/
Article / Book Information

Title	Parallel integration and characterization of nanoscaled epitaxial lattices by concurrent molecular layer epitaxy and diffractometry
Authors	T. Ohnishi,D. Komiyama,T. Koida,S. Ohashi,C. Stauter,H. Koinuma,A. Ohtomo,M. Lippmaa,N. Nakagawa,M. Kawasaki,T. Kikuchi,K. Omote
Citation	Applied Physics Letters, Vol. 79, No. 4,
Pub. date	2001, 7
URL	http://scitation.aip.org/content/aip/journal/apl
Copyright	Copyright (c) 2001 American Institute of Physics

Parallel integration and characterization of nanoscaled epitaxial lattices by concurrent molecular layer epitaxy and diffractometry

T. Ohnishi, D. Komiyama, T. Koida, S. Ohashi, C. Stauter, and H. Koinuma[a),b),c)]
Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan

A. Ohtomo, M. Lippmaa,[c)] N. Nakagawa, and M. Kawasaki[b),c)]
Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8502, Japan

T. Kikuchi and K. Omote
X-Ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima 196-8666, Japan

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 multilane 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 for 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[1] stimulated extensive studies on perovskites and related oxides in order to find new 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,[2] colossal magnetoresistance,[3] high-temperature quantum paraelectricity,[4] and excitonic UV lasing at room temperature.[5] 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,[6] for the exploration of solid materials as well.[7] 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,[8] 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 diffractometries. 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,[9] 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.[10] 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
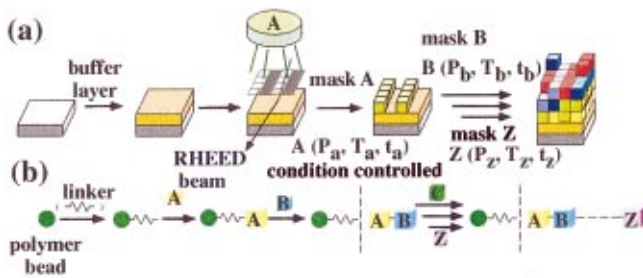
Appl. Phys. Lett., Vol. 79, No. 4, 23 July 2001

Ohnishi *et al.*   537

FIG. 1. (Color) Reaction schemes of the combinatorial molecular layer epitaxy method (a) and the Merrifield method (b).

FIG. 3. (Color) Traces of RHEED specular intensities during the synthesis of ten $[(SrTiO_3)_n/(BaTiO_3)_n]$ 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.

(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 integration by this system, ten $SrTiO_3/BaTiO_3$ superlattices with equimolar ratios and different periodicities were fabricated at an oxygen pressure of 1.0×10^{-6} Torr and a substrate temperature of 700 °C. The use of chemically etched $SrTiO_3$ (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

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 × 0.1-mm stripe on the specimen. Diffracted 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 $[(SrTiO_3)_n/(BaTiO_3)_n]_{30}$ (n = 12,14,16,...,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 2ω picked up from the data for $[(SrTiO_3)_{12}/(BaTiO_3)_{12}]_{30}$ pixel.
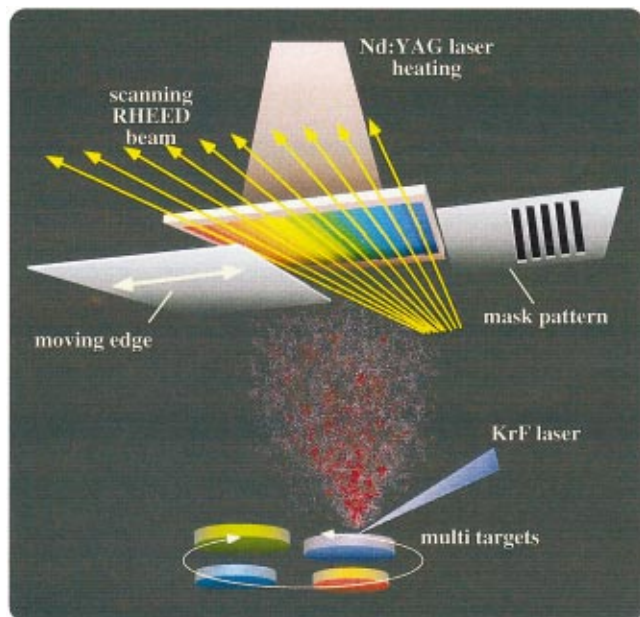

