

Mg₂Ge/Si Composite Electrodes Prepared by Gas-Deposition as Anodes for Lithium
Rechargeable Battery

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Abstract

Mg₂Ge/Si composite electrodes were prepared by a gas-deposition (GD) method and evaluated their electrochemical properties of anodes for Li rechargeable battery. The discharge capacity of the Mg₂Ge/Si composite electrodes increased in comparison with that of Mg₂Ge GD-film electrode. Among them, the Mg₂Ge/Si composite electrode with 30 wt% Si content exhibited good cycle stability, which is 603 mAh g⁻¹ after 200 cycles. At this composition of composite, each Si particle was surrounded with Mg₂Ge layer, and the Mg₂Ge layer appears to be easy to release the stress generated in the Si particle at Li insertion-extraction because Mg₂Ge is more ductile than Si. Thus, we succeeded to develop the electrode which can take advantage of both high capacity of Si and good cyclability of Mg₂Ge.

Keyword: Mg₂Ge/Si composite electrode, gas-deposition, lithium rechargeable battery, anode

1. Introduction

Si-based materials are of great interest due to their excellent specific capacities as negative-electrode materials in lithium secondary batteries. Si has, however, a poor cyclability owing to significant volume changes during lithium insertion and extraction. In order to improve its cyclability, various approaches have been suggested¹⁻⁶⁾, but their results cannot be satisfied yet.

On the other hand, we have investigated Mg_2Ge as a negative electrode material, that the electrochemical reaction of Mg_2Ge is largely based on the reversible insertion and extraction of lithium in the crystal lattice⁷⁻¹⁰⁾. We adopted a gas-deposition (GD) method (also referred to as an aerosol deposition method) as a novel fabricating process for electrode for the first time¹¹⁻¹³⁾. This process has the following advantages: (i) Strong adhesions between the active material particles, as well as between the particles and the electron collector can be expected. (ii) The composition of the film obtained is maintained that of the raw material due to the lack of heat-induced decomposition. The resulting Mg_2Ge GD-thick-film electrode exhibited an excellent cyclability in comparison with the electrode prepared by a conventional method¹¹⁻¹³⁾.

We also tried to improve the poor cyclability of Si electrode by using the GD method, but the expected result has not been achieved yet because of too large expansion-contraction during insertion-extraction of Li.

From the backgrounds, we focused on developing the $\text{Mg}_2\text{Ge}/\text{Si}$ composite electrode. Accordingly, the GD method was adopted to prepare the composite electrode and its electrode performance was investigated.

2. Experimental

Mg₂Ge powders were formed by mechanical alloying⁷⁻¹¹). The size of the material particles was 0.5–3 μm. The commercially available Si powder (Wako pure chemical Industries, Ltd., 99 %) was also used as a raw material. The size of the material particles was 0.1–100 μm. The Mg₂Ge and Si powders were mixed using agate mortar under an Ar atmosphere. The Mg₂Ge:Si weight ratios were 80:20, 70:30, 50:50 and 30:70 respectively. The Mg₂Ge/Si composite film was deposited on a Cu-rolled foil (20 μm thickness ; 99.9 %, Nilaco Co. Ltd.) substrate set up in the evacuated chamber equipped with a guide tube. An aerosol consisting of an argon gas (differential pressure 7×10⁵ Pa) and the mixture of Mg₂Ge and Si powders was generated in the guide tube, and was gushed from nozzle (φ 0.8) toward the substrate. The deposition weight was c.a. 250 μg and the thickness of the deposited film was 3-5 μm.

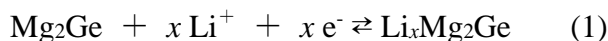
The morphologies of obtained films and distributions of Si were evaluated using Scanning Electron Microscope (SEM, JSM-5200; JEOL Ltd., 15 kV) and Energy dispersive X-ray analysis (EDX, EDS-54033MCK; JEOL Ltd.).

Electrochemical measurements were carried out with a beaker-type three-electrode cell. Working electrodes were consisted of Mg₂Ge, Si and Mg₂Ge/Si composite film formed on Cu foils by the GD method. Both counter and reference electrodes were 1 mm thick lithium metal sheets (Rare Metallic, 99.9% pure). 1 M LiClO₄-dissolved propylene carbonate (PC) (Kishida Reagents Chemicals) was used as an electrolyte. The cell performances were estimated galvanostatically at 303 K and at a current density of 0.36 A g⁻¹ between 2.000 and 0.005 V.

