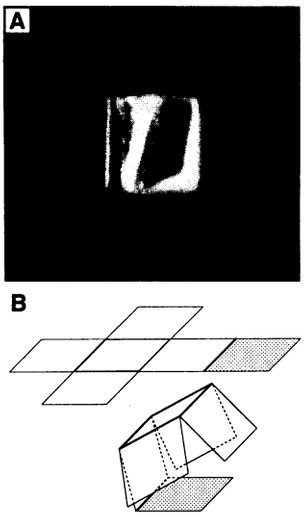

Fig. 6. Actuators with three consecutive rigid elements. (**A**) Photograph of a closed, side-mounted box with three consecutive hinges and the same dimensions as the cube in Fig. 5. (**B**) Schematic illustration.

applying several hundred volts between the plate and the substrate. The key difference between this approach and our approach is that we control the bending of the hinge rather than the position of the plate. The conducting polymer devices can therefore achieve folding of 180° at each joint.

Further applications of the described technology might include valves that close automatically in response to a chemical signal or a change in pH and structures for single-cell capture and analysis. More sophisticated folding structures could perhaps be used as microrobot limbs.

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A Combinatorial Approach to Materials Discovery

X.-D. Xiang,* Xiaodong Sun, Gabriel Briceño, Yulin Lou, Kai-An Wang, Hauyee Chang, William G. Wallace-Freedman, Sung-Wei Chen, Peter G. Schultz*

A method that combines thin film deposition and physical masking techniques has been used for the parallel synthesis of spatially addressable libraries of solid-state materials. Arrays containing different combinations, stoichiometries, and deposition sequences of $BaCO_3$, Bi_2O_3, CaO, CuO, PbO, $SrCO_3$, and Y_2O_3 were generated with a series of binary masks. The arrays were sintered and BiSrCaCuO and YBaCuO superconducting films were identified. Samples as small as 200 micrometers by 200 micrometers in size were generated, corresponding to library densities of 10,000 sites per square inch. The ability to generate and screen combinatorial libraries of solid-state compounds, when coupled with theory and empirical observations, may significantly increase the rate at which novel electronic, magnetic, and optical materials are discovered and theoretical predictions tested.

Currently, there is tremendous interest in materials such as high-temperature superconductors, supermagnetic alloys, metal oxide catalysts, and luminescent materials (*1*). However, few general principles have emerged that allow a priori prediction of the structures of new materials with enhanced properties (*2*). Consequently, the discovery of such materials remains a time-consuming and rather unpredictable trial-and-error process, made even more difficult by the increasing complexity of modern materials. Hence there is a need for a more efficient and systematic way to search through the largely unexplored universe of ternary, quaternary, and higher order solid-state compounds in order to discover materials with novel electronic, optical, magnetic, or mechanical properties.

In biology, molecules with a desired property are often identified by the synthesis and screening of large collections, or libraries, of structures. Perhaps the best such example is that of the humoral immune system, which can generate and screen some 10^{12} antibody molecules to identify one that specifically recognizes and binds a foreign pathogen (*3*). One of the first applications of molecular libraries to chemistry was the development of catalytic antibodies (*4*). Shortly thereafter, a number of methods were developed for generating and screening large populations of biological molecules in vitro for binding, catalysis, or both (*5*, *6*). A great deal of effort is currently devoted toward the application of these combinatorial libraries (libraries generated by combining large numbers of precursors), as well as libraries of small organic molecules (*7*), to the discovery of new drugs.

Here, we report the first application of the combinatorial approach to the discovery of new solid-state materials with novel

X.-D. Xiang, G. Briceño, K.-A. Wang, Molecular Design Institute, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA.

X. Sun, Y. Lou, H. Chang, W. G. Wallace-Freedman, S.-W. Chen, Department of Chemistry, University of California, Berkeley, CA 94720, USA.

P. G. Schultz, Molecular Design Institute, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA, and Department of Chemistry, University of California, Berkeley, CA 94720, USA.

