

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0705-0188	
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE <b>970228</b>	3. REPORT TYPE AND DATES COVERED <b>Technical Reports 1-7, Dec '95-Nov '96</b>		
4. TITLE AND SUBTITLE <b>Synthesis of Ceramics from Solutions: Fuctionally Graded Composites, NanoComposites and Single Crystal Thin Films</b>			5. FUNDING NUMBERS <b>AFOSR F49620-96-1-0003</b>	
6. AUTHOR(S) <b>Fred F. Lange</b>				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Materials Department College of Engineering University of California Santa Barbara, CA 93106-5050</b>			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) <b>Dr. Alexander Pechenik AFOSR/PKA 110 Duncan Avenue, Suite B115 Bolling AFB DC 20332-8080</b>			10. SPONSORING/MONITORING AGENCY REPORT NUMBER  <b>19970313 012</b>	
11. SUPPLEMENTARY NOTES				
12A. DISTRIBUTION/AVAILABILITY STATEMENT <b>A</b>			12B. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) <p>This program has emphasized two topics: 1) the crystallization of metastable, solid-solution structures, their partitioning into equilibrium structures and compositions, and the role of the metastable phase and its partitioning on forming unique, nanometer microstructures important to the mechanics of structural ceramics and their composites, and 2) the formation of single crystal thin films via spin coating single crystal substrates with solution precursors. Results for the first topic are new, namely, the discovery that diffusion limited crystallization concepts used in rapid solidification directly applies to precursors that crystallize at low temperatures during heating. This discovery is significant because solid-solutions can be greatly extended relative to high temperature synthesis and processing routes where equilibrium conditions are rapidly achieved and solid-solutions can be severely limited. Extension of solid-solution fields (and thus defect chemistries) in compositional space is important to synthesize new materials with optical and electronic properties controlled by defect chemistry and/or metastable compositions. Results for the second topic have shown that single crystal thin films can be formed on single crystal substrates with spin-on liquid precursors despite large differences in lattice parameters and/or crystal structures. Several mechanisms have been identified for the growth of single crystal thin films which are very different to the well know vapor phase epitaxy mechanisms. The significance of the second topic is that single crystal (or poly-variant single crystal) thin films of nearly any inorganic material can be produced on any non-reactive (thermodynamically or kinetically) single crystal substrate, despite crystal structure differences between the film and substrate materials. Processing of multi-layer and/or embedded strip line architectures are possible using liquid precursor spin-on techniques for new device technologies.</p>				
14. SUBJECT TERMS <b>Epitaxy, Phase Selection, Solution Synthesis, Ceramics</b>			15. NUMBER OF PAGES <b>5</b>	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT <b>Unclassified</b>	18. SECURITY CLASSIFICATION OF THIS PAGE <b>Unclassified</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>Unclassified</b>	20. LIMITATION OF ABSTRACT	

**Synthesis of Ceramics From Solutions:  
Functionally Graded Composites, NanoComposites and  
Single Crystal Thin Films**

**Contract AFOSR F49620-96-1-0003**

**Technical Reports 1 through 7**

**with a Technical Summary**

**period: December 1995 - November 1996**

**February 1997**

**From**

**Materials Department  
College of Engineering  
University of California  
Santa Barbara, CA 93106**

**Principal Investigator: Fred F. Lange  
805 893 8248  
flange@engineering.ucsb.edu**

## 1. Background

This program has emphasized two topics: 1) the crystallization of metastable, solid-solution structures, their partitioning into equilibrium structures and compositions, and the role of the metastable phase and its partitioning on forming unique, nanometer microstructures important to the mechanics of structural ceramics and their composites, and 2) the formation of single crystal thin films via spin coating single crystal substrates with solution precursors. Results for the first topic are new, namely, the discovery that diffusion limited crystallization concepts used in rapid solidification directly applies to precursors that crystallize at low temperatures during heating. This discovery is significant because solid-solutions can be greatly extended relative to high temperature synthesis and processing routes where equilibrium conditions are rapidly achieved and solid-solutions can be severely limited. Extension of solid-solution fields (and thus defect chemistries) in compositional space is important to synthesize new materials with optical and electronic properties controlled by defect chemistry and/or metastable compositions. Results for the second topic have shown that single crystal thin films can be formed on single crystal substrates with spin-on liquid precursors despite large differences in lattice parameters and/or crystal structures. Several mechanisms have been identified for the growth of single crystal thin films which are very different to the well know vapor phase epitaxy mechanisms. The significance of the second topic is that single crystal (or poly-variant single crystal) thin films of nearly any inorganic material can be produced on any non-reactive (thermodynamically or kinetically) single crystal substrate, despite crystal structure differences between the film and substrate materials. Processing of multi-layer and/or embedded strip line architectures are possible using liquid precursor spin-on techniques for new device technologies.