3. Results and Discussion

Figure 1 shows the charge-discharge (Li insertion-extraction) curves of the first cycle for Mg₂Ge and Si GD-film electrodes in order to discuss the charge-discharge reaction for the Mg₂Ge/Si composite GD-film electrode. The discharge capacity of Mg₂Ge GD-film electrode was 600 mAh g⁻¹, which is higher than that obtained by the conventional electrode fabrication process ¹¹⁾. In contrast, the discharge capacity of Si GD-film electrode is 2300 mAh g⁻¹, which is the same as the reported value ¹⁴⁾ though the current density is large. Thus, it was confirmed that the GD-film electrodes exhibited same or higher capacity than conventional electrode.

In the discharge profile of Mg₂Ge GD-film electrode, two plateaus were observed at 0.2 and 0.6 V. They are regarded to correspond to the following reaction previously reported ¹¹⁾.



As for the Si GD-film electrode, the plateau was observed at 0.4 V, which corresponds to be due to the following reaction ¹²⁾.

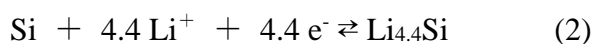


Figure 2 illustrates the cycle performance of these electrodes. The discharge capacity of the Si GD-film electrodes decayed significantly and showed ca. 320 mAh g⁻¹ after 200 cycles. The significant capacity decay is due to the exfoliation of the Si active materials. On the other hand, the capacity of the Mg₂Ge GD-film electrode maintained a capacity of more than 260 mAh g⁻¹ after 200 cycles, exhibiting an excellent cyclability. It was found that the Si GD-film electrode exhibits high initial discharge capacity but low cyclability, whereas the Mg₂Ge GD-film electrode exhibits the opposite properties. Thus, we tried to develop the new composite anode which takes advantage of both high capacity of Si and good cyclability of Mg₂Ge.

Figure 3 shows the charge-discharge curves of the first cycle for Mg₂Ge/Si composite GD-film electrodes with various Si composition ratios. The discharge capacities were larger for the every composite GD-film electrodes than for the Mg₂Ge GD-film electrode. It was found that the discharge capacity increased with Si ratio. On the discharge profiles, three plateaus were observed at 0.2, 0.4 and 0.6 V. They appear to derive from the aforementioned reactions (1) and (2), suggesting that both Mg₂Ge and Si were acted as active materials. As for the capacity reversibility at the first cycle, no remarkable improvement was observed in both Mg₂Ge and Si GD-film electrodes in comparison with the conventional electrodes ¹¹). Since the capacity reversibility of Si electrode, ca. 70 %, was superior to that of Mg₂Ge electrode, ca. 55 %, the Mg₂Ge/Si composite electrode exhibited the value between the two.

It has been found that the capacity reversibility of Si GD-film can be improved by optimizing the particle size at gas-deposition. Therefore, the capacity reversibility of composite electrode would increase if the size-optimized Si powder will be used.

The dependence of discharge capacity on the number of cycles for the Mg₂Ge / Si composite electrodes is shown in Fig. 4. For the composites with higher Si contents, such as 70 and 50 wt%, the significant capacity decay was still observed, though the improvement of cyclability was certainly confirmed in comparison with the Si electrode. It could be considered that the composites in such ratios cannot take advantage of good cyclability of Mg₂Ge. In contrast, the discharge capacity of the composite with 20 wt% Si content was relatively low, but the capacity retention became quite stable. Consequently, the optimum Si content in Mg₂Ge/Si composite was found to be 30 wt%, and the resulting composite electrode still maintained a discharge capacity of 600 mAh g⁻¹ even after 200 cycles.