*To whom correspondence should be addressed. World Wide Web URL: http://www.inetbiz.com/matcombi

physical or chemical properties. Specifically, methodology has been developed that allows the parallel synthesis of spatially addressable arrays containing superconducting copper oxide thin films. Thin film deposition methods are synthetically quite versatile; they offer the ability to construct artificial lattices, epitaxial overlayers, and patterned films of a variety of materials. By sequentially depositing the individual precursors of interest through a series of physical masks, it is possible to generate a spatially defined library of solid-state thin films. Each sample can be varied with respect to elemental composition, the sequence in which the layers are deposited, and the thickness of each layer (including thickness gradients). Subsequent thermal processing provides a library of materials (or devices) whose physical properties can be screened with contact or rapid scanning probes. The number of compounds that can be simultaneously synthesized by this technique is limited by the spatial resolution of the masks and detectors and by the degree to which synthesis can be carried out on a microscale.

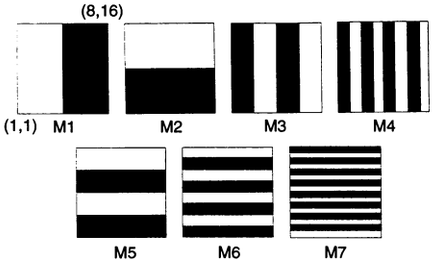

Fig. 1. Binary masks used for library synthesis. The numbers at the lower left and upper right corners of mask M1 indicate its orientation with respect to the coordinates of the library members; the other masks were similarly oriented.

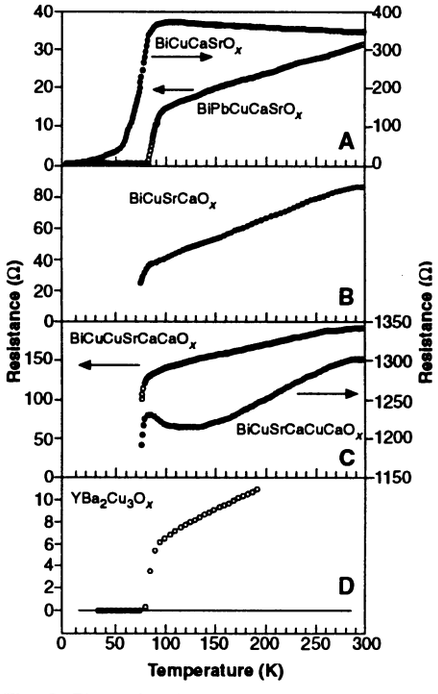

Fig. 2. Plots of resistance versus temperature. (**A**) BiPbCuCaSrO$_x$, BiCuCaSrO$_x$; (**B**) BiCuSrCaO$_x$; (**C**) BiCuSrCaCuCaO$_x$, BiCuCuSrCaCaO$_x$; (**D**) YBa$_2$Cu$_3$O$_x$.

We generated libraries by sputtering target materials through physical masks using an RF magnetron sputtering gun (*8*). Polished MgO or $LaAlO_3$ single crystals were used as substrates, and CuO, Bi_2O_3, CaO, PbO, $SrCO_3$, Y_2O_3, and $BaCO_3$ were used as sputtering targets. The library was generated by overlaying a primary physical mask, containing a grid of either 16 or 128 openings, with a series of secondary masks (Fig. 1). Precursors were sputtered through a series of binary masks in a stepwise fashion. The resulting array contains all 2^n combinations that can be formed by deleting one or more steps from the entire series of n deposition-masking steps (*6*). Alternative masking schemes can also be used to generate libraries, yielding, for example, a library of quaternary compounds from a group of seven precursors. Currently, six identical libraries can be generated simultaneously and processed under different conditions.

