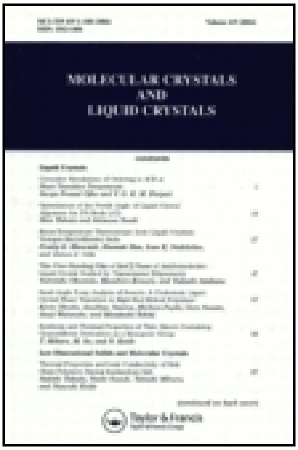


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Preparation of Metallic Crystals by Langmuir-Blodgett Technique

Hong Lin [a] [b] , Nobuhiro Kuroiwa [a] , Won-Seon Seo [a] , Katsumi Kuwabara [a] & Kunihito Koumoto [a]

[a] Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-01, Japan

[b] Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu, 611, Japan

Version of record first published: 04 Oct 2006

To cite this article: Hong Lin, Nobuhiro Kuroiwa, Won-Seon Seo, Katsumi Kuwabara & Kunihito Koumoto (1997): Preparation of Metallic Crystals by Langmuir-Blodgett Technique, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 295:1, 129-132

To link to this article: http://dx.doi.org/10.1080/10587259708042813

Mol. Cryst. Liq. Cryst., 1997, Vol. 295, pp. 129–132
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION OF METALLIC CRYSTALS BY LANGMUIR-BLODGETT TECHNIQUE

HONG LIN*, NOBUHIRO KUROIWA, WON-SEON SEO, KATSUMI KUWABARA AND KUNIHITO KOUMOTO
Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan, *Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

Abstract Preferentially oriented Ag crystals with platy surface morphology were prepared under appropriate Langmuir monolayers by using electrodeposition plating method at a small current. On the other hand, randomly oriented Ag crystals with needle-like morphology grew at the air/subphase interface in the absence of a monolayer, or under a monolayer at a relative large current. It was noted that two dimensionally oriented Langmuir monolayers promote the two dimensional crystallization of metallic crystals through chemical interactions at inorganic-organic interfaces.

INTRODUCTION

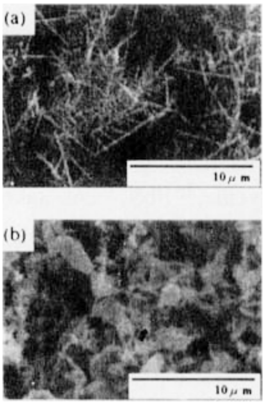
It is well known that it is the functionalized surface of the organized organic matrix that serves as a template for inorganic nucleation and controls the kinetics and direction of crystal growth due to their interactions in natural biomineralization processes.[1] Recent studies[2] have shown that the orientation and the architecture of inorganic crystals can be controlled under ambient conditions by manipulating surface energies through chemical modification of the biomimetic organic surfaces, such as the use of Langmuir-Blodgett (LB) technique. Oriented crystallization of glycine,[3] PbS,[4] etc. takes place under Langmuir monolayers floating on the surface of aqueous subphases containing corresponding molecules or ions. These clearly suggest that the structural information of LB films can be transferred to three-dimensionally growing crystals. We have synthesized preferentially oriented hydroxyapatite crystals from supersaturated simulated body fluid due to the presence of Langmuir monolayers at 309.5 K.[5] On the present study, we prepared metallic Ag crystals under oriented organic matrices of Langmuir monolayers by using electrodeposition plating method. The effect of Langmuir monolayers on the crystallization of metallic crystals in terms of chemical interactions at inorganic-organic interfaces was investigated.

EXPERIMENTAL

Monolayers of stearic acid were prepared in a moving-wall LB trough. $AgNO_3$ was added in distilled water subphase to form an aqueous solution with the ionic concentration of 1.7×10^{-4} M. A platinum (Pt) electrode was fixed just at the air-solution interface. Then chloroform solution (5×10^{-3} M) of the surfactant molecules was spread onto the aqueous subphase. The monolayer was kept under the surface pressure of 25 mN/m at 293.5 K for a certain period of time. A constant current flow produced by DC voltage current standard (Auwano SV-261) resulted in metal reduction under the monolayer. The slide glass substrate was used to horizontally transfer a monolayer and a metal crystal layer together from the subphase with smallest damage to the deposited crystal layer. Characterization of the deposited films was carried out by X-ray diffraction (XRD; Rigaku Rad-C) measurements and scanning electron microscope (SEM; Hitachi S-510) observation.