The changes in coulomb efficiency of the Mg_2Ge , Si and $\text{Mg}_2\text{Ge}/\text{Si}$ composite electrodes with cycle number are illustrated in Fig. 5. The remarkable decrease in coulomb efficiency, which is due to disintegration of active material layer during charge-discharge cycling, was observed for the Si electrode, whereas the $\text{Mg}_2\text{Ge}/\text{Si}$ composite electrode exhibited an excellent stability of coulomb efficiency as well as the Mg_2Ge electrode. The changes in coulomb efficiency of the Mg_2Ge , Si and $\text{Mg}_2\text{Ge}/\text{Si}$ composite electrodes with cycle number are illustrated in Fig. 5. The remarkable decrease in coulomb efficiency, which is due to disintegration of active material layer during charge-discharge cycling, was observed for the Si electrode, whereas the $\text{Mg}_2\text{Ge}/\text{Si}$ composite electrode exhibited an excellent stability of coulomb efficiency as well as the Mg_2Ge electrode. The decrease in coulomb efficiency does not go on continuously and should be halted by releasing the accumulated internal energy. Since the adhesion between the active material particles, as well as between the particles and the electron collector in GD-film electrode is superior to that in the electrodes fabricated by the conventional method, the exfoliation of the active material layer from the electron collector may be suppressed under a certain level. Consequently, the coulomb efficiency appears to rise again in GD-film electrodes. Figure 6 also shows the change in coulomb efficiency of $\text{Mg}_2\text{Ge}/\text{Si}$ composite electrodes with $\text{Mg}_2\text{Ge}/\text{Si}$ ratio. The rate of decrease in efficiency during initial tens of cycling was reduced by the addition of Mg_2Ge . Especially, in the $\text{Mg}_2\text{Ge}:\text{Si}=70:30$ composite GD-film electrode, no decrease in coulomb efficiency was observed. Although the Mg_2Ge layer must suppress the disintegration of the composite electrode, the distribution of Si particles in Mg_2Ge layers appears to be an important factor to obtain the best performance of cyclability.

The reasons for the remarkable improvements of the Mg₂Ge/Si composite GD-film electrodes in comparison with the Mg₂Ge electrode are discussed below. Figure 7 displays surface SEM images of the Mg₂Ge/Si composite GD-film electrodes, while Figure 8 shows the distribution of Si in the electrodes analyzed by Si-K α of EDX. In the composite electrodes with 70 and 50 wt% Si contents (Fig. 8 (d), (c)), Si particles locally existed, so that these electrodes exhibited poor cyclability. As for the composite electrode with 20 wt% Si content (Fig. 8 (a)), since there are a few Si particles in the electrode, a large amount of discharge capacity was not observed in the electrode. On the other hand, it was found that Si particles were homogeneously distributed in the composite electrode with 30 wt% Si content (Fig. 8 (b)). At this optimum composition of Mg₂Ge and Si in the composite, each Si particle was surrounded with Mg₂Ge layer, and the stress generated in the Si particle at Li insertion-extraction was considered to be released by the Mg₂Ge layer because Mg₂Ge is more ductile than Si. Thus, we succeeded to develop the new composite anode which takes advantage of both high capacity of Si and good cyclability of Mg₂Ge.

4. Conclusions

Mg₂Ge/Si composite electrodes were prepared by a gas-deposition (GD) method, and their electrochemical properties were estimated. The resulting Mg₂Ge/Si composite electrodes exhibited larger discharge capacity than the Mg₂Ge GD-film electrode. The best anode performance among the composite electrodes was obtained at a content of 30 wt % Si. Si distributed homogeneously in the composite electrode.

Acknowledgement

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Figure Captions

Fig. 1 Charge-discharge curves of the Mg₂Ge and Si GD-film electrodes.

(a) (— —) Mg₂Ge and (b) (—)Si.

Fig. 2 Cycle life performance of the Mg₂Ge and Si GD-film electrodes.

(a) (□) Mg₂Ge and (b) (▲)Si.

Fig. 3 Charge-discharge curves of the Mg₂Ge/Si composite GD-film electrodes.

(a) (— —)Mg₂Ge:Si = 80:20, (b)(—) Mg₂Ge:Si = 70:30, (c)(— - —) Mg₂Ge:Si = 50:50 and (d) (•••)Mg₂Ge:Si = 30:70.

Fig. 4 Cycle life performance of Mg₂Ge/Si composite GD-film electrodes.

(a) (▲)Mg₂Ge:Si = 80:20, (b)(●) Mg₂Ge:Si = 70:30, (c)(◆) Mg₂Ge:Si = 50:50 and (d) (■)Mg₂Ge:Si = 30:70.

Fig. 5 Coulomb efficiency for (a) (□)Mg₂Ge, (b) (▲) Si and (c) (●)Mg₂Ge/Si

GD-film electrodes.

Fig. 6 Coulomb efficiency for (a) (▲)Mg₂Ge:Si = 80:20, (b)(●) Mg₂Ge:Si = 70:30,

(c)(◆) Mg₂Ge:Si = 50:50 and (d) (■)Mg₂Ge:Si = 30:70 composite GD-film electrodes.

