Growth of MoSi₂ by Molten Salt Technique Using Mo-Based Compounds*

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The hexagonal phase MoSi₂ was grown using MoS₂ powder as the source material by the molten salt method. The structural and morphological properties of the resultant silicides are characterized. As a comparison, the structural and compositional characterizations were made for the Mo-silicides grown on a Mo substrate and a Mo-Ti alloy compact. It was revealed that the homogeneity of the chemical composition of the silicides grown using MoS₂ is improved, except for the existence of the Si source powders, though a small amount of S remained in the powder. The layered structure of MoS₂ with a hexagonal crystalline structure would affect the growth morphology and enhance the formation of the hexagonal MoSi₂. A simple growth procedure to fix the crystalline structure using an appropriate starting material under a preferable growth environment is proposed.
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I. INTRODUCTION

Recently, semiconducting silicides, which consist of non-toxic and abundant materials, have attracted much attention for their potential to create new classes of environmentally conscious electronics [1]. The group VI metal silicides are classified in this material group [2]. MoSi₂ with stable tetragonal (t-) phases is metallic and has been used in electrode wire materials. On the other hand, the hexagonal (h-) phase MoSi₂ has lattice constants of $a = 0.4622$ nm and $c = 0.6646$ nm, and is known to be a narrow gap semiconductor. It is reported that the low temperature phase, h-MoSi₂, is expected to be one of the novel silicide semiconductors, which has improved thermoelectric properties [2]. However, the electrical and thermoelectric property of the bulk crystal h-MoSi₂ have not been experimentally clarified. Since t-MoSi₂ is transformed into h-MoSi₂ with the Ti addition by a Mechanical Alloying (MA) technique in the Mo-Ti-Si system [3], it has been reported that Mo-silicides were grown using Mo substrates and Mo-Ti alloy (Mo(Ti)) compacts by the molten salt method. However, the tetragonal phase was formed as well as the hexagonal phase in the silicides. A nonhomogeneous compositional distribution of Mo and Si atoms was observed in the silicides when using the Mo substrate and Mo(Ti) compact [4]. The single phase growth of h-MoSi₂ and improved compositional homogeneity of the silicide are required.

On the other hand, MoS₂ has a hexagonal structure with lattice constants of $a = 0.31612$ and $c = 1.22985$ nm. The detailed structure of MoS₂ and extraordinary chem-

ical properties of the two-dimensional MoS₂ nanoclusters are described in Refs. [5] and [6], respectively. MoS₂ has a characteristic layered structure, i.e., metal chalcogenide slabs are formed by two layers of close-packed chalcogenide atoms sandwiching one metal layer between them. These slabs are stacked with only van der Waals forces between the slabs [7]. It is considered that the use of the thin separated slabs would improve the homogeneity of the atomic distribution in the resultant alloys, because the diffusing species easily can pass through the materials during the treatment. Moreover, it has also been reported that the crystalline structure of the resultant compounds is strongly affected by that of the starting materials. For example, the formation of the zincblende-MnTe phase was demonstrated using ZnTe [8]. Single phase Ca₂Si was obtained using Mg₂Si as the starting material [9]. In the same manner, it is expected that the h-MoSi₂ would be easily obtained using MoS₂ as the source material.

In this study, the synthesis of h-MoSi₂ was examined using MoS₂ powder to overcome the previously mentioned difficulties. The structural and morphological properties of the resultant silicides were also characterized.

II. EXPERIMENTAL

The Mo-silicide powder was synthesized using MoS₂ powder and a molten salt, comprised of 36.58 mol% NaCl–36.58 mol% KCl–21.95 mol% NaF–4.89 mol% Na₂SiF₆. The salt mixture and silicon powder (99.999%, 21.85 mol% for the salt mixture) were placed in an SiO₂–Al₂O₃ crucible with the MoS₂ powder (99.9% up, 2.73 mol% for salt mixture). They were thermally treated at 873 K for 4 h. After the heat treatment, the salt was removed from the sample using deionized H₂O. As a comparison, a Mo-silicide layer was grown on a Mo 99.9(% up) substrate. They were thermally treated at 973 K for 4 h. The de-

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TABLE I: Typical chemical compositions of Mo silicides measured by EDS point analyses for the positions shown in Figs. 1 and 2.