FIG. 2. (Color) Illustration of the combinatorial molecular layer epitaxy system. A continuous wave Nd:yttrium–aluminum–garnet laser heating provides high substrate temperature (up to 1400 °C) in an atmosphere ranging from ultrahigh vacuum to 1 atm oxygen. *In situ* scanning RHEED and a moving mask system are included in order to control the deposition thickness of each region.
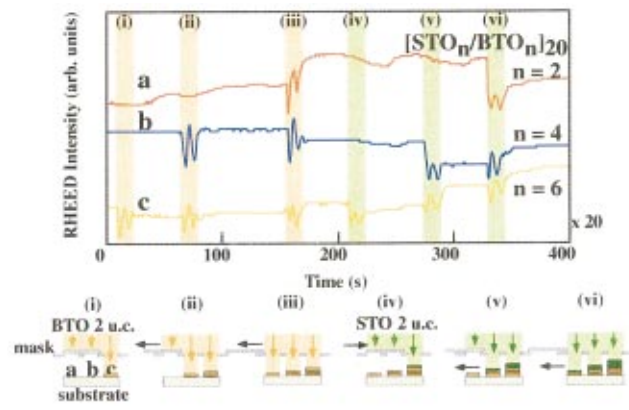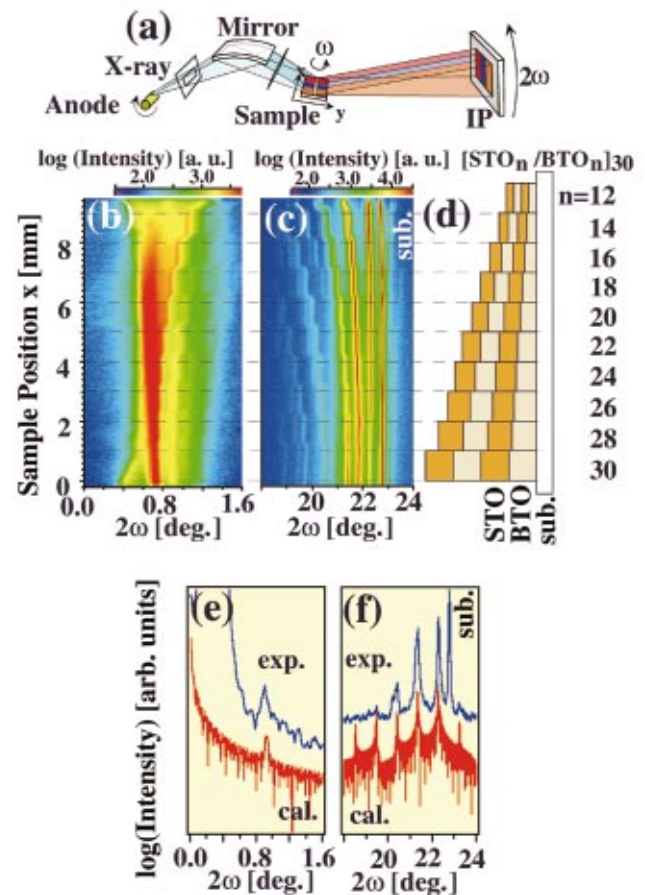
charge coupled device camera looking at the RHEED screen. Synchronization between the RHEED beam sweeping and image acquisition was performed with the computer. Using this technique, combined with moving physical masks, we were able to control simultaneously the growth of as many as ten (at present) 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 growth of $SrTiO_3/BaTiO_3$ 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 $[(SrTiO_3)_2/(BaTiO_3)_2]$, $[(SrTiO_3)_4/(BaTiO_3)_4]$, and $[(SrTiO_3)_6/(BaTiO_3)_6]$ 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 oxide (ZnO, TiO_2, etc.) films solid soluted with transition metals, composition spread dielectrics ($Ba_{1-x}Sr_xTiO_3$, etc.), and $SrTiO_3/SrVO_3$ superlattices. A nonlinear conductivity indicating a specific property of the low-dimensional system[14] was reconfirmed in the $SrTiO_3/SrVO_3$ superlattices. This combinatorial laser MBE system using a conventional electron beam for RHEED is designed to produce as many as ten striped films at present and is being upgraded to grow as many as 10 000 superlattices on a $10\,mm \times 10\,mm$ $SrTiO_3$ substrate in a 100×100 cell matrix by using a RHEED gun with field 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 ($Cu K_{\alpha 1}$), a conventional powder diffraction goniometer, and a two-dimensional detector, an imaging plate. X-ray beam having a dispersion of 2° is formed by a rotating anode x-ray source and proper x-ray optics, including a Johann-type mirror. The beam is focused into a line of $10\,mm \times 0.1\,mm$ 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 (ω) over 2° and the other axis represents sample position (x). It takes only a few seconds for this measurement or a few minutes for covering the diffraction angle between 0° and 90°, i.e., more than ten times faster than conventional x-ray diffractomers. The resolution of $\Delta\omega$ and Δx are 0.01° and 100 μm, respectively. Depicted in Figs. 4(b) and 4(c) are the images taken for a library of ten superlattices; $[(SrTiO_3)_n/(BaTiO_3)_n]_{30}$ ($n = 12, 14, 16, \sim, 28$ and 30). In addition to the specularly reflected band near 0.70° [Fig. 4(b)] and the reflected $SrTiO_3$ (001) band near 22.75° [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 $[(SrTiO_3)_{12}/(BaTiO_3)_{12}]_{30}$ 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,[15] 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[7] 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.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).

