Combinatorial solid state materials science and technology

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Abstract

Conventional ‘one by one’ synthesis approach has been a major rate limiting step in the systematic exploration of increasingly complex materials for the demanding new technologies. New concepts of ‘combinatorial chemistry’ are presented for the substantially efficient and cost-effective parallel synthesis and optimization of variety of multicomponent compounds as well as artificially designed lattices and devices. Effectiveness of variety of application areas developed by us is discussed with typical examples and brief review of the merits, challenges, current status and the future directions. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Extensive efforts have been expended in trying to understand and predict the electronic, optical and physical properties of various materials in thin film form and to discover new materials. Remarkable progress has been made in the areas of interplay between deposition/processing and analysis/properties. Nevertheless, with the increasing complexity of new materials for the novel technologies, the conventional ‘one by one’ approach of synthesis, which is predominantly a process of trial and error, yields a low success rate needing high expenditure and long timelines. Combinatorial approach offers a novel unique way to overcome this barrier. Combinatorial chemistry is a development which has already had its most profound impact in the field of organic and bio-organic synthesis in general and medicinal synthesis in particular [1–3]. Subsequent to several reports on composition spread approach to metal alloys [4] and oxides [5], the concept of combinatorial chemistry was successfully extended to solid state materials [6]. The combinatorial approach involves synthesis of vast number of compounds by reacting a set of components in the pre-designed combinations within a single experiment. This yields the microscale quantities of diverse materials in a library format which can be then evaluated to quickly identify the ‘most promising’ candidates.

In this paper, we present the basic concept of combinatorial chemistry and its applications to various solid state materials and processes, together with the key factors for this technology and future development.

2. Advanced concepts and systems for combinatorial materials synthesis

Materials synthesis whether in bulk or thin film form is a chemical reaction which is influenced by many factors. Fig. 1 summarizes combinatorial synthesis vis-à-vis the classical synthesis [7]. Process optimization is often a huge task. Applying combinatorial approach, several key parameters such as temperature, pressure, atmosphere, thickness etc. can be quickly adjusted for the optimal performance.

The pioneering work of Xiang et al. involved the fabrication of 128-member library of copper oxide superconducting thin films by the deposition of precursors of BaCo\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3}, CaO, SrCo\textsubscript{3} and CuO through a series of binary masks, one at a time onto the substrates of either MgO or LaAlO\textsubscript{3} [6]. This library contained films with varying compositions and stoichiometries. After annealing first at low temperature (200–400°C) and next sintering at 840°C, different superconducting sample pixels such as BiSrCa-CuO\textsubscript{3} and YBaCuO\textsubscript{3} were successfully identified. Their process consisted of film deposition at room temperature, controlling the film composition by deposition time, followed by a sintering step for crystallization to occur. This limits the products to those occurring in thermal equilibrium. This limitation can be overcome by developing a system combining a combinatorial masking arrangement with condition controlling mechanism. Fig. 2 shows the
schematic of conventional and advanced combinatorial thin film deposition systems. In the following sections, some of our systems developed for the advanced versions are described.

2.1. Combinatorial laser molecular beam epitaxy

We have developed combinatorial laser molecular beam epitaxy (CLMBE) (Fig. 3), which features a multitarget holder and a disk plate consisting of eight distinctly patterned masking plates. The combinatorial masking plate is located between the target and the substrate, 3 mm from the substrate surface. The targets are typically placed 70 mm away from the substrate in order to improve the film thickness uniformity. A desired mask pattern-target combination can be selected by the appropriate computer controlled rotation of masking plate and multitarget holder. Besides, the laser pulse counting is also automated. We have tested the capability of this CLMBE system by carrying out the band gap engineering of ZnO [8]. Recently, our group discovered and reported the ultraviolet laser emission from ZnO nanocrystal thin films at room temperature (RT) and that under the moderate excitation, the optical gain responsible for this emission was of excitonic nature [9]. Thus, band gap engineering of ZnO constitutes a vital part in the fabrication of ZnO based laser diode. Highly Mg doped ZnO thin films were combinatorially synthesized in as grown crystals to control the band gap.

