The Nobel prize in physics 2014

Incandescent light bulbs lit the 20th century but the 21st century will be lit by LED lamps—thanks to discoveries recognized by the Swedish Academies of Science

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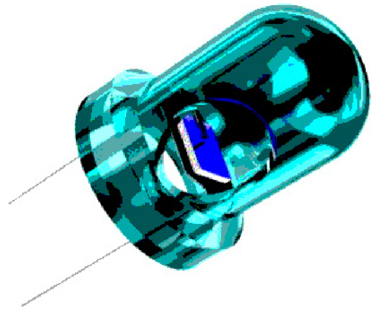
On October 7th, 2014, the Royal Swedish Academy of Sciences announced that the 2014 Nobel Prize in Physics will be awarded to the three Japanese professors, Dr. Isamu Akasaki at Meijo University, Dr. Hiroshi Amano at Nagoya University, and Dr. Shuji Nakamura at University of California, Santa Barbara, for "the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources".

The advent of the white light source according to the practical application of blue light emitting diodes (LED) brings great benefit to mankind, in the form of home lighting, display devices such as public signals, display backlighting, etc. Conventional white light bulbs create light by heating filaments, making them glow with a low conversion efficiency. Instead, an LED utilizes the recombination of electrons and holes, with good energy conversion efficiency for changing the electric power directly into light. The efficiency of this white light creation is promising for energy saving, as well as its longer-lasting nature. It is also favorable for human health and is environmentally friendly since it does not contain hazardous elements, such as mercury. The blue LED was the final technology necessary for practical white light LED-based illumination based on the triad of red, green and blue LEDs. Red and green LEDs have been available for almost half a century but creation of an effective blue LED has been an elusive challenge for many decades.

An important material responsible for blue light emission is GaN (gallium nitride) semiconductor thin film. Due to its nature of high breakdown voltage and its capability of high temperature operation, GaN had been attracted a great deal of attention for use in power electronic devices, as well as in the research surrounding the blue LED. However, the crystal growth of GaN proved to be very difficult because large, single-crystalline, native substrates to grow single crystalline epitaxial thin films were not known. In contrast, red and green LEDs, composed from (Al, Ga) As or Ga (As, P) solid solutions (mixed crystals), can be fabricated on GaAs single crystal substrates by



epitaxial growth. This favorable situation arises from the fact that these materials have the same crystal structure, i.e., a zinc-blende type. Though the crystal structure is the same, this type of epitaxial growth is classified as "Heteroepitaxial growth", since the compositions are different.

The lack of sufficiently large high-quality native GaN substrates led to the employment of sapphire substrates for the production of GaN blue LEDs. There exists a symmetric similarity for *c*-axis growth of GaN (hexagonal) on *c*-plane of Sapphire (trigonal). However, these two materials are totally different in the crystallographical view point, such as atomic coordinations, or nature of bonding, etc. This fact can be found in the significant difference in their lattice constants (axis length) of unit cells (the so called lattice mismatch), and in the large difference of their thermal expansion coefficients(1).

In order to obtain single crystalline epitaxial GaN films on sapphire substrates in spite of the bad accommodation between these two materials, Akasaki and Amano's group introduced a thin AlN buffer layer grown at low temperature prior to the high-temperature GaN film growth(2). A thin GaN layer grown at low temperature was revealed to improve the crystalline quality of following GaN epitaxial films grown at high-temperature by Nakamura's team(3). A great paradigm shift in thinking about epitaxial growth was required for their discoveries since high quality epitaxial films were believed to be grown on flat and clean surfaces of substrates. To further enhance LED performance, Akasaki and Amano's group made improvements in the

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growth chamber of the MOVPE (Metal-Organic Vapor Phase Epitaxy) growth method[4]. The efficient light emission in GaN doped with Mg as the *p*-type dopant, followed by irradiation treatment with a low-energy electron beam was reported[5] from the same group. This was the important breakthrough for the fabrication of the *p–n* junction in the LED structure. Fast GaN film growth for industrial processing was realized by a novel MOCVD (Metal-Organic chemical Vapor Deposition) reactor with dual gas flows[6], proposed by Nakamura's group of Nichia Chemical Industries, Ltd. They also demonstrated the improvement of the LED performance via thermal annealing treatment in N_2 atmosphere, by revealing the dependency of the electrical conductivity of GaN films on the residual hydrogen atoms[7].

