

Mg<sub>2</sub>Ge/Si Composite Electrodes Prepared by Gas-Deposition as Anodes for Lithium  
Rechargeable Battery

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## Abstract

Mg<sub>2</sub>Ge/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 Mg<sub>2</sub>Ge/Si composite electrodes increased in comparison with that of Mg<sub>2</sub>Ge GD-film electrode. Among them, the Mg<sub>2</sub>Ge/Si composite electrode with 30 wt% Si content exhibited good cycle stability, which is 603 mAh g<sup>-1</sup> after 200 cycles. At this composition of composite, each Si particle was surrounded with Mg<sub>2</sub>Ge layer, and the Mg<sub>2</sub>Ge layer appears to be easy to release the stress generated in the Si particle at Li insertion-extraction because Mg<sub>2</sub>Ge 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 Mg<sub>2</sub>Ge.

Keyword: Mg<sub>2</sub>Ge/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 suggested<sup>1-6)</sup>, but their results cannot be satisfied yet.

On the other hand, we have investigated  $\text{Mg}_2\text{Ge}$  as a negative electrode material, that the electrochemical reaction of  $\text{Mg}_2\text{Ge}$  is largely based on the reversible insertion and extraction of lithium in the crystal lattice<sup>7-10)</sup>. 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 time<sup>11-13)</sup>. 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  $\text{Mg}_2\text{Ge}$  GD-thick-film electrode exhibited an excellent cyclability in comparison with the electrode prepared by a conventional method<sup>11-13)</sup>.

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

Mg<sub>2</sub>Ge powders were formed by mechanical alloying<sup>7-11</sup>). 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 Mg<sub>2</sub>Ge and Si powders were mixed using agate mortar under an Ar atmosphere. The Mg<sub>2</sub>Ge:Si weight ratios were 80:20, 70:30, 50:50 and 30:70 respectively. The Mg<sub>2</sub>Ge/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 7×10<sup>5</sup> Pa) and the mixture of Mg<sub>2</sub>Ge 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.

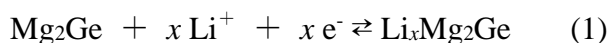
The morphologies of obtained films and distributions of Si were evaluated using Scanning Electron Microscope (SEM, JSM-5200; JEOL Ltd., 15 kV) and Energy dispersive X-ray analysis (EDX, EDS-54033MCK; JEOL Ltd.).

Electrochemical measurements were carried out with a beaker-type three-electrode cell. Working electrodes were consisted of Mg<sub>2</sub>Ge, Si and Mg<sub>2</sub>Ge/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 LiClO<sub>4</sub>-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<sup>-1</sup> 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 Mg<sub>2</sub>Ge and Si GD-film electrodes in order to discuss the charge-discharge reaction for the Mg<sub>2</sub>Ge/Si composite GD-film electrode. The discharge capacity of Mg<sub>2</sub>Ge GD-film electrode was 600 mAh g<sup>-1</sup>, which is higher than that obtained by the conventional electrode fabrication process <sup>11)</sup>. In contrast, the discharge capacity of Si GD-film electrode is 2300 mAh g<sup>-1</sup>, which is the same as the reported value <sup>14)</sup> 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 Mg<sub>2</sub>Ge 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 <sup>11)</sup>.



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

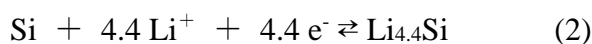


Figure 2 illustrates the cycle performance of these electrodes. The discharge capacity of the Si GD-film electrodes decayed significantly and showed ca. 320 mAh g<sup>-1</sup> after 200 cycles. The significant capacity decay is due to the exfoliation of the Si active materials. On the other hand, the capacity of the Mg<sub>2</sub>Ge GD-film electrode maintained a capacity of more than 260 mAh g<sup>-1</sup> 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 Mg<sub>2</sub>Ge 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 Mg<sub>2</sub>Ge.

