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論　文　内　容　要　旨

Since reflectance difference spectroscopy (RDS) has been introduced as a new surface sensitive optical technique by Aspnes et al. in 1985, many studies have been performed to characterize static surface structures and to monitor dynamic surface processes in the growth of various material systems. RD signal can be detected from a semiconductor surface even when the material is optically isotropic, if it has anisotropic surface chemical bonds. Hence RDS is sensitive to surface chemical bonds, while the local structure can be analyzed by RHEED. Figure shows the basic conceptual diagram of RDS. When the linearly polarized light is incident on the surface having anisotropic surface dielectric function (As-stabilized GaAs surface as an example), the reflected light will be elliptically polarized due to the difference of reflectance between two directions. The analysis of elliptically polarized reflect light gives the information about the difference of dielectric function between two principal optical axes.

While RDS is very effective tool to investigate a subtle change of surface state as discussed in the above section, quantitative physical analysis of RD spectrum is difficult as described in the previous section. So with the aid of complementary measurement by well established RHEED technique, which is very useful for obtaining the geometrical information such as lattice constant, RDS can be a powerful tool to study the epitaxial processes in MBE. The purpose of this study is to get insight into MBE processes of compound semiconductors by using in-situ RDS and RHEED.
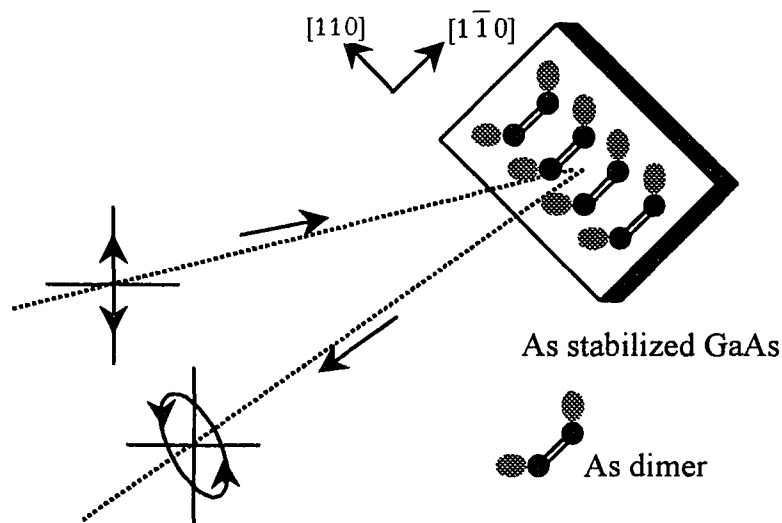
Figure Conceptual diagram of RDS

This dissertation consists of 5 chapters. Chapter 1 gives the introduction of this dissertation. The motivation of this study, previous studies on MBE growth processes with RDS/RHEED, principle of RDS and RHEED, and the scope of the dissertation are described.

Chapter 2 explains experimental details of MBE growth and optical formalism of RDS. MBE system used in the present study consists of two growth chambers (III-V chamber and II-VI chamber), which are equipped with 25 kV RHEED systems and an Auger electron spectroscopy (AES) chamber. RHEED patterns are recorded by Polaroid camera and charge coupled device camera connected to an image processing system. RDS system is positioned outside the MBE system and used for the *in-situ* optical measurement through a quartz window. Our home-made RDS setup is similar to the one developed by Aspnes *et al*. It uses a 75 W Xe lamp as a light source, covering an energy range from 1.5 to 5.5 eV. Focal length of monochromator is 10 cm and its energy resolution is about 10 meV. The incident light is polarized by calcite Glan-Taylor prism and the reflected light was phase modulated by photo elastic modulator (PEM) at 50 kHz to obtain the anisotropy signal. All measuring units are controlled by IBM computer through General Purpose Interface Bus (GPIB) card.

For AES analyses, the samples prepared in the MBE chamber was transferred to the AES chamber through a vacuum tunnel. Samples were characterized using various analytical techniques including atomic force microscopy (AFM), photoluminescence (PL), double crystal x-ray diffraction (DXRD) and transmission electron microscopy (TEM).