Source Material	Position	Compositions (at.%)						Remarks
		Mo	Si	Ti	Fe	Cr	S	
Mo substrate	+1	97.61	2.39					
	+2	23.41	76.59					
Mo(Ti) compact	+1	52.28	3.02	5.16	30.66	8.88		MA
	+2	14.09	59.95	19.06	5.19	1.71		
MoS ₂	+1	25.16	68.73				6.11	
	+2	17.66	74.92				7.43	
	+3	—	~100				—	

tailed growth procedure is described elsewhere [4]. In addition, Mo-silicide compacts were synthesized using Mo powder with added Ti powder. The Mo (150 μm 99.8%) and Ti (45 μm 99.9%) powders were mixed in the molar ratio of Mo:Ti= 85:15, then mechanically alloyed for 50 h using 1/4 inch $\times$ 4 stainless steel balls. The resulting powders were cold pressed at 200 MPa for 15 min, then thermally treated in the molten salt for 2 h to synthesize the Mo-silicide compacts containing Ti (Mo(Ti)-silicide). The detailed growth procedure is described elsewhere [4]. The structural properties of the powder, layer and compact were characterized by scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with EDS.

III. RESULTS AND DISCUSSIONS

Figures 1(a) and (b) show the cross-sectional SEM images and corresponding EDS mappings of the Mo- and Mo(Ti)-silicides grown using a Mo substrate and a Mo(Ti) compact, respectively. For both cases, two regions are mainly observed. One is the region with the brighter contrast shown as (+1), and the other is observed with the darker contrast shown as (+2). The typical results of the compositional analyses are shown in Table I. During the EDS measurements, additional Na, K, F, Cl and O elements were also detected in addition to Mo and Si, and they originated from the mixed salts, and probably oxidation and other contaminants in the air. In the table, only the signals of Mo and Si are shown. In addition, for the Mo(Ti) compacts, Fe and Cr were also detected, and they originated from the contamination by the steel vial and balls during the MA process. It was found that the regions including (+1) and (+2) are Mo and Si rich in the figures, respectively, and that Si atoms are significantly distributed on the surface of the voids formed in the Mo and Mo(Ti). It is considered that the molten salt can penetrate into the substrates or the compacts through voids. The significant nonhomogeneous distributions of the Mo and Si atoms are observed, which is caused by the limited interdiffusion between the deposited Si and Mo or Mo(Ti). Considering the co-existence of the tetragonal phase [4], the growth procedure should be modified to grow the hexagonal MoSi₂ single phase with homogeneous compositional distributions.

Figure 2 shows an SEM image and corresponding EDS

FIG. 1: Cross-sectional SEM images and corresponding EDS mappings of (a) Mo- and (b) Mo(Ti)-silicides grown using a Mo substrate and a Mo(Ti) compact. Typical results of the compositional analyses are shown in Table I.

mappings of the Mo silicide powders grown using MoS₂ as the source material. The typical results of the compositional analyses are shown in Table I. The average composition of the local area on the resultant silicide is approximately Mo:Si $\approx$ 1:2~4. The region with pure Si is also observed. According to the Mo-Si phase diagram, no stable phase exists between MoSi₂ and Si [10]. The excess Si is due to the presence of Si powder as the source material. This revealed that the homogeneity of the compositional distributions of Mo and Si atoms was improved, except for the residual Si compared to the silicide cases shown in Fig. 1.

Figure 3 shows an STEM image and corresponding EDS mappings of one of the powders grown using MoS₂ as the source material. It was confirmed again that the Mo

FIG. 2: SEM image and corresponding EDS mappings of Mo silicide powders grown using MoS_2 as the source material. Typical results of the compositional analyses are shown in Table I.

FIG. 3: STEM image and corresponding EDS mappings of one of the powders grown using MoS_2 as the source material.

and Si are homogeneously distributed, and the average chemical composition of the powder is about $\text{Mo}:\text{Si}=1:2$, though a small amount of S ($\sim 0.4\%$) remained in the powder.