[2] R. Kleiner, F. Steinmeyer, G. Kunkel, and P. Müller, Phys. Rev. Lett. **68**, 2394 (1992); K. Tamasaku, Y. Nakamura, and S. Uchida, *ibid.* **69**, 1455 (1992).

[3] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994); Y. Tokura, A. Urushibara, Y. Morimoto, T. Arima, A. Asamitsu, G. Kido, and N. Furukawa, J. Phys. Soc. Jpn. **63**, 3931 (1994).

[4] Y. Inaguma, J.-H. Sohn, I.-S. Kim, M. Itoh, and T. Nakamura, J. Phys. Soc. Jpn. **61**, 3831 (1992).

[5] P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Solid State Commun. **103**, 459 (1997); Y. Segawa, A. Ohtomo, M. Kawasaki, H. Koinuma, Z. K. Tang, P. Yu, and G. K. L. Wong, Phys. Status Solidi B **202**, 669 (1997).

[6] M. J. Plunkett and J. A. J. A. Ellman, Sci. Am. **276**, 68 (1997).

[7] X.-D. Xiang, X. Sun, G. Bricno, Y. Lou, K. Wang, H. Chang, W. G. W. G. Wallace-Freedman, S. W. Chen, and P. G. Schultz, Science **268**, 1738 (1995); X.-D. Xiang, Annu. Rev. Mater. Sci. **29**, 149 (1999); H. Koinuma, Solid State Ionics **108**, 1 (1998).

[8] H. Koinuma, MRS Bull. **19**, (1994).

[9] R. B. Merrifield, Fed. Proc. **21**, 412 (1962).

[10] Y. Matsumoto, M. Murakami, Z. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, and H. Koinuma, Jpn. J. Appl. Phys., Part 2 **38**, L603 (1999).

[11] S. Ohashi, M. Lippmaa, N. Nakagawa, H. Nagasawa, H. Koinuma, and M. Kawasaki, Rev. Sci. Instrum. **70**, 178 (1999).

[12] M. Yoshimoto, H. Nagata, T. Tsukahara, and H. Koinuma, Jpn. J. Appl. Phys., Part 2 **29**, L1199 (1990).

[13] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, Science **266**, 1540 (1994).

[14] H. Koinuma, M. Yoshimoto, H. Nagata, and T. Tsukahara, Solid State Commun. **80**, 9 (1991).

[15] E. D. Isaacs, M. Marcus, G. Aeppli, X.-D. Xiang, X. Sun, P. Schultz, H.-K. Kao, G. S. Cargill III, and R. Haushalter, Appl. Phys. Lett. **73**, 1820 (1998).