was designed and verified by the coupling of atomic scale control in thin film growth and combinatorial chemistry. In view of the facts that every crystalline material is composed of molecular layers stacked periodically and that modern electronic devices have nano-scale layer structures, it is desired to develop a scheme for parallel fabrication of such layered structures so that we could quickly find the best matching of layered lattices and optimum fabrication conditions. In order to materialize this scheme this five years project started in 1996 by the collaboration with Miyamoto in Tohoku U., Yamamoto and Kawasaki in TIT, and Segawa in RIKEN who played roles for design, synthesis, and physics, respectively (Fig.1). Hardwares and softwares were made to align a number of artificial lattices or heterojunctions of each layer composition, thickness, and sequence controlled on an atomic scale into an integrating materials chip. This innovative technology is schematically illustrated in Fig.2 (a) as compared with the conventional combinatorial chemistry using the Merrifield synthesis (Fig.2 (b)). Molecular layers are deposited from several kinds of solid sources through a series of physical masks on a heated substrate so as to crystalize the deposited materials in as-grown state. Synchronizing the target exchange with mask movement, a number of nano-structures can be integrated on a single substrate. The results of this project are summarized in the following sections, which are classified into three categories: (1) system development for high speed fabrication and characterization of material chips, (2) combinatorial computational chemistry for materials design and system control, and (3) quick optimization and discovery of new materials.

For high speed synthesis are two types (giant and mobile) of combinatorial laser molecular beam epitaxy (CLMBE), which are illustrated in Fig.3. For structural analysis, a concurrent X-ray diffractometer was assembled by the collaboration with Rigaku Ltd. We also verified the usefulness of such rapid scan probe analyses as microwave microscope and scanning SQUID for high throughput characterization of dielectric and magnetic properties, respectively, of materials chips. Electronic conductivity was evaluated by the infrared reflectivity and multi-channel 4-probes measurements.

Figure 1. Combinatorial MLE project team and their roles.

Figure 2. Scheme of combinatorial nano-technology.

Figure 3. Giant (all round) and mobile (compact) CLMBE systems with circular and linear operation masks, respectively. The chamber diameter of the latter is 250mm.
was proposed by Miyamoto for systematic screening of designed materials and optimizing the reaction conditions. The softwares programmed in this project for computing a large integrated materials library are summarized in Table 1.14 Automatic system operation is done mainly by Lab View program.

Table 1 Software for combinatorial computational chemistry

<table>
<thead>
<tr>
<th>Program Name</th>
<th>Language</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerated Quantum Chemical Molecular Dynamics Program“Colors”</td>
<td>Fortran</td>
</tr>
<tr>
<td>Crystal Growth Simulator”MOMOODY“</td>
<td>Fortran</td>
</tr>
<tr>
<td>Molecular Dynamics Program</td>
<td>Fortran</td>
</tr>
<tr>
<td>Coarse Grained Molecular Dynamics Program “Dual-MOMOODY”</td>
<td>Fortran</td>
</tr>
<tr>
<td>Integrated Molecular Dynamics Simulator “NEW-RYUJO“</td>
<td>C</td>
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are represented in Figs. 4 through 8 on the libraries of perovskite oxide superlattices,15 molecular layer composition spreads for (La,Sr)MnO3 magnetic phase diagramming,16 ZnO band-gap engineering,17 organic light emitting device,18 and Co-doped TiO2,19 respectively. In addition to quick optimization, there is another broad advantage in combinatorial material technology when rapid synthesis is coupled with high throughput characterization. A good example is the discovery of transparent magnetism in TiO2 anatase films doped with Co.20 Libraries of 3d transition metal doped TiO2 were originally fabricated by CLMBE in a search for photocatalysts. When their magnetic properties were checked with a scanning SQUID, Co-doped TiO2 was found, surprisingly, to exhibit ferromagnetism while maintaining its transparency and single phase up to a

Figure 4 Concurrent XRD machine and data measured on a library of the [SrTiO3-x][BaTiO3-x] (x=12,14,15) superlattices (Ref.6) made by CLMBE on a SrTiO3 single crystal substrate. The data verified the formation of 10 superlattices as designed.

