

4-1-2014

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Recommended Citation

Tatsuoka, Hirokazu; Li, Wen; Meng, Erchao; Ishikwa, Daisuke; Nakane, Kaito; Oda, Shingo; Matsushita, Tomoji; and Kurebayashi, Natsuki (2014) "Preparations of Nanostructured Silicide Bundles and Oxide Arrays," *Makara Journal of Technology*. Vol. 18: Iss. 1, Article 4.

DOI: 10.7454/mst.v18i1.2935

Available at: <https://scholarhub.ui.ac.id/mjt/vol18/iss1/4>

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Preparations of Nanostructured Silicide Bundles and Oxide Arrays

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Abstract

A variety of nanostructured silicide bundles and oxide nanowire arrays with abundant, non-toxic materials we are prepared. The CrSi₂ nanowire and Mg₂Si/MgO composite nanowire bundles were synthesized using a Si substrate and a SiO_x nanofiber bundle, respectively. The hexagonal MoSi₂ nanosheet bundles were also synthesized using a MoS₂ layered material as a template. In addition, ZnO, CuO/Cu₂O and α -Fe₂O₃ nanowire arrays were prepared on semiconductor or metallic substrates. The growth phenomena and the structural properties of the nanostructured materials were investigated. In addition, the preparations of axial and radial nanowire structures were examined.

Abstrak

Pembuatan Berkas Silisida dan Rangkaian Oksida Ternanostruktur. Beragam jenis berkas silisida dan rangkaian kawat nano oksida ternanostruktur dapat dibuat dengan bahan baku tidak beracun yang jumlahnya berlimpah. Kawat Nano CrSi₂ disintesis dengan substrat Si, sedangkan berkas-berkas kawat nano komposit Mg₂Si/MgO disintesis dengan berkas serat nano SiO_x. Berkas-berkas lembaran nano MoSi₂ heksagonal juga disintesis dengan bahan baku berlapis MoS₂ sebagai contoh dasar. Selain itu, rangkaian-rangkaian kawat nano ZnO, CuO/Cu₂O, dan α -Fe₂O₃ juga dibuat pada substrat semikonduktor atau metalik. Penyelidikan dilakukan terhadap fenomena perkembangan dan sifat-sifat struktural pada bahan-bahan baku ternanostruktur. Selanjutnya dilakukan pula pengamatan terhadap pembuatan struktur-struktur kawat nano aksial dan radial.

Keywords: nanosheet, nanowire, nanowire array, oxides, silicides

1. Introduction

Semiconducting silicides and oxides have been extensively investigated for environmentally conscientious electronics [1–2]. Silicides such as CrSi₂, Mg₂Si, and hexagonal (h-) MoSi₂ have been proposed as low energy gap semiconducting materials for low cost thermoelectric applications [3–5]. On the other hand, oxides, for example, ZnO, CuO/Cu₂O and α -Fe₂O₃, have been suggested for photovoltaic and photoelectrochemical cell applications [6–8]. In addition, low-dimensional materials have attracted much interest due to their enhanced or modified optical, electronic and mechanical properties compared with those of bulk materials.

Nanostructured devices, or electric devices containing nanostructured textures, have been proposed, and nanowires consisting of Si, III-V and II-VI compounds, have been extensively investigated [9–11]. However, it is important to control their morphological and structural

properties such as the composition, size and crystalline quality. These properties greatly depend on the growth conditions wherein the morphology is widely changed into dots, wires, ribbons, belts, sheets, and so on. The growth window for the specific morphology is narrow, and it is usually difficult to obtain a large area of uniformly distributed nanostructures. Yet applications such as thermoelectric generators, solar cells or photoelectrochemical cells require nanostructures to be uniformly distributed over large areas at low cost. Thus, a variety of silicide and oxide nanostructures, such as nanowires, nanorods and their nanowire arrays have been synthesized and characterized. Bundle structures consisting of nanowires or nanosheets can also be considered as high-efficiency nanostructured materials for thermoelectric applications. However, these semiconducting nano-sized bundle structures have been rarely synthesized. In addition, further refinement of the nanowires and arrays will be required for further development of sophisticated nanodevice technology.

