PNL-SA-26436

BIOMIMETIC THIN FILM DEPOSITION

P.R. Rieke   S. Baskaran
G.E. Graff   L. Song
A.A. Campbell   B.J. Tarasevich
B.C. Bunker   G.E. Fryxell

September 1995

MASTER

BIOMIMETIC THIN FILM DEPOSITION

P. C. Rieke, G. E. Graff, A. A. Campbell, B. C. Bunker,
S. Baskaran, L. Song, B. J. Tarasevich, G. E. Fryxell
Materials Science Department
Pacific Northwest Laboratory
Richland WA, 99301, USA

ABSTRACT

Biological mineral deposition for the formation of bone, mollusk shell and other hard tissues provides materials scientists with illustrative materials processing strategies. This presentation will review the key features of biomineralization and how these features can be of technical importance. We have adapted existing knowledge of biomineralization to develop a unique method of depositing inorganic thin films and coating. Our approach to thin film deposition is to modify substrate surfaces to imitate the proteins found in nature that are responsible for controlling mineral deposition. These biomimetic surfaces control the nucleation and growth of the mineral from a supersaturated aqueous solution. This has many processing advantages including simple processing equipment, environmentally benign reagents, uniform coating of highly complex shapes, and enhanced adherence of coating. Many different types of metal oxide, hydroxide, sulfide and phosphate materials with useful mechanical, optical, electronic and biomedical properties can be deposited.

KEY WORDS: Coatings, Thin Films, Biomimetic

1. INTRODUCTION

Biological hard tissues (e.g. bone and mollusk shell) are ceramic/polymer composites with remarkable mechanical properties [1]. The composition is better than 90% mineral phase, and the remainder consists of structural proteins and polysaccharides. The choice of mineral phase is dictated by availability rather than intrinsic mechanical properties. The calcium phosphate and calcium carbonate found in bone and shell, respectively, would traditionally be considered very poor choices as structural materials. The impressive structural strength and fracture resistance arise from the organization of the two constituents; the result is greater than the sum of the parts. Practical application of biomineralization concepts requires a general understanding of the biology involved and identification of physical and chemical principles that can be applied to materials science. In this paper, we briefly describe how biomineralization principles can be applied to control the deposition of thin film materials of technical importance. Specific examples of surface-controlled nucleation and growth are presented.

Because of its importance to biology, medicine, and dentistry, the mechanism of biomineralization has been the subject of much research [2,3]. This cannot be adequately reviewed here and only a simplified model is presented as background. Hard tissue formation begins with deposition of structural biopolymers. In bone, collagens are the primary constituent; in mollusk shell, silk-fibroins and polysaccharide fibrils are used. The organization of these into a three dimensional, skeletal framework determines the form and function of the resulting hard tissue. Within the void spaces, nucleation proteins are deposited and the solution invading this network is brought to supersaturation with respect to the desired mineral phase. The nucleation proteins are thought to induce nucleation at the desired location. Crystal growth ensues and the void spaces are filled with mineral to form a fully dense ceramic/polymer composite. The overall process is cyclic or incremental: a small fringe of unmineralized substrate forms, the mineral growth front advances, another small fringe of unmineralized substrate forms, ad infinitum.

A wide variety of minerals are deposited by organisms including metal oxides, sulfides, carbonates, and phosphates [4]. Thus, biomineralization appears to be a general phenomenon the concepts of which should be applicable to deposition of minerals not found in nature. Furthermore, the mineral deposition process is not under direct cellular control and only the structure and composition of the nucleation protein appear to be controlling the mineralization. With this rationale, our researches have focused on understanding how organic substrates control nucleation and crystal growth of both biominerals and technically important minerals [5-15].

Our primary practical objective has been to develop a novel thin film deposition technology based on the above basic observations of biomineralization. The primary difference between biomimetic and other liquid or vapor phase thin film deposition techniques is that the substrate drives deposition. As shown in Fig. 1, this is achieved by derivatizing the surface of the substrate with bifunctional organic molecules. One end of the interfacial layer is designed to covalently bind to the substrate while the other is designed to induce thin film deposition. This simple model mimics the strategy used by living organisms to induce mineral growth. Thin films can be deposited on metal, polymer, and oxide substrates by tailoring the interfacial layer to the specific, desired substrate.

