ELECTRON MICROSCOPY OF III-NITRIDE THIN FILMS AND SIC NANOCRYSTALS

Summary of the PhD thesis

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I. Introduction

In the recent 10-12 years there have been many efforts to investigate the wide band gap semiconductor materials. The reason for this is the increasing need for development of the devices with special features made of them. However, the device development to a greater extent needs the strengthening of basic research in this field.

SiC and the III-nitride material group are the most important materials from the wide band gap semiconductor family. I investigated GaN, GaInN, GaAlN epitaxial thin films, and SiC nanocrystals from this group.

The primer application of these materials are the high-power, high-frequency semiconductor devices, which work at high temperature, and the semiconductor optoelectronics. Although working devices can be made of them, the present layers need further structural improvement due to the high number of defects they contain.

The main stream of investigations in the case of SiC film growth: decreasing the number of micropipes or terminate them, elimination of the domain boundaries, obtaining good surface homogeneity. In the case of GaN, the bulk growth is not solved at all. The main research goal is the growth of hexagonal GaN layers with acceptable quality in the form of heteroepitaxial layers.

The III-nitride samples needed for the research work could not been produced in Hungary because of lacking the special technical background. It would be very expensive to purchase special metalorganic chemical vapor deposition reactor dedicated to nitride thin film growth. The samples for my investigations originate mainly from Thales Laboratorie Central de Recherches (previously called Thomson CSF), and from other foreigner partners. The SiC samples were produced at the Budapest University of Technology and Economics, Atomic Physics Department. The base of the domestic research is the electron microscopy laboratory of the Research Institute for Technical Physics and Materials Science, which gives useful results for device developers and film grower partners.

II. Objectives

During my PhD research work I had to learn the sample preparation and the operation of transmission electron microscopes. Beside the investigation of defect structure of special III-nitride thin films, I carried out the analysis of origin of the defects, and the optimization of the growth conditions of some III-nitrid and Si/SiC/SiO_2 film structure.

Targets were:

- characterizing the defect structure using electron microscopy,
- searching relations of origin of special defects with other features,
- making efforts to decrease the defect density in nitride thin films,
- determining the possibilities and limits of SiC growth at Si/SiO_2 interface in CO pressure, and how large the smallest crystal grains are.

III. Investigation techniques

My work was carried out mainly on two transmission electron microscopes. I got professional skills in using of Philips CM20 (200 keV) and JEOL 3010 (300 keV) transmission electron microscopes (TEM). The line-resolution of the JEOL microscope reaches 1.4 Ångström. The sample preparation is the most difficult in this technique. It is very difficult to prepare artifact free, nice sample which reflects the real structure. However, that is possible with great experience and patience. The wide band gap semiconductor samples are thinned by ion beam milling till they become transparent to the electron beam, but thick enough to give information about the original sample.

Many results in my research work are connected to a JEOL JSMT25 and a LEO 1540XB scanning electron microscopes (SEM). The latter one has a field emission gun and can reach 1.1 nm lateral resolution at special circumstances.

IV. New scientific results

1. Investigation of GaN/GaAlN fim structures [R1,R2]

I investigated the defect structure of GaN and GaAlN films, GaN/GaAlN superlattices grown onto sapphire by metalorganic chemical vapor deposition.

a., I showed that pits sized around 0.1 micron in diameter can be found on the surface of GaAlN films grown in definite parameter range. These pits are regular, hexagonal based pyramids turned upside down. I showed that an inversion domain can be found under each pits. These inversion domains started to grow from the substrate. The unambiguous connection of surface pits to the inversion domains gives the solution for their elimination, since the ratio of the inversion domains and the dislocations can be controlled.

b., I proved that similar pits can be found also in GaN/GaAlN superlattice systems. The bending of the individual layers of the superlattices shows that the pits formed already at the nucleation and at the very first stage of growth.

c., I confirmed that the inverted surface pyramid connected to an inversion domain configuration differs from that observed in GaInN, because in that case these pits are always connected to dislocations. I found aluminium segregation at the sidewalls while in the case of GaInN indium segregation is observed.

