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Research and Development of Electronic and Optoelectronic Materials in China

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Abstract: A review on the research and development of electronic and optoelectronic materials in China, including the main scientific activities in this field, is presented. The state-of-the-arts and prospects of the electronic and optoelectronic materials in China are briefly introduced, such as those of silicon crystals, compound semiconductors, synthetic crystals, especially nonlinear optical crystals and rare-earth permanent magnets materials, etc., with a greater emphasis on Chinese scientist´s contributions to the frontier area of nanomaterials and nanostructures in the past few years. A new concept of the trip chemistry proposed by Dr. Liu Zhongfan from Peking University has also been described. Finally the possible research grants and the national policy to support the scientific research have been discussed.

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1 Bulk Materials

1.1 Silicon Materials

Electronic materials play more and more important role in making electronic devices and integrated circuits. It was predicted that up to FY2000 the world electronics market would reach about USD $200 billion, in which 95% is silicon-related electronic devices and systems. Unfortunately, China only has a productive capability of 80tons polycrystal silicon and 300tons silicon single crystals a year, and epi-ready silicon wafers are 0.5% of the total wafers output in the world (4 billion square inch). However, a polycrystal silicon factory with annual produce of 1000 tons and two 200mm wafer mass production lines are under construction, and in the meantime, fabrication of 300mm silicon crystal is in its experimental phase. Hopefully, we would reach 5% of the total world silicon production by the year of 2005.

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1.2 Semi-Insulating GaAs Crystals

Undoped Semi-Insulating (SI) GaAs crystals are widely used for high-speed devices, MMIC and GaAs IC's, which are important to the highspeed computation, mobile optical fiber communications and the military purpose as well. Compared with silicon, the situation of SI-GaAs in China is relatively good. SI-GaAs crystal wafer of 50—75mm can meet the commercial requirements in domestic market, and the pulling SI-GaAs crystals with a diameter 100mm is still in a short production run. SI-GaAs crystal with a diameter of 150mm is prepared in the laboratory. By the end of year of 2005, China is expected to have the annual capability of SI-GaAs crystals of 3 tons, which is about 6% of the world annual yield.

1.3 Synthetic Crystals

Growth and study of the synthetic crystals, especially of the NonLinear Optical (NLO) crystals belong to high-tech fields, in which China is in the leading position. Synthetic crystals can be applied to some important industries, military, scientific and technological fields and daily life, such as the generation and frequency-tuning of lasers, optical communication, optical storage, optical calculations and laser processing and surgery etc.

The crystal research in China has gradually entered into "crystal engineering" stage. According to requirements of the applications, we are now able to design, explore and grow new crystals. A number of new crystals with Chinese characteristic such as Cesium triborate($C_3B_3O_5$, CBO), BBO, Lithium triborate (LBO), KDP (KH_2PO_4), Ce: $BaTiO_3$, etc. have been discovered during the past two decades, during which China occupies the leading position in the world. The NLO crystals are potentially useful materials for the harmonic of high power density in laser systems, especially the tunable UV generation to 185nm by Sum Frequency Generation (SFG).

Techniques for growing of large-sized Ti∶Al_2O_3(Ti∶sapphire) crystals by temperature gradient method have been developed at the Shanghai Institute of Optics and Fine Mechanics in early 90's. High perfection and excellent optical homogeneity $\Delta n \leqslant 10^{-5}$/inch for the laser rods have been obtained, as well as the Ti doping concentration of 0.6wt%, high FOM (Figure of Merit) value of 200—300 and the high optical damage threshold of 15J/cm^2. Combining the semiconductor laser diodes or diode arrays, some kinds of all solid-state tunable lasers are obtained, i.e. a prototype of fs laser with a power of 120mW and a pulse width of 28fs has been produced.

Besides various kinds of artificial crystal, such as Cr∶Tm∶Ho∶YAG laser crystals, a new type of photorefractive crystal, KNSBE, Fe∶Mg∶$LiNbO_3$ crystals and tunable laser materials of Cr^{3+} LiCAF, Cr^{3+} LiSAF, etc. are also synthesized in labs.