Figure 3 shows the charge-discharge curves of the first cycle for Mg<sub>2</sub>Ge/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 Mg<sub>2</sub>Ge 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 Mg<sub>2</sub>Ge and Si were acted as active materials. As for the capacity reversibility at the first cycle, no remarkable improvement was observed in both Mg<sub>2</sub>Ge and Si GD-film electrodes in comparison with the conventional electrodes <sup>11</sup>). Since the capacity reversibility of Si electrode, ca. 70 %, was superior to that of Mg<sub>2</sub>Ge electrode, ca. 55 %, the Mg<sub>2</sub>Ge/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 Mg<sub>2</sub>Ge / 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 Mg<sub>2</sub>Ge. 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 Mg<sub>2</sub>Ge/Si composite was found to be 30 wt%, and the resulting composite electrode still maintained a discharge capacity of 600 mAh g<sup>-1</sup> even after 200 cycles.

The changes in coulomb efficiency of the  $\text{Mg}_2\text{Ge}$ , 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  $\text{Mg}_2\text{Ge}$  electrode. The changes in coulomb efficiency of the  $\text{Mg}_2\text{Ge}$ , 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  $\text{Mg}_2\text{Ge}$  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  $\text{Mg}_2\text{Ge}$ . 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  $\text{Mg}_2\text{Ge}$  layer must suppress the disintegration of the composite electrode, the distribution of Si particles in  $\text{Mg}_2\text{Ge}$  layers appears to be an important factor to obtain the best performance of cyclability.

The reasons for the remarkable improvements of the Mg<sub>2</sub>Ge/Si composite GD-film electrodes in comparison with the Mg<sub>2</sub>Ge electrode are discussed below. Figure 7 displays surface SEM images of the Mg<sub>2</sub>Ge/Si composite GD-film electrodes, while Figure 8 shows the distribution of Si in the electrodes analyzed by Si-K $\alpha$  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 Mg<sub>2</sub>Ge and Si in the composite, each Si particle was surrounded with Mg<sub>2</sub>Ge layer, and the stress generated in the Si particle at Li insertion-extraction was considered to be released by the Mg<sub>2</sub>Ge layer because Mg<sub>2</sub>Ge 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 Mg<sub>2</sub>Ge.

#### 4. Conclusions

Mg<sub>2</sub>Ge/Si composite electrodes were prepared by a gas-deposition (GD) method, and their electrochemical properties were estimated. The resulting Mg<sub>2</sub>Ge/Si composite electrodes exhibited larger discharge capacity than the Mg<sub>2</sub>Ge 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 Mg<sub>2</sub>Ge and Si GD-film electrodes.

(a) (— —) Mg<sub>2</sub>Ge and (b) (—)Si.

Fig. 2 Cycle life performance of the Mg<sub>2</sub>Ge and Si GD-film electrodes.

(a) (□) Mg<sub>2</sub>Ge and (b) (▲)Si.

Fig. 3 Charge-discharge curves of the Mg<sub>2</sub>Ge/Si composite GD-film electrodes.

(a) (— —)Mg<sub>2</sub>Ge:Si = 80:20, (b)(—) Mg<sub>2</sub>Ge:Si = 70:30, (c)(— - —) Mg<sub>2</sub>Ge:Si = 50:50 and (d) (•••)Mg<sub>2</sub>Ge:Si = 30:70.

Fig. 4 Cycle life performance of Mg<sub>2</sub>Ge/Si composite GD-film electrodes.

(a) (▲)Mg<sub>2</sub>Ge:Si = 80:20, (b)(●) Mg<sub>2</sub>Ge:Si = 70:30, (c)(◆) Mg<sub>2</sub>Ge:Si = 50:50 and (d) (■)Mg<sub>2</sub>Ge:Si = 30:70.

Fig. 5 Coulomb efficiency for (a) (□)Mg<sub>2</sub>Ge, (b) (▲) Si and (c) (●)Mg<sub>2</sub>Ge/Si

GD-film electrodes.

Fig. 6 Coulomb efficiency for (a) (▲)Mg<sub>2</sub>Ge:Si = 80:20, (b)(●) Mg<sub>2</sub>Ge:Si = 70:30,

(c)(◆) Mg<sub>2</sub>Ge:Si = 50:50 and (d) (■)Mg<sub>2</sub>Ge:Si = 30:70 composite GD-film electrodes.

