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Growth of $CrSi_2$ Nanostructures Using $CrCl_2$ Powder on Si Substrates

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Abstract

Chromium disilicide ($CrSi_2$) nanostructures were grown by the exposure of Si (111) substrates to $CrCl_2$ vapor in an argon gas flow at atmospheric pressure without using any metal catalyst. Dependence of the growth condition on the structural property was investigated. Hexagonal-shaped $CrSi_2$ microrods were grown at 750 °C with 0.05 g of $CrCl_2$. As the quantity of $CrCl_2$ increased to 0.1 g, the bundle of $CrSi_2$ nanowires with microrods and web-liked $CrSi_2$ nanostructure with turning angles were grown at 750 °C and 700 °C, respectively. The preliminary discussion on the growth mechanism of $CrSi_2$ micro- and nanostructures was carried out.

Abstrak

Pertumbuhan Struktur Nano $CrSi_2$ dengan Serbuk $CrC1_2$ pada Substrat Si. Struktur-struktur nano kromium disilisida ($CrSi_2$) dapat dikembangkan dengan paparan substrat Si (111) pada uap $CrCl_2$ di dalam aliran gas argon dengan tekanan atmosfer tanpa menggunakan katalis metal apa pun. Ketergantungan kondisi perkembangan pada elemen struktural juga diselidiki. Mikrorod $CrSi_2$ berbentuk heksagon dikembangkan pada suhu 750 °C dengan $CrCl_2$ sebanyak 0,05 g. Ketika kuantitas $CrCl_2$ meningkat menjadi 0,1 g, bundel kawat-kawat nano $CrSi_2$ dengan mikrorod dan struktur nano $CrSi_2$ berbentuk jaring dengan sudut putar mengalami perkembangan yang masing-masing terjadi pada suhu 750 °C dan 700 °C. Pembahasan pendahuluan juga diberikan mengenai mekanisme pertumbuhan struktur mikro dan nano $CrSi_2$.

Keywords: *$CrSi_2$, microrods, nanostructures, thermoelectric material*

I. Introduction

Chromium disilicide ($CrSi_2$) is an indirect narrow-gap (Eg=0.35 eV) semiconductor that has been targeted and used for robust, stable, and inexpensive thermoelectric (TE) materials and has shown promise for photovoltaic applications [1-2]. Although $CrSi_2$ possesses many advantages such as low cost, excellent thermal stability and outstanding oxidation resistance, it has modest ZT value compared with those of the more well-known TE materials [3]. Nano-scale thermoelectric materials are considered to have potential ability to enhance the energy conversion performance of thermoelectric materials [4]. Theoretical calculations and proof of principle experiments of nanoscale systems have demonstrated both a decrease in thermal conductivity and an increase in the power factor σS^2 relative to the corresponding bulk systems [4-8]. Hochbaum et al. [8] reported that the Si nanowires with diameters of about 50 nm exhibit 100-fold reduction in thermal conductivity, yielding ZT = 0.6 at room temperature. Recently, various nanostructures of $CrSi_2$ have been successfully synthesized, such as nanowires, nanowebs, and core-shell nanocables [2-3,9-10]. However, it is important to develop a simple and controllable growth process for the fabrication of the $CrSi_2$ nanostructures.

In this study, the preliminary growth of $CrSi_2$ nanostructures was carried out, and dependence of the growth condition on the structural property was investigated. In addition, the preliminary discussion on the growth mechanism of $CrSi_2$ micro- and nanostructures was carried out.

2. Experiment

$CrSi_2$ nanostructures were grown by the exposure of Si(111) substrates to $CrCl_2$ vapor in an argon gas with the flow rate of 4500 sccm at atmospheric pressure. The

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Si(111) substrates covered with native oxide layers were placed approximately 10 cm downstream apart from the $CrCl_2$ powder in the furnace [2]. 0.05 g-0.1 g of $CrCl_2$ source was maintained at 872 °C, and Si substrates were reacted at different temperatures in the range of 700 °C-750 °C and kept for 10 min. In this study, the source material and substrate are moved into the furnaces after the temperature of the furnaces up to the reaction temperature, in order to ensure the source material reacted at the reaction temperature and control the growth process easier.

The morphological and structural properties of samples were characterized by filed emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). In addition, the compositional analysis of the samples was carried out using energy dispersive spectroscopy (EDS).