1.4 Rare-Earth Permanent Magnet Materials

China has an abundance of rich rare-earth, with the reserves being about 80% of the total in the world. The verified and the prospective reserves of rare-earth elements in China are 48million tons and over 100 million tons respectively, which are distributed over

Baotou of Inner Mongolia and Jiangxi province. In 1999, the total output of rare-earth is 6×10^4 tons and that of pure oxides and metals are 2.5×10^4 tons, as shares about 70% of the global market.

The rare-earth permanent magnet materials, especially NdFeB magnets, have been explored widely in recent years both in China and out of China. The global output of sintered NdFeB was 285 tons in 1987 and 9600 tons in 1998, while the output of NdFeB magnets in China was 4000 tons in 1998 and 5180 tons in 1999. However, the grade of the production yielded in China is still very low.

On the other hand, the rare-earth giant magnet stricture materials, Tb-Dy-Fe with < 110> oriented, and 20mm in diameter, has been developed and of the international advanced standard. Research on the rare-earth element related to the electroluminescence materials is also in progress.

1.5 Ceramics Powder with High Dielectric Constant for Multilayer Ceramic Capacitors

More than 200 tons of ceramics powder with high dielectric constant and low firing temperature have been produced in China, ten percent of which was exported in 1998. About 5 billion pieces of MultiLayer Ceramics Capacitors (MLCC) were fabricated.

Two kinds of $BaTiO_3$, based and relaxed the ferroelectric composite materials, are studied systematically, and the dielectric constant, in the range of 4600—5200, has been obtained.

2 Superlattice and Quantum Well Structures

In early 80′s, Chinese scientists and engineers began to work with the GaAlAs/GaAs (InGaAsP/InP etc.) superlattice and quantum well materials using the home-made MBE (MOCVD) system. After their solving many unexpected problems caused by the home-made machines, the stability of the system and growth conditions were greatly improved. The electron mobility of GaAlAs/GaAs two dimensional electron gas (2DEG), of $1.14\times10^6 cm^2/(V\cdot s)$, was obtained at 4.8K in 1993, which demonstrates that the quality of 2DEG materials reached the international advanced state. The experimental results, as shown in Fig. 1, demonstrate that the roughness of 2DEG GaAlAs /GaAs interface grown by us is less than one atomic layer.

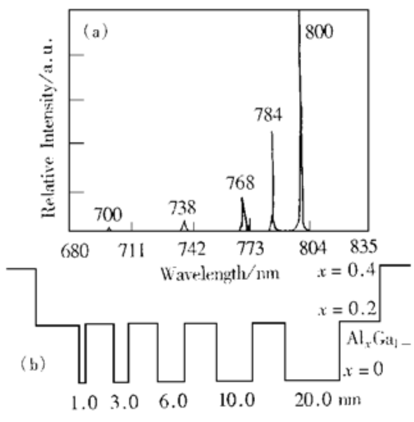


FIG. 1 AlGaAs/GaAs Quantum Well Structure (a) and Corresponding PL Spectra (b)

On the basis of high quality 2DEG materials, HEMT and PHEMT devices with excellent performance (for an example, GaAs based PHEMT, g_m = 690mS/mm, f_T = 82GHz) are realized at labs. In the meantime, high power quantum well lasers in pilot production and the module of 1.55μm Distributed Feed-Back (DFB) lasers/ EA modulator for optical fiber communication are successfully fabricated. In addition, the heterostructures have also been prepared for the vertical cavity surface emission laser and Self-Electronic-Optic Effect Devices (SEED), etc. in some institutes and universities in China.

High performance semiconductor laser in the mid-infrared region are desired to be applied to the remote chemical sensing, infrared countermeasures, biomedical diagnosis and free space optical communication, etc. In recent years, the Quantum Cascade (QC) laser based on both intersubband[1] and interband[2] transitions have been demonstrated successfully in InGaAs/InAlAs and type Ⅱ InAs/InGaSb/AlSb quantum well structures, respectively, with the wavelength ranging from 3.4 to 13μm. The intersubband QC lasers based on InGaAs/InAlAs quantum well structures have been fabricated at Institute of Shanghai Metallurgy, Chinese Academy of Sciences (CAS) and Institute of Semiconductors, CAS as well. The mid-infrared QC laser emitting at the wavelength of 5μm and 8μm respectively were operated in pulsed mode at the temperature up to 220K. Figure 2 (left) is the schematic band diagram of the active and the injective regions for InGaAs/InAlAs intersubband QC laser, while the Figure 2 (right) is the high-resolution cross-section TEM image for the QC laser structure. They indicate that the high quality structure has been obtained with dislocaton-feee and smooth interfaces.

