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学位授与の要件	課程博士（学位規則第４条第１項）
学位授与の題目	Interface-control technique of semiconductors for layered thin-film electronic devices （積層型薄膜電子デバイス作製のための半導体界面制御技術）
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学位論文要旨

Interface–control technique of semiconductors is studied in prospect of integrated devices with layered structure composed of ferroelectric oxide films or Ⅲ－Ⅴ nitrides and conventional semiconductors such as Si and GaAs. SiO_2/Si interface control is also performed for establishing the well–ordered ultrathin–oxide formation technique. Orientation control of MgO films on (100)GaAs and (100)Si is accomplished. Highly [100]–oriented perovskite phase $Pb(Zr,Ti)O_3$ (PZT) films are obtained on (100)GaAs and (100)Si substrates with MgO buffer layer without fatal interdiffusion or fatal formation of the alloying layer at the interface. PZT films on (100)Si with MgO layer of 50 Å thickness show the ferroelectric hysteresis loop. Nitrided layer of GaAs, which is often employed as the excellent buffer layer between cubic GaN and GaAs substrate, is in detail studied using X–ray photoelectron spectroscopy changing the photoelectron take–off angle. Several tens Å of GaN layer with high oxidation resistance is formed by the NH_3–plasma nitridation under appropriate conditions. Plasma oxidation of Si is also examined for obtaining the high quality SiO_2/Si interface and for controlling the ultrathin–oxide–layer thickness. N accumulation at the SiO_2/Si interface is observed in the case of N_2O–plasma oxidation.

In this article three examples of interface–control technique for semiconductors are shown. These techniques will contribute to fabrication of integrated devices with layered thin–film structure composed of newly developed electronic materials and conventional semiconductors such as Si and GaAs.

Firstly, preparation of oxide ferroelectrics on GaAs and Si substrates using MgO buffer layer is studied. MgO films were prepared on both (100)Si and (100)GaAs by electron–beam evaporation under various deposition conditions. The orientation of MgO films on Si and GaAs changed from [111] to [100] with an increase in the substrate temperature or a decrease in the deposition rate. It also became apparent that MgO films become [100] oriented on (100)GaAs at lower temperature as compared with those on (100)Si. These results suggest the possibility of the orientation control of MgO films on semiconductor substrates by changing the deposition conditions. Highly [100]-oriented perovskite-phase Pb(Zr,Ti)O_3 (PZT) films were obtained by pulsed laser ablation (PLA) on both (100)GaAs and (100)Si substrates with MgO buffer layer which was also prepared by PLA. It was shown that MgO buffer layer acts as an excellent barrier against the oxidation of the substrate, against the diffusion of Pb into the substrate and that of Ga and As into the PZT films, and also against the vaporization of As. No fatal interdiffusion was observed at the interfaces both between PZT and MgO and between MgO and GaAs or Si. [100]-oriented PZT films with almost perovskite phase were obtained on (100)Si with MgO buffer layer of only 50 Å thickness, as shown in Fig. 1. This sample showed the ferroelectric hysteresis loop. This technique promises realization of integrated devices composed of semiconductors and ferroelectric materials, such as metal-ferroelectric-semiconductor field-effect transistors (MFS-FETs).

Secondly, NH_3-plasma nitridation of (100)GaAs with a planar magnetic field was carried out at various temperatures and for various times. The surface reaction of GaAs with NH_3 plasma was studied in detail using X-ray photoelectron spectroscopy (XPS) changing photoelectron take-off angle. It is revealed that the surface composition varies with the plasma-nitridation time and temperature. First, an unstable As-N or Ga-As-N layer is formed on the GaAs surface. Then, such unstable layer disappears with increasing treatment time or temperature. The formation of a GaN layer on GaAs surface can be achieved with the appropriate treatment time and temperature. The surface-nitridation mechanism is schematically illustrated and summarized in Fig. 2. NH_3-plasma nitridation mainly proceeds without the thermal reaction and/or the thermal diffusion. The nitridation proceeds faster for (111)GaAs than for (100)GaAs. Although the nitridation rate for (111)B is equal to that for (111)A, a larger number of As-N bonds are observed in (111)B surface than in (111)A surface. Successive laser irradiation after the plasma nitridation decreases the number of As-N bonds in the unstable surface layer and enhances the GaN formation. This process is confirmed to be also one of the promising candidates for the surface passivation of GaAs.

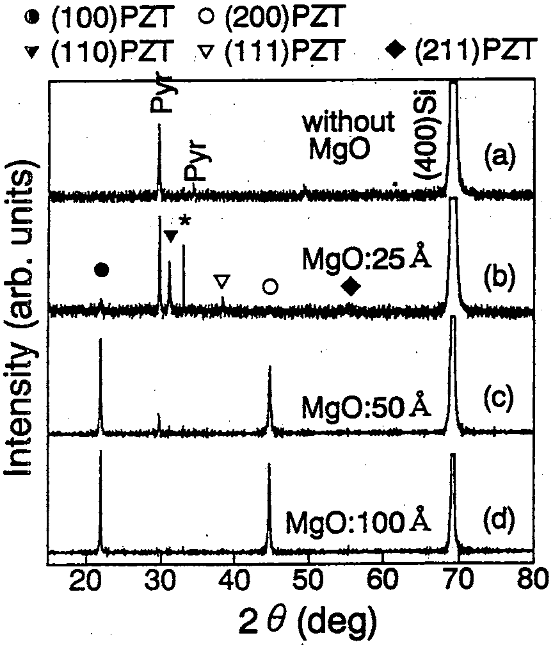

Fig. 1. X-ray diffraction patterns for PZT/MgO/(100)Si structures. MgO-layer thickness is changed.