Initially, a 16-member binary library derived from Bi_2O_3, PbO, CuO, CaO, and $SrCO_3$ was synthesized (*9*); each site was 2 mm by 2 mm in size. Approximately 660 Å of CuO was deposited and the molar stoichiometry of each element relative to Cu was ~1:1. The library was then sintered at 840°C in air with no apparent melting or evaporation of the samples. The resistance of each site was measured as a function of temperature (T) down to 4.2 K with a parallel in-line four-point probe configuration and a multichannel switching system. Superconductivity was found in two films, BiCuCaSrO$_x$ and BiPbCuCaSrO$_x$, with critical temperatures (T_c's) of 80 and 90 K, respectively (Fig. 2A) (*10*, *11*). A 128-member library was then generated to further examine the effects of stoichiometry and deposition sequence on the properties of the BiSrCaCuO$_x$ films (Fig. 3). In general, films with low resistances showed metallic behavior with onset T_c's of 80 to 90 K. Films with excess Ca and Cu (Bi:Sr:Ca:Cu ratios of 2:2:4:4 and 2:2:4:5) showed a 110 K phase, consistent with the formation of $Bi_2Sr_2Ca_2Cu_3O_{10}$. A number of films with identical stoichiometries but different deposition sequences displayed distinct profiles of resistance versus temperature (for example, BiCuSrCaCuCaO$_x$ and BiCuCuSrCaCaO$_x$ in Fig. 2C), which suggests that different phases may be accessible by controlling the sequence in which the layers diffuse (*12*).

One important figure of merit in the synthesis of combinatorial libraries is the library density (samples per unit area). To explore synthetic limitations on sample size, we used physical masks to generate films ranging from 1mm by 1 mm down to 100 mm by 100 μm (*13*). Superconductivity was found in BiSrCaCuO$_x$ samples as small as 200 μm by 200 μm in size (T_c's of 80 to 90 K). Below 200 μm by 200 μm, sample evaporation became a significant factor, although methods may be found to overcome such problems. We can currently synthesize copper

Fig. 3. A 128-member binary library prior to sintering. Each site is 1 mm by 2 mm; the color of each is the natural color of reflected light from a white light source. The library was deposited according to the sequence 1, Bi, M0 (no secondary mask); 2, Bi, M1; 3, Cu, M0; 4, Cu, M2; 5, Cu, M3; 6, Sr, M0; 7, Sr, M5; 8, Ca, M6; 9, Cu, M4; 10, Ca, M7 (*9*). The molar stoichiometry for each layer was 1:1 relative to Bi (which was deposited as a 300 Å layer), with the exception of steps 3 and 5 in which the Cu:Bi ratio was 0.5:1.

oxide libraries with sites of 200 μm by 200 μm and spacings of 50 μm between sites.

Because this approach differs from conventional bulk synthesis and thin film fabrication methods, standard synthetic conditions may require modification in some instances. For example, synthesis of the $YBa_2Cu_3O_{7-x}$ superconductor (*11*) from a film generated by sequential deposition of BaF_2, Y_2O_3, and CuO in a 1:2:3 molar ratio (~400 Å of CuO) required low-temperature annealing of samples (200 to 400°C) before high-temperature sintering (840°C). Diffusion processes at low temperatures may facilitate formation of a homogeneous intermediate without nucleation of stable lower-order phases (*12*). We used this protocol to reproducibly synthesize $YBa_2Cu_3O_{7-x}$ superconducting films of sizes as small as 200 μm by 200 μm with metallic behavior and a T_c of ~90 K (Fig. 2D). A 128-member library derived from $BaCO_3$, Y_2O_3, Bi_2O_3, CaO, $SrCO_3$, and CuO was then generated to determine the compatibility of different families of copper oxide superconductors with a common processing condition. After annealing and high-temperature sintering (840°C), sites containing $BiSrCaCuO_x$ and $YBa_2Cu_3O_x$ were found to be superconducting.