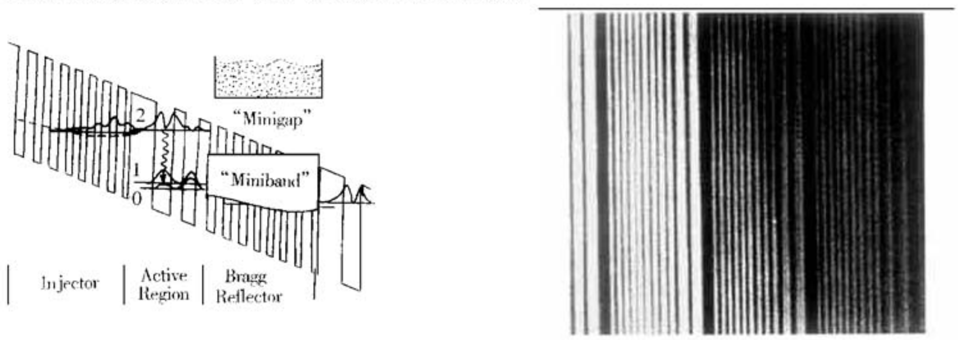


FIG. 2 Schematic Band Diagram of InGaAs/InAlAs Intersubband QC Laser (Left), High-Resolution Cross-Section TEM Image of Structure (Right)

Similar idea has been proposed in early 70s by a Chinese scientist, about the high power laser structure based on the interband quantum tunneling and the photon coupling between the multi quantum well active regions. A 5-W Continuous-Wave (CW) laser operation of three active regions coupling at room temperature with wavelength of 980nm has been demonstrated recently, which indicates its potential application in the optical pumping source of optical fiber amplifier.

3 Studies on Nanomaterials and Nanostructures in China

The preferable properties of nanomaterials and nanostructures (or low dimensional materials and quantum devices), which are quite different to those of bulk materials, have attracted much attention during the past decades. To these materials, the effects of quantum's size, quantum tunneling, quantum interference, surface and interface, as well as the non-linear optical effect will all lead to their distinctive properties. A new type of the device with these materials has been proposed and demonstrated. The important contributions to this new field made by Chinese scientists in past few years are reported briefly in this paper.

3.1 Carbon Nanotubes and Gallium Nitride Nanorods

Many groups in China are working on the study of carbon nanotubes. Prof. Xie Sishen *et al*. from Institute of Physics, Chinese Academy of Sciences, have succeeded in preparing "very long" (~ 1cm) well- aligned carbon nanotube arrays, which makes it easier to study the mechanical and electrical properties of the carbon nanotubes. And a single well carbon nanotube with a diameter of 0.5nm was fabricated recently by his group, which is very close to the theoretical limitation of 0.4nm. Prof. Fan Shoushan's group, from Tsinghua University, on the other hand, has made GaN nanorods via a carbon nanotubes-confined reaction[3], in which Ga_2O vapor reacts with NH_3 gas in the presence of carbon nanotubes to form GaN nanorods. The nanorods have a diameter of 4—50 nanometers and a length up to 25 micrometers. It is proposed using the carbon nanotubes as a template to confine the reaction, as results in the free-standing hexagonal wurtzite GaN nanorods, which have a similar diameter to that of the original nanotubes after the evaporation of the carbon nanotubes via heat treatment at a higher temperature. Fan Shoushan *et al*.[4] have succeeded in the synthesis of massive arrays of monodispersed carbon nanotubes on patterned porous silicon substrates and the plain ones. The well-ordered self-oriented nanotubes have been tested, which are uniformly on typical 2cm × 2cm silicon substrates and acting as electron field emitter arrays with the results shown in Fig. 3.