Patterning controls site of deposition

Interfacial groups control phase and orientation of mineral deposit

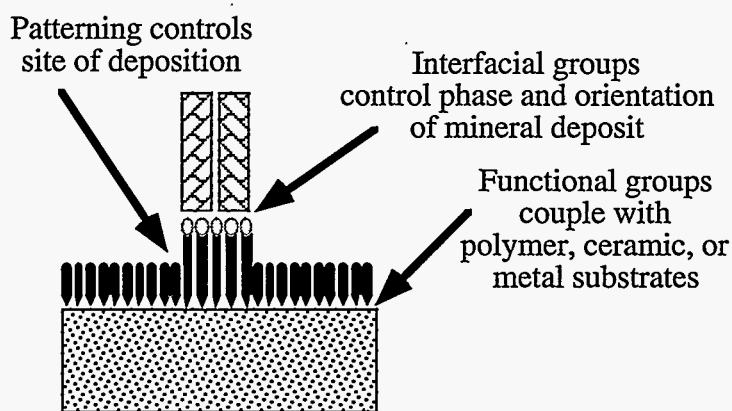Functional groups couple with polymer, ceramic, or metal substrates

Fig. 1 Objective is to mimic biological nucleation proteins with a bifunctional organic interface.

Biomimetic thin film deposition has a number of advantages over vapor phase and solution phase deposition technologies. It is a low temperature (<100 °C), aqueous solution process. No complex vacuum equipment is required nor does the process require organic solvents. This results in energy savings and reduced emission of volatile organic compounds. Because the surface promotes mineralization, very good film adhesion is obtained. Further, porous and complexly shaped substrates can be easily coated.

Control of thin film microstructure is possible by manipulating the type and density of functional group on the surface. Thus biomimetic thin film deposition provides the ability to 1) control the phase of mineral deposited on the substrate, 2) control the orientation of the crystal lattice with respect to the surface, and 3) direct deposition to only those locations properly derivatized with the mineralization inducing functional group.

2. DERIVATIZATION OF SUBSTRATES

As noted above, preparation of the substrate interface by derivatization is key to achieving proper film deposition. The discussion of nucleation proteins suggests that a surface with high density of functional groups with strong acid/base character or ligand binding ability is the primary requirement for controlling mineralization. Artificial surfaces could be prepared with these groups to mimic the nucleation proteins. Each type of substrate requires a different tactic to achieve this. Selective chemical reactions can be performed on the surface of many plastics. We have explored surface derivatization methods on polyethylene and self-assembled monolayers (SAMs) and developed methods for the introduction of hydroxyl, phosphate, thiol, sulfonate, carboxylate, amine, and methyl groups.

As the very simplest example, sulfonate groups can be introduced to polystyrene surfaces by exposure to either sulfuric acid or SO_3 gas. The sulfuric acid method is difficult to control and severely etches the substrate surface. In the second method, SO_3 gas is introduced into an evacuated chamber containing the substrates. Effusion of the gas over the polystyrene samples results in reproducible sulfonation. This method is applicable to many aromatic containing polymers.

Polyethylene and other nominally inert polymers can be derivatized by covalent attachment of primary amines to the oxidized surface via an amide linkage. Details of preparation are described elsewhere [13]. Low density polyethylene is first oxidized in chromic acid to introduce carboxylate groups. Treatment in a saturated solution of PCl_5 in ether gives the reactive acyl chloride. Immersion in a solution of a primary amine dissolved in 50/50 volume percent triethylamine and pyridine formed the amide derivative. Using appropriate primary amines the surface end groups can be tertiary amines, esters, thiols, alcohols, sulfonates and phosphates.

Self-assembled monolayers (SAMs) can be used to derivatize metal and oxide interfaces. We use alkyltrichlorosilanes terminated in either bromine, vinyl or trifluoroester groups. The trichlorosilane reacts with surface hydroxyl groups to form a covalent siloxane linkage to the surface. As most metals have an oxide layer, this same scheme can be applied to both metal and oxides. Shown in Fig. 2 is a schematic for derivatizing silicon substrates with a vinyl terminated monolayer. The vinyl groups are easily converted to sulfonate groups by exposure to SO_3 gas. By using mixed monolayers consisting of alkyl chains with and without the vinyl groups, the average

Fig. 2 Formation of sulfonated SAMs.