Pioneering research activities by these three scientists through their long series of various improvements led to the invention of the blue LED and consequently bright and efficient white light for humans.

Of particular interest in this article is the relationship of Rigaku with blue-LED research, with respect to material characterizations or process evaluations. The Rigaku Journal included special feature articles highlighting GaN-related materials just one year before, as "GaN for Opto- and Power-electronic Applications"[1], [8].

The core part of a GaN-LED is single crystalline epitaxial multilayers (superlattice) of several nanometers thick. Parameters, such as their crystalline quality, thickness (including the repetition period of superlattice), compositions of solid solutions (mixed crystal), and lattice strain/deformation, are the major issues of characterization, as are the same with other epitaxial films. These parameters can be deduced by using high-resolution XRD techniques[8]. Their thicknesses may be analyzed via X-ray Reflectivity (XRR) analysis, but this analysis is not necessarily easy due to the significant curvature in samples, caused by the large mismatch in thermal expansion coefficients between films and substrates. X-ray Fluorescence (XRF) spectroscopy techniques have become important non-destructive tools to detect the metallic contaminants for process control[9]. Since the aim of the characterization is the detection of surface contaminants originated from factory environments or from chambers of thin film growth or processes, the Total Reflection X-ray Fluorescence spectroscopy (TXRF) has come to be recognized as one of the most powerful and indispensable tools for this purpose. It is recently reported that the X-ray radiography technique has been employed as a check to identify electrodes that are peeling in the molded final chip products.

It is natural in technological history that various characterization techniques have progressed in accordance with the evolution of devices. The rocking curve characterization of twist spreading (the orientation variation of lattices within the surface plane and around the crystallographic axes of growth of films)[1] has come to be widely employed. This situation derived from the fact that the physical parameters determined from identical rocking curves were found to be crucially correlated with the large lattice mismatch present for the GaN-LED materials. Lattice misorientations between epitaxial films and substrates, or curvatures of substrate crystals are now recognized as the important parameters for the characterization of heteroepitaxial systems with large lattice mismatches. A great demand of faster Reciprocal Space Mapping (RSM) measurements in wider reciprocal space areas in GaN-LED materials was one of the largest driving forces for developing a fast RSM measurement technique utilizing a 1-dimensional X-ray detector. This led to the use of a 1-dimensional detector was also applied to the XRD measurements for bulk ceramic materials or powder samples.

There also exists a need for *in-situ* characterization during film growth in MOVPE chambers, where electron diffraction techniques cannot be applied due to low vacuum conditions. An *in-situ* XRD/XRR monitoring system combined with MOVPE chambers has recently appeared[10].

Since the crystal structure of GaN is known as a hexagonal wurtzite type, which lacks centrosymmetry, GaN crystals show piezoelectricity. This means the device performance in *c*-axis grown GaN-LED is affected by the intrinsic spontaneous and/or piezoelectric polarization field due to the electric carrier transportation properties. A nondestructive determination technique of the crystallographic polar direction of GaN epitaxial films by XRD in conventional XRD system was proposed[11]. In recent years, approaches to grow GaN epitaxial thin films along semi-polar or non-polar direction have been widely studied[8]. In the cases of the semi-polar or non-polar GaN single crystal growth, the symmetry around the growth axis of GaN films should be treated as anisotropic. Furthermore, semi-polar or non-polar GaN growths are performed on non-isotropic lattice planes (not isotropic around the axes perpendicular to the lattice planes) on substrates. Therefore, lattice strains for these films should be analyzed with complex stress field models.

As Materials Science advances, improvements and evolutions in various technologies will also advance. Novel discoveries or revolutionary technologies will contribute to the evolutions in Materials Science and process developments. The blue LED will light the world of Materials Science.

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