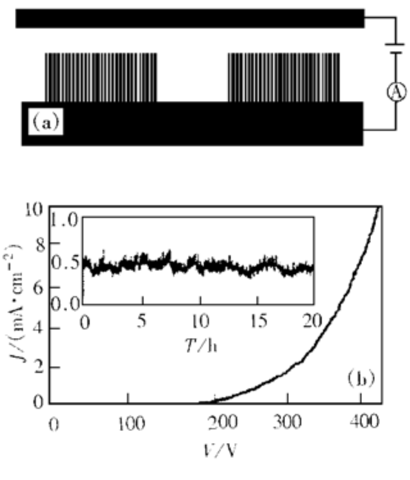
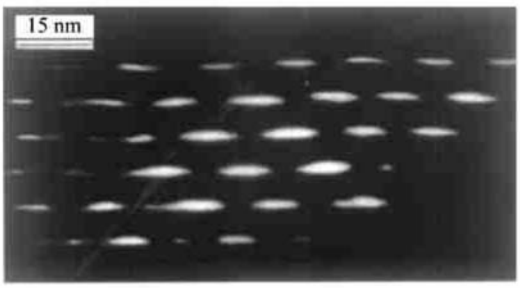


FIG. 3 Self-Oriented Nanotube Arrays as Electron Field Emitter Array. (a) Experimental Setup. The cathode consists of a n^+-type porous silicon substrate with 250μm by 250μm nanotube blocks. The height of the blocks is 130μm. Aluminum-coated silicon substrate serves as the anode and is kept 200μm away from the sample by a mica spacer containing a hole in the center. (b) Current Density Versus Voltage Characteristics.

In addition, Chinese scientists have also made important contributions to the discovery of nanobalance for the following purpose of: (1) measuring the mass of a single nanoparticle, (2) preparation of large-sized C_{60} single crystal (~ 13mm long and ~ 6mm in diameter), (3) hydrogen storage with carbon nanotubes, (4) identification of Buckyball (a C_{60} molecular) orientation on silicon surface and (5) preparation of nanocables, such as SiC core with SiO_2 sheathing, TaC superconductivity core with graphite or SiO_2 sheathing, etc.

3.2 Strain-Induced Self-Assembled Quantum Dots and Quantum Wires[5—7]

The strain-induced self-assembled technique in lattice mismatched system, which is on the basis of Stranski-Krastonow (SK) growth mode, has been widely applied in fabrication of density-packed defect-free QDs, which might lead the great developments of nanoscale optoelectronic devices in future. However, the uniformity and density of QDs, especially the quantum wires (QWRs), are extremely difficult to control, as makes it impossible to obtain the favorable performance of nanoscale devices as theoretical predictions. Recently, it is found by Zhanguo Wang′s group in Institute of Semiconductors, CAS that by adjusting the growth conditions, the density and ordering of self-assembled InGaAs/GaAs, InAs/InAlAs/InP and InAs/InGaAs/InP QDs and QWRs can be controlled, which are grown by SK growth mode using MBE technique. At the same time, we observed the surprising alignment of dots and their remarkable elongation under specific condition. Spontaneous formation of InAs QWRs in InAlAs/InP (001) via sequential chain-like coalescence of QDs along[1—10] is realized. Theoretical calculation based on the energetic of interacting steps proves the experimental results. Sequential coalescence of initial isolate dots reduces the total free energy greatly. Thus the wire-like structure is rather favorable. This fascinating crossover from QDs to QWRs might become a new approach to the fabricate high-density QWRs. Multi-stacked bilayer InAs/InAlAs has been grown with the purpose of proving the uniformity and shapes of QWRs. Contrary to the result observed in vertically coupled InAs/GaAs QDs array, the anti-correlation in the growth direction of InAs/InAlAs multilayer array was firstly discovered in our lab (see Fig.4).