Fig. 7 Surface SEM images of the Mg<sub>2</sub>Ge/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  $\text{Si-K}\alpha$ .

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

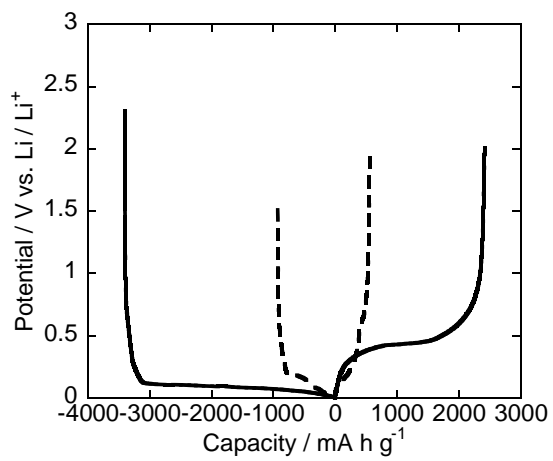


Fig. 1

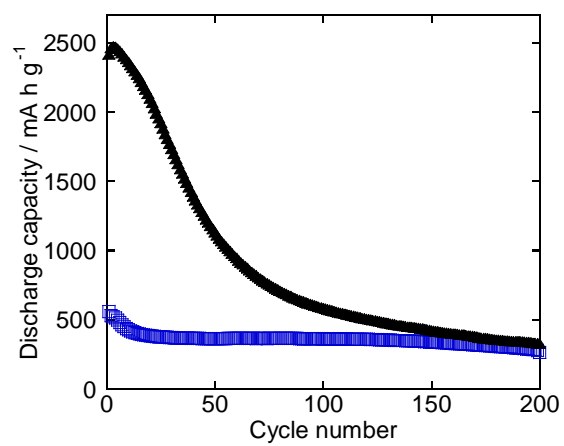


Fig. 2

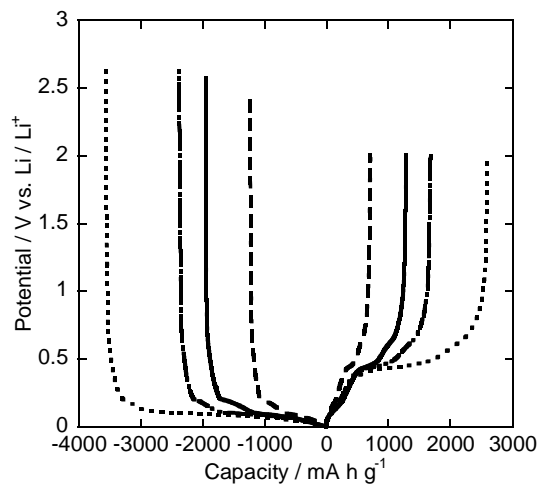