density of sites can be controlled. Bromine and trifluoroethylester terminated SAMs provide reactive routes to other types of terminal groups. We have applied this technique to derivatize aluminum, titanium, stainless steel, silicon and glass. From a practical standpoint the use of long chain monomers is not required but does allow easy solution phase deposition of the SAM. Shorter chain silanes can be deposited by vapor deposition. For metals without an oxide coat, such as gold, a thiol linkage can be used to attach the SAM to the surface.
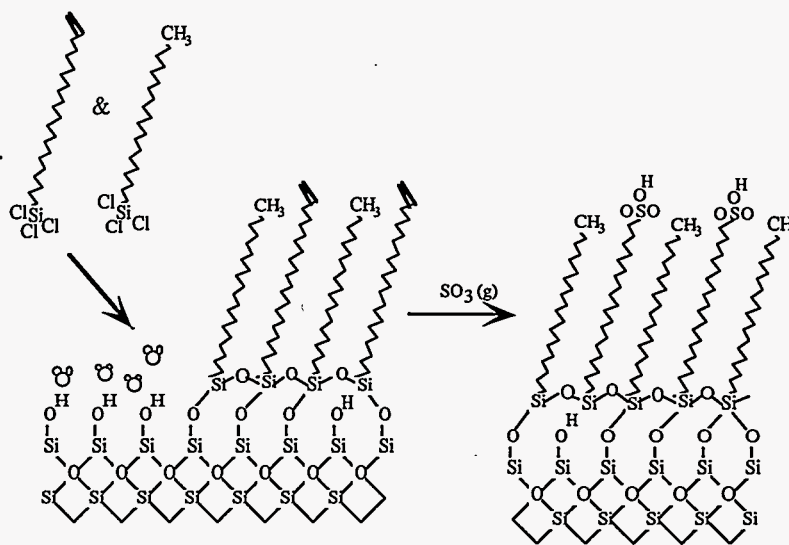
3. DEPOSITION OF THIN FILMS

Experiments with various mineral systems and various surface systems have shown that artificial substrates can be used to control the phase of materials deposited, the orientation of the crystal lattice, and the location of deposition. We have explored a number of thin film depositions including CdS, FeOOH, AlOOH, TiO_2, SnO_2, CeO_2, hydroxy apatite (calcium phosphate), $CaCO_3$, and ZrO_2. Described below are selected systems that illustrate the advantages of biomimetic thin film deposition. Details of the precipitation schemes can be obtained from the literature [5-15].

The approach is to prepare a solution supersaturated with respect to the desired mineral. The solution should not be so supersaturated so as to precipitate spontaneously. Upon immersion of the derivatized substrate, precipitation occurs on the surface by heterogeneous nucleation. Often a very precise set of solution conditions are required to promote heterogeneous nucleation without inducing solution precipitation. In other cases, heterogeneous nucleation occurs just prior to or simultaneously with solution precipitation.

Precipitation can occur by formation of a stable supersaturated solutions. This is the case with $CaCO_3$, hydroxy apatite, and FeOOH. As an example of this, FeOOH films can be deposited from solutions that are no more than 3.0 mM, no more than pH 2.0 and no less than pH 1.8. Hydrolysis and condensation are induced by heating to 70 °C [5,6]. Under these conditions no precipitation is observed in solution. Alternatively supersaturation can be generated by *in-situ* formation of one of the reagents. CdS films can be prepared from 0.1M cadmium nitrate and 1.0M ammonium nitrate solutions at pH values ranging from 8.5 to 10.5 [11]. Sulfide was generated *in-situ* by base decomposition of thiourea at 0.05M concentration. As the sulfide concentration increases conditions become favorable to film formation. As decomposition continues a precipitate forms in solution. The films are removed from solution prior to bulk precipitation.

A dark-field TEM micrograph of a 3000 Å FeOOH film is shown in Fig. 3. In general, the films are dense with uniform microstructure and thickness. The dark filed image revealed crystals with a columnar structure and 20 nm in diameter, while the bright field image revealed that each column consisted of lamellar features of about 20 Å in dimension. Microspot electron diffraction analysis revealed that the mineral deposited was goethite and that the crystal lattice was highly oriented with respect to the substrate. Micrographs of other mineral thin film deposited biomimetically show similar properties in that the films are consistently very dense with little porosity.

Fig. 3 TEM cross section of FeOOH thin film. Film is 300 nm thick.

We have used biomimetic processing to coat very complex and porous shapes [7]. Shown in Fig. 4 is a titanium bone implant test piece. It consists of a titanium metal core with a sintered titanium bead coating. Bone grows into the bead coating and forms a strong mechanical interlock. Unfortunately bone does not grow well into bare titanium and the implant is usually coated with a calcium phosphate that promotes bone ingrowth. Plasma sprayed coating has been used to coat the implant but tends to coat only the outer portion

and also to block the pores between the beads. Biomimetic coating overcomes many of these problems. A thin calcium phosphate coat issa deposited on the beads without clogging the pores. From this example it is possible to envision uniform coating of other complex shapes such as tubes, curved surfaces, and gear teeth.