The following two chapters describe the topics studied. Chapter 3 deals with the mechanism of nitridation

on GaAs (001) surface, in which nitridation processes on GaAs (001) surfaces exposed to nitrogen plasma were investigated by in-situ RDS and RHEED, and in-line AES. The nitridation reaction has been reported to be an important process to obtain high quality zincblende GaN, which is a parasitic reaction in the initial stage of GaN growth on GaAs. In the critical examination of extensive nitrided GaAs surface, it was shown that an extensive nitridation results in an anisotropically rough surface morphology, which island was directed to [110] direction. The anisotropic island exposes surface planes including <111> familiar plane and the growth of GaN on rough GaAs surface is known to form wurtzite structure GaN on (001) GaAs.

Next, the influences of the As background pressure and of the reconstruction of the initial GaAs surfaces on the nitridation process have been investigated with *in-situ* RDS and RHEED. It was known that nitridation rate is strongly dependent on the background As pressure. A rough GaN can be formed only under sufficiently low As background pressure, while a high background pressure of As suppresses the nitridation process. However, the initial As surface coverage is not significantly affected on nitridation. Several groups succeeded in growing zincblende GaN on GaAs by employing a high As flux in initial growth stage or throughout growth. Our results presented above indicate that such successful growth of zincblende GaN is a consequence of suppressed nitridation of GaAs under a relatively high As flux. Our results clarify the relation between these two observations: a controlled supply of As can suppress the nitridation processes on the GaAs surface, facilitating the growth of high-quality cubic GaN. The results of the RDS and RHEED characterizations reported above are expected to be useful reference data when one would try to determine the optimal As pressure for GaN growth.

Zincblend structure GaAsN layer was successfully grown based on the nitridation study on GaAs surface. It was shown that the nitrogen composition could be estimated from the results of RDS observation during the growth of GaAsN layer.

Chapter 4 discussed the surfactant effect of Sn in Zn(Cd)Se MBE growth. All the species which have been successfully employed as surfactants have in common a tendency to passivate the surface and to segregate strongly on top of the growing film, which means that it is energetically favorable for the surfactant to be driven to the surface. Massies *et al.* classified the surfactants as two types, reactive- and non-reactive surfactants.[1] The reactive surfactant decreases the migration length of ad-atoms through an increase in nucleation sites, which is useful to enhance two dimensional growth in highly strained heteroepitaxial systems. Non-reactive surfactant

enhances migration of ad-atoms by reducing the surface energy, which is useful for low temperature 2D layer-by-layer growth of lattice matched systems.

There has been no report on the SM-MBE of ZnSe related wide band gap II-VI semiconductors although there have been many studies on their epitaxial growth and material properties due to possible applications to blue-green light emitting devices. The surface morphology of ZnSe-related II-VI materials is known to be rough. Moreover, the surface diffusion length of host atoms at normal growth temperature is much less than that of GaAs and it gives difficulty in observing RHEED oscillations during ZnSe growth.

In order to see the effect of initial surface chemistry before Sn deposition, Sn was deposited either onto the Zn terminated c(2x2) surface and onto the Se exposed (2x1) ZnSe surface. The Zn-stabilized surface was prepared by exposing the surface of the ZnSe buffer layer with Zn flux and Sn was evaporated without Zn flux. However the desorption of Se from the ZnSe surface was not negligible at a substrate temperature of 300 °C. Hence Se in addition to Sn was deposited onto the surface to preserve (2x1) reconstruction. In hetero-epitaxy of CdSe on ZnSe, CdSe was grown on a Sn-treated ZnSe surface either by atomic layer epitaxy (ALE) or MBE. Epitaxial processes were compared with the conventional (without Sn) ALE and MBE growth of CdSe. The quantity of segregated Sn onto Zn(Cd)Se surface was measured by AES. The surface morphology of the layers was investigated by atomic force microscopy (AFM) and the crystal quality was investigated with photolumiscence (PL).

First of all, it is interesting that the dynamic behavior after Sn deposition on two initial surface reconstructions, Se stabilized (2x1) and Zn stabilized c(2x2) ZnSe, shows significantly different properties. Sn deposited onto Zn-stabilized c(2x2) ZnSe surface shows surface segregation during further ALE growth, while it was incorporated into ZnSe layer in case of Sn deposition onto Se stabilized (2x1) ZnSe surface. SnSe is known to form an orthorhombic structure (distorted NaCl structure) having lattice parameter (a=5.928 Å, b=5.97 Å, c=12.282 Å) and typical growth temperature of SnSe is around 200 ~ 300 °C. Therefore, it is suggested that Sn forms a compound with surface Se or Se simultaneously supplied with Sn when Sn is deposited onto Se stabilized ZnSe surface(θ_{Se} =1) and it is incorporated into subsurface. Sn on the Zn-terminated ZnSe surface induced a (2x1) reconstruction in the RHEED results. Here, a tentative model is suggested with above information that the position of Sn on the Zn-terminated ZnSe surface is the center of four Se atoms. Sn incorporated onto Zn-terminated ZnSe surface will form complex with four Se atoms, which are also bonded with surface Zn atoms.

