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主 論 文 の 要 旨

論文題目 Study on plasma-enhanced metal-organic chemical vapor deposition for future gallium nitride devices
（次世代窒化ガリウム系デバイスのためのプラズマ励起有機金属化学気相成長法に関する研究）

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論 文 内 容 の 要 旨

Plasma-enhanced chemical vapor deposition (PECVD) technique was widely available for industrial use from semiconductor fabrication to protective coating. The energetic electron and highly reactive radicals generated from plasma can induce reactions between precursor molecules that would otherwise be very improbable at low temperatures, so this technique is capable for a low-temperature high-speed growth on many thermo-sensitive structures. A major breakthrough can be expected from the promising application of gallium nitride (GaN) for the high-power high-frequency devices, such as power MOSFETs and HEMTs. Unfortunately, the development of GaN-based devices has been under limitations of the conventional metal-organic chemical vapor deposition (MOCVD) technique. In spite of the advantage of MOCVD technique in high growth rate with big growth area, high growth temperature over 1000°C restricted its use range due to its big difference of thermal expansion coefficients with the substrate (e.g. silicon), and the high cost from huge assumption of ammonia gas severely hindered its popularization in industrial interests. To solve these, plasma-enhanced MOCVD (PEMOCVD) was proposed about two decades ago. However, it proved to be still far to an industrial application by applying PEMOCVD which were performed with inductively coupled plasma (ICP) generated by radio frequency of 13.56 MHz and electron cyclotron resonance (ECR) by microwave frequency of 2.45 GHz in the previous studies. On the other hand, SiO_2 films can be used as gate oxide layer in GaN MOSFETs, and used as sacrificial layer in self-aligned double patterning (SADP) for GaN FinFET fabrication. Previously, Ultrathin and conformal SiO_2 films were deposited at low temperature under 100 ^{o}C by plasma-enhanced atomic layer deposition (PE-ALD), as one of PE-CVD. However, the reaction as well as its difference with the conventional thermal ALD has not clarified yet. We therefore developed a very-high-frequency (60 MHz) capacitively coupled plasma (CCP) system, which achieved a large plasma density with a possibly high uniformity over more than a 300 mm diameter. In this study, GaN epitaxial growth at 800^{o}C was realized successfully in this newly-developed VHF-CCP-MOCVD system without using ammonia gas, and the PE-ALD mode deposition of SiO_2 films was also achieved at a room temperature in this system. The effect of growth time, precursor flow rate and VHF power on the grown GaN quality was investigated. The reaction mechanisms of GaN growth and SiO_2 deposition with the relatively low temperatures of plasma processing were discussed.

The content for each chapter in this thesis is interpreted as following:

Chapter 1 Research background and introduction

It is introduced about the basic properties of GaN. Relevant fabrication techniques for GaN growth and their development are interpreted. Recent PE-MOCVD for GaN growth and PE-ALD for SiO_2 deposition are also introduced in this chapter.

Chapter 2 Diagnostics and characterization techniques

It introduced on the principal of plasma diagnostic and film characterization analysis methods. Among them, optical emission spectroscopy (OES) is used to monitor plasma status. Scan electronic spectroscopy (SEM) and atomic force spectroscopy (AFM) are used to learn the sample surface's morphology. X-ray diffraction (XRD) is employed to investigate the crystalline quality of GaN film.

Chapter 3 Epitaxial growth of GaN films on sapphire employing very-high-frequency remote-plasma-enhanced metal-organic chemical vapor deposition (VHF-RPE-MOCVD)

Gallium nitride (GaN) films were epitaxially grown at 800^{o}C by using the developed very high frequency remote plasma-enhanced metalorganic chemical vapor deposition (VHF-RPE-MOCVD) system. This system applied VHF power source of 60 MHz and CCP discharge structure in order to improve the plasma density and uniformity. A mixture of H_2

and N_2 gases was introduced into the discharge region to generate nitrogen radicals and they were supplied to grow films under a remote plasma arrangement with suppressing charged ions and photons by employing a Faraday cage. By this new system, I studied the effect of the trimethylgallium (TMG) source flow rate and the plasma generation power on the GaN crystal quality by SEM and XRD. The results proved, by using the mixture of N_2 and H_2 as the plasma gas with introducing TMG gas separately from the discharge region, the epitaxial growth of GaN film could be achieved without using costly ammonia gas. It was found that the increase of TMG gas itself decreased the crystal quality in the case of lack of sufficient N source while the increase of VHF power was effective to increase the growth rate and to improve the crystal quality because of the sufficient supply of nitrogen source.