Fig. 7 Surface SEM images of the Mg₂Ge/Si composite GD-film electrodes before charge-discharge cycling test.

(a) $\text{Mg}_2\text{Ge}:\text{Si} = 80:20$, (b) $\text{Mg}_2\text{Ge}:\text{Si} = 70:30$, (c) $\text{Mg}_2\text{Ge}:\text{Si} = 50:50$ and (d) $\text{Mg}_2\text{Ge}:\text{Si} = 30:70$.

Fig. 8 EDX area analysis of the $\text{Mg}_2\text{Ge}/\text{Si}$ composite GD-film electrodes before charge-discharge cycling test by Si-K α .

(a) $\text{Mg}_2\text{Ge}:\text{Si} = 80:20$, (b) $\text{Mg}_2\text{Ge}:\text{Si} = 70:30$, (c) $\text{Mg}_2\text{Ge}:\text{Si} = 50:50$ and (d) $\text{Mg}_2\text{Ge}:\text{Si} = 30:70$.

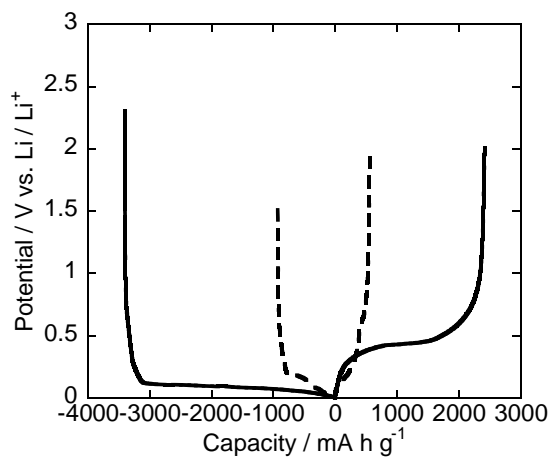


Fig. 1

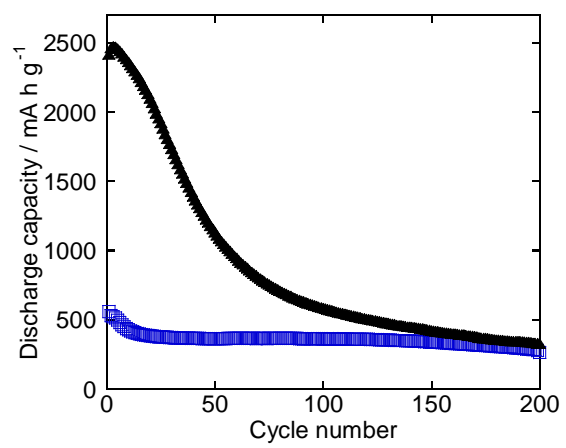


Fig. 2

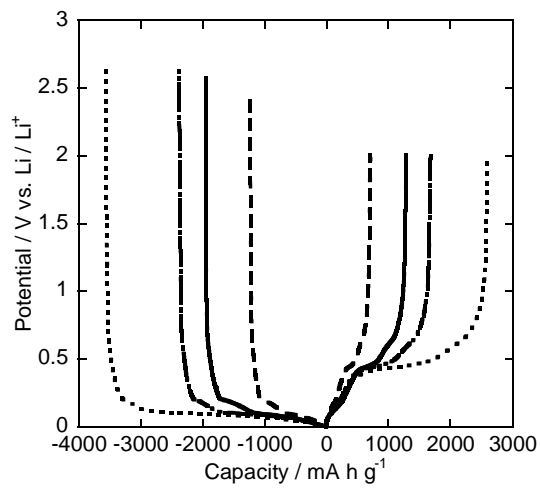


Fig. 3

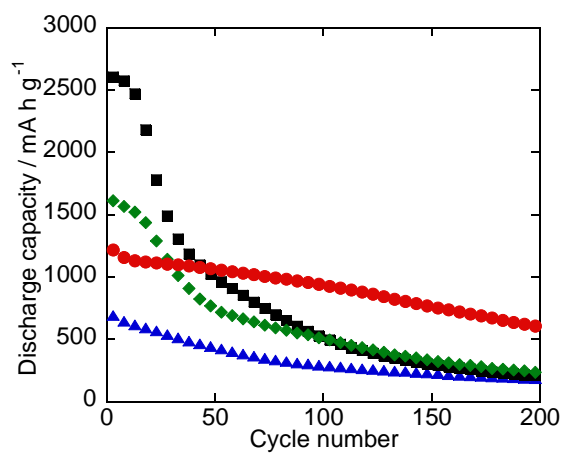


Fig. 4

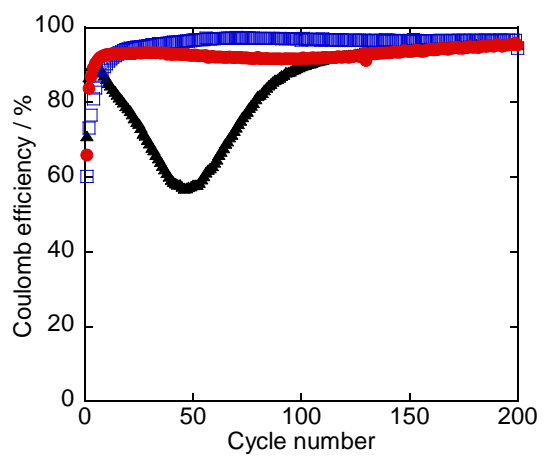


Fig. 5

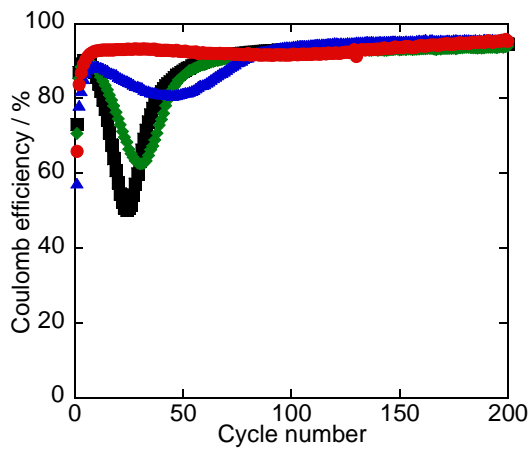
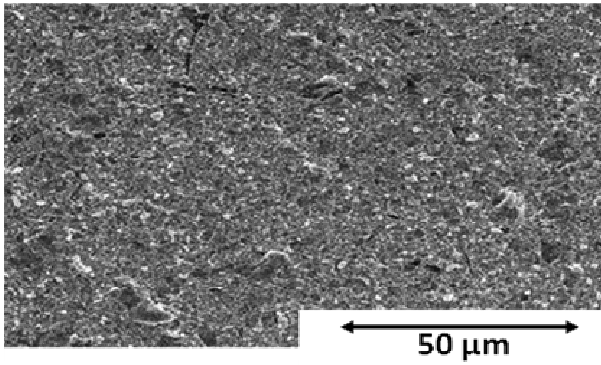
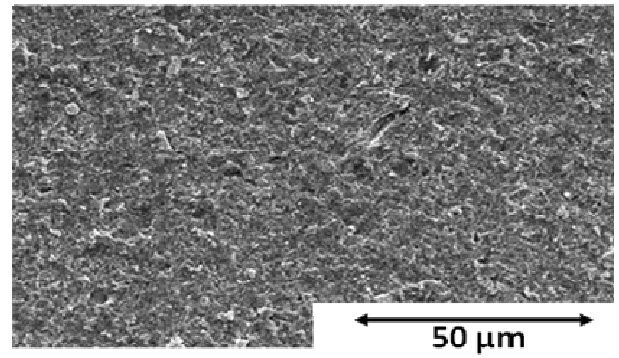


Fig. 6

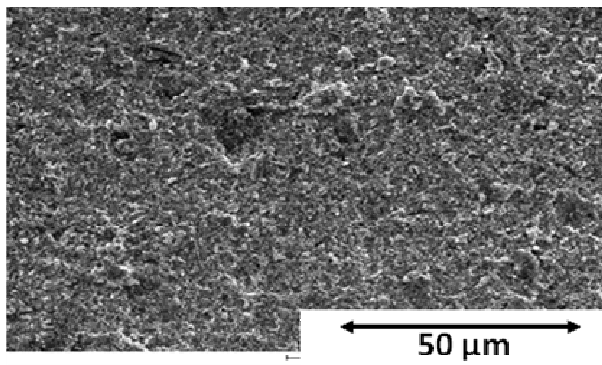
(a) $\text{Mg}_2\text{Ge}:\text{Si}=80:20$



