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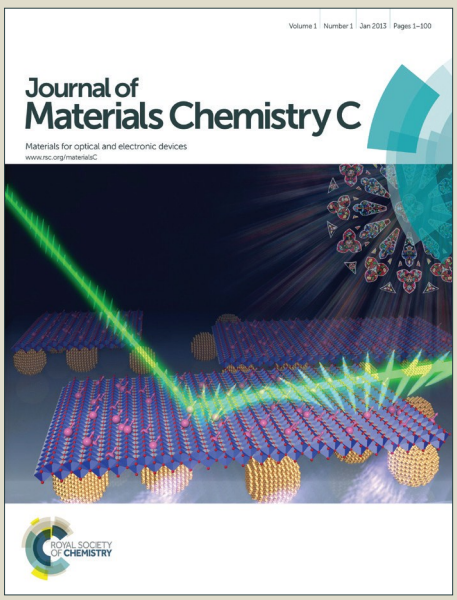

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Control of verticality and (111) orientation of In-catalyzed silicon nanowires grown by the vapour-liquid-solid mode for nanoscale device applications

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Vertically aligned silicon nanowires (Si NWs) with (111) orientation were developed using vapor-liquid-solid growth mode with control of the interface between the In nanodroplets (In NDs) and the Si substrate. We found that the contact angle of the In NDs is critical for the growth of vertically aligned Si NWs. The diameter of the Si NWs was also scaled down to 18 nm.

Recently, efficient nanoscale devices structures have been increasingly in demand because of the need to reduce device cost and enhance performance. Much effort has been devoted to the modifications of band gap by exploiting the quantum size effect through the reduction of the diameter of silicon nanowires (Si NWs).[1] In particular, nanoscale devices, such as transistors[2] and sensors[3,4], require such Si NWs to achieve enhanced characteristics. The use of vapor-liquid-solid (VLS) growth mode enables us to investigate the crystalline structures of individual NWs. In the VLS mode, growth parameters such as temperature, the introduction of dopants,[5,6] and the type[7] and size[8] of the metal catalyst particles control the density, orientation, and periodicity of the obtained nanostructures. The recent studies of the use of VLS mode for Si NW growth has invigorated the research of nanotechnology devices using various catalytic materials such as Au, In, and Zn.[8-11] Vertically aligned Si NWs have already been grown using an Au catalyst in the VLS mode.[10] However, Au is not a useful candidate material for use in solar cells and nanoscale devices that inevitably require the presence of shallow acceptor levels which can be produced by In.[12]

Even though nanoscale devices and high performance solar cells require vertically aligned and single-crystal Si NWs, simultaneous control of vertical alignment and (111) orientation were not rigorously investigated for In-catalyzed Si NWs grown by the VLS mode. Development of vertically aligned Si NWs with diameters of a few nm is essential for the harnessing of the quantum size effect in highly efficient tandem solar cells.[1,13] Kurokawa *et al.* reported, in theory, a modified band gap for Si NWs embedded in SiO_2 that can be utilized in the top cell of a tandem solar cell.[1] Conversion efficiency of over 30% can be achieved in tandem structure where a Si NWs top cell and Si heterojunction bottom cell are stacked monolithically or mechanically.[13] Reducing the diameter of Si NWs to as low as 3–4 nm and a growth of longer Si NWs are required to achieve the concept of tandem solar cells based on Si NWs.[1,13] Therefore, the control of the verticality and (111) orientation of Si NWs grown by the In-catalyzed VLS mode is necessary. In this study, the interface conditions of indium nanodroplets (In NDs) on Si substrate were primarily investigated in order to control the verticality and (111) orientation of Si NWs using the In-catalyzed VLS mode growth. The process of Si NWs growth used in this study is comparable to that used in the modern CMOS industry[14] and may make this approach practicable for fabrication of nanoscale devices.