High quality c-axis oriented Mg doped ZnO thin films were grown on as polished 16 × 16 mm² sapphire (α-Al2O3) (0001) substrates in 1 × 10⁻⁶ Torr oxygen at 900 K by alternating KrF excimer laser (λ = 248 nm) ablation of a 10 mol% Mg doped ZnO and a pure ZnO ceramic target (99.999% purity). Typical laser fluence and repetition rate were 3 J/cm² and 5 Hz, respectively. Fig. 4 shows the combinatorial process for the fabrication of Mg doped ZnO films. The deposition sequence was repeated 80 times. This sequential process gave a combinatorial library with nine different Mg doped ZnO films. The Mg content in ZnO films can be easily designed by counting the laser pulses with the knowledge of deposition rates for each target and the enrichment factor. In this combinatorial work, the Mg content was roughly designed to vary from 1 to 15 mol%. The Mg content obtained from Rutherford Backscattering (RBS) measurements on different Mg–Zn–O films agreed closely with the designed values. From the XRD patterns, all the Mg doped ZnO films exhibited a single wurtzite phase in spite of the excess Mg doping in ZnO. The evaluated c-axis length and the band gap (estimated from the UV measurements) showed a linear dependence on the Mg content. The c-axis length is shortened and band gap is increased systematically with increase of Mg content as shown in Fig. 5(a) and (b), respectively. The data obtained from conventional one by one experiments is also compared in these figures. It is seen that the scatter of the data points obtained in combinatorial fashion (●) is drastically reduced in contrast with that of conventional (□) experiments. It is thought that the statistical error in the conventional experiments is due to possible small changes of various process parameters between the depositions. The unique advantage of the CLMBE deposition technique is its ability to stabilize kinetically controlled phases which would not occur under thermodynamic
equilibrium conditions. Besides, the present capability of this system offers another powerful aspect of parallel in situ processing of ‘substrate pre-treatment’, ‘film deposition’ and ‘annealing’.

In another application of CLMBE system, we have fabricated an integrated library of epitaxial ZnO films doped with all the 3d transition metal (TM) ions to address the general solubility behaviour of TM ions in ZnO thin films and the effect of doping on the optical properties. The solubility limits were investigated employing X-ray diffraction measurements. Transmission spectra were obtained at RT for all the 3d ion doped samples from 185 to 3200 nm. Specially designed holders were used for the different characterization of our combinatorial libraries. Typical photograph of Co doped ZnO film library deposited with our CLMBE is shown in Fig. 6. Assuming that the deposition rates of both pure ZnO ($r_z$) and Zn$_{1-x}$TM$_x$O ($r_{TM}$) are kept constant during the deposition process, the doping concentration in the film is given as $\left[\frac{r_{TM}n_{TM}X}{r_zn_z + r_{TM}n_{TM}}\right]$ where $n_z$ and $n_{TM}$ are the number of laser pulses in a cycle for ZnO and Zn$_{1-x}$TM$_x$O targets, respectively, and $x$ is the dopant concentration in the target. The solubility behavior of 3d ion species in ZnO thin films was found to depend mainly on their ionic radii and valence states. In this study, among all the doped 3d ions, Mn$^{2+}$ and Co$^{2+}$ exhibited the highest solubility.

2.2. Combinatorial lattice engineering

Oxides exhibit the wide range of exotic properties such as superconductivity, colossal magnetoresistance, quantum paraelectricity, giant piezoelectricity with immense technological implications. In all the applications of the emerging ‘oxide electronics’, crystal engineering of oxides plays a central role [10–12].

The CLMBE is viable for the synthesis of artificially designed materials, lattices and heterostructures which can be in thermodynamic non-equilibrium states. This combinatorial molecular layer technology is schematically illustrated in Fig. 2(b). Molecular layers can be deposited from different solid sources through a series of physical masks on heated substrate so as to crystallize the deposited materials in the as-grown state. Synchronizing the solid source target exchange with the mask switching, we can realize several artificially designed heterostructures on a single substrate. This process can be compared with that of Merrifield method which is the root of combinatorial chemistry in the organic synthesis of one-dimensionally (1D) bonded chemicals by a series of chemical reactions for example peptides from amino acids [13]. Accordingly, our combinatorial approach is a sort of 2D version of parallel Merrifield synthesis. Incorporating the specially designed masking system and the scanning reflection high energy electron diffraction (RHEED) into a basic high temperature laser MBE chamber, we have realized the combinatorial lattice engineering of oxides. Details of this process schematically shown in Fig. 7 are reported elsewhere [14]. The use of atomically flat substrates was necessary to observe the clear RHEED intensity oscillations which is a typical indication of atomically controlled layer by layer epitaxy [15]. One oscillation period corresponds to the growth of a unit cell layer (typically ~0.4 nm) of each
oxide. The growth of several thin films on the same substrate can be controlled by sweeping the RHEED beam. In this method, electron beam is scanned across the substrate surface with a pair of coils, the detection being done by monitoring the RHEED screen with a CCD camera.