(b) $\text{Mg}_2\text{Ge}:\text{Si}=70:30$



(c) $\text{Mg}_2\text{Ge}:\text{Si}=50:50$



(d) $\text{Mg}_2\text{Ge}:\text{Si}=30:70$

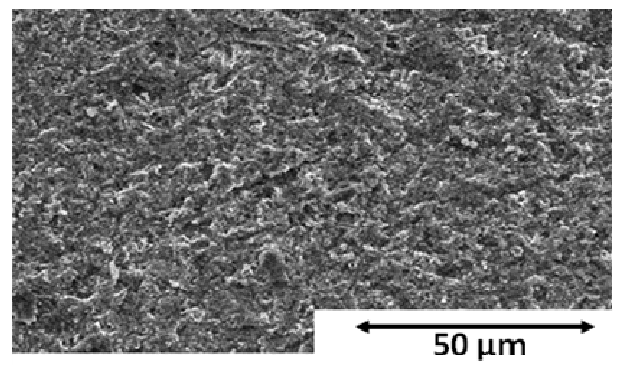
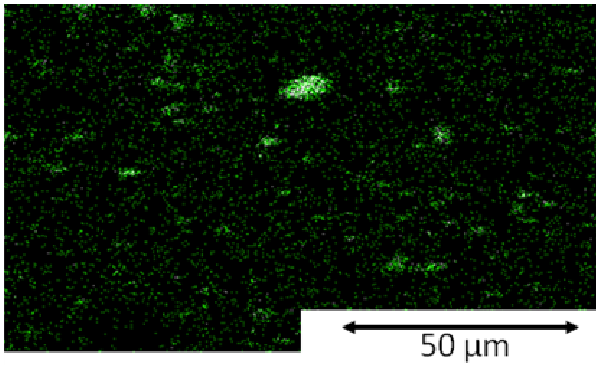
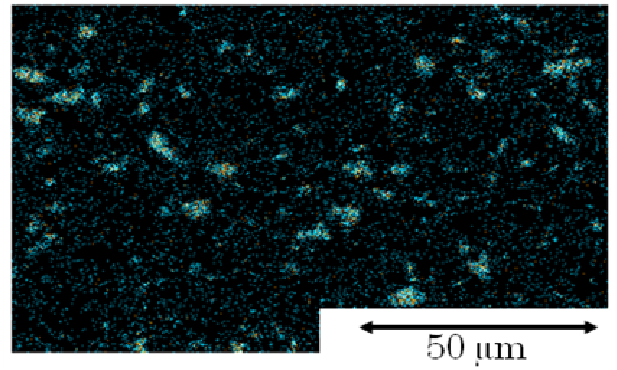


Fig. 7

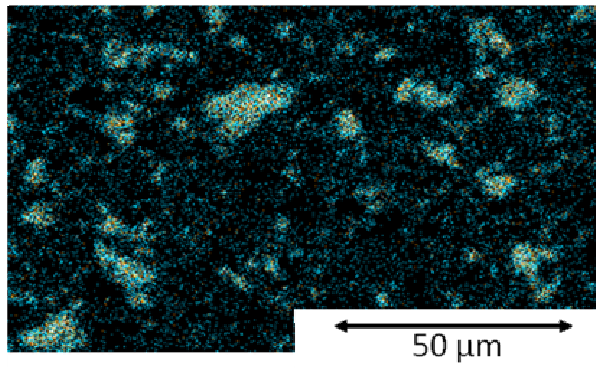
(a) $\text{Mg}_2\text{Ge}:\text{Si} = 80:20$



(b) $\text{Mg}_2\text{Ge}:\text{Si} = 70:30$



(c) $\text{Mg}_2\text{Ge}:\text{Si} = 50:50$



(d) $\text{Mg}_2\text{Ge}:\text{Si} = 30:70$

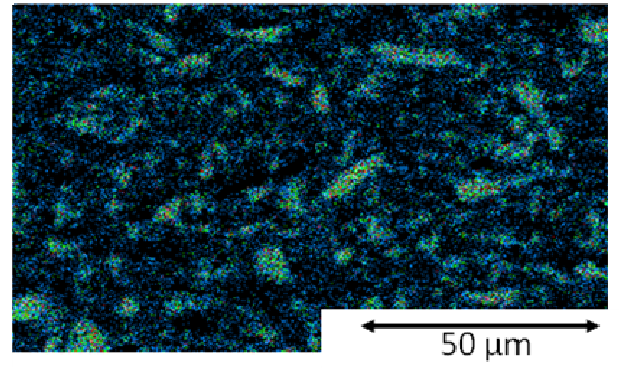


Fig. 8