Recovery of Constituent Elements and Crystal Growth of Compound Semiconductors using Marine Bacteria

Yoriko Tominaga[1*], and Yoshiko Okamura[2]

[1]Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1, Kagamiyama, Higashihiroshima, Hiroshima 739-8530, Japan, E-mail: ytominag@hiroshima-u.ac.jp, TEL: +81-82-424-7049
[2]Graduate School of Integrated Sciences for Life, Hiroshima University, 1-3-1, Kagamiyama, Higashihiroshima, Hiroshima 739-8530, Japan

Keywords: Crystal growth, Biomineralization, Sulfide and GaAs-based compound semiconductors

Abstract

We report here the growth of PbS spherical nanocrystallites and thin film crystals using marine bacteria, as well as the recovery of In, Ga, and As to develop the novel crystal growth techniques of compound semiconductors using microorganisms. Moreover, we present a summary of our current findings and discuss future prospects for this study.

Introduction

The recovery of rare metals from industrial effluents, waste, and the natural environment has gained much importance in recent years. Towards solving this problem, we focus on the function of biomineralization, in which microorganisms produce minerals. Some biominerals are known to be formed as the oriented nanocrystals[1,2]. Moreover, it has been reported that it is possible to recover various metals and synthesize compound semiconductors using microorganisms[3,4]. Our long-term goal is to use biomineralization to recover rare metals from industrial wastewater and the natural environment, and to establish the new technology to reuse them as semiconductor devices with low cost and low power consumption because these biological reaction occurs at normal temperature and pressure. We already succeeded in growing PbS spherical nanocrystallites and thin film crystals [5], as well as the simultaneous recovery of In, Ga, and As[6,7] using marine bacterial consortium. There are few studies of biomineralization on III-V compound semiconductors, and this field is still unexplored. In this presentation, we will discuss the crystallinity of biogenic GaAs-based compound semiconductors by comparing with that of PbS, and explain a summary of our current findings and future prospects for this study.

Experimental Methods

Some bacterial consortia which we had screened from marine bacteria were used to recover Pb[5], In, Ga, and As[6,7]. As for synthesis of PbS, lead acetate was added to RCVBN medium at a final Pb^{2+} concentration of 1 mM. For recovery of In, Ga, and As, indium chloride, gallium nitrate, and potassium arsenate were added to RCVBN medium at a final concentration of 500 μM. Each bacterial consortium was incubated at room temperature under fluorescent light. Bacterial growth curves were obtained using a photoelectric colorimeter during incubation period. After the incubation, the bacteria and minerals were observed using transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDS), and the crystallographic properties of the minerals were investigated using X-ray diffractions (XRD) measurement. Optical absorption measurements were performed to reveal the optical properties of the minerals using a tungsten lamp and a InGaAs CCD detector. The metal ion concentrations in culture supernatant were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) to measure the removal rate from the medium for each ion. Thermal treatment after the material synthesis including In, Ga, and As, especially, was performed at over 300 °C under the N_2 atmosphere for 10 minutes.

Results and Discussion

Figure 1 shows the culture color of bacterial consortium which can synthesize PbS being dependent on incubation days after lead acetate was added. The color becomes darker with increasing the days, suggesting that the bacteria are growing. To confirm this, bacterial growth curves were measured as shown in Fig. 2. Compared to the first day of bacterial passage, optical density increases rapidly within 3 days, and after that, the value of the optical density saturated. We can confirm that the bacteria can be alive even under the presence of Pb^{2+}. The polycrystalline formation of PbS by the bacteria was confirmed using XRD measurement, and the

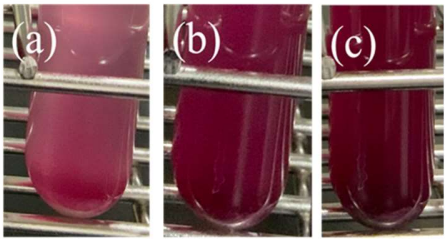

Fig. 1. Changes in the culture color being dependent on incubation days for synthesis of PbS. (a) one day after, (b) three days after, and (c) five days after adding lead acetate.

