Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 576-578 **PC-1-23**

Effect of Radical Oxygen for Epitaxial Growth of Al_2O_3 on Si

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Epitaxial Al_2O_3 films were grown on Si substrates by metalorganic molecular beam epitaxy (MOMBE) method using radical oxygen excited with remote rf (radio frequency) plasma and TMA (trimethylaluminum) as source gases. The epitaxial temperature of Al_2O_3 on Si went down from 800°C to 700°C by this method. The growth rate of the Al_2O_3 films increased to 1.4-1.6 times compared with that without rf plasma excitation. The Auger electron spectroscopy (AES) measurement showed that the carbon contamination in the Al_2O_3 film was reduced by the radical oxygen during the growth.

1. Introduction

Heteroepitaxial growth of an insulator layer on Si and the successive growth of single crystalline Si on the insulator are great interest in the formation of silicon on insulator(SOI) structures. We have reported epitaxially grown Al_2O_3 films on Si as a insulator material and epitaxial stacked structures of $Si/Al_2O_3/Si$[1]. The Al_2O_3/Si structures have been studied by low-pressure chemical vapor deposition[2] (LPCVD) and metalorganic molecular beam epitaxy[3] (MOMBE) using O_2 and TMA(trimethylaluminum) as source gases. For device applications of Al_2O_3/Si stacked structure, it is necessary to improve the crystalline quality of grown films and to decrease the strain of heteroepitaxial interface.

In this study, effects of radical oxygen were studied in epitaxial Al_2O_3 film on Si. The epitaxial $Al_2O_3(100)$ films were grown on Si(100) substrates by MOMBE method using radical oxygen excited with remote rf plasma and TMA as source gases. We expected that the direct excitation of O_2 source gas could be effective to decrease the growth temperature and to improve the film quality, because the excited species can accelerate the film growth reaction. The epitaxial temperature, the growth rate and the carbon contamination were investigated.

2. Experiment

The MOMBE system consists of a growth chamber, an analysis chamber and a sample exchange chamber. The growth chamber was maintained about $5x10^{-8}$Pa and was equipped with an atom beam source (Oxford Applied Research), in-situ reflection high energy electron diffraction (RHEED) and a quadrupole mass spectrometer (QMS). The analysis chamber had an Auger electron analyzer. The n-type 2-inch Si(100) wafers with resistivities 3-6ohm were chemically cleaned and dipped in 2.5% HF to remove the native oxide. After rinsing them with de-ionized water, they were loaded in the growth chamber.

The Al_2O_3 epitaxial growth was carried out by introducing TMA and O_2 gases simultaneously to the growth chamber at substrate temperatures of 650-850°C. The O_2 gas was excited by remote rf plasma a few minutes later than the source gases were introduced because of the adjustment of rf power. Typical growth conditions were as follows: TMA flow rate was 0.02sccm, O_2 flow rate was 0.5sccm, the substrate temperature was 800°C, the excitation power of rf plasma was 400W and the growth rate was 120Å/hour under these conditions. The pressure in the chamber during the growth was about $2x10^{-3}$Pa.

The crystallographic features and the composed element of grown layers were examined by RHEED and AES, respectively. The film thickness of grown films were also measured by ellipsometry.

3. Results and discussion

The relationship between growth rates and TMA flow rates with the excitation rf powers of 0W and 400W are shown in Fig. 1. The growth rate increased with the increase of TMA flow rate under the epitaxial growth condition. At the rf power of 400W, the growth rate increased to 1.4~1.6 times compared with that without the excitation. The direct excitation of O_2 gas was effective to increase the growth rate. The Al_2O_3 films were not grown epitaxially at the TMA flow rate of more than 0.03sccm without the excitation. However, using radical oxygen, the Al_2O_3 films were grown on Si at the maximum TMA flow rate of more than 0.04sccm. This result show that the epitaxial growth conditions can be expanded using the radical oxygen. In the present condition, it was confirmed that the maximum growth rate was about 400Å/hour under the TMA flow rate of 0.1sccm, O_2 flow rate of 0.5sccm and the substrate temperature of 850°C.

A relation between growth rates and excitation rf powers is shown in Fig. 2. The growth rates increased with the rf powers of more than 250W. Radical oxygen excited with rf power was estimated by the light emission intensity of the rf plasma discharge which was measured by the optical emission detector. Light emission intensity increased with rf powers of more than 250W, but did not increase with the power until 250W. It is seen that radical oxygen is effective to increase the growth rate of the Al_2O_3 film.