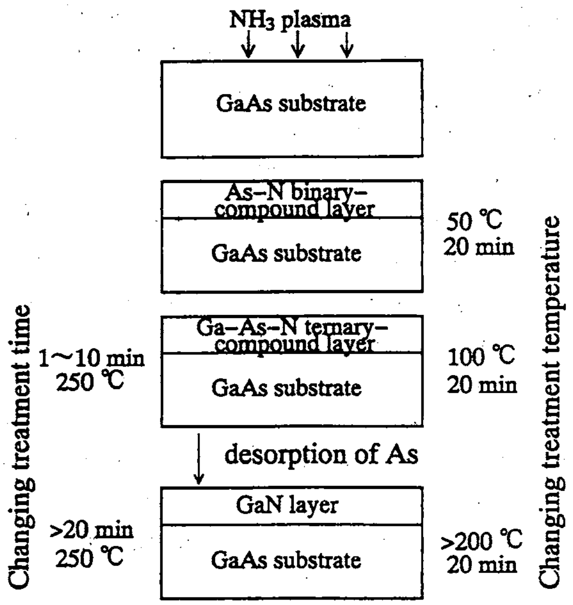

Fig. 2. Schematic diagram of the model for surface nitridation of GaAs with NH_3 plasma.

Thirdly, plasma oxidation of (100) and (111)Si on the anode electrode was carried out using O_2 plasma or N_2O plasma. The rapid oxide-growth in the early stage is observed irrespective of the substrate orientation and the type of the oxidant. Accumulation of N atoms at or near the SiO_2/Si interface was observed by XPS, as shown in Fig. 3, for the N_2O-plasma oxidation of Si in the same way as in the case of rapid thermal process (RTP) of Si in N_2O ambient. The increase in the incorporated N content is observed only at the early stage of the oxidation, and the content of accumulating N remains constant with the oxidation for longer time. It is supposed that the oxide-growth mode on Si by the plasma oxidation is the two-dimensional growth regardless of the substrate orientation or the type of the oxidant. Electron spin resonance (ESR) observation reveals that at the SiO_2/(111)Si interface formed by the plasma oxidation there are Si dangling bonds (DBs) similar to those in amorphous Si in addition to *Pb* center. The *Pb*-center density at the SiO_2/(111)Si interface formed by the N_2O-plasma oxidation is comparable to that formed by a thermal oxidation.

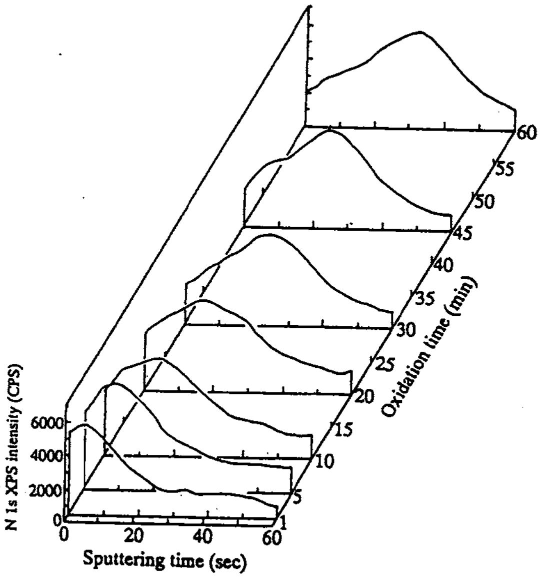

Fig. 3. N 1*s* XPS intensities against the sputtering time during XPS measurements for samples oxidized for various times.

学位論文の審査結果の要旨

提出された学位論文及び資料を審査委員が個別に検討を行い，平成８年１月31日に行われた口頭発表で質疑を行った後，審査委員会において以下のような結論を得た。本学位論文は電子デバイスの高機能化のために重要な積層型電子デバイス作製の基礎となる半導体界面制御に関する下記の３つの研究に関するものである。まず第１は，他の強誘電体薄膜と比較して成膜条件の厳しいPZT薄膜をMgOバッファ層を用いることによってSiならびにGaAs基板上に高配向成長させることに成功したものである。この技術はMISトランジスタ型メモリや一体型レーザスキャナ等の強誘電体と半導体を集積した新規デバイスの開発に貢献するものと思われる。第２はGaAsの表面プラズマ窒化の初期窒化過程をＸ線光電子分光（XPS）を用いて詳細に明らかにした研究である。この窒化技術はGaAsの表面パッシベーションならびにGaAs上へのGaNの成長にとって有益なものである。GaNは青色発光材料として近年脚光を浴びている材料である。また，上記窒化過程の評価に際して角度依存XPSを用いた点に特徴がある。この手法は非破壊で極薄膜の深さ方向の組成分析を可能とするものであり，従来法での試料破壊に伴う種々の測定誤差の要因を除去できる点ですぐれている。第３はSi結晶表面のプラズマ酸化に関するものでN_2Oプラズマを用いることによって酸化膜とSiの界面近傍にNが集積することによって界面欠陥を減少させることを明らかにしている。以上のように申請者の研究は多岐にわたっており，半導体界面制御技術に貢献するものと思われ，博士の学位に値するものと認定する。