We have also demonstrated a novel lithographic techniques based on biomineralization [6,8]. Fig. 5 is a schematic of the procedure for lithography. First a hydrophobic SAM that does not support mineralization is deposited over the entire substrate. The SAM is etched using an energetic beam to reexpose the underlying silicon wafer. In the etched area, a functionalized SAM is

Fig. 4 SEM of calcium phosphate coating on the beaded titanium bone implant shown in the inset.

deposited that promotes the heterogeneous nucleation of the inorganic mineral. The now-patterned surface is placed in an aqueous deposition solution, from which the mineral precipitates as a thin film on the functionalized regions of the surface. Resolution of the SAM patterning step was 1-3 μm; while resolution of the mineral deposition step was 10-15 μm.
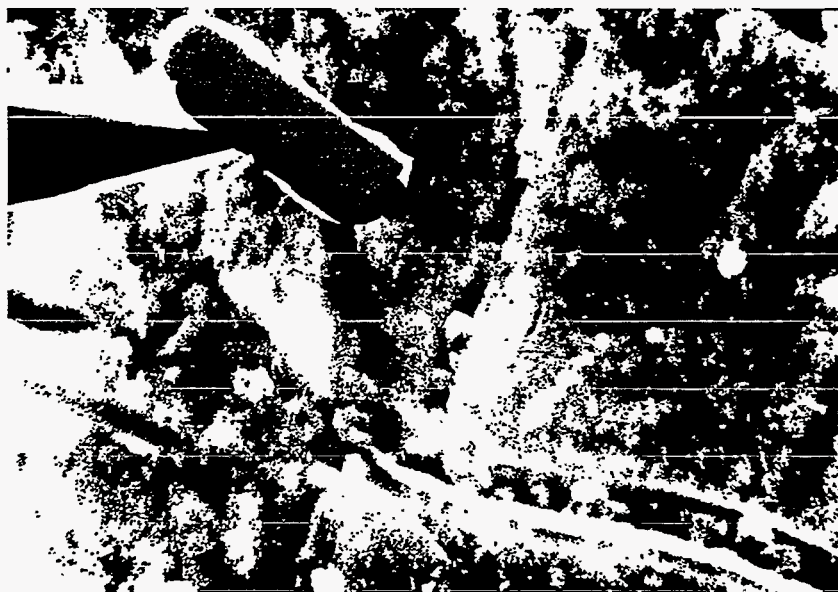
Many minerals have useful optical, piezoelectric, magnetic and other sensor/transducer properties. These materials, difficult to etch by conventional chemical and ion beam techniques, are easily and rapidly patterned by this process. This technique should find application in miniaturization of sensor devices and their integration into electronic circuits. The method is applicable to patterning on a larger scale as the derivatization step can easily be accomplished by modified printing techniques.

4. CONCLUSIONS

In this article we have introduced the concepts of biomineralization and related how this information can be utilized in developing new materials processing methods. To realize this advancement required development of new organic surface synthesis methods, extensive characterization of these surfaces, and a more detailed understanding of the mineral solution chemistry. In this limited space we have tried to show some of the advantages of biomimetic thin

① Deposit an inert SAM on substrate
Substrate

② Etch selected regions with ion or electron beam

③ Deposit a second SAM terminated with functional end group in etched regions

④ Mineral growth from aqueous solution occurs only on patterned region
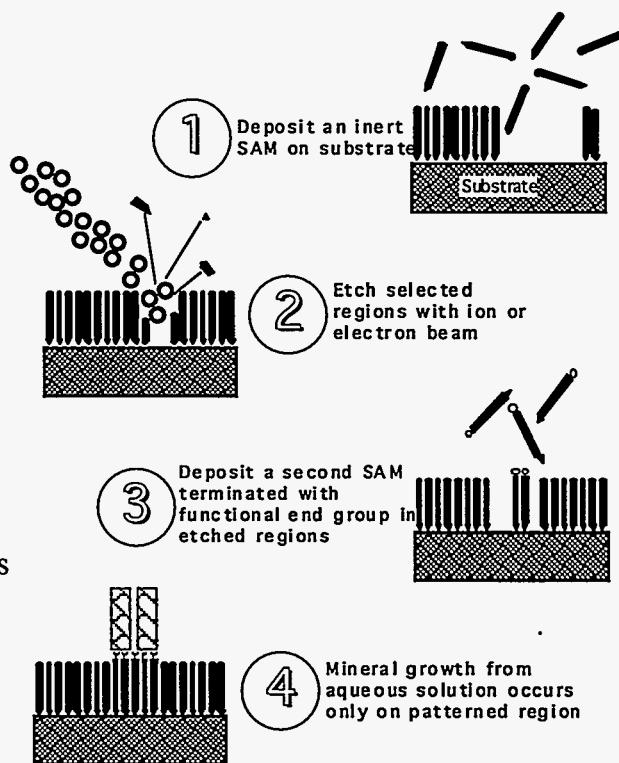
Fig. 5 Schematic of Biomimetic Lithography

film processing. In particular, we have shown that oriented dense thin films can be deposited and that the technique is applicable to many industrially relevant materials. Biomineralization is by no means limited to the minerals discussed here and we are continually developing new methods for deposition of other minerals with new applications. Complex and porous shapes can easily be coated and mineral deposition can be patterned on the micron scale