RESULTS AND DISCUSSION

In the absence of a monolayer (a general electrodeposition plating method), some needle-like crystals of Ag were observed around the Pt electrode (see Figure 1 (a)). The



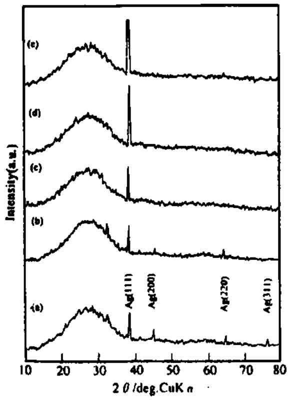


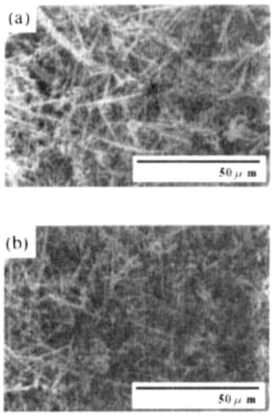
FIGURE 1 (left) SEM photographs of Ag deposited for 2 h at 25 μA (a) in the absence of a monolayer; (b) under a stearic acid monolayer.

FIGURE 2 (right) XRD patterns of Ag deposited for various periods of time (a) in the absence of a monolayer; (b-e) under a stearic acid monolayer. Current was 25 μA except (b) which was at 50 μA.

current was maintained at 25 μA and the growth time was 2 h. This kind of morphology does not change with the changes in current and growth time. The morphology of deposited Ag under a stearic acid monolayer was found to be similar when the current was relatively large (i.e. 50 μA). While a small current of 25 μA resulted in a very different growth mode of Ag crystals under the monolayer. Figure 1 (b) shows a typical SEM image of deposited Ag crystals grown for 2 h under a stearic acid monolayer. Platy crystals of micro meter or submicron meter size indicate a two-dimensionally spreading growth mode.

XRD patterns of Ag crystals deposited with and without a monolayer are shown in Figure 2. In the absence of a monolayer, Ag crystals deposited were not preferentially oriented (Figure 2 (a)). The orientation of deposited Ag crystals under a stearic acid monolayer was similar as above at 50 μA (Figure 2 (b)). While crystallization of Ag under a stearic acid monolayer at 25 μA resulted in the growth of preferentially oriented Ag crystals with a sharp reflection of the (111) plane (Figure 2(c)), which increased with an increase in growth time (Figure 2 (c-e)).

Two more experiments were carried out in which the amphiphilic molecules were uncompressed (in a gas-state), and the compressed monolayer was damaged. In both



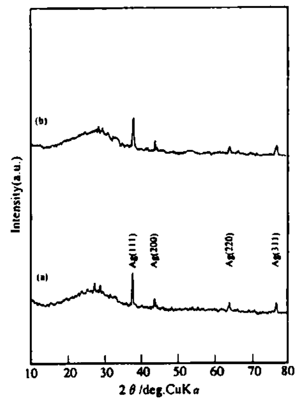


FIGURE 3 (left) SEM photographs of Ag deposited for 2 h at 25 μA under (a) uncompressed stearic acid molecules, (b) damaged monolayer.

FIGURE 4 (right) XRD patterns of deposited Ag crystals. The conditions were the same as in Figure 3.

cases, crystals deposited showed almost a needle-like growth mode as that in the absence of a monolayer but had a little higher density (Figure 3), and were randomly oriented as confirmed by XRD (Figure 4).

The above results strongly indicated that it is the compressed organized monolayer which promote the oriented nucleation of Ag crystals. This crystallization process should be carried out at a small current to arrange deposited crystals. The interfacial interaction between the carboxyl group and Ag ions in the subphase resulted in the formation of a Stern layer[6] which is reduced preferentially, and it appeared a two-dimensionally grown architecture of Ag crystals. No special lattice matching existed between the inter-headgroup spacing of stearic acid molecules (0.481 nm) and Ag-Ag distance (0.289 nm) on the (111) plane of Ag. Electrostatic interactions inducing the formation of a layer of Ag-stearic acid salt molecules are considered to be responsible for the preferred orientation of the crystals grown under a monolayer. These factors can override the structural mismatch at the interface in most cases.[6]

SUMMARY

Orientation and morphology of the prepared Ag crystals were different depending on whether the appropriate oriented organic matrices existed or not under the present conditions. The growth rate depending on the amount of electrolytic current seems also critical for the growth mode. Two dimensionally oriented Langmuir monolayers promote the two dimensional crystallization of metallic crystals through chemical interactions at inorganic-organic interfaces.

REFERENCES

1. S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum, N. J. Reeves, Science, 261, 1287 (1993).
2. B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Campbell, G. E. Fryxell, G. L. Graff, L. Song, J. Liu, J. W. Virden, G. L. McVay, Science, 264, 48 (1995).
3. E. M. Landau, M. Levanon, L. Leiserowitz, M. Lahar and J. Sagiv, Nature, 318, 353 (1985).
4. X. K. Zhao, Y. X. Yuan, L. D. McCormick and J. H. Fendler, J. Phys. Chem., 96, 9933 (1992).
5. H, Lin, W. S. Seo, K. Kuwabara and K. Koumoto, J. Ceram. Soc. Japan, 104(4), 291 (1996).
6. S. Mann, S., Heywood, B. R., Rajam, S. and Birchall, J. D., Nature, 334, 692 (1988).