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授与学位	博士（工学）
学位授与の年月日	平成13年3月26日
学位授与の根拠法規	学位規則第４条第１項
研究科，専攻の名称	東北大学大学院工学研究科（博士課程）応用物理工学専攻
学論文題目	Plasma-assisted molecular beam epitaxy of ZnO based II-VI semiconductor oxides and their heterostructures（プラズマ分子線エピタキシによるZnOをベースとしたII-VI族酸化物半導体及びヘテロ構造の成長）
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論文内容要旨

The emergence of ZnO owes to recent explosions in three independent research fields. One is of wide bandgap semiconductors, which can be applied to short wavelength solid-state emitters highly desired for full color illumination and dense optical storage. The second is of excitonic processes in a photonic crystal, which reveals numerous possibilities in developing new photonic devices. The third is of oxide electronics, for which heterostructures combined with various functional oxide materials are being explored. ZnO has a direct bandgap of 3.37 eV at room temperature, strong bond strength of 1.89 eV per bond, and large exciton binding energy of 60 meV. These properties ensure ZnO a prospective material impacting on these research fields and deserving extensive studies. For all the three different research fields a reliable epitaxial growth technique for growing high-quality thin films and heterostructures is essential, however not well developed so far for ZnO. The difficulties exist in that the state-of-art epitaxial growth techniques developed for conventional semiconductors, such as molecular beam epitaxy (MBE) and chemical vapor deposition, have not been well applied to the growth of oxide materials. Thus, numerous technical problems still remain unsolved. The absence of suitable substrate materials for ZnO heteroepitaxial growth further challenges the research work and turns out to be a vital issue being confronted. The present research set out from the technical base of MBE to develop a reliable epitaxy growth technique for achieving device quality ZnO thin films and heterostructures, and to understand the fundamental growth processes and material properties of ZnO epilayers. The concentration has been paid on how to overcome the long-standing problem of large lattice mismatch in the heteroepitaxy of ZnO on low cost, widely used substrate α-Al_2O_3 (0001), and the studies on excitonic processes in the lasing mechanism of ZnO.

The key point to surmount the problems associated with various mismatches including lattice mismatch (18.6%), thermal mismatch, crystallographic mismatch and chemical mismatch between covalent semiconductor ZnO and ionic oxide Al_2O_3 is using a thin MgO buffer layer as a template between the epilayer and the substrate. Because of the similar crystal and chemical properties, MgO can wet the Al_2O_3 (0001) surface, which lowers the surface energy so that the lateral growth of ZnO becomes favorable after the Al_2O_3

substrate is covered by MgO. Furthermore, the MgO layer, whose growth mode transits from two-dimensional nucleation (2D) to three-dimensional (3D) island growth, provides nucleation cores for the initial ZnO nucleation. As a result, the columnar growth, which dominates in the case of direct growth of ZnO on Al_2O_3, is completely suppressed and 2D growth evolves during the subsequent ZnO epitaxy on the MgO buffer layer. The detailed studies by using high-energy electron reflection diffraction (RHEED) show that MgO buffer grows under Stranski-Krastanov mode with a critical thickness around one monolayer. The total thickness needed for MgO buffer is only 1-2 nm. Although the growth mode transition results in surface roughening, the relaxation in the MgO layer, which releases the built-in strain energy, is indispensable for achieving smooth surface in following ZnO growth. On the other hand, the thickness, the growth temperature and the growth rate of the buffer layer have subordinate effects. The post-growth characterizations confirm that the crystal quality of the ZnO films grown on Al_2O_3 with an MgO buffer is greatly improved compared with that without an MgO buffer. X-ray diffraction peak width, deep-level emission intensity, and background carrier concentration, can be reduced by more than one order. Finally, by using a few monolayer thick MgO buffer, smooth surface morphology and excellent crystal quality became available in epitaxial grown ZnO on large mismatched substrate Al_2O_3.

Owing to the achievement of a flat surface and the 2D growth, the surface structure and dynamical growth processes of ZnO were precisely investigated by using RHEED and atomic force microscopy (AFM). The surface polarity plays an important role in epitaxial growth and consequently, affects the crystal quality of epilayers. This fundamental feature of ZnO epilayers grown on Al_2O_3 with an MgO buffer was determined to be oxygen polarity (000 $\bar{1}$) surface by chemical etching method. A (3×3) surface reconstruction was found for the (000 $\bar{1}$) surface and the phase transition diagram was determined. It was found that the anisotropy of a step edge and asymmetric energy barriers associated with a step edge define the surface morphology evolution showing two representative features. One is that the terraces have a step height of 5.20 Å (*c* lattice constant) and the other is that the terrace width evolves towards uniform during step-flow growth. The typical growth mode transition from 2D nucleation and step-flow mode was found to be at 700 °C for samples with an average terrace width of 90 nm. With an increasing in terrace width, the transition temperature increases. The growth stoichiometry was obtained by analyzing the growth rate as a function of Zn flux at various growth temperatures and the characters of the sticking coefficients of both Zn and O^* were identified. Zn is much more dependent on the growth temperature than O^*. This must be due to the higher chemical reactivity of energetic oxygen radicals. These experimental finding feedbacks to the optimization of the growth conditions, which leads to further improvements of the crystal quality of ZnO epilayers. It was found that the (3×3) reconstructed surface and step-flow mode are favorable factors for growing high-quality ZnO epilayers. On the other hand, the near stoichiometry oxygen rich condition is critical to the reduction of the background carrier density.