Fig. 3

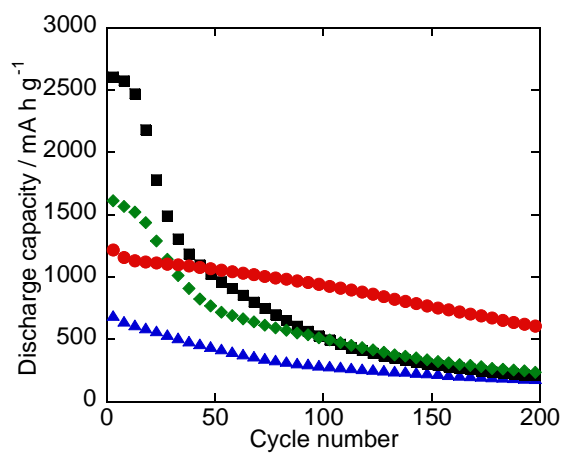


Fig. 4



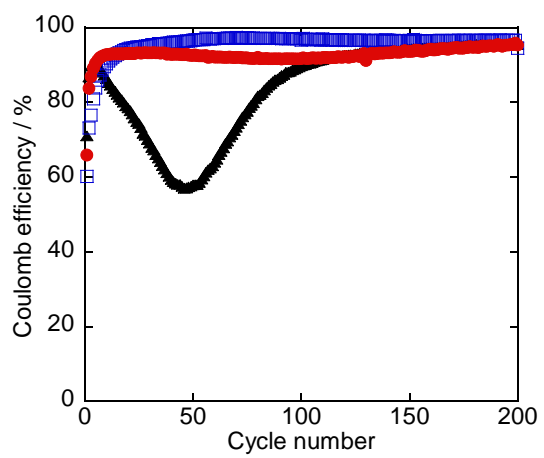


Fig. 5

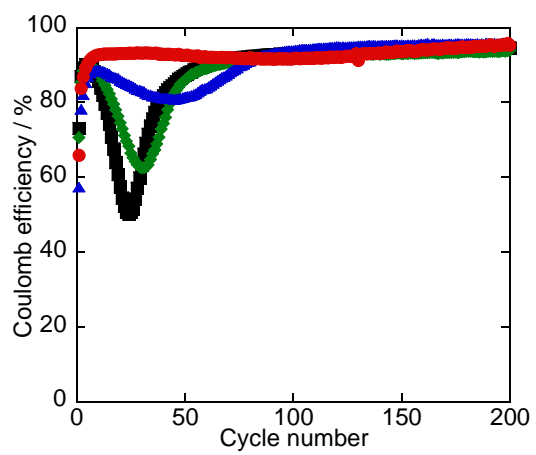
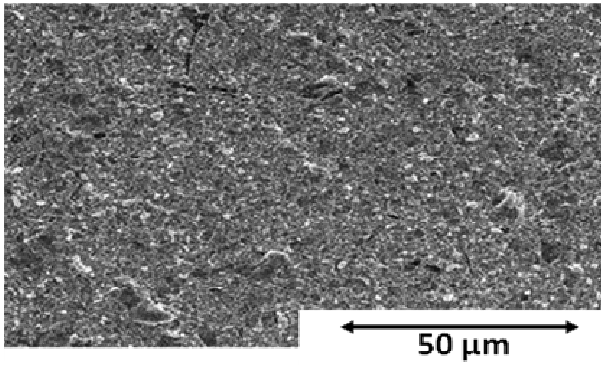
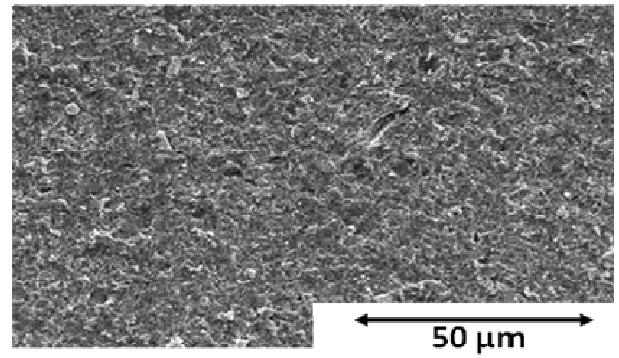


Fig. 6

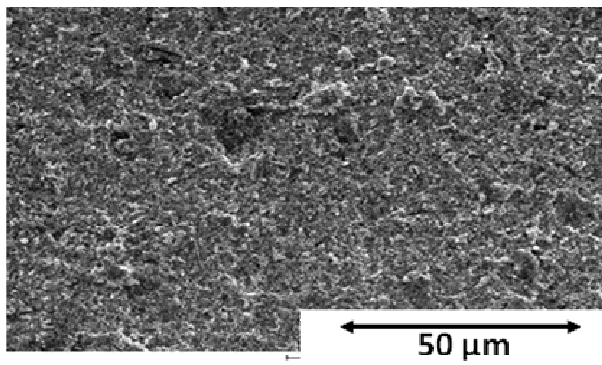
(a)  $\text{Mg}_2\text{Ge}:\text{Si}=80:20$



