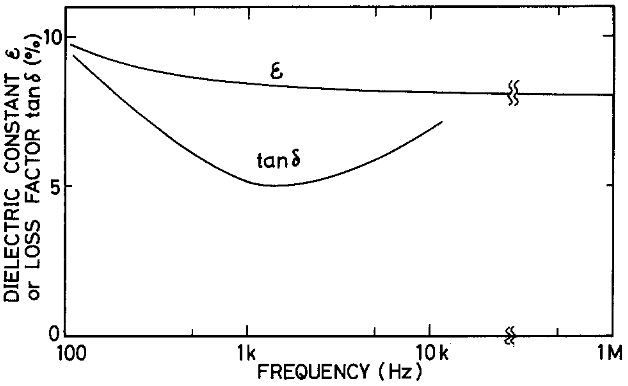

Fig. 7. Frequency dependence of the dielectric constant and the loss factor. The sample was prepared at T_{sub} of 265°C and at the ATI flow rate of 100 ml/min.

and tan δ show a large dispersion at low frequencies, and the value of tan δ is large. This fact shows that these samples include polarization centers whose response time is rather long, which coincides with the results in dc resistivity measurement. Such frequency dispersions have been reported also by Tanaka *et al.* (3). Similar but smaller dispersions were also found for the samples prepared at higher temperatures in the surface reaction limited region. The origin of the increase in tan δ at 10 kHz observed in Fig. 6 and 7 is not clear at this stage.

Kobayashi *et al.* (5) have reported from Auger electron spectroscopic (AES) analysis that CVD-Al_2O_3 films prepared below T_{sub} of 300°C include carbon atoms, which were thought to form organic molecules. In our samples prepared at 265°-355°C, carbon signal was not detected by AES (signal ratio of O/Al was less than 0.015). But signal ratio differs by measuring conditions and is difficult to discuss without comparing the conditions in detail. Therefore, the possibility that such organic molecules contribute to the slow polarization cannot be excluded. And they may also be the origin of rather large values of tan δ. However, since from AES the content of carbon does not seem to increase with lowering the substrate temperature, large frequency dispersion in the samples prepared under the surface-reaction limited region should be attributed to an additional origin. In fact, these films were revealed to be weak under ion beam etching. Such structural weakness, rather than the increase in numbers of molecular centers, seems to enhance polarization at low frequencies and contribute to the large frequency dispersions.

The low temperature deposition reported in this paper is important for III-V and II-VI compound semiconductors to avoid surface degradation at higher temperatures.

Summary

Smooth Al_2O_3 thin films were deposited reproducibly by reduced-pressure CVD through heterogeneous reactions of aluminum tri-isopropoxide. Substrate temperatures (250°-420°C) and source gas supply were systematically varied, and the dependence of the deposition rate on these parameters was determined. From the Arrhenius plot, the activation energy of the decomposition reaction was determined to be 18.2 kcal/mol. DC electrical resistivity is ranged from 10^{13} to 10^{15} Ω cm and increases gradually with the substrate temperature. The dielectric constant and the loss factor are 8-9 and 1-2%, respectively. The samples prepared under surface-reaction limited conditions show frequency dispersions at low frequency, that is, they include slowly polarizing centers. The structural weakness in these samples seems to enhance such polarizations. CVD-Al_2O_3 films reported will be useful for the combination with III-V and II-VI compound semiconductors, whose surfaces tend to degrade at higher temperatures.

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