## 2. Summary of Research

### 2.1 Metastability of the Fluorite, Pyrochlore and Perovskite Structures in the PbO-ZrO<sub>2</sub>-TiO<sub>2</sub> System, Andrew D. Polli, Fred F. Lange, and Carlos G. Levi

#### Technical Report No. 1

**Abstract:** The crystallization, transformation, and partitioning of amorphous PbO-ZrO<sub>2</sub>-TiO<sub>2</sub> powders produced by pyrolytic decomposition of mixed alkoxide precursors were investigated. Materials have the general formulation  $Pb_{1+\chi}Ti_{[1/(1+\phi)]}Zr_{[\phi/(1+\phi)]}O_{3+\chi}$ , where  $-0.2 \leq \chi \leq 0.2$  is the fraction PbO excess/deficiency and  $0 \leq \phi \leq 1$  is the Zr/Ti molar ratio. Most compositions first crystallized as a metastable fluorite structure with varying degrees of pyrochlore-like cation ordering, which transformed to a single perovskite phase upon additional heat treatment. Higher Zr/Ti ratios enhanced the retention of fluorite and reduced the incidence of cation ordering. Compositions with off-stoichiometric amounts of PbO often yielded extended solid solutions prior to partitioning. For example, metastable perovskites with as much as 20% PbO deficiency ( $\chi = -0.2$ ) could be prepared for  $0 \leq \phi \leq 1$ , but only ~10% PbO excess could be incorporated in solution for  $0.33 \leq \phi \leq 1$ . Increasing PbO content was found to promote crystallization, suggesting that this oxide acts as a network modifier enhancing mobility within the initial amorphous precursor powder. Higher PbO was also noted to favor cation ordering in the metastable phase and to accelerate the transformation to perovskite, as well as to promote partitioning for hyperstoichiometric compositions. The findings are discussed in light of structural relationships between the fluorite, pyrochlore and perovskite phases, as well as current understanding of the thermodynamics of the system.

### 2.2 Epitaxial Growth and Structure of Highly Mismatched Oxide Films with Rock-Salt Structure on MgO, P.A. Langjahr, T. Wagner, F.F. Lange, and M. Rühle

#### Technical Report No. 2

**Abstract:** CaO thin films were grown on (001) MgO single crystal substrates by a chemical solution deposition method to study the influence of a relatively high lattice mismatch (14%) on the epitaxial growth. In order to minimize an influence of a different crystal structure and chemistry between film and substrate, film and substrate were chosen to have the same structure (NaCl) and a similar chemistry. The films were heat treated until they broke up into single crystal islands on the MgO substrate. X-ray pole figure analysis and TEM observations of the CaO-films showed that most of the grains had a single out-of-plane orientation (111)CaO || (001)MgO, corresponding to two non-redundant, symmetry related in-plane variants [110](111)CaO || [110](001)MgO and [110](111)CaO || [110](001)MgO. A  $\Sigma 7/\Sigma 8$  Near Coincidence Site Lattice (NCSL) model could be constructed for the interface, that suggests good lattice and charge

matching for the observed orientation relations. The mechanisms and energetics leading to the experimentally observed orientation relations are discussed.

### **2.3 Lattice Mismatch Accommodation in Perovskite Films on Perovskite Substrates, P.A. Langjahr, F.F. Lange, T. Wagner, and M. Rühle**

#### **Technical Report No. 3**

**Abstract:** Cubic perovskite films with different compositions were grown on perovskite substrates to investigate the influence of a large lattice mismatch on growth phenomena via the chemical solution deposition method, using toluene solutions of different 2-ethylhexanoates and neodecanoates. The films were pyrolyzed to crystallize the perovskite of the desired composition and then heated to 1000°C to promote epitaxial grain growth. Pole figures obtained via X-ray diffraction as well as selected area diffraction (SAD) of TEM specimen with lattice mismatches of 2.5% (SrTi<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>3</sub> on SrTiO<sub>3</sub>), 5% (SrZrO<sub>3</sub> on SrTiO<sub>3</sub>), 7.4% (BaZrO<sub>3</sub> on SrTiO<sub>3</sub>) and 8.2% (SrZrO<sub>3</sub> on LaAlO<sub>3</sub>) reveal only the epitaxial orientation [100](001) film || [100](001) substrate. The XRD and TEM results also indicate increasing polycrystallinity with increasing lattice mismatch. High resolution electron microscopy (HREM) of films on SrTiO<sub>3</sub> demonstrated that an array of misfit dislocations is present at the interface. The misfit dislocations have line vectors **l** of a<100>-type and Burgers-vectors **b** of a<010>-type. Dislocation separation distances obtained with HREM and XRD lattice parameter measurements show that the strain energy within the films, due to lattice mismatch, is nearly fully relaxed. The mechanisms of epitaxial growth and dislocation formation are discussed.

