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Simple Synthesis of a Variety of Nano-structures Using Silicide Alloys with Ga Droplets

K. Ogino[a], S. Honda[a], T. Yasuda[a], H. Tatsuoka[a,], T. Inaba[a], H. Kominami[b], Y. Nakanishi[b] and K. Murakami[b].

[a] Faculty of Engineering, Shizuoka University, Hamamatsu 432-8561, Japan
[b] Research Institute of Electronics, Shizuoka University, Hamamatsu 432-8011, Japan

A variety of nano-structures, such as nanofibers, nanotubes, nanocapsules, nanoribbons and nanorods, were synthesized using silicide alloys with Ga droplets. It was found that the growth morphology and the structural property of the nanostructures significantly depended on the silicides seed materials. In addition, the amorphous SiO_x nanofibers show strong ultraviolet and/or visible light emissions, and the PL spectra of the nanofibers depended on the seed materials. For some of the nanofiber syntheses, the formation of nanoflakes or nanoribbons of β-Ga_2O_3 occurs, and a variety of growth morphologies for the β-Ga_2O_3 nanostructures was obtained. The series of morphological and structural images are shown for a variety of nanostructures. The obtained SiO_x nanofibers are expected to be materials for use in cheap, abundant and safe luminescent devices for visible light applications.

Introduction

Nano-sized materials have attracted much interest due to their optical, electronic and mechanical properties compared to those of bulk materials. Nanowires and nanotubes made of various kinds of materials have been intensively synthesized. Nanowires of metallic oxides are considered to be one of several photoluminescence materials (1), and they are also expected to be used for scanning near-field optical microscopy, nanoscale connections in future integrated optical devices and low-loss optical wave guiding (2), which have interesting properties such as a tight-confinement ability, enhanced evanescent fields and large waveguide dispersions that are very promising for developing future microphotonic devices with subwavelength-width structures (3). On the other hand, nano-filters have been used in industrial and consumer filtration applications. The filter will retain not only toxic metals, but also virus and bacteria. In addition, nanofibers provide dramatic increases in the filtration efficiency with relatively small decreases in the permeability for a broad range of environments and contaminants. In addition, metal oxide nanomaterials are of tremendous interest due to their potential use in gas sensing, and as photocatalyst materials (4).

Generally, the growth of nanofibers or nanowires requires nano-sized catalysts. Recently, a simple growth procedure has been developed, namely, silica nanofibers can be grown around FeSi and β-$FeSi_2$ plates without any nano-sized catalysts, though molten Ga is used as a catalyst (5). For development of the procedure, the choice of seed materials is an important issue for the synthesis of nanostructures. Silicides are alloys consisting silicon and metal atoms, and they have been the focus for electronic materials such as contact metals, semiconductors and magnetic materials. Silicides can be

considered as seed materials for the synthesis of nano-sized structures, and would play important roles in the nanostructure preparation procedure. In this study, the synthesis of nano-structured materials, with a variety of morphologies, using silicide alloys is demonstrated. In addition, the morphological and structural properties of the nanostructures are investigated, and the detailed synthesis condition dependence of the nanostructures is shown. Moreover, the photoluminescent property is also evaluated.

Experimental

The nanostructures were synthesized by the heat treatment of silicide plates or powders with Ga droplets. The Ga was melted around 35-40 ^{o}C, then applied to the silicides by manually using a steel or wood stick. As a result, the mm size Ga droplets stick to the plates or the powders. The silicides with Ga droplets were placed in the vacuum chamber, which was then evacuated to a base pressure of 10^{-4} Torr. The nanostructure synthesis was performed by exposure of the silicides to residual O_2 for several hours at a temperature between 700 – 900 ^{o}C. Most of the nanostructures were synthesized by a heat treatment at 900 ^{o}C for 24 h.

The resultant nanostructures were observed using a scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy analyzer (EDS–SEM), and transmission electron microscopy (TEM). The photoluminescence (PL) spectrum was measured at room temperature under the excitation of He-Cd at 325nm with the spectral resolution of 0.5 nm.

Results and Discussion

Figure 1(a) shows the cross-sectional SEM micrograph of nanofibers grown on the FeSi plates by heat treatment at 900 ^{o}C for 114 h. It was observed that the highly oriented, well-aligned nanofibers grew in an orderly fashion with a high density on the plates. Figure 1(b) shows a TEM image of part of the nanofibers. The diffraction pattern of the nanofibers is also shown in the inset. It was observed that the nanofiber is thin with about a 20 nm uniform diameter. The diffraction pattern shows that the nanofiber is amorphous. The EDS analysis showed that the nanofibers mainly contain Si and O in most of the fibers, and it was found that the amorphous SiO_x nanofibers grew from the FeSi plates (1).

