主　論　文　の　要　約

論文題目　**Studies on precisely controlled isotropic etching and its application to semiconductor device fabrication (高精度等方性エッチングとその半導体デバイス製造への応用に関する研究)**

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論　文　内　容　の　要　約

To deal with the increased data traffic due to the spread of IoT applications, low power consumption and high data capacity are required for semiconductor devices including photonic devices, logic devices and memory devices. The structure of semiconductor devices has thus changed from planar two-dimensional (2D) ones to integrated, miniaturized three-dimensional (3D) ones for integrated laser diodes (LD), fin-type field effect transistors (FinFET), and 3D NAND flash memories. To meet the small size requirement of the devices, precisely controlled isotropic etching is important.

This work was motivated by the need for precisely controlled isotropic etching of III-V semiconductors and nitride films for next-generation semiconductor devices that must consume less power. To achieve these goals, the author developed the means of isotropically etching InGaAsP and InGaAlAs for fabricating reliable, low-drive-current laser diodes. Moreover, the author developed a means of isotropic, atomic-layer etching (ALEt) of Si_3N_4 and TiN for making atomic-scale 3D devices.

Chapter 1 describes the technology trends of 10-Gbit/s optical transceivers, integrated photonic devices, and logic/memory devices. The requirements for low-power-consumption laser diodes for smaller optical transceivers and atomic-scale logic devices such as nanowire FETs are described. It was shown that low-power-consumption lasers could be developed with isotropic non-selective InGaAlAs/InP etching and isotropic selective InGaAlAs etching over InP. Furthermore, the requirements for isotropic ALEt of Si_3N_4 for fabricating nanowire FETs are described.

Chapter 2 describes the theory of plasma diagnostics for optical emission spectrometry (OES). The theory behind various film evaluation techniques, including X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry, atomic force microscopy (AFM), and scanning electron microscopy (SEM), is also described.

Chapter 3 describes the development of isotropic, non-selective etching of InGaAsP and InP for removing damage from buried heterostructures of laser diodes fabricated by dry etching. By comparing the etching characteristics of various solutions, a mixture of HBr, Br_2, and H_2O was chosen for non-selective etching. A solution with the optimum composition, which contains 0.4-mol/liter of HBr and 0.0021-mol/liter of Br_2, enabled non-selective etching of InGaAsP and InP. The non-selective etchant produced smooth etched sidewalls, which resulted in a smooth regrowth profile. A simple transport-limited model of InP/InGaAsP etching in a HBr/Br_2/H_2O solution is proposed. The amount of etching calculated by the model is in good agreement with experimental results. A ten-fold improvement in the lifetime of the laser diode was demonstrated by using this non-selective etchant instead of a conventional etchant. The author developed a process for fabricating dry-etched-mesa buried heterostructures that are ideal for low-current operation.

Chapter 4 describes the development of isotropic, selective etching of InGaAlAs over InP for making short-cavity lasers capable of low-current operation. Theoretical calculations showed that the optimum cavity length for low-current operation is between 10 and 100 μm, which is difficult to form by conventional cleaving. A key to fabricating the short-cavity structure is the selective etching of InGaAlAs multiple quantum wells (MQW) and subsequent epitaxial regrowth of InGaAsP distributed Bragg reflector (DBR). After the theoretical examination, mixtures of various acids, H_2O_2, and H_2O were experimentally investigated. H_2SO_4-based and H_3PO_4-based solutions exhibited highly selective etching of InGaAlAs over InP; the selectivity was as high as 500. An InGaAlAs active waveguide and an InGaAsP DBR were butt-jointed by using this highly selective etching. The optical loss at each butt-jointed interface was estimated to be 2-3%, which was sufficiently low for actual applications. A fabricated short-cavity laser exhibited a record-low drive-current of 14 mA for 10-Gbit/s operation at 100°C.

Chapter 5 describes the development of selective, isotropic ALEt of Si_3N_4. The process involves repeated cycles of CHF_3/O_2 plasma exposure for modification of the surface and heating for desorption of the modified surface. An *in-situ* XPS analysis revealed self-limiting formation of ammonium hexafluorosilicate ($(NH_4)_2SiF_6$) on the surface of Si_3N_4 after exposure to CHF_3/O_2 plasma. The *in-situ* XPS analysis also revealed sublimation of ammonium hexafluorosilicate by heating the sample up to 100°C. Thermal desorption spectroscopy indicated that the ammonium hexafluorosilicate decomposes into SiF_4, NH_3, and HF. The thermal decomposition of the ammonium hexafluorosilicate was found to be in good agreement with thermodynamic calculations. On the basis of these findings, a 300-mm etching tool for rapid thermal-cyclic ALEt was developed. Using this tool, it was found that the etching depth increased as the number of cycles increased. It was 2 nm after one cycle of etching. Selective Si_3N_4 ALEt relative to SiO_2 was obtained. The process had self-limiting characteristics in terms of the plasma-exposure time and infrared-heating time. Conformal, highly selective ALEt of Si_3N_4 was confirmed with patterned samples by using an optimum gas chemistry.

Chapter 6 described the development of isotropic ALEt of TiN. The process is composed of cycles of CHF_3/O_2 plasma exposure followed by infrared heating and is basically the same as the one for Si_3N_4 ALEt. An *in-situ* XPS analysis revealed the formation of a modified layer, which was tentatively ascribed to reactions involving ammonium fluorotitanate, on the surface of TiN after plasma exposure. The ammonium fluorotitanate disappeared after heating at 110°C. The thermal-cyclic ALEt of TiN was performed using a 300-mm ALEt tool. The etching depth increased as the number of cycles increased. It was 0.6 nm for one cycle of etching. The process had self-limiting characteristics in terms of the plasma-exposure time and infrared-heating time.

Chapter 7 describes the summary of this dissertation. This dissertation presents the results of development of precisely controlled isotropic etching of various materials: InGaAsP/InP etching for removal of dry etching induced damage, InGaAlAs etching for fabricating low-drive-current laser diodes, thermal-cyclic ALEt of Si_3N_4, and thermal-cyclic ALEt of TiN. These isotropic etching procedures modify the surface and then remove the modified surface. For example, surface oxidation and subsequent dissolution of the oxide were used for etching III-V semiconductors. Nitride films were etched by forming and then sublimating ammonium salt. Throughout this study, it was found that a combination of carefully controlled surface modification and complete removal of the modified surface is a key to realizing precisely controlled isotropic etching. These findings will be fundamental to the development of isotropic etching for other materials.

The outcomes of the present study will be of use in the development of the next generation of semiconductor devices. The knowledge obtained in the study of isotropic etching of III-V semiconductors will be useful for the development of devices such as InGaAs tunnel FETs. The isotopic ALEt of nitride films will be useful for the development of devices such as gate-all-around FETs. The author concludes that these precisely controlled isotropic etching will lead to novel ways of nanofabrication for the next generation of semiconductor device manufacturing.