Figure 5 Systematic optical properties on a ZnO/MgO MQWs library. Coupling strength between exciton and LO phonons (solid circles) and the exciton binding energies (open circles) in bulk ZnO and MQWs of different well thicknesses (Ref. 12)

Figure 6 Structural-magnetic-optical properties of a La1-x Sr x MnO3: sample as a function of Sr concentration x. (Ref. 9) (a) A concurrent x-ray diffraction spectra. The horizontal scale bar indicates length scale along the film. (b) The out-of-plane lattice constants calculated from (a) (blue curve). The vertical dashed lines indicate the phase boundaries between ferromagnetic insulator (FI), ferromagnetic metal (FM), and antiferromagnetic metal (AFM). (c) The strength of the out-of-plane magnetic field (|Bz|) measured with a scanning superconducting quantum interference device microscope at 3 K. (d) The contour map of infrared reflectivity as a function of photon energy at 293 K. (e) At 5 K. Color bars denote the magnitude of the reflectivity.
composition of 8% Co.

Patents have been filed and applied for these research products from JST. Some of them are licensed for commercial production.

![Figure 7 Double layered structures of Poly (PP-co-Py) and Poly (PPy-co-MPy) for blue light emitting.](image)

After optimizing thickness, the emitting efficiency reached 16 times as high as that of Poly p-Phenyline (PPP). (Ref. 10)

![Figure 8 A library of TiO2-CeO2 (D-x=0.08) anatase films was made by CMBE. Transparent solid solution films were found to be ferromagnetic from conventional and scanning SQUID measurements.](image)

5. **FUTURE OF COMBINATORIAL TECHNOLOGY**

can be prospected in comparison with the history of electronics. As the key to advanced science and technology, electronics experienced two breakthroughs: down-sizing to solid state transistors and its integration to IC. Considering that the currently interested nano technology corresponds to ultimate down-sizing of materials, the next step should be directed towards its integration by combinatorial technology. The concept of combinatorial technology has wide applicability to a variety of materials, processes, and devices. The priority in advanced materials and devices would be claimed by those who take initiative in this promising technology.¹⁴

**Acknowledgment**

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**References**

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**Patents**

8 patents filed and 6 others open in Japan:
JP 2000-3,018,000, etc.
4 international patents open and 2 others in application
Parallel integration and characterization of nanoscaled epitaxial lattices by concurrent molecular layer epitaxy and diffractometry

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A material highway for building up crystal lattices and heterojunctions from molecular layers has been developed based on a concept of combinatorial lattice integration. The atomic-scale precision of automated multilayer paving of multilayered thin films is in situ monitored by concurrent reflection high-energy electron diffraction. The designed nanolayered structures are rapidly verified by a concurrent x-ray diffractometer which has been developed for the purpose of this technology. This scheme corresponds to the concurrent two-dimensional Merrifield synthesis to form a variety of sequence-controlled layer structures in parallel and should be widely applicable to systematic fabrication and property screening of nanostructured materials and devices. © 2001 American Institute of Physics. [DOI: 10.1063/1.1385587]

The discovery of high-$T_c$ superconductivity in layered perovskite cuprates stimulated extensive studies on perovskites and related oxides in order to find novel materials, properties, and device applications. As a result of enormous time-consuming efforts, various new materials and phenomena have been discovered in metal oxides, e.g., intrinsic Josephson effect, colossal magnetoresistance, high-temperature quantum perelectricity, and excitonic UV lasing at room temperature. On the other hand, several research groups have realized the benefit of the smart time-saving method of combinatorial chemistry, which is well recognized as a technique to increase dramatically the rate of new drug discovery by parallel solution chemical processes, for the exploration of solid materials as well. The current combinatorial material process is composed first with the deposition of a large number of thin films of different or continuously spread compositions on a substrate, usually at room temperature, second with annealing of the films to turn them into homogeneous amorphous films, and finally with high-temperature heating to crystallize them. Since this process is essentially the same as classical sintering, in which the products are dominated by thermodynamics, it is hardly applicable for the fabrication of atomically controlled layered materials. In other words, the products of this process are not controlled in the direction normal to the substrate.

In view of the facts that every crystalline material is composed of molecular layers stacked periodically and that modern electronic devices have nanoscaled layer structures, we have designed a scheme for parallel fabrication of such layered structures with atomic-scale precision by integrating the concepts and methods of combinatorial chemistry, laser molecular beam epitaxy, and concurrent electron and x-ray diffractometers. This scheme makes it possible to pave a substrate with a number of artificial lattices or heterojunctions of each layer composition, thickness, and sequence controlled on an atomic scale. The structure of resulting lattices or devices library is rapidly characterized by the concurrent x-ray diffractometer. We present here the concept of combinatorial lattice integration and some details of component systems and demonstrate the operation of this scheme in the parallel fabrication of superlattices of perovskite oxides.