3. Results and Discussion

Figure 1 shows cross-sectional SEM images of the $CrSi_2$ samples grown at different temperature of substrates with different quantity of $CrCl_2$. Free-standing microrods less than 10 μm in length and less than 5μm in width are grown at 750 °C with 0.05 g of $CrCl_2$ and microparticles are also observed, as shown in Fig.1 (a). As the quantity of $CrCl_2$ increased to 0.1 g, the width of the microrods is slightly increased and the length up to 30 μm, as shown in Fig. 1 (b). However, the size of microrods depends on the quantity of $CrCl_2$. Additionally, the bundle of nanowires is grown at the top of the microrods, and the white nanoparticles are attached to the apexes of the nanowires, as shown in the inset in Fig. 1 (b). It is considered that the sufficient $CrCl_2$ vapor supply in the growth process leads to growth of the nanowires. It has been reported that $CrSi_2$ nanowires grow out perpendicularly and evenly from both sides of the microrod-like $CrSi_2$ stems using Cr powder and $NiCl_2$ as source materials [11]. The film with the thickness of 30 μm, consists of the microparticles, is formed at 700 °C with 0.1 g of $CrCl_2$, as shown in Fig. 1 (c), and nanowires are grown at the top of the film, as shown in the inset in Fig. 1 (c). It is seen that the mophology property of the samples depends on the quantity of $CrCl_2$ and the temperature of substrates.

Figure 2 shows XRD spectra of the $CrSi_2$ samples grown at different temperature of substrates with different quantity of $CrCl_2$. The peaks in the spectra, except the peaks from the Si substrates, can be indexed to the hexagonal crystal structure of $CrSi_2$. No other chromium silicide phases or impurities are detected. $CrSi_2$ is the most thermodynamically favorable phase to form among various phases of chromium silicides [2]. It is confirmed that the samples are mainly composed of $CrSi_2$. The silicide can be formed either by the direct reaction of halide source with Si substrate or through a

The growth of the $CrSi_2$ microrods or nanowires could be described by the following plausible reaction equations [2].

$$2CrCl_2\,(g) + 5Si\,(s) \rightarrow 2CrSi_2\,(s) + SiCl_4\,(g) \quad (1)$$

$$CrCl_2\,(g) + 2SiCl_4\,(g) \rightarrow CrSi_2\,(s) + 5Cl_2\,(g) \quad (2)$$

Figure 3 shows SEM images and corresponding EDS results of the $CrSi_2$ sample grown at 750 °C with 0.05 g of $CrCl_2$. It is observed that the microrods and microparticles are distributed on the surface of the Si substrate. Magnified SEM image shown in the inset in Fig.3 indicates that the microrods have hexagonal structure, which is consistent with the crystalline structure of $CrSi_2$. EDS results reveal that the atomic ratio between Cr and Si in microrods and microparticles is approximately 1:2. It is considered that the growth

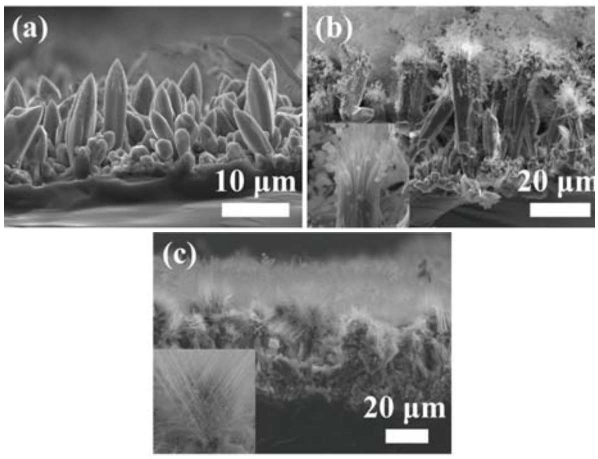


Fig. 1. Cross-sectional SEM Images of the $CrSi_2$ Samples Grown at (a) 750 °C with 0.05 g of $CrCl_2$, (b) at 750 °C with 0.1 g of $CrCl_2$ and (c) at 700 °C with 0.1 g of $CrCl_2$. Magnified SEM Images of the Nanowires in (b) and (c) Shown in the Inset

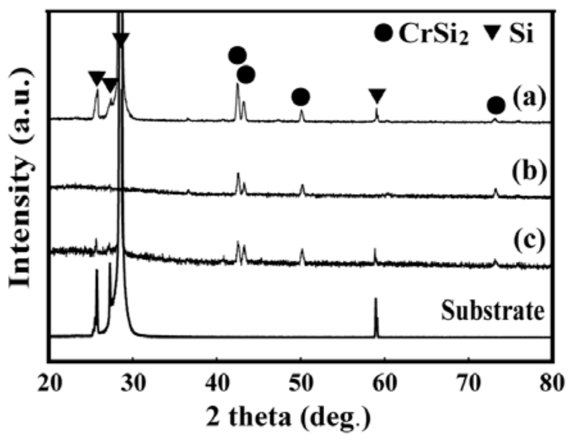


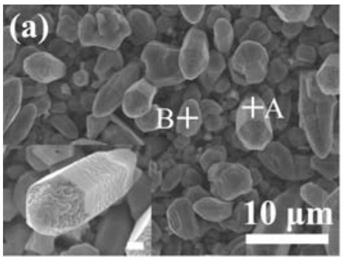
Fig. 2. XRD Spectra of the $CrSi_2$ Samples Grown at (a) 750 °C with 0.05 g of $CrCl_2$, (b) at 750 °C with 0.1 g of $CrCl_2$ and (c) at 700 °C with 0.1 g of $CrCl_2$

direction of the microrods with hexagonal structure is parallel to the $CrSi_2$ [0001] [3].