In this paper, CrSi₂ nanowire and Mg₂Si/MgO composite nanowire bundles were synthesized using a Si substrate and a SiO_x nanofiber bundle, respectively. The hexagonal MoSi₂ nanosheets were also synthesized using a MoS₂ layered material as a template. In addition, ZnO, CuO/Cu₂O and α-Fe₂O₃ nanowire arrays were prepared on semiconductor or metallic substrates. The syntheses of axial CuO/Cu₂O and radial ZrO₂/SiO_x core/shell nanowire heterostructures was also examined.

2. Methods

The oxide and silicide nanostructures were prepared as follows. First, SiO_x nanofibers were grown by heat treatment of the FeSi substrates with Ga droplets. Afterward, the substrates were degreased, Ga was melted at around 313 °K, then applied by hand to the FeSi substrates using a steel or wooden stick. As a result, Ga droplets of mm in size were stuck on the substrates. The substrates with Ga droplets were loaded into the vacuum chamber, which was then pumped to a base pressure of 10⁻⁴ Torr. The SiO_x nanofiber growth was performed by exposure of the substrates to the residual O₂ for 114 h at the substrate temperature of 1173 °K [12].

CrSi₂ nanowire bundles were synthesized by the exposure of Si(111) substrates to CrCl₂ vapor with an argon carrier gas at a flow rate of 4500 sccm under atmospheric pressure. The Si(111) substrates with native oxide layers were placed downstream apart from the CrCl₂ powder in the furnace. The Si substrate and the CrCl₂ source were heated up to between 1023–1173 °K [13].

The h-MoSi₂ nanosheet bundles were 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. The detailed growth procedure is described elsewhere [14]. Mg₂Si/MgO composite nanowire bundles were synthesized by the exposure of SiO_x nanofiber bundles to Mg vapor. The detailed thermal treatment condition is described elsewhere [15].

The ZnO nanowire array was synthesized by the heat treatment of ZnS substrates with Ga droplets. Polycrystalline bulk ZnS crystals were used as the source material. Ga was melted around 313 °K, then manually applied to the ZnS substrate using a steel or wood stick. As a result, Ga droplets with a mm size were stuck to the ZnS. The ZnS with Ga droplets were loaded into the quartz tube which was open to the air. The nanowire growth was performed by air exposure of the ZnS, and

the nanowire arrays were grown for 5 h at a temperature of 1073 °K [16].

The CuO/Cu₂O nanowire arrays were synthesized by the thermal oxidation of copper substrates in air. The substrates were placed in a quartz tube, which was loosely sealed at 1 atmosphere of air. The nanostructure growth was performed by exposure of the copper substrates to air in a loosely sealed tube under the following temperature profile. The Cu substrates were heated to the elevated temperature range of 873 °K within 30 min, and were maintained for 1 h [17].

The α-Fe₂O₃ nanostructures were synthesized by the thermal oxidation of iron substrates. The iron substrates were loaded into the quartz tube which was open to the air. The nanostructure growth was performed by exposure of the iron substrates to the air for 3 h at temperatures of 973 and 1073 °K [18].

The ZrO₂/SiO_x core/shell nanowire bundles were grown by the thermal oxidation of ZrSi₂ substrates with molten gallium. ZrSi₂ flat plates were used as the seed substrates. The gallium was melted at around 313 °K, then manually applied to the ZrSi₂ substrates using a stick. As a result, molten gallium layers with a thickness <1 mm adhered to the ZrSi₂ substrates. The source substrates were placed in a vacuum chamber, which was then evacuated to a base pressure of 10⁻⁴ Torr. The synthesis of ZrO₂/SiO_x core/shell nanowire bundles was performed by exposure of the source substrates to the leaked air for 24 h at a temperature of 1173 °K. [19].

3. Results and Discussion

Preparations of silicide nanowire/nanosheet bundles.

Figures 1(a), (b) and (c) show an SEM image of a bundle of CrSi₂ nanowires, a TEM image of a part of a h-MoSi₂ nanosheet bundle and an SEM image of a bundle of Mg₂Si/MgO composite nanowire bundle, respectively. Figure 1(d) shows an SEM image of a SiO_x nanofiber bundle, as a template for the fabrication of the Mg₂Si/MgO composite nanowire bundle.