The combinatorial lattice integration technology we have developed is schematically illustrated in Fig. 1(a). This technology is essentially a development of molecular layer epitaxy, which is required for atomically controlled layer-by-layer epitaxial growth of thin films, for parallel operation. When compared with the Merrifield synthesis, which is the root of combinatorial chemistry in organic synthesis of one-dimensionally bonded chemicals by a series of reactions, e.g., peptides from amino acids [Fig. 1(b)], our technique can be regarded as a two-dimensional and parallel version of the Merrifield synthesis. Molecular layers are deposited from several kinds of solid sources through a series of physical masks on a heated substrate so as to crystallize the deposited materials in the as-grown state. Synchronizing the target exchange with mask switching, we can synthesize a number of artificially designed lattices on a single substrate.

In order to materialize this concept of combinatorial epitaxial crystal lattice integration, we have constructed a deposition system which is illustrated in Fig. 2. Two new additions to our high-temperature laser molecular beam epitaxy
2. SELECTION OF ARTICLES FROM WORKSHOP FOUNDERS AT TOKYO TECH

(MBE) chamber\(^{11}\) are shown in the figure. One is the masking system and the other is the scanning reflection high-energy electron diffraction (RHEED). Target exchange, setting of deposition conditions, reaction diagnostics, and mask exchange are all controlled by a computer. Laser MBE has been widely used for oxide film growth ever since we verified its usefulness for fabricating atomically regulated epitaxial oxide thin films.\(^{12}\)

As a demonstration of combinatorial lattice epitaxy by this system, ten \(\text{SrTiO}_3\)-\(\text{BaTiO}_3\) superlattices with equiatomic ratios and different periodicities were fabricated at an oxygen pressure of \(1.0 \times 10^{-6}\) Torr and a substrate temperature of 700°C. The use of chemically etched \(\text{SrTiO}_3\) (001) substrates with atomically flat surfaces\(^{13}\) enabled us to observe clear RHEED intensity oscillation, which is a typical indication of atomically controlled layer-by-layer epitaxy. A single oscillation corresponds to the growth of a unit cell layer (0.4 nm) of each oxide. The necessity of controlling deposition of each sample simultaneously on the same substrate prompted us to develop a RHEED beam sweeping technique. The electron beam is scanned across the substrate surface with a pair of coils, the detection being done by a

![Image of the combinatorial molecular layer epitaxy system.](image)

FIG. 2. (Color) Illustration of the combinatorial molecular layer epitaxy system. A continuous wave Nd:YAG—selenium—garnet laser heating provides high substrate temperature (up to 1400°C) in an atmosphere ranging from ultrahigh vacuum to 1 atm oxygen. In situ scanning RHEED and a moving mask system are included in order to control the deposition thickness of each region.

![Image of RHEED specular intensities.](image)

FIG. 3. (Color) Traces of RHEED specular intensities during the synthesis of ten \(\left[\text{SrTiO}_3\right]_{n} / \left[\text{BaTiO}_3\right]_{n}\) superlattices. Only three traces, corresponding to \(n=2, 4,\) and 6 are shown for clarity. The deposition sequence and mask positions are shown at the bottom. Each block corresponds to the deposition of two molecular unit cell layers. Intensity oscillations for individual regions were observed by rapidly scanning (10 Hz) the electron beam.

![Image of parallel x-ray diffraction.](image)