Fig. 3 shows the relations between growth rates and O_2 flow rates under the fixed TMA flow rate of 0.02sccm. The growth rate had a peak at the O_2 flow rate of 0.5sccm under 400W rf power and the substrate temperature of 800°C. When the O_2 flow rate was higher or lower than the suitable flow rate to get the maximum growth rate, the growth rate decreased. When the growth conditions varied far from the most suitable condition, the Al_2O_3 films did not grow epitaxially. When the O_2 flow rate was not enough, the grown film quality declined and the RHEED patterns of the grown film were different from the single crystal Al_2O_3

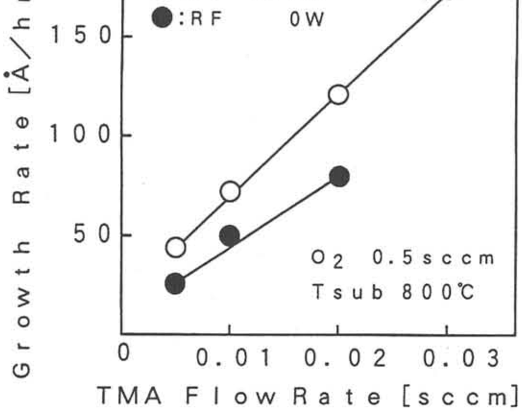

Fig. 1 Relations between growth rates and TMA flow rates at the rf excitation powers of 0W and 400W.

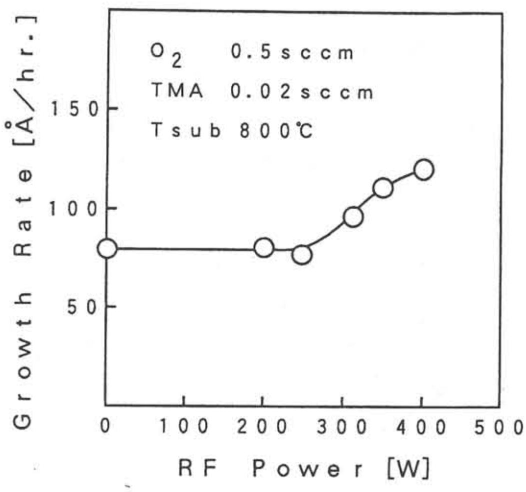

Fig. 2 Relation between growth rates and rf excitation powers.

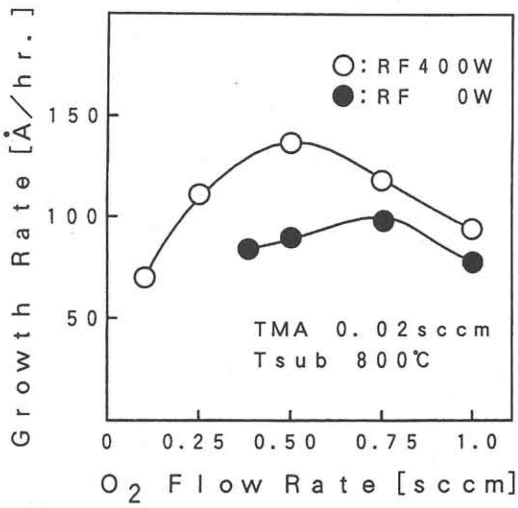

Fig. 3 Relations between growth rates and O_2 flow rates with TMA flow rate of 0.02sccm.

patterns. It is considered the O in Al_2O_3 is less than stoichiometry. When the O_2 flow rate was too much, the film quality declined to become poly-crystalline. It is considered that the silicon surface is oxidized immediately by a lot of O_2 gas before the beginning of Al_2O_3 nucleation at the initial growth stage.

It seems that the TMA molecules can be dissociated sufficiently by the substrate temperature, because the growth rate increases in proportion to the TMA flow rate. But dissociation of the O_2 molecules are insufficient on the substrate, because the growth rate can be increased by the decomposition of O_2 gas using rf plasma excitation as shown in Fig. 2. The growth rate of Al_2O_3 film was very slow such as 120Å/hour in typical growth condition. The percentage of total Al atoms contained in Al_2O_3 film to the number of that in TMA arriving at substrate surface during the growth was estimated at about 2%. The Al atoms were contributed insufficiently to grow the Al_2O_3 film. The adsorption of Al atoms maybe increase with the TMA flow rate, so that the growth rate increases in proportion to the TMA flow rate. The growth rate had a peak at the suitable O_2 flow rate. In the region of large O_2 flow , the growth rate decreased. It can be considered that Al desorption becomes too large due to the excited O atoms arriving at the substrate surface. From these results, it is inferred that the Al_2O_3 growth rate depends on the balance of Al atoms adsorption and desorption.