Figure 2 shows SEM micrographs of nanofibers synthesized using various kinds of silicides as the seed materials. It is interesting that the growth morphology of the fibers significantly depends on the silicide materials. The amorphous SiO_x nanofibers were grown around $ZrSi_2$ and $SrSi_2$ as well as when using the FeSi seed. On the other hand, crystalline β-Ga_2O_3 nanofibers were grown when using the Cu_5Si seed material. It is interesting that the Ga can be a host element to grow β-Ga_2O_3 for use as a Cu_5Si seed material.

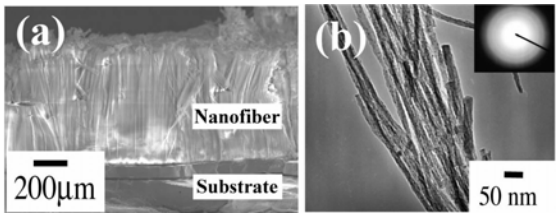

Figure 1. (a) SEM and (b) TEM images of SiO_x nanofibers synthesized at 900 ^{o}C for 114 h on the FeSi plate.

Figure 3 shows a series of TEM images of the nanostructures synthesized using various kinds of silicides as the seed materials. Figures 3(a) and (b) show the amorphous SiO_x nanotubes and nanocapsules grown using FeSi and Mg_2Si seeds, respectively. The nanotubes are observed when the FeSi is thermally treated at 700 ^oC for 20 h. On the other hand, the nanocapsules were grown when Mg_2Si is thermally treated at 700 ^oC for 20 h. The fibers with a diameter of 100 – 500 nm and a rough surface were grown using the $CoSi_2$ seed, as shown in Fig.3(c).

The surface of the fibers is smooth, but the formation of flakes or ribbons of β-Ga_2O_3 occurs when using a $CaSi_2$ seed material, as shown in Fig.3(d). Figure 3(e) shows the β-Ga_2O_3 fibers with a diameter distribution from 20 to 500 nm. Figure 3(f) shows the amorphous SiO_x nanofibers along with β-Ga_2O_3 ribbons. It is interesting that the nanostructure morphology significantly depends on the seed materials and the growth conditions.

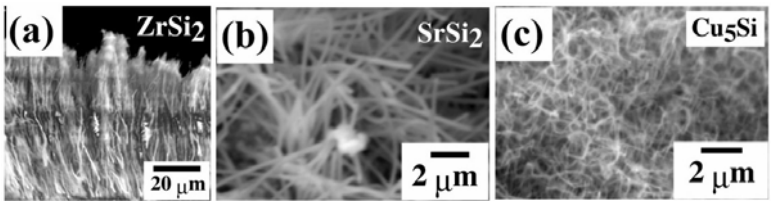

Figure 2. SEM images of nanofibers synthesized using (a) $ZrSi_2$, (b) $SrSi_2$ and (c) Cu_5Si, as the seed materials. The fibers were grown by the heat treatment at 900 ^oC for 24h.

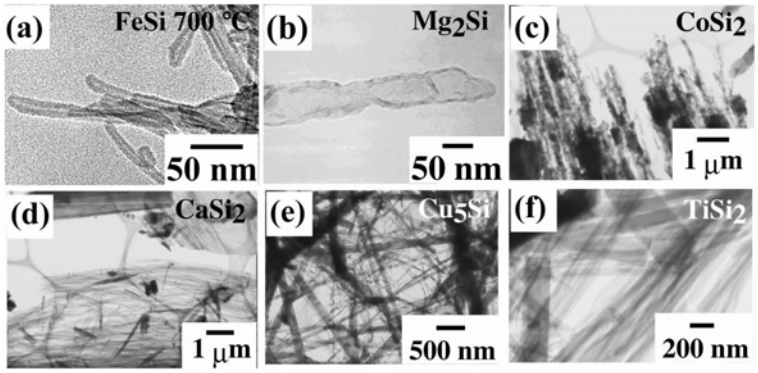

Figure 3. TEM images of a variety of nanostructures synthesized using various kinds of silicides as the seed materials.

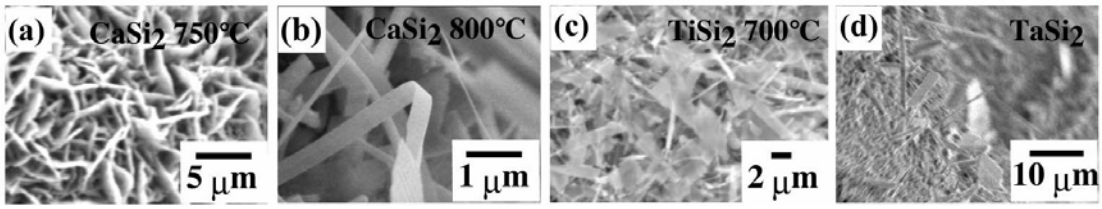

Figure 4. SEM images of a variety of β-Ga_2O_3 nanowalls, nanoribbons and nanorods, synthesized using various kinds of silicides as the seed materials.