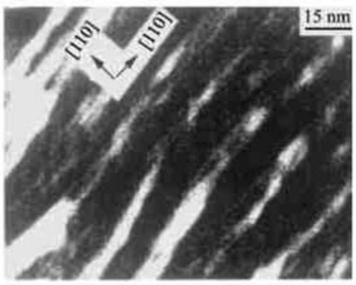


FIG.4 Plan-View TEM Image of Six-Period 6.5ML InAs/20nm InAlAs (Lift) and [1—10] Cross Sectional TEM Image of Six-Period 6ML InAs/10nm InAlAs (Right)

To explain this abnormal feature, the strains of two-dimensional (2D) QWR arrays in infinite isotropic materials are calculated on the basis of principle of minimum energy. Figure 5 shows the calculated strains of 2D QWR arrays. If the vertical distance between QWR arrays is larger enough than the critical value, the materials above the QWRs are laterally compressed while the materials above interstice of QWRs are laterally expanded. The vertical anti-correlation can be obtained when the spatial distance between QWR arrays is larger than the critical value, which is mainly determined by the width of QWRs. The observation is well explained by our model.

Comparing the self-assembled QDs and QWRs, we find their potential applications in quantum electronic or optoelectronic devices. Consequently, based on the optimization of band gap engineering design for QD lasers, structure geometry and the growth conditions of QDs, 3.62W (two facets) CW laser operation of three-stacked vertically coupled InAs/GaAs QDs at Room Temperature (RT) has been demonstrated. The lifetime of the QD laser is over 3000hr, which is of an emitting wavelength about 960nm with CW operating at 0.614 W at RT. At this point the output power was reduced to 0.83db, which is the best result as far as we know.

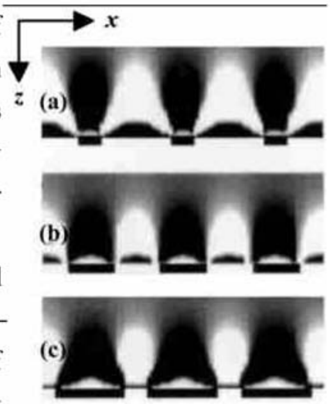


FIG. 5 Calculated Strain Component ϵ_x of Two-Dimensional QWR Arrays in x-z Plane for (a) $w = d/4$, (b) $w = d/2$ and (c) $w = 3d/4$ Here w is the width of the QWRs and d is the in-plane period of the QWR arrays. The black rectangular represents the QWRs.

3.3 Concept of Tip Chemistry[8]

The concept, "tip chemistry", was proposed by Dr. Zhongfan Liu, Peking University. The essence is to study various physicochemical properties of supramolecular assemblies by chemically modified SPM tips with special nanoparticles, which play a leading role in serving as a nanoprobe, nanolens and nanobeaker of a chemical reaction. The contributions made by his group is as follows: (1) AFM tip is used a force probe to examine the local chemical reaction properties. It has been modified with an organic monolayer to have a specific chemical interaction with the sample surface, so that the surface reaction processes can be monitored by measuring the specific tip-sample interaction. The dissociation properties of acid-base SAMs and the electrochemical reduction-oxidation of azobenzene SAMs are also studied in this way, as indicates that it is really an effective approach to explore the local reaction properties of inhomogenous surfaces. (2) Should tip be used as a nanolens to induce spatially-confined chemical reactions, the highly localized surface chemical reaction for nanostructure can be induced due to the highly-localized fields between the SPM tip and the sample surface, which is created by electric field, etc. The nanooxidation of Si and GaAs using conductive AFM tips and the nanolithgraphy have been studied, based on an organized colloidal nanoparticles mask. (3) To study the single electron phenomena, SPM tip is modified, with an organic SAM and colloidal nanoparticles serving as the tunneling barrier and Coulomb island, respectively. Positioning SPM tips on a SAM-modified surface can form a double-barrier tunneling structure with extremely low capacitance. Single electron tunneling phenomena have been investigated in such self-assembled nanostructures at room temperature with Au, CdS and

PbS as Coulomb islands.

And besides, they have succeeded in the chemical treatment on single walled carbon nanotubes and the fabrication of various nanotube assemblies on silicon or gold surfaces with nanotubes on them regularly.

3.4 Solvothermal Preparation of Non-Oxide Nanomaterials

It is worthless for Prof. Yitai Qian's group at the University of Sciences and Technology of China to make a great progress with the solvothermal preparation of non-oxide nanomaterials. As we know, those non-oxide materials, such as Nitride, Carbides and Boride, are prepared conventionally by direct combination of elements at high temperatures. Some non-oxides can be obtained by the complex organometallic precursors in organic solvents at certain temperatures, however, the post-treatment at a higher temperature is needed, as makes it difficult to obtain the nanocrystalline materials. Solvothermal progress is a non-aqueous thermal process, which is relatively simple and easy to control. And the sealed system can effectively prevent the contamination by the toxic and air-sensitive starting materials, too.