The work described above effectively extends the combinatorial approach from biological and organic molecules to the remainder of the periodic table. Improved synthetic methodology may allow the parallel synthesis of larger libraries by means of higher-resolution physical masks or photolithography. Moreover, high-resolution scanning (susceptibility and Eddy current) detectors, as well as multichannel contact probes using spring-loaded contact pins, are being developed to facilitate library analysis. Nonetheless, the methodology, even in its current form, has already shown its effectiveness as a tool for discovering new materials. For example, new giant magnetoresistive oxides (*14*) containing cobalt have been found in libraries of Ln-M-X oxides, where Ln = La or Y, M = Ba, Sr, Ca, or Pb, and X = Mn or Co (*15*).

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9. The library was generated using the following deposition sequence (deposition step, element, secondary mask number): 1, Bi, M1; 2, Pb, M2; 3, Cu, M0 (no mask); 4, Ca, M3; 5, Sr, M4.
10. Seemann-Bohlin x-ray diffraction measurements were carried out with thin films (5 mm by 5 mm) deposited and sintered along with libraries under the conditions described above. The films are generally not highly oriented, and no effort has yet been made to correlate transport properties with x-ray structures.
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Hubble Space Telescope Imaging of Neptune's Cloud Structure in 1994

H. B. Hammel,* G. W. Lockwood, J. R. Mills, C. D. Barnet

Images of Neptune taken at six wavelengths with the Hubble Space Telescope in October and November 1994 revealed several atmospheric features not present at the time of the Voyager spacecraft encounter in 1989. Furthermore, the largest feature seen in 1989, the Great Dark Spot, was gone. A dark spot of comparable size had appeared in the northern hemisphere, accompanied by discrete bright features at methane-band wavelengths. At visible wavelengths, Neptune's banded structure appeared similar to that seen in 1989.

In 1989, the Voyager 2 spacecraft flew by the planet Neptune, revealing remarkable atmospheric activity on the most distant giant planet (*1*). Blue wavelength images were dominated by a single large storm in the southern hemisphere [see, for example, figure 8 in (*1*)]; the feature, dubbed the "Great Dark Spot" (hereafter, GDS-89) because of its prominence, was tracked for months (*2*). However, despite its size, the feature's low contrast put it beyond the reach of subsequent ground-based or Hubble Space Telescope (HST) imaging until HST's 1993 refurbishment. Thus, the feature's long-term survival was the subject of speculation (*3*). Meanwhile, ground-based near-infrared images suggested dramatic changes in Neptune's large-scale atmospheric features: activity appeared to be shifting from the southern hemisphere to the northern hemisphere (*4*). Moreover, the overall brightness of the planet increased by several percent, continuing a long-term trend (*5*), and initial imaging with the repaired HST hinted that GDS-89 might have disappeared, although the time sampling of the observations was insufficient to make a definitive statement (*6*).

In late 1994, we obtained multiwavelength images of Neptune with HST. The images show that the planet's appearance has indeed changed dramatically since 1989: we confirm that GDS-89 is gone and report a new dark feature of comparable size in the northern hemisphere, most clearly visible in blue light (Figs. 1 and 2). At methane-band wavelengths, the planet's appearance is dominated by several large, rapidly changing features at northern mid-latitudes, including clouds clearly associated with the new dark spot. Each set of images, taken a few hours apart, was timed to ensure nearly complete longitudinal coverage on three separate HST visits: 10 to 11 October 1994, a week later on 18 to 19 October 1994, and finally, 3 weeks later on 1 to 2 November 1994 (Table 1).

Neptune's disk (diameter, 2.2 arc sec) extended over 48 pixels on HST's Planetary Camera. One pixel corresponded to 990 km at disk center, about six times better than the resolution in excellent ground-based images. We used the standard image calibration and processing provided by the Space

H. B. Hammel and J. R. Mills, Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.
G. W. Lockwood, Lowell Observatory, Flagstaff, AZ 86001, USA.
C. D. Barnet, Space Astrophysics Laboratory, Institute for Space and Terrestrial Science, North York, Ontario M3J 3K1, Canada.

* To whom correspondence should be addressed.