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Fabrication of Aluminum Oxide Thin Films by Solution-Source Non-Vacuum Process of Mist Chemical Vapor Deposition with Ozone Assistance

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Abstract

Aluminum oxide (AlO_x) thin films were grown by mist CVD, which is based on non-vacuum and energy-saving system configuration with safe solution sources. Discussions are focused on effects of ozone (O_3) for high quality films. With the assistance by O_3, the AlO_x thin films grown at the low temperature of 340°C exhibited breakdown field (E_{BD}) over 8 MV/cm, static dielectric constant (κ_0) over 7, and a dynamic dielectric constant (κ_∞) over 3. It is suggested that O_3 enhances decomposition of OH bonding, which tends to be incorporated in the film, resulting in higher film quality.

1. Introduction

Aluminum oxide (Al_2O_3) is a promising high dielectric constant (high-*k*) material in scaled-down device components and engineering systems in micro- and nano- scale, owing to its wide band gap energy, high breakdown field, and high thermal stability. Also, Al_2O_3 thin films are used for passivation on silicon (Si) surface.

Several deposition processes utilizing vacuum-based equipment, such as sputtering, metal organic chemical vapor deposition[1], plasma-enhanced chemical vapor deposition, and atomic layer deposition[2], have been employed for the controlled fabrication of Al_2O_3 thin films of high quality. On the other hand, safe, energy-saving, and low-cost non-vacuum deposition methods are acknowledged for future green and sustainable industry.

We have investigated the growth of Al_2O_3 thin films by mist chemical vapor deposition (mist CVD). The mist CVD is a non-vacuum fabrication technology with a simple, low cost and environmental friendly system configuration as well as utilizing safe and inexpensive solution sources. Al_2O_3 thin films were grown under the standard condition previously reported[3]. However, the breakdown field (E_{BD}) and dielectric constant (κ) of the AlO_x thin films[a] were not satisfactory for device applications. In this presentation we report the effects of ozone (O_3) assistance, which was expected to improve quality of metal oxide thin films[4], in order to obtain the high-quality AlO_x thin films.

[a] Since the O/Al atomic ratio of the grown film is not always the stoichiometric value (3/2), in this manuscript we denote the chemical formula of aluminum oxide grown in the experiments as AlO_x.

2. Experiments

AlO_x films were grown using a homemade fine-channel mist CVD (FCM-CVD) system as seen in Fig.1. The O_3 line was connected near the reaction chamber. As the source for Al, we used aluminum acetylacetonate diluted in the solution of H_2O:methanol=1:9. The carrier gas was air. The growth was carried out either without O_3 (standard condition; ST) or with the flow of 5000-ppm O_3 in air (O_3 assistance condition; O_3).

In order to evaluate the breakdown field (E_{BD}), AlO_x thin films with the thickness of 50 nm were grown on p^+-Si substrates. For obtaining Fourier transform infrared (FT-IR) spectra and dielectric constant (κ) values, the AlO_x thin films were grown on p^--Si substrates to the thickness of about 200 nm. The breakdown field (E_{BD}) and dielectric constant value (κ) values were evaluated from the current-voltage (*I-V*) and capacitance-voltage (*C-V*) characteristics, respectively.

3. Results and Discussions

Electrical Properties

Breakdown fields (E_{BD}) and dielectric constants (κ) of the AlO_x thin films are shown in Figs.2 and 3, respectively. The AlO_x thin films grown at temperatures above 400°C under the standard condition (ST) exhibited a breakdown field (E_{BD}) over 6 MV/cm, a static dielectric constant (κ_0) over 6, and a dynamic dielectric constant (κ_∞) around 3. On the other hand, the AlO_x thin films grown at temperatures above 340°C at the O_3 assistance condition (O_3) exhibited a breakdown field (E_{BD}) over 8 MV/cm, a static dielectric constant (κ_0) over 7, and a dynamic dielectric constant (κ_∞) over 3, which were the better for the AlO_x thin films grown at 400°C at the standard condition. It is verified that high quality AlO_x thin films can be obtained with assistance of O_3 and O_3 contributes to lower the growth temperature for the fabrication of high quality films from 400 to 340°C.