In the case of (Mg, Zn, Cd)O alloy growth, the studies of growth kinetics revealed different incorporation behaviors of Cd and Mg. By investigating RHEED intensity oscillations, strong segregation of Cd was observed when growing CdZnO. In contrast, Mg holds a unit incorporation rate in a temperature range up to 750 °C. Because both MgO and CdO have a different crystal structure from ZnO, a phase transition occurs when incorporating large amount of either Mg or Cd. By finely controlling the growth temperature and II-VI flux ratio, alloys with up to 40% Cd and 30% Mg can be successfully grown. In order to grow heterostructures with sharp interfaces, migration enhanced epitaxy

(MEE) was developed for improving surface morphology. The MEE technique is based on the discovery that Zn adatom enhances the surface migration on the oxygen polarity (000 $\bar{1}$) surface, so that a growth interruption on the surface under Zn flux facilitates flattening of a surface. Using the MEE technique, multi-quantum-well structures were fabricated. The remaining problem is that surface roughening occurs during growth of (Mg, Zn, Cd)O alloys, which gradually degrades the interface of quantum wells as more wells are grown.

Although very large lattice mismatch still exists in the ZnO/MgO-buffer/Al_2O_3 system, structural characterization by high-resolution X-ray diffraction (HR-XRD) and transmission electron microscopy (TEM) indicate a dramatic reduction in defect density in ZnO epilayers grown with an MgO buffer. HR-XRD studies show that the microstructure of a ZnO epilayer is dominated by twist, rather than tilt. The twist reduces in-plane correlation length and causes a broadening perpendicular to the surface normal, which was directly resolved by 2D mapping of the diffraction peaks in the reciprocal space. Using the TEM two-beam technique, the structural defects of this material system were characterized. It was found that the dominant extending defects are edge, screw and mixed dislocations along *c*-axis. This is different from the ZnO epilayers without buffer, where low-angle gain boundaries are main extending defects. The elimination of low-angle grain boundaries by using MgO buffers results from the dramatic suppression of columnar growth. The screw dislocation is two orders less dense than the edge dislocation owing to the well-controlled layer-by-layer growth. The structure of dislocation revealed by TEM explains why twist rather than tilt dominates the mosaicity as the HR-XRD measurements showed. In order to get further insight into how an MgO buffer improves the crystal quality, the structural properties of interfaces were studied in detail. It was discovered that the dislocations form loops at near interface region and their density abruptly decreases when thickness exceeds above a critical value about 20 nm. Here the MgO buffer plays a critical role in introducing the interaction between dislocations and consequent annihilation. No alloy formation can be found at the interface of either ZnO/MgO or MgO/Al_2O_3, and the crystal structure of the buffer was identified to be rocksalt with the surface normal along the [111] crystallographic orientation. Because of the different crystal structure and chemical bonding, the feature of forming *c*-axis orientated dislocations in wurtzite ZnO is no longer applies to the case where an MgO layer is inserted. Although the buffer is as thin as 1-2 nm, the effect must be large. These observations indicate the mechanism of buffer lies on the dynamic generation of dislocations during epitaxial process with the surface and initial nucleation environment modified by a thin MgO layer.

The optical properties of ZnO were extensively studied 30 years ago in the bulk materials at low temperature. In this research, the optical properties of ZnO epilayers at room temperature were focused. Measurements revealed that the most promising property is that the excitonic features dominate even at high temperatures and under high excitation. This is expected considering the large exciton binding energy of ZnO, but has not been obtained because high-quality samples had not been available so far. At room temperature free exciton recombinations dominate the photoluminescence (PL) spectra. The exciton-phonon coupling is obvious because of the strong ionicity of ZnO. Under high excitation, exciton-exciton scattering becomes dominant in PL and governs the mechanism of stimulated emission and lasing. The excitonic stimulated emission persists even up to the temperature as high as 550 K. Variable stripe length measurements indicated that the excitonic processes contribute mainly to the near threshold optical gain. With increasing in pumping intensity the electron-hole plasma gradually becomes dominant in the optical gain. Dynamics of the carrier relaxation gave further information that the optical gain forms during the cooling procedure of photon-excited hot carriers. Additionally, it was found

that the excitonic optical gain is more easily obtained with near resonant excitation. The gain spectrum is narrower than that of electron-hole plasma indicating that lower threshold density can be expected for excitonic laser diodes.

