Technical Note



Effects of Various Atmospheres on the Reduced-Pressure CVD of Al₂O₃ Thin Films at Low Temperatures

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Aluminum oxide (Al_2O_3) is a stable insulator which has several advantages over SiO₂ for semiconductor device applications. An amorphous Al₂O₃ film makes a better barrier to mobile ionic species (Na, etc.). The radiation resistance is higher. Also, the dielectric constant is larger than SiO₂ by a factor of 2. Chemical vapor deposition of Al₂O₃ films using aluminum-tri-isopropoxide [Al(C₃H₇O)₃, ATI in the following] has been reported by Aboaf (1), Duffy *et al.* (2), and these authors (3). Low temperature deposition is desirable if we consider use with semiconductors such as III-V and II-VI compounds whose surfaces are readily deteriorated at high temperatures.

In this paper, we show the effects of various atmospheres $(N_2, N_2 + H_2, N_2 + O_2, \text{ and } N_2 + H_2O)$ on the CVD of Al₂O₃ thin films and on their properties. All gases added to N₂ gas in this study have enhanced the deposition rate at low temperatures.

Experimental

The deposition apparatus was similar to one reported in a previous paper (3) except a new gas inlet of H_2 , O_2 , or H₂O was added to the reaction chamber. The main carrier gas was N₂ gas. The bubbler containing aluminum triisopropoxide (ATI) was kept at $105^{\circ} \pm 0.1^{\circ}$ C, at which the vapor pressure of ATI is about 1.9 torr. The N₂ gas flow rate through the ATI bubbler (ATI flow rate in the following) was kept constant where the deposition rate of 90 Å/min (N₂, N₂ + H₂, and N₂ + O₂ atmosphere) or 25 Å/min (N₂ + H₂O atmosphere) was obtained in the substrate temperature range of mass-transfer limited region (at high temperatures). The total N2 gas flow rate was 1000 ml/min. Hydrogen or oxygen gas was introduced into the reaction chamber at a rate of 100 ml/min. Water vapor was introduced by bubbling N₂ at 20 ml/min through room temperature water. The vapor pressure of water is about 20 torr at room temperature. The reaction chamber was evacuated to a pressure of about 15 torr during deposition.

Silicon wafers and glass plates were used as substrates. The deposition period was 30 min or 1h. The film thickness was measured on the Si substrates by ellipsometry or by its interference color. The thickness ranged from 600 to 2700Å. Refractive indexes were also determined by ellipsometry. For electrical measurements, Al-evaporated glass substrates were used, and gold or aluminum dots (0.017 cm²) were evaporated on the AI_2O_3 films as upper electrodes. Dielectric properties were measured with a digital impedance analyzer (Waynekerr 6425) in the frequency range of 50 Hz-300 kHz.

In our system, Al_2O_3 films are deposited through heterogeneous reaction on the substrate surface, not through homogeneous reaction in the gas phase, as shown in a previous paper (3).

Results and Discussion

Figure 1 shows the temperature dependence of the deposition rate. The deposition rate in N_2 atmosphere decreased steeply as the substrate temperature was lowered. The activation energy of the Al₂O₃ deposition through the thermal decomposition of ATI was 19.1 kcal/mol, which is very close to the previously reported value of 18.2 kcal/mol (3). However, the absolute values of the deposition rate at low temperatures (in the reaction-limited region) were smaller than the previous data. The deposition rates at the low temperatures were confirmed to increase from a trace of impurity gas (probably water vapor) desorbed from the chamber wall or included in the N_2 carrier gas. In $N_2 + H_2$ and $N_2 + O_2$ atmosphere, the deposition rates were similar and they were higher at low temperatures than in N2 atmosphere, while the deposition rates in the mass-transfer limited region were the same as in N2 atmosphere for the same ATI flow rate. The activation energies for $N_2 + H_2$ and $N_2 +$ O_2 atmosphere were smaller than that for N_2 , 3.5 and 4.5 kcal/mol, respectively. The smaller activation energies show that H₂ and O₂ gas may react with ATI so that high deposition rates result at low temperatures. In the report of Aboaf (1), the deposition rate in $N_2 + O_2$ was higher than that in N_2 , and the deposition rate in $N_2 + H_2$ was the same as in N2 atmosphere. Our results are not fully consistent with his results. The fact that the homogeneous reaction in the gas phase played an important role in his process may be a key factor in the discrepancy. Since the heterogeneous reaction on the substrate surface played a major role in our process (3), our data seem to reflect more directly the reaction between ATI and the atmosphere.

 $In N_2 + H_2O$ atmosphere, the apparent deposition rate increased with decreasing substrate temperature as shown



Fig. 1. Temperature dependence of the deposition rate. For N₂, N₂ + H₂, and N₂ + O₂ atmosphere, ATI flow rate corresponds to a deposition rate of 90 Å/min in the mass-transfer limited region. For N₂ + H₂O atmosphere, the ATI flow rate is smaller and corresponds to a deposition rate of 25 Å/min in the mass-transfer limited region. The broken lines represent the deposition rates in the mass-transfer limited region.