Chemical Structures

Chemical structure, that is, bonding configurations in AlO_x films were evaluated from FT-IR spectra in order to find the clue for the degradation of breakdown field (E_{BD}). The typical spectra for AlO_x thin films grown at temperatures of 300, 350, and 400°C, are shown in Fig.4. At the standard condition, shown in (a), the broad peak at around 3300cm^{-1} which is assigned to stretching vibrations of OH bonding in (Al)O-H is apparently seen for the AlO_x thin films grown at 300 and 350°C. This peek is not seen for the film grown at 400°C, which exhibits reasonable electrical properties. At the O_3 assistance condition, shown in (b), the broad peak assigned to the stretching vibrations of OH bonding is seen in the AlO_x thin films grown at 300°C. the peak is negligible for e films grown at 350 and 400°C.

The above results suggest that residual OH bonding exists in the AlO_x thin films grown at low temperatures, causing the low breakdown field (E_{BD}). It is thought that O_3 contributes to enhance decomposition of OH bonding even at the lower growth temperature, such as 350°C. This seems to be a reason for the formation of AlO_x thin films with higher quality at lower temperatures by the O_3 assistance.

Al_2O_x/InGaZnO Thin Films and Transistors

Bottom-gate thin film transistors were fabricated by successive mist CVD growth of InGaZnO and Al_2O_x films at 360 and 350°C, respectively. Reasonable device operation, as shown in Fig.5, proofs the potential of mist CVD for actual device applications.

4. Conclusions

Mist CVD with O_3 assistance is found to be a promising method for the growth of AlO_x thin films at lower temperatures with simple and energy-saving system configuration with safe and inexpensive sources. The reasonable insulating properties obtained at the growth temperature of 340°C encourage the marked contribution of most CVD for a variety of device processes

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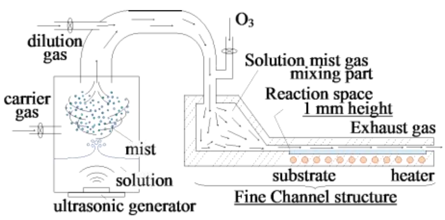

Fig.1 The schematic image of fine channel (FC) type mist CVD system

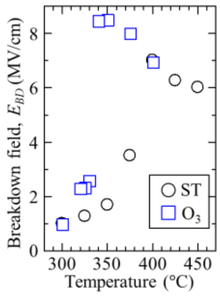

Fig.2 Breakdown field (E_{BD}) of AlO_x thin films grown by mist CVD at the standard condition (ST) or at the O_3 assistance condition (O_3).

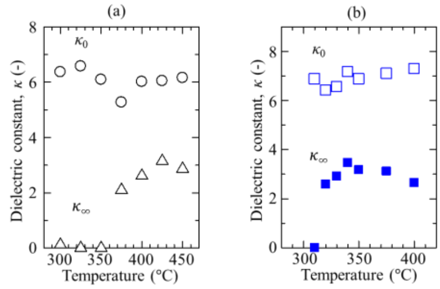

Fig.3 Dielectric constant (κ) of AlO_x thin films grown by mist CVD (a) at the standard condition or (b) at the O_3 assistance condition.

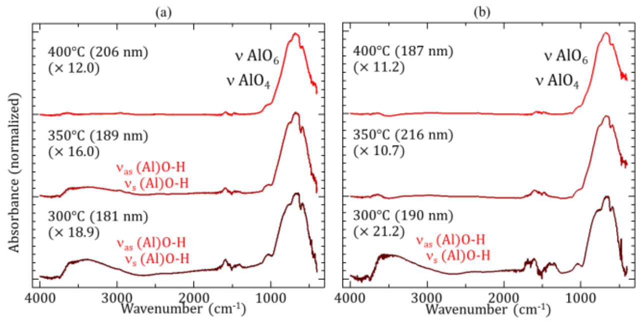

Fig.4 FT-IR spectra of AlO_x thin films grown by mist CVD (a) at the standard condition or (b) at the O_3 assistance condition.

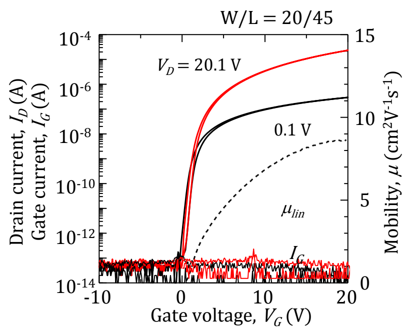

Fig.5 Characteristics of InGaZnO TFTs whose active (InGaZnO) and insulating (Al_2O_3) layers were deposited by mist CVD mode. The on/off ratio was >10^8, gate leakage current was <1pA, and channel mobility was >8 cm^2/Vs, which were nearly the standards tor display applications.