5. ACKNOWLEDGMENTS

6. LITERATURE CITED

1. S. A.Wainwright, W. D. Biggs, J. D. Currey, J. M.Gosline, *Mechanical Design in Organisms*; Princeton University Press: Princeton, NJ, 1976.
2. S. Weiner, *CRC Crit. Rev. Biochem.* 20, 325, 1986.
3. S. Mann, J. Webb, R. J. P. Williams, Eds.; *Biomineralization, Chemical and Biochemical Perspectives*; VCH, Germany, 1989.
4. H. A.Lowenstam, *Science*, 211, 1126, 1981.
5. P. C. Rieke, B. D. Marsh, L. L. Wood, B. J. Tarasevich, J. Liu, L. Song, G. E. Fryxell, *Langmuir* 11, 318, 1994.
6. P. C. Rieke, B. J. Tarasevich, L L. Wood, B. M. Marsh, G. E.. Fryxell, M. H. Engelhard, D. R. Baer, C. M. John, Proceedings of the Fall 1993 Materials Reseach Society *Biomolecular Materials by Design*, 1994.
7. B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Campbell, G. E. Fryxell, G. L. Graff, L. Song, J. Liu, *Science*, 264, 48, 1994.
8. P. C. Rieke, B. J. Tarasevich, L. L. Wood, M. H. Engelhard, D. R. Baer, G. E. Fryxell, C. M. John, M. C. Jaehnig, D. A. Laken, *Langmuir*, 10, 619, 1994.
9. P. C. Rieke, Submitted to *Materials Science & Engineering, C, Biomimetic Materials, Sensors and Systems,* Sept. 1994.
10. A. A. Campbell, G. E. Fryxell, G. L. Graff, P. C. Rieke, B. T. Tarasevich, *Scanning Microscopy* 7, 423, 1993.
11. P. C. Rieke, S. B. Bentjen. *Chemistry of Materials*, 5, 43, 1993.
12. P. C. Rieke, B. J. Tarasevich, G. E. Fryxell, S. B. Bentjen and A. A. Campbell. 1991. In: "Supramolecular Architecture: Synthetic Control in Thin Films and Solids" A.C.S Symposium Series #499, American Chemical Society, Washington, DC. 1992.
13. S. B. Bentjen, D. A. Nelson, B. J. Tarasevich and P. C. Rieke. *Journal of Applied Polymer Science*, 44, 965, 1992.
14. B. J. Tarasevich, P. C. Rieke, G. L. McVay, G. E. Fryxell and A. A. Campbell. In *Chemical Processing of Advanced Materials*, J. Wiley & Sons, New York, 1992.
15. P. C. Rieke, S. B. Bentjen, B. J. Tarasevich, T. S. Autrey and D. A. Nelson. In: *Materials Synthesis Utilizing Biological Processes*, Vol. 174, eds. P.C. Rieke, P.D. Calvert, M. Alper, Material Research Society, Pittsburgh, PA, 1990, pp 69.

Type of release:
Proceeding Paper

Previous clearance # if applicable
NA

Date Clearance Required
5/10/95

Title
BIOMIMETIC THIN FILM DEPOSITION

Lead Author, payrole #, msin
Peter C. Rieke, 3B063, K2-44

Other Authors
P. C. Rieke, G. E. Graff, A. A. Campbell, B. C. Bunker,

S. Baskaran, L. Song, B. J. Tarasevich, G. E. Fryxell

Program Title
Ceramic Composite Sythesis Utilizing Biological
Processes

Org. Code
D7E32
1830 Project # and B&R #
12565 KC-02-03-01-0
Title of Conference
4th Japan International SAMPE symposium
Group or Society
Society of Applied Mechanical and Process Engineers
(SAMPE)
Date of Conference
09/25/94 - 09/28/94
City/State
Tokyo, Japan
Title of Journal
NA
Proceeding will be published
Materials will not be handed out at meeting
Comments
NA