J. Electrochem. Soc., Vol. 136, No. 10, October 1989 © The Electrochemical Society, Inc.

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in Fig. 1. However, after heat-treatment at temperatures higher than 500°C, the thickness of these low-temperature deposited films decreased to the same thickness as the films deposited at higher temperatures. It was elucidated from infrared absorption measurements around 3450 cm^{-1} (4) that a large amount of OH was included in these as deposited films and the amount increased with lowering of the substrate temperature. The amount of OH was decreased by the heat-treatment above 500°C. Therefore, the addition of water vapor is effective in fixing Al₂O₃ into a solid film at low temperatures (even at 170°C), but the resulting films are swelled by incorporated OH.

Figure 2 shows examples of the frequency dispersion of the dielectric dissipation factor $(\tan \delta)$. First we discuss the samples prepared in N_2 , $N_2 + H_2$, and $N_2 + O_2$ atmosphere. High temperature (380°C) deposited films show very low $\tan\delta$ (about 0.5%) and small frequency dispersion in each atmosphere. But low-temperature deposited films show large $tan\delta$ and large dispersion toward low frequencies similarly in each atmosphere. The polarization mechanism at such a low frequency is not clear at this stage, but the value of tano at 100 Hz (the lowest frequency in our study) was studied as a measure of the quality of the films in relation to the deposition temperature and the atmosphere. Figure 3 shows the dependence of $\tan\delta$ at 100 Hz on the deposition temperature. Data taken with the Au and Al upper electrodes are plotted. It is found that a deposition temperature higher than 370°C is desirable to obtain high quality films. At low temperatures, the films have large tano values and almost the same dependence on the deposition temperature irrespective of the atmosphere. The addition of H₂ or O₂ did not degrade the loss factor in spite of the increased deposition rate.

The data with the Au and Al counterelectrodes differ significantly at the low deposition temperatures. The fact that the tan δ values at 100 Hz with the Al electrodes are almost constant at low substrate temperatures seems rather peculiar. In this sense, the Au electrode seems to reveal the film quality better than the Al electrode since the tan δ values increase monotonically with lowering the deposition temperature. However, the difference between the data with the Au and Al electrodes are not explained yet in this study.

Figure 2 also shows an example of the frequency dispersion of tan δ of the films deposited in N₂ + H₂O atmosphere. A remarkable feature commonly observed in the films is that a peak in tan δ appeared in rather high frequency range of 100 Hz-10 kHz and the value of tan δ is large even at higher deposition temperatures. It is considered that the structure including a large amount of OH affects the polarization mechanism.

Refractive indexes at a wavelength of 6328Å decreased monotonically with lowering of the deposition temperatures irrespective of the deposition atmospheres. This decrease in the refractive index seems to correspond well to



Fig. 2. Examples of the frequency dispersion of tan $\delta.$ These data were measured with Au upper electrodes.



Fig. 3. Dependence of tan δ at 100 Hz on the deposition temperature for N₂, N₂ + H₂, and N₂ + O₂ atmosphere. Data with the Au and Al upper electrodes are plotted. At 380°C, data with the Al upper electrodes are not shown. The values are slightly smaller than with the Au electrodes.

the monotonic increase in tan δ at 100 Hz measured with the Au electrode. The value of the refractive index for N_2 + H_2 and N_2 + O_2 atmosphere were about 1.54 at 210°C and about 1.65 at 380°C. As the value for N_2 atmosphere was smaller by about 0.02 at each temperature, the addition of H_2 or O_2 improves the film quality. The value for N_2 + H_2O atmosphere was larger by about 0.02 than for N_2 + H_2 atmosphere at each deposition temperature, which may reflect the fact that the films prepared under N_2 + H_2O atmosphere include a large amount of OH species.

Conclusion

We have studied the effect of atmosphere $(N_2, N_2 + H_2,$ $N_2 + O_2$, and $N_2 + H_2O$) on the deposition of Al₂O₃ films by CVD under reduced pressure using Al(C₃H₇O)₃ as a source material. Hydrogen and oxygen enhanced largely the deposition rate at low temperatures. The activation energies for the deposition in N_2 , N_2 + H_2 , and N_2 + O_2 were determined as 19.1, 3.5, and 4.5 kcal/mol, respectively. The dielectric dissipation factor tand was about 0.5% at 380°C and increased with decreasing deposition temperatures almost irrespective of the atmospheres. The addition of H₂ or O₂ did not degrade tano but improved the refractive index, in spite of the increased deposition rate. The film quality prepared at low temperatures under the $N_2 + H_2$ or $N_2 + O_2$ atmosphere was not sufficiently good but may be improved through after heat-treatment. The process of low temperature deposition and high temperature heat-treatment is sometimes useful for the combination of insulating films with III-V or II-VI semiconductors whose surfaces are readily deteriorated at high temperatures. The overlying insulating film may possibly prevent the deterioration of the semiconductor surfaces during the high temperature treatment, even if the bare surfaces of the semiconductors might degrade at the high temperature. In such a case, the increased deposition rates at the low temperatures are advantageous.

Water vapor was more effective in obtaining high deposition rate at low temperatures, but the resultant films included a large amount of OH species and were swelled by the species. Those films showed different dielectric properties from the films deposited in the other atmospheres.

Acknowledgments

This work was supported financially in part by the Grant-in-Aid from the Ministry of Education, Science and Culture of Japan, 63550235 and also by Nippon Sheet Glass Foundation for Materials Science.

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Manuscript submitted Feb. 15, 1989; revised manuscript received June 19, 1989.

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