GaN with a diameter of 30 nm was successfully prepared by the reaction of gallium halide on Lithium nitride at 300℃ in Benzene. Nanocrystalline InAs was also obtained through the co-reduction of $AsCl_3$ and $InCl_3$ by using metallic Zinc at 180℃. In addition, nanomaterials such as InP, FeAs, SnS_2 and ternary semiconductors of $CuInSe_2$, $CuSbS_2$ etc. were obtained in temperatures of 200℃ below. The morphology of nanomaterials is controlled by the solvents. The nanorods, such as CdSe, InAs, $CoFe_2$ etc., were successfully prepared in corresponding solvents. Recently, PbSe and SnSe nanorods have been fabricated in organic solvent at room temperature under standard atmospheric pressure.

4 Research Grants and National Policy

There are many grants to support various research programs in China, such as National Natural Science Foundation of China (NSFC), National Basic Research Project (NBRP), National High Technology R&D Program (HTR&D, also called as 863 program), National Five-Year Planning Project (FYPP), Foundation of the Education Ministry and Foundation of the Chinese Academy of Sciences, etc. The NSFC and NBRP are mainly for the fundamental studies, while the HTR&D and FYPP especially for the R&D projects. It is in nation's consideration to encourage the combination of institutes and/or universities and the industry or companies for more founding. The total founding is about RMB 10 billion (~ USD＄ 1.2 billion) per annum, not including that from industry and companies nor for some special projects. For example, the founding for No. 909 project (0.35μm IC's production line in Shanghai) amounts to more than RMB 10 billion, about 10% of which is used for the research on materials and engineering. The founding for the study concerned with electronic and optoelectronic materials are less than 5% in total. China is a developing country and relatively poor. To catch up with the developed countries, we have to make more efforts and have a long way to go.

Nearly 15000 Chinese scientists and engineers are working in the fields of materials science and engineering distributed over more than 30 national and ministerial key laboratories and about 300 groups in China. One third of them are engaged in the study on electronic and optoelectronic materials. At least ten or more national conferences in this field have been held in China, and hundreds of researchers take part in various international conferences annually abroad. More than 2000 referred papers per year are published in international authoritative journals.

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References

[1] J. Faist, F. Capasso, D. L. Sivco *et al.*, Science, 1994, **264**: 553.
[2] R. Q. Yang, Superlattices Microstruct., 1995, **17**: 77.
[3] Weiqiang Han, Shoushan Fan, Qunqing Li and Yongdan Hu, Science, 1997, **277**: 1287.
[4] Shoushan Fan *et al.*, Science, 1999, **283**: 512.
[5] F. Q. Liu, Z. G. Wang *et al.*, Phys. Lett., 1998, **A249**: 555.
[6] J. Wu, Z. G. Wang *et al.*, J. Crystal Growth, 1999, **197**: 95.
[7] H. X. Li, Z. G. Wang *et al.*, Appl. Phys. Lett., 1999, **75**: 1173.
[8] Z. F. Liu, Universitatis Pekinensis, 1998, **34**: 161.

Brief Resume

WANG Zhan-guo(Z. G. Wang), male, Academician of The Chinese Academy of Sciences, a physicist of semiconductor materials and materials physics, was born in Henan Province, China, on 29 December, 1938. He joined the Institute of Semiconductors, Chinese Academy of Sciences (IS, CAS) after graduating from Department of Physics, Nankai University, Tianjin, China. He is currently a professor of IS, CAS, Director of the Laboratory of Semiconductor Materials Science, IS, CAS. Now his research interests are mainly concentrated on self-assembled In(Ga)As/GaAs, InAlAs/GaAsIn(Ga)As/InAlAs/InP quantum wire, quantum dot materials growth and quantum device applications.

He has published 180 refereed papers in many authoritative journals since 1983. And he was awarded a number of prizes from the State and Chinese Academy of Sciences.