Fig. 4 shows the result of Auger electron spectroscopy measurement of Al_2O_3 films grown on Si. The dN/dE signals from the samples grown by O_2 and radical oxygen are shown in Figs. 4(a) and 4(b), respectively. The grown Al_2O_3 films were analyzed by AES after removal of the surface contamination during handling by Ar ion at the acceleration

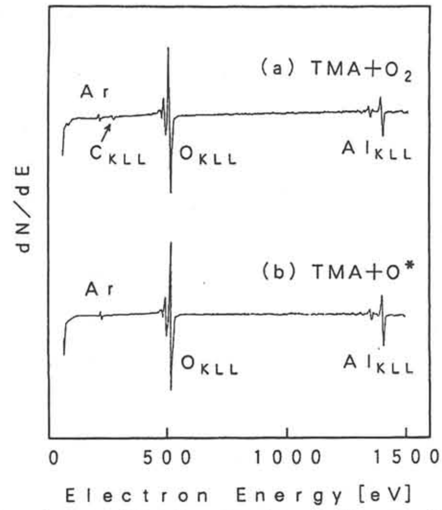

Fig. 4 Auger spectrum from Al_2O_3 grown with O_2(a) and Al_2O_3 with O radical atoms(b) after Ar ion sputtering.

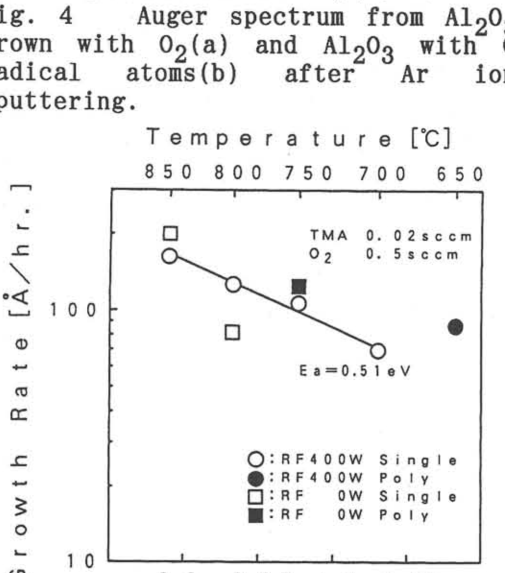

Fig. 5 Substrate temperature dependence of the epitaxial growth rates of Al_2O_3 with excitation rf powers of 0W and 400W.

voltage of 3kV. O_{KLL} peak and Al_{KLL} peak were observed. The C_{KLL} peak of 272eV was observed in Fig.4(a), but it disappeared in Fig. 4(b). The Auger peak of 210eV shows the Ar peak. It is considered that the carbon atoms adsorbed on the Al_2O_3 surface during growth reacted on the O species and desorpted out as CO and CO_2 molecules. From this result, it is confirmed that the carbon contamination in the grown Al_2O_3 film was effectively decreased using the radical oxygen compared with the O_2 gas.

Fig. 5 shows the relationship between of growth rates and growth temperatures for the rf powers of 0W and 400W. The Al_2O_3 film was not grown epitaxially at the temperatures below 800°C without the rf plasma excitation. But with the rf excitation of O_2 gas, the epitaxial temperature of Al_2O_3 on Si went down from 800°C to 700°C. Arrhenius plot of the growth rates above 700°C is shown. The activation energy was 0.51eV. In previous study, we showed that the effects of ArF excimer laser(193nm) irradiation for epitaxial growth of Al_2O_3 on Si by MOMBE[4]. In case of the laser irradiation horizontal to the substrate, the activation energy was about 0.5eV and the growth rate increased 1.6 times compared with that without the laser irradiation. These results were explained by the decomposition of N_2O source gas due to ultraviolet light in vapor phase. At the present experiment using radical oxygen, the increase of the growth rate and the activation energy are the same as those in horizontal laser irradiation. Therefore, the effects using radical oxygen can be considered the similar effects in horizontal laser-irradiated MOMBE. It can be seen that the radical oxygen atoms enhance the growth of Al_2O_3 on the surface and can remove the surface contamination such as carbon. These effect are also useful to reduce the epitaxial temperature.

4.Conclusions

In conclusions, the epitaxial growth of Al_2O_3/Si structure was carried out by MOMBE method using radical oxygen excited with remote rf plasma and TMA. It was confirmed that the radical oxygen was effective in reduction of epitaxial growth temperature, increase of growth rate and removal of carbon contamination in the Al_2O_3 films.

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