In Figure 1(a), it is observed that well-aligned CrSi nanowires were densely grown to form the bundle [13]. On the other hand, as shown in Figure 1(b), h-MoSi₂ thin layered sheets were synthesized, which are due to the layered structure of the MoS₂ starting material. It is also found that the surface of the thin layers is (0001) [14].

In addition, the bundle, which consists of Mg₂Si and MgO, is observed as shown in Figure 1(c). Even though Mg₂Si and MgO are randomly distributed, the bundle structure maintains as the SiO_x nanofiber bundle [15, 12]. As shown in Figure 1(d), it is observed that the highly oriented, well-aligned nanofibers grew in an

orderly fashion with a high density on the substrates. It has also been observed that the nanofiber is thin with about a 20 nm uniform diameter, and the nanofiber is amorphous [12]. From the experimental results mentioned above, the nanofibers are found to be amorphous SiO_x nanofibers.

Preparations of oxide nanowire arrays. Figure 2(a) shows an SEM image of the ZnO nanowire array. The diameters of the nanowires vary from 20 nm, and the maximum length extends to tens of micrometers. It is noted that small amounts of Ga or S remain in the ZnO layer. The co-existence of ZnGa_2O_4 in deeper regions of the substrate is also observed [16].

Figure 2(b) shows an SEM image of the Cu-oxide nanowires on a Cu substrate. High density nanowires with an average length of about 10 μm were observed [17].

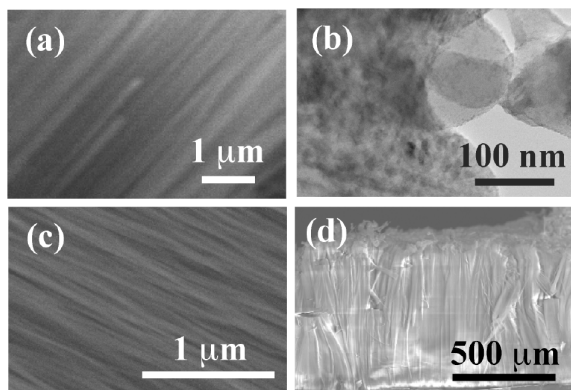


Figure 1. Nanostructured Bundles of (a) CrSi_2 Nanowires, (b) h-MoSi_2 Nanosheets and (c) $\text{Mg}_2\text{Si/MgO}$ Composite Nanowires, which are Used as a Template for the Synthesis of $\text{Mg}_2\text{Si/MgO}$ Composite Nanowires

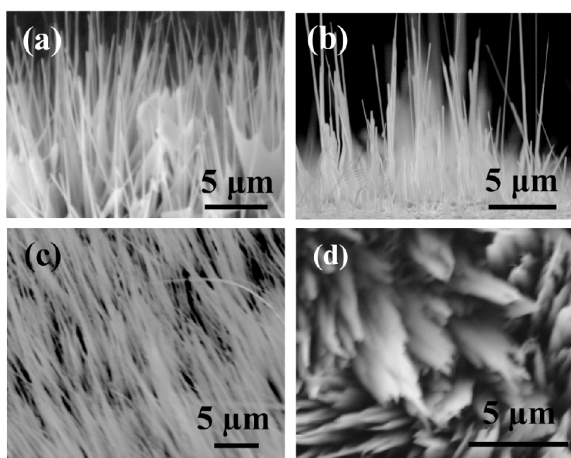


Figure 2. Arrays of (a) ZnO Nanowires, (b) CuO/Cu₂O Nanowires, (c) $\alpha\text{-Fe}_2\text{O}_3$ Nanowires and (d) $\alpha\text{-Fe}_2\text{O}_3$ Nanobelts

Figure 2(c) and (d) show SEM images of $\alpha\text{-Fe}_2\text{O}_3$ nanostructure arrays synthesized by thermal oxidation of iron substrates in the air at 973 and 1073 $^\circ\text{K}$, respectively.

The nanowires and nanobelts cover the surface of the iron substrates. Most of the nanowires and nanobelts become narrow towards the tip, and the length extends to tens of micrometers. In addition, the nanowires are generally thinner than the nanobelts. The detailed structures of the nanowires and nanobelts are described elsewhere [18].

