



Approcci combinatoriali alla scoperta di nuovi materiali

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iNRiM, Torino, 18/09/2008

M. Anderle, Approcci combinatoriali alla scoperta di nuovi materiali





Outline

Scienza combinatoriale

Tavola di Mendeleev e possibili combinazioni

Approcci sperimentali

Nuovi materiali e nuove interfacce

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MANY AT A TIME Program head Andreas Marzinik (front to back) and lab specialists Raphael Gattlen and Urs Rindisbacher of Novartis Pharma AG, Basel, Switzerland, pipette coupling reagent into 96-well reaction blocks.

COMBINATORIAL CHEMISTRY

Chemical & Engineering News, August 2001

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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.

Science 268, 1738 (95)







April 2002, Volume 27, No. 4

Serving the International Materials Research Community A Publication of the Materials Research Society



Combinatorial Materials Science



COMBINATORIAL APPROACH TO MATERIALS

Sample size <mark>—</mark> = 50µm to 1mm

> Thin-film deposition techniques, or parallel injection delivery systems

Processing temperature, atmosphere, pressure

Variable temperature parallel / scanning detection systems Large scale synthesis / analysis Sintesi di materiali tramite approccio combinatoriale in FCS adattando e utilizzando l'apparato già esistente CLUSTER LAB





Correlation between materials complexity and physical properties





Take 60 "useful" elements.

There are about 30,000 known inorganic compounds.

Binary compounds have the form AB. (e. g., MgF, SiC, ZnO,....) 60 x 60 x different combinations: **most are known**.



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Combinatorial libraries of inorganic materials



Semiconductor gas sensor library, "electronic nose", Appl. Phys. Lett. **83**, 1255 (2003)

Magnetic shape memory alloy library, Nature Materials **2**, 180 (2003)

Quaternary Masks



A

С

H H H +H H H \square H H + \square H H H \square \square +H H + \square +

В





Quaternary Masking



Quaternary Masking: 1st mask, 1st position



Quaternary Masking: 1st mask, 2nd position



Quaternary Masking: 1st mask, 3rd position





Quaternary Masking: 1st mask, 4th position





Quaternary Masking: after 1st mask



Quaternary Masking: 2nd mask, 1st position



Quaternary Masking: 2nd mask, 2nd position





Quaternary Masking: 2nd mask, 3rd position





Quaternary Masking: 2nd mask, 4th position





PbTiO ₃	PbZrO ₃	BaTiO ₃	BaZrO ₃
PbNb ₂ O ₆	PbTa ₂ O ₆	BaNb ₂ O ₆	BaTa ₂ O ₆
SrTiO ₃	SrZrO ₃	CaTiO ₃	CaZrO ₃
SrNb ₂ O ₆	SrTa ₂ O ₆	CaNb ₂ O ₆	CaTa ₂ O ₆

- # depositions: 4 x n A
 # combinations: 4ⁿ
- 5 masks:
- 4 x 5 = 20 depo's 4⁵ = 1024 samples



В



+				





(Right) Luminescent image of the same library after thermally processed under UV excitation.

Science 279, 1712 (1998)

Various combinatorial experimental designs

discrete libraries vs composition spreads



- Composition spreads allow continuous mapping of physical properties and phase boundaries
- Run to run variation in ordinary experiments is removed

Combinatorial UHV Co-sputtering (P_{base} ~1x10⁻⁹ Torr) CCS-Continuos Composition Spread Approach



distance between _ guns & substrate

Composition Spreads of Ternary Metallic Alloy Systems



Scanning SQUID microscope based on YBa₂Cu₃O₇ thin film (F. Wellstood, UMD)



Room temperature samples are measured

Scanning SQUID image of a Ni-Mn-Ga spread wafer (room temperature)



Combinatorial search of ferromagnetic shape memory alloys



"Sistema di monitoraggio rapido del gruppo sanguigno e per la rivelazione di reazioni immunoematologiche"





macro \rightarrow micro \rightarrow nano

Morpho thamyris (Nymphalide)



5.0kV

LEI

X5,500

 $1\mu m$

de si se

WD 7.4mm

Morpho thamyris (Nymphalide)


Spatially Programmable Equipment Design for Combinatorial CVD

New paradigm for intelligent design and control of semiconductor process equipment





G. W. Rubloff, R. Adomaitis, et. al.

Combinatorial CVD Reactor







Combi-CVD Programmability



- Spatially programmable CVD enables combinatorial studies
- Post-process mapping of thickness/rate
- Composition mapping (IRST microcombi project)

Combinatorial W CVD from WF_6/H_2

Reactant flow distributions

	Seg 1.	Seg 2.	Seg 3.
Ar	0	60	30 [sccm]
WF6	12	0	6 [sccm]
H2	48	0	24 [sccm]
Total	60	60	60 [sccm]



Film thickness distributions

- Growth rate $\propto [P_{H2}]^{1/2}$
- Heater T: 400 °CChamber P: 1 torrGap: 1mmProcess time : 10 min



<u>Combi-CVD</u> Materials Synthesis



"Combinatorial Chemical Synthesis of Thin Film Materials: CVD and ALD" G.W.Rubloff, R.A.Adomaitis, L.Henn-Lecordier and M.Anderle Invited to 4th International Workshop on Combinatorial Materials Science and Technology, December 4-6, 2006, San Juan, Puerto Rico

Atomic Layer Deposition



BUT...