2.3. Combinatorial pulsed laser deposition of polymer films

There has been tremendous interest in the conjugated polymer materials from the viewpoint of their technological applications [16–18]. Vacuum evaporation is a common method used for the synthesis of polymer films. It is possible to fabricate the polymer films with the absorption maxima close to their bulk counterparts using this technique. We have adopted a combinatorial pulsed laser deposition (PLD) approach for the synthesis of libraries of various polymer materials. As an example, in Fig. 8, we present the UV–visible spectra of combinatorially deposited poly-(p-phenylene) i.e. PPP polymer films on glass substrate under different laser fluence conditions (50, 60, 70 and 90 mJ/cm²). The other deposition conditions were pulse frequency of 1 Hz, substrate temperature of 30°C with the film thickness of 250 Å for 30 min deposition. It is seen that with the increasing laser fluence, the absorption maxima shifts continuously to lower wavelengths indicating the formation of ‘short chain’ polymer films. Thus it is possible to control the polymer chain size using PLD. Using the combinatorial approach, this technique can be very promising in searching novel polymer structures.

2.4. Combinatorial plasma enhanced chemical vapor deposition

We have also developed a combinatorial PECVD system for a-Si:H based alloys and devices which are critical to the promising low-cost large area microelectronics [19,20]. In this technique, typically, a ‘contact’ mask with predefined pixel matrix is placed over the substrate/s of interest and a sequence of different depositions is carried out along x-axis of the substrate by moving a ‘slit’ mask over the ‘contact’ mask exposing one pixel row to the plasma at a time. This is followed by the substrate rotation (90°) and another
sequence of depositions along $y$-axis with a different deposition variable. As a demonstration of this method, we have successfully fabricated a $7 \times 7$ combinatorial library of a-Si:H thin film transistors (TFTs) with a-SiN:H as the gate insulator by varying the time of a-SiN:H and a-Si:H deposition along the two axis as the combinatorial parameter. Fig. 9 shows the photograph of the combinatorial (a-Si:H/a-SiN:H) bilayer library on (ITO/Glass) substrate. Forming the source and drain electrodes on these bilayers by ‘Al’ metal evaporation using another mask gives a TFT library with ‘bottom gate-inverted staggered’ structure as shown in Fig. 9. Employing such a combinatorial strategy, in a single pump down experiment, we have identified the thicknesses of a-Si:H and a-SiN:H for the optimal TFT performance which are 1000 and 6000 Å, respectively. Observed device characteristics are consistent with the reported literature of conventionally synthesized TFTs. These results demonstrate the usefulness of combinatorial PECVD for low-cost, high-throughput fabrication and optimization of a-Si:H based materials and heterostructures. We
are currently exploring the extension of this technique to the fabrication of a-Si:H field effect solar cells [21]. Besides these device applications, the combi-PECVD has been exploited for systematic exploration of effects of various plasma treatments on the growth and properties of amorphous silicon and its alloys [22].

2.5. Combinatorial atmospheric pressure cold plasma processing

We have developed a combinatorial low temperature, atmospheric pressure pulsed plasma generator which can supply activated chemical species into open air space [23]. This apparatus (Fig. 10) has a shower type cathode with several gas exits. On application of rf 13.56 MHz power to cathode, a stable homogeneous plasma was generated in helium or argon gas flow passing through the gap between the electrodes and carried out of the nozzle into the air. This cold plasma system was characterized by optical emission and single probe methods [24] to give the electron and gas temperatures below 2.0 eV and 400 K, respectively. By mixing the reactive gases such as CH4, O2 and CO2 and different organic compounds in the plasma, different materials can be effectively processed. Using a roll-to-roll polymer film substrate arrangement and a motor drive control, we have realized the combinatorial version of this set up. Depositions under various conditions can be continuously...
carried out in this system by first depositing the desired material on a given area of the polymer substrate under the one set of conditions and then rolling up the substrate to bring the next bare portion of the substrate for the deposition under the next set of conditions and so on. Various parameters that can be varied combinatorially are rf power, reaction time, carrier gas, reaction gas, gas concentration, flow rate, pulse width and temperature. This soft plasma system under open air conditions can be exploited in important applications such as surface modification of polymers and air exposed materials, CO$_2$ fixation, surface sterilization and plasma treatment of biomedical materials. Such work is currently in progress in our laboratory.