The longest wavelength ever emitted from wurtzite II-VI oxides was achieved by CdZnO/ZnO multi-quantum-wells (MQWs), which gives the room temperature emission peak at 2.9 eV. This suggests a significant tunable range of bandgap in CdZnO alloys. Stimulated emission and optical gain spectrum of ZnO/MgZnO MQWs were also investigated. A large red shift of the stimulated emission with respect to spontaneous emission was observed. The emission intensity increases quadrically with the excitation intensity. These observations suggest the existence of localized excitons. Since the exciton Bohr radius is as small as 18 Å in ZnO, in order to achieve significant quantum confinement, narrow wells have to be used. Thus the fluctuation of the well width caused by the interface roughness induces the localized states, which inhomogeneously broadens the energy levels of quantum wells. The localized states result in a tail in the optical gain spectrum, which causes the large red shift on stimulated emission. The quadric intensity dependence can be explained by considering non-radiative recombination processes subject to the localized state.

In conclusion, we have developed plasma-assisted MBE growth technique for ZnO heteroepitaxy. A novel buffer has been invented to solve the long-standing problem of large lattice mismatch. The excitonic processes have been demonstrated to dominate the optical properties of MBE grown ZnO epilayers. Heterostructures based on ZnO have also been investigated. Recently, ZnO with its unique properties has stimulated worldwide interest and research activities. In the present research, the material base of crystal growth has been concretely anchored to a new ground required for the applications to optoelectronics and photonics, where high-quality epilayer and heterostructures become available through well developed epitaxial growth technique (plasma-assisted MBE) on widely used low cost substrate (sapphire). Optical studies strongly suggest that extremely stable excitons in ZnO can play a dominant role in a new generation of excitonic devices.

審査結果の要旨

ZnOとその関連するII-VI族化合物半導体は短波長帯における新しい光エレクトロニクス素子材料として有望であるが、光エレクトロニクスデバイス応用のためには、高品質薄膜成長技術の確立が必須である。この物質系に対する薄膜成長では、適切な基板が得られないため、サファイヤ基板などの大きな格子不整を持つヘテロエピタキシが不可欠となっている。格子不整系ヘテロエピタキシでは、種々の格子欠陥が発生し良好な品質を持つ薄膜を得ることが困難である。著者は、酸素プラズマ援用分子線エピタキシ法を開発するとともに、MgOバッファー層を導入した成長プロセスを開発することによって、ヘテロエピタキシにおける結晶工学的な問題点を解決し、高品質のZnO系酸化物エピタキシ技術を確立した。この薄膜技術によって、初めて室温における励起子機構による光励起レーザ発振を実現し、さらに高温までの励起子誘導放出を実証するなど、励起子機構に基づく光デバイスのフィージビリティーを示した。本論文は、この研究成果についてまとめたもので、全文7章よりなる。

第１章は序論であり、本研究の背景及び目的を述べている。

第２章は本研究で開発した酸素プラズマ援用分子線エピタキシ法と薄膜の評価法について記述している。

第３章はサファイヤ基板を用いた薄膜成長において、MgOバッファー層導入によって格子不整、結晶不整、価電子不整が解決されることを述べている。MgOバッファー層を用いて成長したZnO薄膜と、用いない場合のZnO薄膜をX線回折法、フォトルミネッセンス測定、表面モフォロジー測定などにより詳細に比較し、結晶学的にも光学的にも高品質のZnO薄膜が成長できることを示した。

第４章はZnO薄膜成長時における反射高速電子線回折を駆使した表面再配列構造と表面過程のダイナミックスに関する研究成果を記述している。表面再配列構造の原子構造モデルの提案、表面テラスの展開、表面原子の表面泳動、MgやCdの取りこみ過程、Cdの偏析効果などについて記述している。ZnO膜の２次元成長プロセスの実現は、ヘテロ構造の原子オーダー制御を可能にするもので、特筆される。

第５章はZnO薄膜中の格子欠陥の性質、ミクロスこピックな構造、ZnOとサファイヤ基板の界面構造について記述している。これらの研究を通して、ZnO成長過程、欠陥形成過程、界面形成におけるMgOバッファーの役割を明らかにしている。

第６章はZnOエピタキシ膜および(Zn, Mg, Cd)O系ヘテロ構造の室温における高励起下での光学特性について記述している。室温における初めての光励起励起子レーザ発振、高温での励起子誘導放出の実現などについて記し、励起子光デバイスのフィージビリティーを示した。

第７章は本論文の結論である。

以上要するに本論文は、ZnOとその関連するII-VI族化合物を対象として、酸素プラズマ援用分子線エピタキシ法を開発するとともに、新しいバッファー層を導入した成長プロセスを開発することによって、高品質のZnO系酸化物エピタキシ技術を確立し、励起子機構に基づく光デバイスのフィージビリティーを示したものであり、応用物理学ならびに結晶工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。