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



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



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

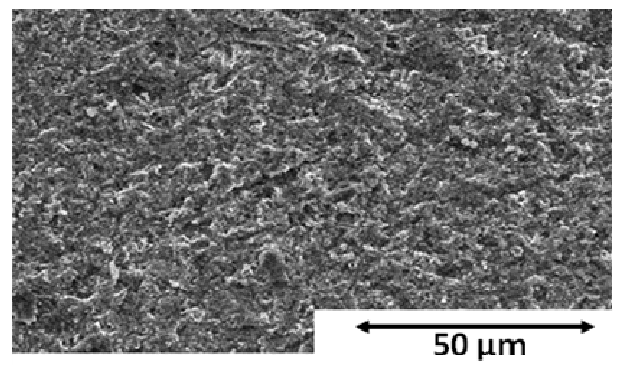
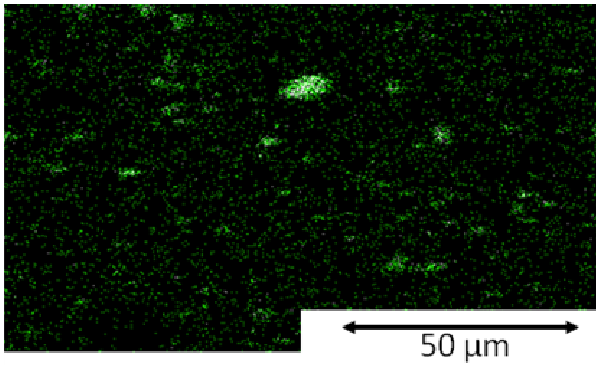
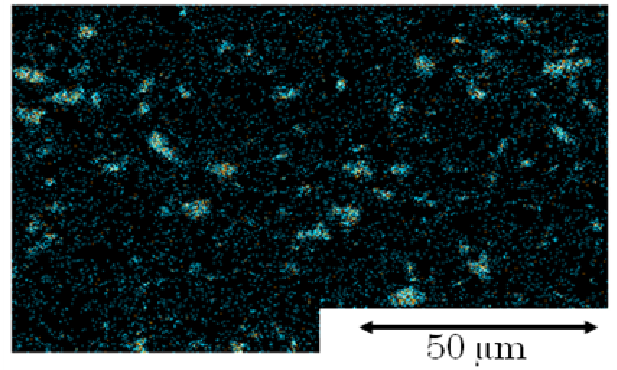


Fig. 7

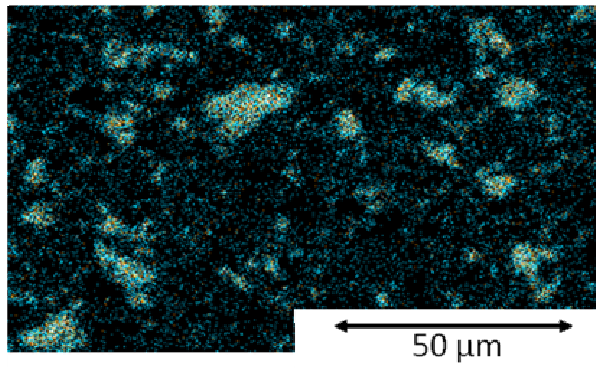
(a)  $\text{Mg}_2\text{Ge}:\text{Si} = 80:20$



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



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



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

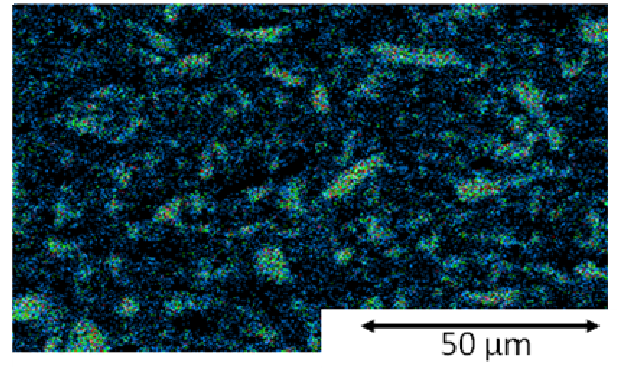


Fig. 8