FIG. 4. (Color) A demonstration of parallel x-ray diffraction. (a) depicts a schematic of the system. Point source x-rays are focused to form a 10 mm x 0.1-mm stripe on the specimen. Diffraacted x-rays are collected with a two-dimensional detector (imaging plate). The intensity mapping for low angle (b) and high angle (c) diffraction for a combinatorial superlattice chip, which contains ten superlattice pixels of \(\left[\left(\text{SrTiO}_3\right)_{10} / \left(\text{BaTiO}_3\right)_{10}\right]_{n}\) for \(n=12, 14, 16, \ldots, 28\) and 30. The lines appeared at the angles corresponding to the superlattice periodicities. (d) Schematic illustration of sample configuration. (e) and (f) Intensity profiles as a function of \(2\theta\) picked up from the data for \(\left(\text{SrTiO}_3\right)_{10} / \left(\text{BaTiO}_3\right)_{10}\) pixel.
2. SELECTION OF ARTICLES FROM WORKSHOP FOUNDERS AT TOKYO TECH

change coupled device camera looking at the RHEED screen. Synchronization between the RHEED beam sweeping and image acquisition was performed with the computer. Using this technique, combined with moving physical masks, we were able to control simultaneously the growth of as many as ten (at present) thin films in parallel on a single substrate. By rotating the substrate by 90° and repeating the procedure, it is possible to fabricate a 10 × 10 matrix of superlattices.

Figure 3 shows the RHEED intensity variations monitored during the parallel growths of SrTiO3/BaTiO3 superlattices (data from only three points on the substrate are shown for clarity). A schematic drawing of the deposition sequence and mask positions is shown in the inset. The top, middle, and bottom curves correspond to [(SrTiO3)12/BaTiO3]2, [(SrTiO3)8/BaTiO3]4, and [(SrTiO3)6/BaTiO3]6 superlattices, respectively. Deposition thickness was controlled by counting RHEED intensity oscillations. We have fabricated other oxide lattice and superlattice libraries by this method as well. Some of the examples are epitaxial oxides (ZnO, TiO2, etc.) films solid solution with transition metals, composition spread dielectrics (Ba1−x Srx TiO3, etc.), and SrTiO3/SrVO3 superlattices. A nonlinear conductivity indicating a specific property of the low-dimensional system was reconfirmed in the SrTiO3/SrVO3 superlattices. This combinatorial thin film library allows for a conventional electron beam for RHEED to produce as many as ten stripped thin films at present and is being upgraded to grow as many as 10,000 superlattices on a 10 mm × 10 mm SrTiO3 substrate in a 100 × 100 cell matrix by using a RHEED gun with film-emitted electron beam for concurrent diagnostics of surface reaction.

Structural characterization of these superlattices by x-ray diffraction is a time-consuming part of the experiments. For achieving high-throughput characterization of such a lattice integrated chip, we have developed a concurrent x-ray diffractometer that is schematically illustrated in Fig. 4(a). The system is composed of a convergent x-ray beam source (Cu Kα), a conventional powder diffraction goniometer, and a two-dimensional detector, an imaging plate. X-ray beam having a dispersion of 2θ is formed by a rotating anode x-ray source and proper x-ray optics, including a Johann-type mirror. The beam is focused down to a line of 10 μm × 0.1 mm on an integrated superlattice chip to generate a two-dimensional intensity image on the detector [Fig. 4(a)], one axis of which corresponds to a diffraction angle (2θ) over 2θ and the other axis represents sample position (x). It takes only a few seconds for this measurement or a few minutes for covering the diffusion angle between 0° and 90°, using the resolution of 0.01° and 100 μm, respectively. Depicted in Figs. 4(b) and 4(c) are the images taken for a library of ten superlattices; [(SrTiO3)12/BaTiO3]2 (n=12, 14, 16, 18, 20, and 30). In addition to the specularly reflected band near 0.7° [Fig. 4(b)] and the reflected SrTiO3 (001) band near 22.7° [Fig. 4(c)], we could clearly observe reflection lines at the angles corresponding to the designed periodicities of the individual superlattices. The line profiles extracted from the [(SrTiO3)12/BaTiO3]20s diffraction patterns are shown in Figs. 4(e) and 4(f). The positions of the reflection peaks well agree with the simulated ones. The lattice-engineered structure was also confirmed by transmission electron microscope. Compared to the scanning x-ray diffractometry on a combinatorial materials library with a focused synchrotron radiation x-ray beam, this technique is easily accessible by normal laboratory users.

The well-defined control of deposition conditions and film thickness in conjunction with a mask operation enables the production of a number of lattices, superlattices, and junctions in the as-grown and as-programmed form, thus differentiating this process from the conventional combinatorial precursor method: parallel deposition and sintering process where only thermodynamically dominated film structure is formed at each deposition site. We believe that the combinatorial molecular layer technology provides a key to accelerate the search for new structures and their properties of oxides as well as of artificially designed materials in general.

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