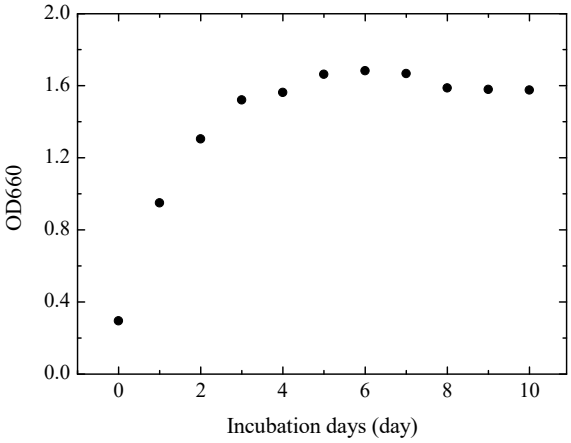

Fig. 2. Bacterial growth curve for the bacterial consortia which can synthesize PbS.

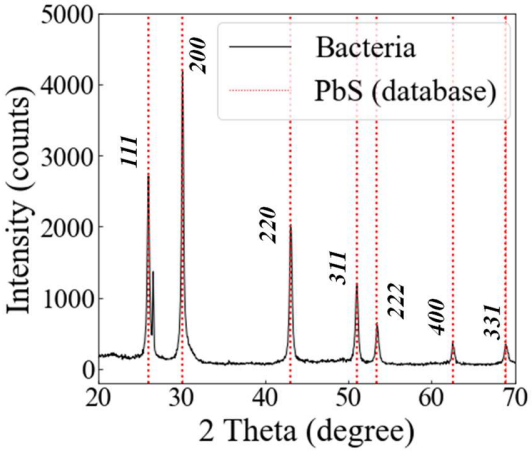

Fig. 3. XRD curve of PbS synthesized by the bacteria and diffraction peaks of the PbS of Galena registered in database.

measured curve was agreed with the PbS of Galena registered in database as show in Fig. 3. These clear peaks and good agreements between measured and simulated curves were also confirmed using synchrotron-source powder XRD[5]. These results of XRD indicate that almost no crystalline impurities are incorporated into the crystalline PbS synthesized by the bacteria. Figure 4 shows TEM image of one of the bacterial cells and PbS synthesized by the bacteria. Synthesis of PbS was also confirmed by EDS and electron diffraction pattern[5]. PbS could be seen deposited on the bacterial cell (Fig. 4(a)). On the TEM image at a high magnification (Fig. 4(b)), lattice fringes of PbS and the formation of spherical PbS nanocrystallite with diameters of ~5 nm were observed. In our study, the size of these crystals was dependent on the concentration of lead acetate, and the optical absorption edge can be confirmed to shift to shorter wavelength with decreasing the size of the crystalline PbS[5]. To exhibit high crystalline quality and future practical use of

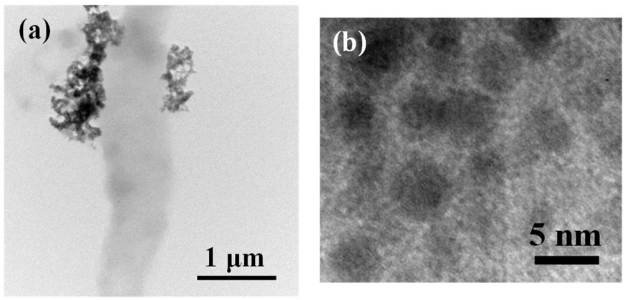

Fig. 4. TEM image of one of the bacterial cells and synthesized PbS. (a) Low magnification, and (b) high magnification of PbS area.

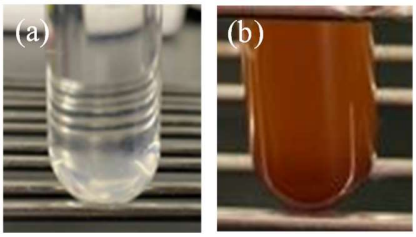

Fig. 5. Changes in the culture color for the recovery of In, Ga, and As. RCVBN medium with indium chloride, gallium nitrate, and potassium arsenate added without bacterial consortium ((a)), and with bacterial consortium ((b)).

our biogenic PbS, quantum size effect should also be demonstrated for the emission from the PbS formed by our bacterial consortiums in the future.