3. High throughput screening

This is a key component of combinatorial materials science and technology. The three main stages involved in the successful application of combinatorial strategies for the innovative materials technology are: (i) design; (ii) high throughput synthesis; and (iii) rapid characterization. Thus, potential of combinatorial techniques can be completely exploited only if high throughput synthesis methods are coupled with different mass screening analysis techniques. Often, analysis is more time consuming than the synthesis. This is presently a major limitation. However, with the focussed research on this aspect, new rapid automated characterization methods are just evolving.

One of the constraints in characterization of such combinatorial material chips pertains to their structural analysis. We have achieved the high throughput structural characterization of lattice engineered combinatorial chips by developing parallel X-ray diffraction system consisting of a convergent X-ray beam source (CuK$_\alpha_1$) employing a conventional goniometer for powder diffraction system and a 2D detector [25]. It is noteworthy to mention here that Issacs et al. reported a synchrotron X-ray microbeam (spot size $3 \times 20 \, \mu$m$^2$) diagnosis method for the nondestructive characterization of as-grown combinatorial libraries [26]. Although highly effective and exhaustive, it is difficult to access such a sophisticated set-up for a normal laboratory user. The convergent X-ray based method developed by us offers a much simpler alternative.

Generally, it is easier to screen the material constants based on the optical properties. Dr Xiang’s group at LBNL, Berkeley and the group at Symyx Technologies have designed special optical characterization systems to map the properties of luminescent materials libraries
Berkeley group has developed a novel electro-optical coefficient measurement system to screen for the better electro-optical materials, a variable temperature magneto-optical measurement technique to map the surface magnetization and an optical measurement system to characterize the piezoelectric or strain effects. To screen the combinatorial libraries of electronic materials, the group has also developed a novel scanning evanescent microwave microscope capable of quick, nondestructive and quantitative mapping of the complex electrical impedance (of any material) with submicron resolution [29]. The microwave frequency of this instrument suits for most electronic applications and can be routinely employed for quantitative characterization of linear and nonlinear dielectric constants of ferroelectrics and dielectrics. The low-temperature version of this microscope has been developed to characterize the superconductor materials [30].

4. Applicability and impact

Combinatorial synthesis has shown the great potential in the serendipitous discovery of diverse class of advanced materials. Several industries and research groups have embraced this high throughput approach. A summarized survey of reported studies of different groups is given in Table 1. In addition to the different areas outlined here, combinatorial methods have already found a key role in other important fields such as catalysis [38]. In the immediate past, there has been a surge of research activity in this area. The concept of
combinatorial chemistry seems amenable to literally any material and process. This is summarized in Fig. 11. Several spin-offs are expected as fruit of the research equipped with combinatorial methodologies. Current revolution in materials synthesis and discoveries owing to combinatorial methods can be compared with that of the evolution of the high-density integrated circuits starting from vacuum tube electronics as depicted in Fig. 12. Combinatorial material libraries, analogous to integrated circuit chips are integrated materials chips containing several compounds/materials.

5. Concluding remarks

The breadth of applications of combinatorial synthesis across the spectrum of materials technologies is illustrated with the focus on the different processes developed by us. The art of high throughput, low-cost synthesis by novel combinatorial approaches with the potential to address diverse applications is proving to be key tool in the arsenal of materials science techniques. We envision that this technique will become a common synthetic practice for the convenient and economic fabrication of thin films in wide variety of applications. This can significantly enhance the speed of exploring the large materials universe thus providing a major impetus for progress in the materials research.