Nucleation & surface condition dependence

Temperature-dependent growth

Dose dependencies

Incomplete layer adsorption & reaction

Multilayer adsorption & reaction

ALD reactor design



Our approach to combi ALD

Final objective:

Compositional gradient for ternary systems requires thickness gradient across wafer



Tuning of materials properties via compositional gradient

Process flow sequence for combi Hf-Al-O films



Effect of TMA dose on thickness profiles



Fixed saturating water dose

 Decrease in TMA dose (3.6 to 0.43) results in increasing but continuous thickness nonuniformities (<30%)

 Below critical dose, discontinuous profile

Higher growth rate at inlet

 May result from localized OH* oversaturation as H2O/TMA increases and multilayer deposition

Higher growth at inlet aggravates TMA depletion near outlet

ALD cross-flow arrangements makes it easy to see when reaction is unbalanced as it amplifies consequent non uniformities

Ex-situ wafer characterization under water-starved conditions (0.8 µmol)

Spect. ellipsometry







AVG constant = 1.48E-010 F STD constant = 2.59E-011 F, or 17.48% Estimated dilectric constant in center: 6.222 for 150 A thickness AVG and STD determined from 190 points





STD constant = 1.41E-012 A, or 37.82% Estimated leakage current in center 7.7124e-007 A for 150 A thickness AVG and STD determined from 163 points



Film properties across wafer under water-starved conditions (0.8 µmol)



Film properties across wafer for TMA-underdosed films



Combinatorial ALD

Numerous process recipe permutations in real-world ALD



Phleum pratense Codolina

X2,300

10µm

WD 24.3mm

2.0kV

LEI



Loto





H.Y. Erbil et al, "Transformation of a Simple Plastic into a Superhydrophobic Surface" Science 299, 1377 (2003)

Superhydrophobic Surface





Choi and Kim, Physical Review Letters 2006



Nanotubi di carbonio



A.Tagliaferro et al, PoliTo

200µm

VVD = 5 mm __Mag = __87 X Aperture Size = 20.00 μm EHT = 5.00 kV

Signal A = SE2 Stage at T = 45.0 ° Date :27 Mar 2006 Time :11:51:03 User Name = ANGELI







CEALP_1709

L x250 300 um

Dolomiti Invisibili 2006









FONDAZIONE BRUNO KESSLER





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Substrate Size	Ø 50 mm (recommended)	
	2x10-4 to 5x10-2 mbar	
Plasma Density	109 to 1012 cm-3	
Ion Current Density	0,01 to 1,0 mA/cm2	
Ion Energy	30 to 200 eV	
Frequency	13,56 MHz	
Max Power	600 W	
Process Gas	O ₂ , N ₂ , CO ₂ , NH ₃ , Ar and other	
Uniformity	± 10%	





































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ADESIONE DELLA GENGIVA AD UN PROTESI DENTALE



ECM proteins and integrin receptors



Titanium alloy functionalization: Overview

Step 1: amide bond through the N-hydroxysuccinimide ester (NHS)Step 2: thiol chemistry (Vinylsulfone)



Fluorescent derivative PEG: 5.5 · 10¹³ molecules/cm²

Titanium alloy functionalization 3: Human gingival cells (HGF-1) adhesion

titanium alloy



Cell images obtained with a laser scan microscope (a and b) and with a scanning electron microscope (a1 and b1)

RGD modified titanium alloy





17.500 cell/cm²

Incubation 24 h in serum free medium plus cycloheximide (25 ug/ml)
Various combinatorial experimental designs

discrete libraries vs composition spreads



Composition spreads allow continuous mapping of physical properties and phase boundaries

Using composition spreads to design multifunctional materials

Mixing properties: ferromagnetism, ferroelectricity, ferroelasticity, superconductivity, hydrogen storage capabilities, optical transparency, band gap, catalytic properties, various sensing, biological ..., ...



Microstructure: composites, nanocomposites, solid solutions

Fabrication of epitaxial continuous composition spread



W. M. Keck Laboratory for Combinatorial Nanosynthesis and Multiscale Characterization

Ichiro Takeuchi, Gary W. Rubloff, Ellen D. Williams





Composition spread characterization technique



Scanning Microwave Microscope



Dielectric constant characterization using microwave microscope



Dielectric constant at 1 GHz

Scanning SQUID microscope based on YBa₂Cu₃O₇ thin film (F. Wellstood, UMD)



Room temperature samples are measured

Magnetic property characterization using a scanning SQUID microscope



Magnetic and dielectric properties of PbTiO₃-CoFe₂O₄ system



Scanning X-ray microdiffraction



Continuous change in nanostructure across the nanocomposite spread



Combinatorial Library

Systematic study of the exchange coupling with small changes of the magnetic parameters



12.5 mm x 12.5mm Substrates

Ming-hui Yu, Jason Hattrick-Simpers, Ichiro Takeuchi, Jing Li, Z. L. Wang, J.P. Liu, S.E. Lofland, Somdev Tyagi, J. W. Freeland, D. Giubertoni, M. Bersani, M. Anderle, "Inter-phase Exchange Coupling in Fe/Sm-Co Bilayers with Gradient Fe Thickness" Journal of Applied Physics 98, 063908 (2005).

Combinatorial material experiment & analysis



HIGH THROUGHPUT EXPERIMENT

The material discovery/optimization PROCESS



"Data analysis in combinatorial experiments: applying supervised principal components to predict thin film ternary composition spreads from TOF-SIMS spectra"

R. Dell'Anna, P. Lazzeri, R. Canteri, C.J. Long, J. Hattrick-Simpers, I. Takeuchi and M. Anderle

QSAR & Combinatorial Science 2008, 27, 171-178

Ringraziamenti





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Ichiro Takeuchi, Gary Rubloff, Laurent Lecordier