Figure 4 shows a TEM image and an enlarged lattice image of the Mo silicides using MoS_2 as the source material. The Fast Fourier Transformation (FFT) pattern of the images and corresponding crystalline orientations of the domains are shown in the figure. As shown in Fig. 4(a), thin silicide films were synthesized, which are due to the layered structure of the MoS_2 starting material. The enlarged lattice fringes show a hexagonal symmetry and the lattice spacing of the fringe is 0.23 nm which corresponds to that of $\text{h-MoS}_2(110)$ as shown in Fig. 4(b). The six-fold FFT pattern is consistent with the electron diffraction patterns of the h-MoS_2 observed along the $[0001]$ zone axis.

Based on the results mentioned above, it was found that single phase h-MoS_2 growth and compositional homogeneity are improved compared to that for the previously reported [4], which is due to the use of MoS_2 as the starting material. The MoS_2 has the shape of a thin piece of hexagonal crystal, and it has layered structure [5]. The deposited Si atoms from the molten salts easily diffused through the thin piece of the layered structure, and the Si atoms replace the S atoms in the MoS_2 host crystals to form the MoSi_2 . From the resultant powders, only a small amount of S was detected.

The replacement of Si atoms with S sites in the hexagonal MoS_2 leads to the formation of the single phase

FIG. 4: (a) TEM image and (b) an enlarged lattice image of Mo silicides using MoS_2 as the source material. The FFT pattern of the images and corresponding crystalline orientations of the domains are shown in the inset.

hexagonal MoSi_2 crystals. It has also been reported that the crystalline structure of the resultant compounds is affected by that of the starting materials. For the zincblende- MnTe growth using ZnTe , it is considered that the interdiffusion of Mn and Zn atoms effectively takes place between the MnSb-ZnTe diffusion couple by keeping the stoichiometric composition of the initial and resultant layers [8]. For the Ca_2Si growth on Mg_2Si , Ca diffusion into Mg_2Si leads to the formation of $\text{Ca}_2\text{Si}/\text{CaMgSi}$ near the Mg_2Si surface. When a sufficient Ca flux is supplied to the silicide surface, no other Si-rich silicide is formed, and single phase Ca_2Si was obtained [9]. In this reaction, the enthalpy of formation of the resultant compounds should be greater than that of the starting material or precursor. However, the enthalpy of formation of MoS_2 (65.8 kcal/mol) is greater than that of MoSi_2 (31.5 kcal/mol) [11]. This means that MoS_2 is more stable than MoSi_2 . By only considering the enthalpy of formation, MoSi_2 is not formed from MoS_2 . However, it is certain that MoSi_2 can be formed from MoS_2 in a molten salt. In fact, it is reported that Mo can be extracted from MoS_2 by the molten salt method [12, 13]. In the molten salt, S atoms dissociated as S^{2-} ions into the molten salts. MoS_2 is intrinsically stable, however, it is active enough to react in the molten salt. The MoS_2 is decomposed to form MoSi_2 by the replacement of Si at the S sites. It is expected that the quality of the grown crystals will be further improved, when the treatment conditions, such as the growth temperature, the salt species and their compositions, are optimized.

Concerning semiconducting silicides, it is usually difficult to grow high quality single phase crystals due to the existence of multiple phases in the metal-silicon system. It is useful to discuss the appropriate choice of the “silicidation path” to fix the chemical compositions during the growth. For example, the single phase Ca_2Si growth using Mg_2Si has been demonstrated [9]. On the other hand, the MoSi_2 growth using MoS_2 shown in this study demonstrates the appropriate choice of the crystalline structure of the grown silicides. In addition, it is shown that the molten salt environment makes the intrinsically stable MoS_2 to be active in order to react and play an important role as a precursor. It is expected that this simple growth procedure to fix the crystalline structure using the appropriate starting material or a precursor un-

der the preferable growth environment would open a new field of silicide semiconducting technology.

IV. CONCLUSIONS

The h-MoSi₂ was grown using MoS₂ powder as the source material by the molten salt method. It was revealed that Mo and Si are homogeneously distributed, except for the existence of Si source powders, and the average chemical composition of the powder is about Mo:Si=1:2, though a small amount of S remained in the powder. The layered structure of MoS₂ with hexagonal crystals would affect the growth morphology and enhance

the formation of h-MoSi₂. The deposited Si atoms from the molten salts easily diffused through the thin piece of the MoS₂ layered structure. It is expected that this simple growth procedure to fix the crystalline structure using the appropriate starting material under the preferable growth environment would open a new field of silicide semiconducting technology.

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