Chapter 4 Epitaxial growth of GaN films employing radical-enhanced metal-organic chemical vapor deposition (RE-MOCVD) in the downflow of a very-high-frequency (VHF) excited plasma

GaN epitaxial growth was performed in the newly developed very-high-frequency radical-enhanced metalorganic chemical vapor deposition (VHF-RE-MOCVD). Based on the results from our previous VHF-RPE-MOCVD system, the inner structure of the reactor had been re-arranged in order to achieve GaN expitaxial growth with a higher growth rate and a better crystal quality. Sample films were grown in the downflow of N_2/H_2 plasma at $800^{o}C$. The distance between plasma discharge region and the sample stage was increased to avoid parasitic reaction by suppressing the TMG cracking before reaching the films. I studied the effect of the growth time and TMG flow rate on the films morphology and crystal structure, which were characterized by SEM, AFM and XRD. The epitaxial GaN films were successfully grown on sapphire substrates by the RE-MOCVD system which was newly developed in our laboratory by using N_2 and H_2 plasma. From these results, GaN epitaxial growth was proved to be achieved by growing in the downflow of the N_2/H_2 plasma without any TMG cracking could be observed by OES. A transformation from 3D to 2D growth with increasing the growth time from 40 min. to 60 min. could be observe by SEM and AFM views. The growth rate was increased as a function of TMG flow rate, and it reached to about 1.7 μm/hr with TMG of 0.4 sccm. The crystal quality proved to be the best as TMG flow rate was between 0.025 and 0.05 sccm.

Chapter 5 SiO_2 plasma-enhanced atomic layer deposition (PE-ALD) at near room temperature using in-situ attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) for a clarification of the mechanism of surface reactions

I reported the temporal evolution of surface species observed in situ using attenuated total reflection Fourier transform infrared absorption spectroscopy (ATR-FTIR) during PE-ALD of SiO_2 films employing aminosilane and an O_2/Ar plasma at a near room temperature. Reversals in the appearance of IR absorbance features associated with C-H_x and Si-H proved to coincide with the self-limiting reaction property in ALD. In previous studies, conventional low-temperature ALD was shown to be unsuitable for SiO_2 film formation because of the difficulties in removing alkylamine by-products and hydroxylating SiH groups by oxidant exposure during each cycle. In our IR results, dissociative adsorption of the aminosilane precursor could be observed by a decrease in the absorbance ratio C-H_x/Si-H. In the O_2/Ar plasma, residual ligands involving alkyl groups could be dissociated and removed entirely, and SiH ligands could be completely oxidized to form SiOH surface species. Newly formed Si-O bonds were incrementally observed at every ALD cycle. A reaction model constructed based on our results verified that the O_2/Ar plasma treatment played two roles of removing the residues of precursor ligands and surface hydroxylation even at a low temperature. Thus, the present study clarified the reasons why PE-ALD of SiO_2 can be carried out at near room temperature.

Chapter 6 Conclusions

Finally, the results in this study are summarized and the future scope is described. GaN was successfully epitaxially grown by our developed VHF-RPE-MOCVD and VHF-RE-MOCVD system. By modifying the reactor structure, the growth rate and crystal quality were improved. However, it is necessary to further optimize the growth conditions in order to achieve the crystal quality competing with that of conventional MOCVD grown GaN. The present result infers a possibility to obtain high quality hetero-epitaxial GaN films without using ammonia gas and at relatively low growth temperature. A further lower growth temperature potentially leads to a lower residual stress compared with that from the conventional MOCVD. In the other hand, SiO_2 PE-ALD at near room temperature was achieved in our developed VHF-PE-MOCVD system. The reaction mechanism was clarified by observing the temporal evolution of surface species using in-situ ATR-FTIR. A further research on the improvement on the stoichiometry and conformality of PE-ALD deposited SiO_2 films will be carried out based on the present results.