Figure 3(a) shows an enlarged SEM image of the CuO/Cu₂O nanowires shown in Figure 2(b). It is noted that each nanowire is divided into two regions. One is the top half part of the nanowire with a diameter of about 100 nm, and the other part is the bottom half of the wires with diameters of several hundred nm. Their features are shown by the arrows in the figure. The nanowire consists of two regions: one is the top half part of the nanowire with thin CuO, and the other part is the bottom half of the wires with thicker Cu₂O. The CuO/Cu₂O interface is clearly seen at the middle part of the nanowire as shown in Figure 3(b).

Figure 4(a) and (b) show SEM and TEM images of the CrSi_2 nanowire bundle prepared for 10 min. The detailed growth temperature profile is shown elsewhere [13]. It is found that the CrSi_2 nanowires have core/shell structures.

Figure 4(c) and (d) show SEM and TEM images of the synthesized $\text{ZrO}_2/\text{SiO}_x$ core/shell nanowires. As shown in Figure 4(c), the bundle of the high density of the nanowires is observed. In addition, the core/shell nanowires with diameter ~ 50 nm are clearly shown in Figure 4(d).

In the paper, the bundle is defined as a collection of long nanowires that are highly oriented, well-aligned, dense and tied together, and have longer and higher densities than so-called arrays of wires or rods fabricated on substrates. On the other hand, the array is formed on the substrates, and nanowires in the array are well aligned, densely grown, but are clearly separated from one other, and are standing one by one. The appropriate distance is kept between them.

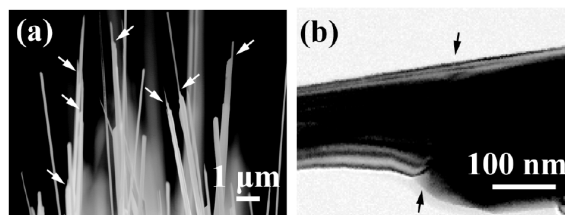


Figure 3. (a) Enlarged SEM Image of CuO/Cu₂O Nanowire Array, (b) STEM Image of CuO/Cu₂O Axial Interface

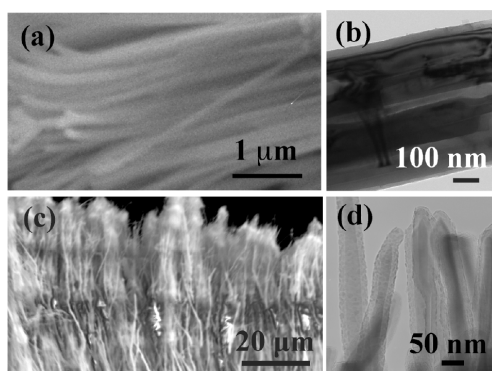


Figure 4. (a) Enlarged SEM Image of CrSi_2 Nanowire Array, (b) TEM Image of the $\text{CrSi}_2/\text{SiO}_x$ Core/Shell Structure, (c) SEM Image of $\text{ZrO}_2/\text{SiO}_x$ Nanowire Bundle and (d) TEM Image of $\text{ZrO}_2/\text{SiO}_x$ Core/Shell Structure

First, the preparations of the nano structured bundles are discussed. As shown in Figure 1, CrSi_2 silicide, $\text{Mg}_2\text{Si}/\text{MgO}$ composite nanowire bundles were successfully fabricated. According to the detailed analyses, it is found that the growth orientation of the CrSi_2 nanowire is (0001). It is considered that these dense nanowire bundles were formed by the dense distribution of SiCl_4 , which is formed by the reaction between Si and CrCl_2 . To obtain such a structure, it is important that a high density of CrCl_2 should be supplied, then CrSi_2 (0001) rods on the Si substrates formed prior to the nanowire growth. It is not difficult to synthesize a variety of nanostructured materials. However, it is not easy to fabricate the required shapes of nanostructures consisting of appropriate materials. For thermoelectric applications, the bundle structure is preferable. To fabricate a bundle structure, the distribution and reactions of catalyst particles should be considered. For the case of the synthesis of CrSi_2 nanowire bundle structures, Si atoms are supplied from the substrate, not only through the CrSi_2 rods, but also through the vapor phase as SiCl_4 . Though only the direct growth of CrSi_2 nanowire bundles is shown in the paper, it is possible that the preparation process for the direct growth of the nanowire bundles can be applied to a wide range of other silicide bundle fabrications.