2. Influence of the Al concentration on the defect structure of GaAlN [R5]

I investigated the relationship between the concentration of Al and the defect structure in $Ga_{1-x}Al_xN$ ternary thin films grown by metalorganic vapor deposition.

a., I showed that the density of surface pits not linearly changes with the Al concentration, there is a maximum at X_{Al}= 9-10 at%, and after that the pit density starts to decrease strongly. The surface pits fully disappear at X_{Al}≈15 at%.

b., I proved that cracks appear on the surface from Al concentration of X_{Al}= 10 at%. The amount of cracks increases with increasing Al concentration.

c., I found that the optimization of growth conditions could result in eliminating the inversion domains, therefore the formation of surface pits and cracks can be avoided.

3. Decreasing the dislocation density with SiN_x thin film interlayer [R3, E2]

a., I confirmed that the direction of most dislocations in GaN grown by metalorganic chemical vapor deposition can be influenced by a thin amorphous SiN_x mask system and by setting the optimal parameters in the different growth steps. If the GaN growth direction above the mask has a component parallel to the surface, most of the dislocations bend, consequently the dislocation density decreases with the increasing distance from the level of the mask layer.

b., I proved that amorphous SiN_x grains deposited randomly onto the substrate act as masking grains, thus most of the dislocations bend to the plane parallel to the surface.

c., I showed that the density of dislocations can be decreased up to two magnitude of order in both cases mentioned above. In my samples the defect density decreased from 2-4x10^9 cm^{-2} to 4-7x$10^7$$cm^{-2}$.

4. Investigation of buried SiC nanocrystals [R4, R6, E1]

SiC nanocrystals are formed at Si/SiO_2 interface during annealing of (111) and (100) oriented, SiO_2 covered Si for different times and at different temperatures in CO ambient pressure. I investigated these nanocrystals by TEM and SEM.

a., I showed that the density of the Si nanocrystals grown epitaxially to the Si substrate is 1-10 x 10^9 cm^{-2}, The nanocrystals contain stacking faults characteristically. Higher quality and more regular shaped SiC grains were grown on (100) oriented Si wafer at 1190°C than on (111) at 1100°C. The fastest growth direction of SiC is <111> on both (100) and (111) oriented Si.

b., I proved that the Si surface move away from the SiC nanocrystals due to the applied Si oxidation by post-annealing in oxygen atmosphere. Pyramids made of Si remain behind under the SiC nanocrystals because the nanocrystals act as masking grains for the surface of the Si substrate oxidation. The distance between the tip of the pyramids and the SiC nanocrystals depends on the post-annealing time.

c., I confirmed that layers of SiC nanocrystals buried in amorphous SiO_2 at different levels can be formed by repeating the SiC nanocrystal forming process and the oxidation of the Si surface.

V. Utilization of the results

Results related to GaAlN are utilized by THOMSON LCR (THALES R&T). Many companies (Osram, Novasic, Lumilog, etc.) used the results related to GaN defect reduction technique in optimization of thin film growth and lifetime of devices.

The work described in my thesis assisted some projects in successfulness. The most important ones are:

- FP5 – EURONIM: European Sources of Nitride Materials, (G5RD-CT-2001-00470)
- Growth mechanisms, structure and contacts of the wide band gap semiconductors – OTKA T03044
- Development of cross sectional sample preparation using gaseous ion beam sputtering – OTKA T035267
- Ion beam techniques in the physical nanotechnology (IONNANO) – OTKA T043704

V. List of publications related to my PhD work

Last updated of the data:	2005.06.06.
Summa impact factor (IF):	14,071 (based on Y2003 data)
Number of independent citations:	27
Number of referred publications:	6

Referred publications

R6. **Makkai Zs**, Pécz B, Bársony I, Vida Gy, Pongrácz A, Josepovits KV, Deák P
Isolated SiC nanocrystals in SiO_2
Applied Physics Letters, accepted for publication