In addition, different RD spectra and RHEED patterns during shutter operations depending on the initial surface chemistries suggest the timing of the moment of surface segregation of Sn. If Sn deposited on Zn-stabilized ZnSe surface segregates onto the Se-stabilized surface (or during Se expose), the Sn segregated onto Se surface will show the same result as in the case of Sn deposition on Se-stabilized ZnSe surface and it must be incorporated into the over layer. It means that Sn deposited on Zn-stabilized ZnSe surface does not segregate during Se exposure but segregate during Zn exposure. Surface morphology was investigated with AFM. RMS value for Sn used sample was 1.086 nm and that of normal sample was 1.567 nm.

In the study of the role of Sn in the highly strained CdSe heteroepitaxy on ZnSe, the surface morphology of the CdSe layer grown by ALE mode with Sn as surfactant materials was relatively rough compared to that of normal MBE growth. And in the RHEED study during MBE growth of CdSe layer, three periods of RHEED intensity oscillation was obtained in the normal MBE growth, which means two dimensional layer by layer growth. However, no oscillation was observed in the Sn SMMBE. It was supported by the results of surface lattice relaxation measured with RHEED analysis.

From such results, it is suggested that the role of Sn used in the growth of ZnSe related II-VI compound semiconductors is to enhance the surface diffusion length of ad-atoms. Sn in Zn(Cd)Se can be classified as a non-reactive surfactant.

審査結果の要旨

　反射率差分光（RDS）は物質の誘電率の光学的異方性を探る実験方法である。もし、表面化学結合に異方性があるならば、たとえバルク的な光学的異方性が見られないときでも、反射率差（RD）信号は観察することができる。それゆえ、RDS は表面化学結合に敏感である。他方、局所的な構造解析は反射高速電子線回折（RHEED）により可能であり、半導体エピタキシャル成長中の表面状態の包括的な解析は RDS と RHEED により可能である。つまり、表面解析において、RDS と RHEED は互いに補完的な評価方法になる。それにも関らず、分子線エピタキシャル（MBE）成長に関するほとんどの研究は RHEED により行われており、RDS と RHEED の両方法を用いた研究例は少ない。

　本論文は、RDS と RHEED のその場観察により原子的な観点から化合物半導体の MBE 成長プロセスに関する知見を得ることを目的としたもので、全体で五章からなる。

　第一章は序論であり、本論文の背景を述べ、意義及び目的を明確化している。

　第二章では、実験方法について述べている。この章では、MBE 法による結晶成長と RHEED の原理、RDS の光学系の詳細について述べている。

　第三章では、GaAs(001)表面の窒化のメカニズムについて述べている。GaAs(001)表面の窒化は窒素プラズマを基板表面に入射することにより行い、窒化過程の表面を RDS 及び RHEED によりその場観察し、超高真空トンネルにより接続されたオージェ分光法（AES）により評価した。成長室中の As 背圧が十分に低いときにのみ、安定した GaN 層が形成され、逆に As 背圧が高いときは窒化が抑制されることを明らかにした。窒化過程のメカニズム及び立方晶 GaN 成長への応用が論じられている。過剰な窒化による表面荒れについても論じられている。さらに、窒化の応用として、RDS 及び RHEED による成長中のその場観察の結果を用い、GaN_xAs_{1-x} の MBE 成長について論じている。

　第四章では、ZnSe の MBE 成長における Sn のサーファクタント効果について論じている。他方 Sn を添加した(2x1) Se 安定化面では層成長が実現しにくいのに対し、Sn を添加した c(2x2) Zn 安定化面は成長表面を安定化し層成長が促進されることを明らかにした。さらに、ZnSe 表面上の CdSe 量子ドット形成に対する Sn の効果を評価した。

　第五章は結論である。

　以上要するに本論文は、誘電率の異方性の観察が可能でありながら、その実験的、理論的複雑さにより研究例が少なかった RDS が、RHEED 観察と組み合わせることによって、MBE 成長中の新たなるその場観察の手段として優れた能力を有していることを明らかにしたもので、半導体工学及び材料物性学の発展に寄与することが少なくない。

　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。