The β-Ga_2O_3 nanostructures were selectively grown with the appropriate choice of growth conditions, as shown in Fig.4. The β-Ga_2O_3 predominantly grew at a lower treatment temperature, such as nanowalls at 750 ^oC, nanoribbons at 800 ^oC using the $CaSi_2$ seed. The flake-like β-Ga_2O_3 nanoribbons were also obtained using a $TiSi_2$ seed at the treatment temperature of 700 ^oC. In addition, β-Ga_2O_3 nanorods were grown on a $TaSi_2$ seed. It was also found that small amount of the β-Ga_2O_3 nanostructures grew, when only the Ga metal was thermally treated without any silicides. On the other hand, larger amount of β-Ga_2O_3 nanostructures was obtained when the silicides were thermally treated with the Ga metal.

It has been demonstrated that silicides are useful materials to produce a variety of nanostructures, such as nanofibers, nanotubes, nanocapsules, nanoribbons and nanorods, which are mainly amorphous SiO_x, accompanied with crystalline β-Ga_2O_3 in some cases. The growth morphology and the structural property of the nanostructures significantly depend on the silicide seeds. The growth mechanism of the nanostructures is not fully understood at this time. The constituents in the silicides are considered to react as catalysts with the Ga and residual O_2. However, the vapor-liquid-solid (VLS) growth would play an important role (6), and the phase diagram including Ga and the constituents of the silicides should be considered to clarify the growth mechanism of the nanostructures.

In addition, some of the fibers show strong ultraviolet and/or visible light emissions, and broad photoluminescence (PL) emissions from the nanofibers were observed, as shown in Fig.5. This emission is due to the oxygen vacancy as reported in ref. 7. The variety of the PL spectra from the SiO_x nanofibers has already been reported (1, 8, 9). It is interesting that just SiO_x eliminates various kinds of PL emissions when the SiO_x fibers were grown using various seed silicides and growth conditions. The PL spectra depend on the defect structure (7) and probably the impurity levels in the SiO_x nanofibers. The constituents in the silicides would cause the formation of specific defects or impurity levels in the fibers.

The variety of nanostructures obtained here could be applied to the luminescence materials, nano-scale optical guides, nanofilters, etc. Especially, silicon oxide is expected to be a candidate photoluminescence material. The obtained amorphous SiO_x nanofibers can be promising materials for use in cheap, abundant and safe luminescent devices for visible light applications.

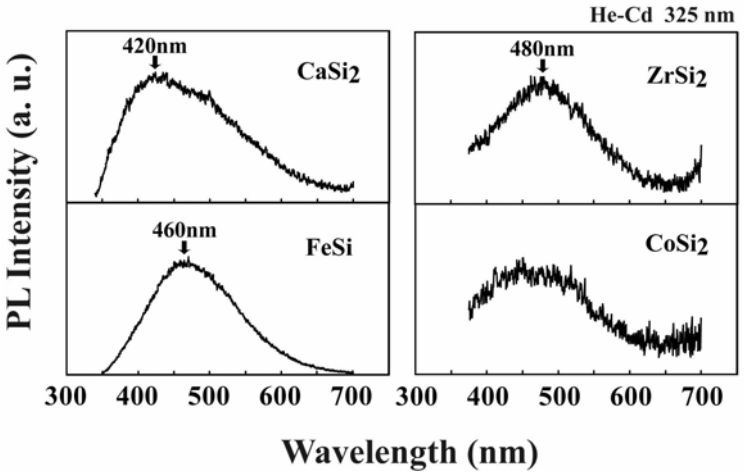

Figure 5. PL spectra of the amorphous SiO_x nanofibers grown using a variety of silicides as the seed materials.

Conclusion

It has been demonstrated that silicides are useful materials to produce a variety of nanostructures, such as nanofibers, nanotubes, nanocapsules, nanoribbons and nanorods. The growth morphology and the structural property of the nanostructures significantly depend on the silicide seeds. In addition, the amorphous SiO_x nanofibers show strong ultraviolet and/or visible light emissions, and the PL spectra of the nanofibers depend on the seed materials. It is expected that this simple growth technique allows the easy fabrication of nanostructures with various kinds of morphological, structural and optical properties. For some of the nanofiber syntheses, the formation of nanoflakes or nanoribbons of β-Ga_2O_3 occurs, and a variety of growth morphologies for the β-Ga_2O_3 nanostructures were obtained.

These results have encouraged us to fabricate a variety of nanostructures using simple growth procedures. The choice of the silicide seeds is especially important. In a series of reactions, the constitutent metals of the silicides play important roles in the synthesis of the nanostructures. The detailed control of the growth morphology and structural and optical properties of the nanostructures will be required, and further characterizations are expected for a wide range of nanostructure applications in the future.

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