Figure 4 shows SEM images and corresponding EDS results of the $CrSi_2$ sample grown at 750 °C with 0.1 g of $CrCl_2$. The bundle of nanowires with microrods is densely distributed on the surface of the Si substrate, as shown in Fig. 4 (a). The microrods also possess hexagonal structure as same as the sample grown at 750 °C with 0.05 g of $CrCl_2$, and the nanowires are grown at the top and along the surface of the microrods. EDS results in Fig. 4 (b) indicate that the atomic ratio between Cr and Si in nanowires and microrods is approximately 1:2, while a lot of O is contained in nanowires. Additionally, Si and O are the main elements contained in the nanoparticles, which reveals that the naonparticles probably consist of silicon oxides. The formation of silicon oxides could be described by the following plausible reaction equation [13]:

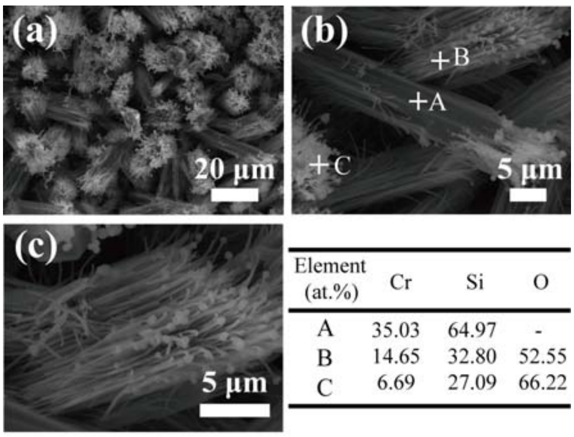
$$SiCl_4\,(g) + 2H_2O\,(g) \rightarrow SiO_2\,(S) + 4HCl\,(g) \qquad (3)$$

As shown in Fig. 4 (c), the bundle of nanowires is well-aligned and has high density.



Element (at.%)	Cr	Si
A	30.47	69.53
B	36.93	63.07

Fig. 3. SEM Images and Corresponding EDS Results of the $CrSi_2$ Sample Grown at 750 °C with 0.05 g of $CrCl_2$. Magnified SEM Image of a Microrod in (a) Shown in the Inset



Element (at.%)	Cr	Si	O
A	35.03	64.97	-
B	14.65	32.80	52.55
C	6.69	27.09	66.22

Fig. 4. SEM Images and Corresponding EDS Results of the $CrSi_2$ Sample Grown at 750 °C with 0.1 g of $CrCl_2$. Coefficient

Figure 5 shows SEM images of the $CrSi_2$ sample grown at 750 °C with 0.1 g of $CrCl_2$. It is clearly observed that the structure of the sample is composed of microrods, nanowires and nanoparticles, as shown in Fig.5 (a). Magnified SEM images show that a lot of nanopariticles are attached on the surface of the microrod and the top of the nanowires, as shown in Fig. 5 (b) and (c). It is considered that the nanoparticles act as the catalyst for the growth of the nanowires. The interface between microrod and nanowires indicates that the secondary nucleation occurred on the surface of the microrods, and then the sufficient vapor supply in the system leads to growth of the nanowires.

Figure 6 shows SEM images of the $CrSi_2$ sample grown at 700 °C with 0.1 g of $CrCl_2$. $CrSi_2$ with web-liked structure is densely distributed on the surface of the Si substrate, as shown in Fig. 6 (a) and (b). The web-liked structure is composed of nanowires with a thickness less than 100 nm. No nanoparticles are observed at the top of the nanowires. Magnified SEM image in Fig. 6 (c)