In cases where the direct growth of the nanowire bundle is difficult, one alternative preparation method is the template-assisted fabrication technique. The $\text{Mg}_2\text{Si}/\text{MgO}$ composite nanowire bundles are prepared using the SiO_x nanofiber bundles. In this case, the Mg_2Si is polycrystalline with a nanoscaled domain structure, and the domains are randomly distributed and oriented in the nanowires. Another alternative bundle structure is the nanosheet bundle. In this work, the h-MoS_2 nanosheet bundle is proposed. The silicide nanosheets were fabricated using MoS_2 as a template material. The MoS_2 has a layered structure, and the replacement of Si atoms

with S sites in the hexagonal MoS_2 leads to the formation of the single phase h-MoS_2 crystals [14]. The applications of the nanostructured silicide bundles to thermoelectric generators are now under investigation.

On the other hand, Wen *et al.* reported the fabrication of the Mg_2Ge and Mg_2Si nanorods using Ge nanorod templates grown on Si substrates [19], which encourages us to fabricate further sophisticated silicide nanostructures, using well designed Si nanostructures or large scaled Si nanorods, as templates [20].

Preparations of oxide nanowire arrays are now discussed. As shown in Figure 2, ZnO , $\text{CuO}/\text{Cu}_2\text{O}$, $\alpha\text{-Fe}_2\text{O}_3$ nanowire arrays were successfully prepared. Their detailed structures were reported elsewhere [16–18]. These nanowire arrays can be formed on semiconducting or metallic substrates, which is preferable for further fabrication of solar cells or photoelectric devices. The developments of dye-sensitized, oxide solar cells and photoelectrochemical cells are now under investigation. In addition, the preparations of other oxide nanostructures, such as TiO_2 , WO_3 , MoO_3 , are also under investigation. For the case of the solar cells and photoelectrochemical cell applications, the array structure is preferable, and the nanowires are densely grown. However, there should be appropriate spaces between the wires. In this case, a two-dimensional ordered arrangement is usually not required. The oxides are fortunately appropriate for photovoltaic and photoelectrochemical cell applications.

The morphological control from the nanowire to the nanobelts is demonstrated for the case of $\alpha\text{-Fe}_2\text{O}_3$ growth. The morphological property of the nano arrays much depends on the thermal treatment condition of the oxide. In particular, it is essential to discuss the crystalline anisotropy, surface energy, defect structures, nucleation behavior at the initial stage of the growth, and the diffusion anisotropy of the constituents of the compounds during the growth. In this sense, the $\text{CuO}/\text{Cu}_2\text{O}$ axial structure was obtained by controlling conditions during growth. Oxygen deficiency during growth causes the formation of Cu_2O and $\text{CuO}/\text{Cu}_2\text{O}$ structures. It is also demonstrated that the $\text{ZrO}_2/\text{SiO}_x$ core/shell bundle structure, namely the radial heterostructure, was fabricated instead of the formation of three-dimensional alloy compounds. The results encourage us to fabricate further sophisticated nanowire structures using silicide and/or oxide. The silicide-silicide, silicide-oxide or oxide-oxide heterostructures would open development of nanoscaled-semiconductors technology.

4. Conclusions

It has been demonstrated that silicide nanowire, nanosheet bundles, and oxide nanowire arrays can be

prepared for low cost thermoelectric devices, dye-sensitized, oxide solar cells and photoelectrochemical cell applications. In this study, CrSi₂, Mg₂Si/MgO composite nanowire bundles and h-MoSi₂ nanosheet bundles were successfully prepared. In addition, ZnO, CuO/Cu₂O and α-Fe₂O₃ nanowire arrays were also fabricated successfully. A variety of novel preparation techniques are proposed to obtain the nanostructured bundles and arrays mentioned above. The results encourage us to develop the high efficient thermoelectric and photovoltaic devices.

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