As for the materials synthesized with In, Ga, and As, we first confirmed that there was no change for the color in the test tube containing RCVBN medium with indium chloride, gallium nitrate, and potassium arsenate added without bacterial consortium, while the color was seen in RCVBN medium including indium chloride, gallium nitrate, and potassium arsenate with the consortium as shown in Fig. 5. It was also confirmed that the bacteria are growing in the medium containing these metal compounds by bacterial growth curves, and the growth rate of the bacteria was slower than that of the bacteria that synthesized PbS. Figure 6 shows TEM image of one of the bacterial cells and the synthesized material. Similar to the case of PbS, the material deposited on the bacterial cell. Analysis with EDS revealed that the elements of In, Ga, and As were incorporated in the material region. However, the images and electron diffraction patters obtained using TEM (Fig. 6) showed that the materials were amorphous because there were no lattice fringes in the image, and no ring-shaped and spotty patterns were confirmed in electron diffraction. And therefore, no diffraction peak appeared in XRD curve. Optical absorption edge of one of the samples was located within the range of band gap of $In_xGa_{1-x}As$. This indicates that it is possible to recover In, Ga, and As

using these bacterial consortia as at least amorphous InGaAs.

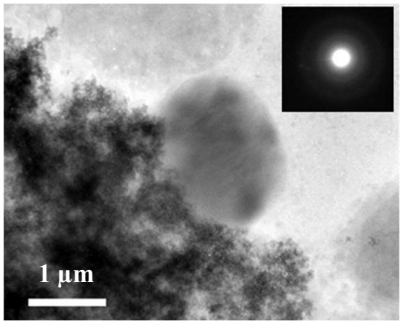

Fig. 6. TEM image of the bacterial cell and the material including In, Ga, and As synthesized by the bacterial consortium which we used in this study. Inset shows electron diffraction pattern of the minerals[5].

On the other hand, the result of ICP-OES indicated that the removal rates of In using the bacterial consortium was calculated to be over 95% which was much higher than those of Ga and As. Therefore, at present, it can be thought that synthesized material was composed primarily of In. After thermal treatment for the materials including In, Ga, and As, clear lattice fringes were confirmed on TEM images. However, lattice planes obtained from electron diffraction patterns did not agree with those in database for InGaAs-related materials. We conclude that it is difficult to crystallize InGaAs using bacteria under current synthesis conditions, and we need other processes to crystallize such as thermal treatment. Even at performance of thermal treatment, it is necessary to acquire other bacteria with high Ga and As recovery capacity comparable to that of In, and to mix materials by symbiosis with them.

CONCLUSIONS

Towards the growth of compound semiconductors using marine bacteria, it was demonstrated that crystallinity of PbS was higher than those of materials including In, Ga, and As. The crystalline PbS tended to be formed as spherical nanocrystallite, and the size of the crystals depended on the concentration of added lead acetate to medium. In XRD curve, no diffraction peak for impurity was confirmed. As for materials including In, Ga, and As, it is necessary to perform some kind of improvement to crystallize biogenic InGaAs.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Dr. Makoto Maeda of the Natural Science Center for Basic Research and Development (N-BARD) at Hiroshima University for the operation of TEM and EDS. This work was partially supported by the Canon Foundation, CASIO Science Promotion Foundation, JSPS KAKENHI [Grant Numbers JP 21K18911, and JP 23K17888], JST FOREST Program JPMJFR213R, and the Research Center for Biomedical Engineering.

REFERENCES

[1] H. Cölfen and S. Mann, Angew. Chem., Int. Ed., 42, 2350 (2003).

[2] H. Imai, J. Ceram. Soc. Japan, 122, 737 (2014).

[3] C.T. Dameron, et al., Nature, 338, 596 (1989).

[4] M. Kowshik, et al., Adv. Mater., 14, 815 (2002).

[5] Y. Okamura, et al., Int. J. Mol. Sci., 24, 14149 (2023).

[6] Y. Okamura, Y. Tominaga, and R. Shimizu, Jpn. Patent No. 7095871.

[7] A. Mukuki, et al., The 41st Elect. Mat. Symp. Th3-7, October 2022, Nara, Japan.