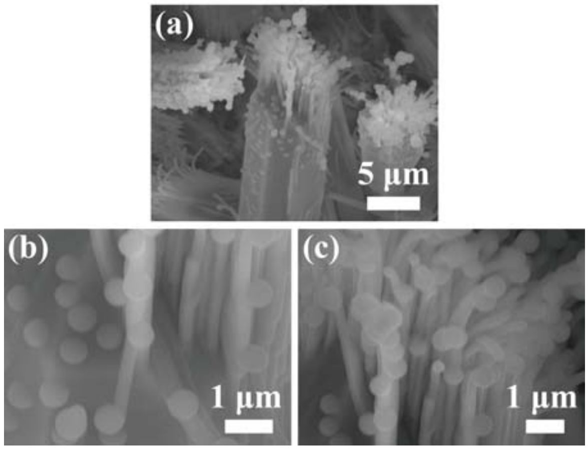


Fig. 5. SEM Images of the $CrSi_2$ Sample Grown at 750 °C with 0.1 g of $CrCl_2$

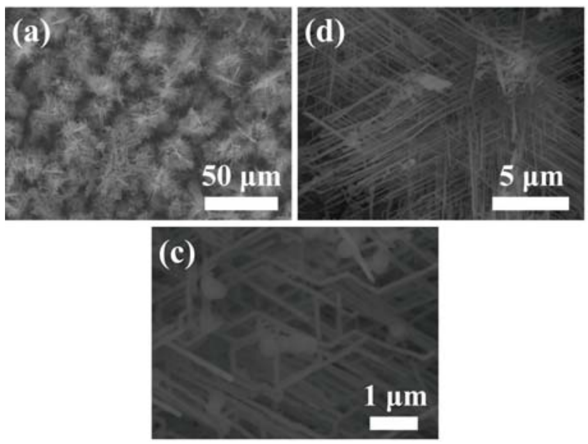


Fig. 6. SEM Images of the CrSi2 Sample Grown at 700 °C with 0.1 g of $CrCl_2$

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illustrates that the turning angles about 60 ° are observed in the nanowires. It is estimated that the growth direction of the nanowires with turning angles is parallel to $CrSi_2$ <11-20> [9].

$CrSi_2$ nanowires are developed by a simple and controllable growth method. According to the results mentioned above, the quantity of $CrCl_2$ and the temperature of substrates affect the final morphology of the samples. The growth mechanism is not clear, but it is considered as follows. Because of no additional catalytic metal particles are employed in the growth process, the growth of $CrSi_2$ microrods and nanowires presented here is not due to the vapor-liquid-solid (VLS) mechanism. The growth of the $CrSi_2$ microrods or nanowires is carried out by two reaction equations. Equation (1) is the dominant reaction on Si substrates.

The Si substrates play a dual role as the source of Si and substrates. The $CrSi_2$ microrods are formed on the surface of Si substrates through (1), and byproduct $SiCl_4$ is produced. According to the nanoparticles, probably consist of silicon oxide, attached at the top of the microrods and nanowires, the nanoparticles act as catalyst to form $CrSi_2$ nanowires at the top of microrods. The nanowires are grown after that the Si substrates are covered by the $CrSi_2$ microrods, which provide a low Si supply from the substrates. Thus, it is considered that the growth of the $CrSi_2$ nanowires at the top of the microrods is carried out through (2), and the byproduct $SiCl_4$ of the (1) is supplied as Si source. As the temperature of Si substrate as low as 700 °C, the nucleation ratio of $CrSi_2$ is increased and the formation of $CrSi_2$ microparticles is enhanced simultaneously due to high supersaturation of $CrCl_2$. It is considered that the growth of nanoparticles is carried out through (1) at the beginning, and it is transformed to (2) as the thickness of microparticles film on the surface of the Si substrates increased, which limit the Si supply from the substrates. In addition, the diffusion rate of Si in the substrates is also reduced at low temperature. The consumption of $SiCl_2$ to form $CrSi_2$ nanoparticles reduces the concentration of $SiCl_2$ in the growth system, and it also suppresses the produce of $SiCl_2$. It has been reported that the difference of the reactant concentration in the growth system could affect the growth direction of the nanowires [14,15]. The above discussions are speculations based on the various experiments conducted in different growth conditions, and systematic studies are still needed to fully illuminate the growth mechanism of various structures.

4. Conclusions

$CrSi_2$ nanostructures were grown by the exposure of Si (111) substrates to $CrCl_2$ vapor in an argon gas flow at atmospheric without using any metal catalyst. The sufficient $CrCl_2$ vapor supply and proper temperature of Si substrates are the crucial factors for the growth of $CrSi_2$ nanostructures. Hexagonal-shaped $CrSi_2$ microrods weregrown at 750 °C of the substrate with 0.05 g of $CrCl_2$. The bundle of $CrSi_2$ nanowires with microrods and web-liked $CrSi_2$ nanostructure with turning angles were grown at 750 °C and 700 °C of the substrates with 0.1 g of $CrCl_2$, respectively. This result leads us to expect that further optimization of growth condition and pretreatment of the substrates grow well-aligned and high density of $CrSi_2$ nanostructures for thermoelectric applications.

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