### **2.4 Epitaxial Growth and Structure of Cubic and Pseudocubic Perovskite Films on Perovskite Substrates, P. A. Langjahr, T. Wagner, M. Rühle and F. F. Lange**

#### **Technical Report No. 4**

**Abstract:** Cubic and pseudocubic perovskite films on perovskite substrates are used to study the influence of the lattice mismatch on the epitaxial growth of thin films on substrates of the same structure. For the growth of the films, a metalorganic deposition route (MOD) using 2-ethylhexanoates and neodecanoates as precursors, was developed. The decomposition of the precursors was investigated with thermogravimetric analysis (TGA) and x-ray diffraction (XRD). The films were spin-coated on (001)-oriented SrTiO<sub>3</sub>- and LaAlO<sub>3</sub>-substrates, pyrolyzed and afterwards annealed between 600°C and 1200°C. XRD-investigations and conventional transmission electron microscopy (CTEM) show, that epitaxial films with the orientation relationship [100](001) film || [100](001) substrate can be grown. With XRD, it could be shown, that not only ternary oxide films (SrZrO<sub>3</sub>, BaZrO<sub>3</sub> and BaCeO<sub>3</sub>), but also perovskite solid solution films (SrTi<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>3</sub> and BaCe<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>3</sub>) can be prepared. Strong interdiffusion, detected by a shift of the

film lattice parameter towards the substrate lattice parameter was found in SrZrO<sub>3</sub>- and BaZrO<sub>3</sub>-films on SrTiO<sub>3</sub>, annealed at temperatures above 1050°C. High resolution electron microscopy (HREM) studies of SrZrO<sub>3</sub> on SrTiO<sub>3</sub> show that a crystalline semicoherent interface with a periodical array of misfit dislocations is present.

## **2.5 Epitaxial Growth of $\beta$ -SiC Thin Films on a 6H-SiC Substrate Using the Solution Precursor Method, D. Heimann, T. Wagner, J. Bill, and F. Aldinger**

### **Technical Report No. 5**

**Abstract:** A polyvinylmethylsilane precursor has been used for the epitaxial growth of SiC thin films on 6H-SiC single crystal substrates. The films were prepared by dipping the single crystalline 6H-SiC substrates into the precursor polymer solution with subsequent thermal treatments at different temperatures. Transmission electron microscopy (TEM) was used to characterize the microstructure and chemistry of the different SiC films. At 1100 °C, the film was amorphous and contained substantial oxygen. At 1600 °C, an epitaxial, single crystalline  $\beta$ -SiC film was observed.

## **2.6 Nano-Meter, Binary Composites Produced from Liquid Precursors via Metastable Phases and Phase Partitioning, F. F. Lange**

### **Technical Report No. 6**

**Abstract:** Chemical routes to synthesize inorganics start with solutions containing different metal-organic molecules that remain well mixed during evaporation to a solid precursor. The solid precursor decomposes and crystallizes during heating. Because decomposition (pyrolysis) occurs at very low temperatures relative to the melting temperature of the inorganic, a large free energy change exists for crystallization. This large free energy change is responsible for two very interesting phenomena. First, the size of the critical nucleus for spontaneous crystallization and growth is very small. Thus the grain size of the initial inorganic material produced during crystallization is  $\leq 2$  nanometers. Second, crystallization occurs at very low temperatures, i.e., either during or subsequent to pyrolysis. Thus diffusion is very limited, resulting in the crystallization of metastable phases, i.e., phases with unexpected (non-equilibrium) structures and/or phases with a solid-solution that is much greater than found for equilibrium conditions (high temperature heat treatments). With this understanding, nano-crystalline materials can be made that are very stable at high temperatures using the following procedure. The first step is to formulate a precursor composition that would produce at least two phases under equilibrium conditions. During and/or subsequent to pyrolysis, only one, metastable crystalline phase will form; it will have a nanometer grain size. Heating to higher temperatures where long range diffusion can occur will cause the single, metastable phase to partition to its stable phases. Since the second phase(s) partition with a smaller size than the initial metastable phase, a multi-phase composite is produced when the size of each phase can be  $\leq 100$  nano-meters. This nano composite can be stable at high temperatures because the growth of either phase requires long-range diffusion.

These issues are detailed for three binary systems: t-ZrO<sub>2</sub>/c-ZrO<sub>2</sub>, ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>.

## 2.7 Chemical Solution Routes to Single Crystal Thin Films, F. F. Lange

### Technical Report No. 7

**Abstract:** Epitaxial thin films of inorganic single crystals can be grown on single-crystal substrate through with a variety of different solution chemistries. This review emphasizes chemical solution deposition, in which a solution is used to deposit a layer of precursor molecule that decompose to low-density, polycrystalline films during heating. Ways to control film cracking during deposition and heat treatment and why many precursors synthesize metastable crystalline structures are discussed, and the different mechanisms th convert the polycrystalline film into a single crystal are reviewed. Hydrothermal epitaxy in which single crystal thin films are directly synthesized on templating substrates in a aqueous solution at temperatures < 1500 °C, is also discussed.