R5. **Makkai Zs**, Pécz B, di Forte-Poisson MA
TEM investigation of defect structure in GaAlN/GaN heterostructures
Vacuum 71 (1-2): 159-163 (2003) – IF: 0,612

R4. **Makkai Zs**, Pécz B, Vida Gy, Deák P
TEM characterization of epitaxial 3C-SiC grains on Si(100) and Si(111)
Inst. Phys. Conf. Ser. 180, 265-268 (2003) – IF: 0,194

R3. Frayssinet E, Beaumont B, Faurie JP, Gibart P, **Makkai Zs**, Pécz B, P. Lefebvre, P. Valvin
Micro epitaxial lateral overgrowth of GaN/sapphire by metal organic vapour phase epitaxy
MRS Int. J. of Nitride Semicon. Res. 7,8 (2002) – IF: 4,565

R2. Pécz B, **Makkai Zs**, di Forte-Poisson MA, Huet F
V-shaped defects connected to inversion domains in AlGaN layers
Applied Physics Letters 78 (11): 1529-1531 (2001) – IF: 4,049

R1. **Makkai Zs**, Pécz B, di Forte-Poisson MA, Huet F
Characterization of GaAlN/GaN superlattice heterostructures
Material Science Forum 353-3: 803-806 (2000) – IF: 0,602

Other publications

E2. Pécz B, **Makkai Zs**, Frayssinet E, Beaumont B, Gibart P
Transmission electron microscopy of GaN layers grown by ELO and micro-ELO techniques
Physica Status Solidi (c) 2, No. 4, 1310-1313 (2005) – IF: még nincs

E1. **Makkai Zs**, Vida Gy, Josepovits KV, Pongrác A, Bársony I, Pécz B, Deák P
Electron Microscopy of SiC nanocrystals
European Microscopy Congress, poszter előadás, Belgium, Antwerpen, 2004. augusztus 21-27.
CONF PROC. Vol II, 2004, 191-192

Conference participations

K7. Pécz B, **Makkai Zs**, Frayssinet E, Beaumont B, Gibart P
Transmission electron microscopy of GaN layers grown by ELO and micro-ELO techniques
7th Expert Evaluation & Control of Compound Semiconductor Materials & Technologies, poster pres., France, Monpellier, 1-4.06.2004.

K6. Riemann T, Christen J, **Makkai Zs**, Pécz B, Frayssinet E, Beaumont B, Faurie JP, Gibart P
Lateral overgrowth of in situ SiN masks for low dislocation density GaN on sapphire
MRS Fall Meeting, poster pres., USA, Boston, 01-05.12.2003.

K5. **Makkai Zs**, Pécz B, Vida Gy and Deák P
TEM characterization of epitaxial 3C-SiC grains on Si (100) and Si (111)
XIII. Microscopy of Semiconducting Materials, poster pres., England, Cambridge, 03.04 - 29.03.2003.

K4. **Makkai Zs**, Pécz B, di Forte-Poisson MA
TEM investigation of defect structure in GaAlN/GaN heterostructures
9th Joint Vacuum Conference, poster pres., Austria, Leibnitz, 16-20.06.2002.

K3. **Makkai Zs**, Pécz B, di Forte-Poisson MA
TEM investigation of defect structure in GaAlN/GaN heterostructures
Diffusion and Reactions at Solid-Solid Interfaces, poster and oral pres., Germany, Halle, 25.09 - 03.10.2001

K2. **Makkai Zs**, Pécz B, di Forte-Poisson MA and Huet F
Characterisation of GaAlN/GaN superlattice heterostructures
European Conference on Silicon Carbide and Related Materials, poster pres., Germany, Closter Banz, 3-7.09.2000.

K1. **Makkai Zs**
GaN filmstructures
Conference of the Hungarian Microscopy Association, oral pres., Balatonalmádi, 25-27.05.2000.