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References

[1] M.A. Gallop, et al., J. Mol. Chem. 37 (1994) 1233.
[2] M.J. Plunkette, J.A. Elman, Sci. Am. April 256 (1997) 55.
[3] C. Chen, A.A. Randell, R.B. Miller, A.D. Jones, M.J. Kurth, Tetrahedron 53 (1997) 6595.
[4] J.J. Hanak, J.I. Gittleman, Physica 55 (1971) 555.
[5] H. Koinuma, H. Nagata, A. Takano, M. Kawasaki, M. Yoshimoto, Jpn. J. Appl. Phys. 27 (1988) L1887.
[6] X.D. Xiang, X. Sun, G. Briceno, Y. Lou, K. Wang, H. Chang, W.G. Wallace-Friedman, S.W. Chen, P.G. Schultz, Science 268 (1995) 1738.
[7] H. Koinuma, Solid State Ionics 108 (1998) 1.
[8] Y. Matsumoto, M. Murakami, Z. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, H. Koinuma, Jpn. J. Appl. Phys. 38 (1999) L603.
[9] Y. Segawa, A. Ohtomo, M. Kawasaki, H. Koinuma, Z.K. Tang, P. Yu, G.K.L. Wong, Phys. Status Solidi 202 (1997) 669.
[10] H. Koinuma, Mat. Res. Soc. Bull. 19 (1994) 21.
[11] R. Tsuchiya, M. Kawasaki, J. Nishino, H. Sato, H. Akou, H. Koinuma, Appl. Phys. Lett. 71 (1997) 1570.
[12] M. Kawasaki, A. Ohtomo, R. Tsuchiya, J. Nishino, H. Koinuma, Mat. Res. Soc. Symp. Proc. 474 (1997) 303.
[13] R.B. Merrifield, in: J.M. Stewart, J. Yong (Eds.), Solid Phase Peptide Synthesis, Federation Proc, vol. 21, W.H. Freman and Co, San Francisco, CA, 1969, p. 412.
[14] H. Koinuma et al., in preparation.
[15] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, H. Koinuma, Science 226 (1994) 1540.
[16] R. Srinivasan, B. Braren, Chem. Rev. 89 (1989) 1303.
[17] C.P. van der Vorst, C.J.M. van Weerdenburg, Proc. SPIE 1337 (1990) 246.
[18] Y. Shuto, A. Amano, T. Kaino, Jpn J. Appl. Phys. 30 (1991) 320.
[19] P.G. Lecomber, W.E. Spear, A. Gaith, Electron. Lett. 15 (1979) 179.
[20] Y. Kuo, Electrochem. Soc. 141 (1994) 1061.
[21] H. Koinuma, H. Fujioka, C. Hu, T. Koida, M. Kawasaki, Mater. Res. Soc. Symp. Proc. 426 (1996) 95.
[22] H. Koinuma, N. Matsuki, R. Maruyama, S. Yasuda, Proc. Am. Phys. Soc. 43 (1998) 1.
[23] H. Koinuma, H. Ohkubo, T. Hashimoto, Appl. Phys. Lett. 60 (1992) 816.
[24] K. Inomata, N. Aoki, H. Koinuma, Jpn J. Appl. Phys. 33 (1994) L197.
[25] T. Kikuchi, I. Harada, Proceedings of the 41st Seminar on Science and Technologies of Crystallography, Osaka, Japan, vol. 51 1998.
[26] E.D. Issacs, M. Marcus, G. Aeppli, X.D. Xiang, X. Sun, et al., Appl. Phys. Lett. 73 (1998) 1820.
[27] J. Wang, Y. Yoo, C. Gao, I. Takeuchi, X. Sun, et al., Science 279 (1998) 1712.
[28] E. Danielson, H. Golden, E.W. McFarland, C.M. Reaves, W.H. Weinberg, X.D. Wu, Nature 389 (1997) 944.
[29] C. Gao, T. Wei, F. Duwer, X.D. Xiang, Appl. Phys. Lett. 71 (1997) 1817.
[30] I. Takeuchi, F. Duwer, X.D. Xiang, Appl. Phys. Lett. 71 (1997) 2026.
[31] H. Koinuma et al., J. Appl. Phys. 27 (1998) L376.
[32] G. Briceno, H. Chang, X. Sun, P.G. Schultz, X.D. Xiang, Science 270 (1995) 273.
[33] X. Sun, C. Gao, J. Wang, X.D. Xiang, Appl. Phys. Lett. 70 (1997) 3353.
[34] E. Danielson, M. Devenney, D.M. Giaquinta, J.H. Golden, R.C. Haushalter, et al., Science 279 (1998) 837.
[35] X.Q. Liu, Z.F. Li, W. Lu, S.C. Shen, C.M. Chen, D.Z. Zhu, J. Hu, M.Q. Li, Appl. Phys. Lett. 75 (1999) 2611.
[36] R.B. van Dover, L.F. Schneemeyer, R.M. Fleming, Nature 392 (1998) 162.
[37] X.D. Xiang, Annu. Rev. Mater. Sci. 29 (1999) 149.
[38] B. Jandeleit, W.H. Weinberg, Chem. Ind. 19 (1998) 795.