Indium metal has a low melting point, and the eutectic temperature of the In–Si binary system is approximately 157°C.[15] The In–Si eutectic alloy exhibits a relatively low Si solubility (~10^{-4} at.% in Si) and a steep liquidus line. The liquid alloy is promptly supersaturated with Si at a wide range of temperatures (up to approximately 800°C).[10] Therefore, the In NDs can act as a facilitator for Si deposition. The high-sticking coefficient of In NDs compared to that of solid surfaces also helps to grow Si NWs from In NDs.[17] Growth of Si NWs is observed after a steady state condition of the flux of Si through the particle and the precipitation of Si on the substrate is reached.[12,16]

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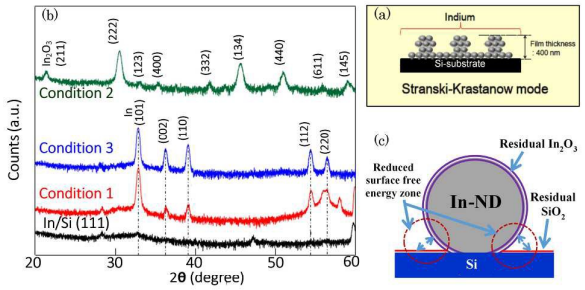

Fig. 1 (a) Stranski–Krastanow mode, (b) In-plane 2θ XRD patterns of as-deposited In NDs on Si substrate after thermal annealing at 200°C for 30 min (condition 1), after thermal annealing at 630°C for 360 min (condition 2), and In NDs after H_2 plasma treatment at 200°C for 30 min (condition 3), and (c) schematic view of cross-sectional In NDs on Si (111) substrate (relative sizes are not shown to scale).

In the first experiment, p-type Cz–Si (111) substrate (thickness: 300 µm, resistivity: 1–10 Ωcm), was cleaned using the RCA process. In NDs were deposited in a conventional thermal evaporation system using an In wire with a background pressure (P_B) of 4.4 × 10^{-4} Pa. The In NDs growth was followed by the Stranski–Krastanow (SK) mode. The SK mode is not a two-dimensional growth mode such as the film growth, but rather gives rise to islands of deposited In, as shown in Fig. 1a. After air-breaking, In NDs were thermally annealed at 630°C for 360 min in a glass tube and were then treated by a H_2 plasma at substrate temperature (T_S) of 200°C and a pressure of 10 Pa applied for 30 min using a sputtering chamber (P_B = 3.0 × 10^{-6} Pa). Finally, Si NWs were grown at T_S = 630°C and a pressure of 1 Pa applied for 30 min by a radio frequency (RF) magnetron sputtering in the same chamber without air-breaking. In the second experiment, RCA-washed p-type Cz–Si (111) substrate was loaded into the chamber (P_B = 5.0 × 10^{-6} Pa), where In NDs were deposited by RF magnetron sputtering at 3 Pa for 20 min at room temperature and were then continuously treated by a H_2 plasma in the same chamber at T_S = 600°C and pressure of 10 Pa applied for 3 min. Finally, Si NWs were grown via the VLS mode using In NDs at T_S = 600°C and a pressure of 10 Pa applied for 60 min in the same chamber without air-breaking.

To investigate the interface of In NDs and Si (111), in-plane 2θ X-ray diffraction (XRD) spectra before and after thermal annealing and after the H_2 plasma treatment were measured. The shape, density, and contact angle (θ_C) of In NDs on Si and the cross-sectional view of the Si NWs were obtained by high resolution scanning electron microscopy (HR-SEM) operated at 1–5 kV. The crystallinity and dimensions of Si NWs were observed through selected area of electron diffraction (SAED) and cross-sectional view of transmission electron microscope (TEM) operated at 200 kV.

The weak crystalline (101), (002), (110), (112), and (200) In peaks are apparent in Fig. 1b after thermal annealing at 200°C for 30 min (condition 1). After further thermal annealing in the glass tube furnace at 630°C for 360 min, typical In_2O_3 peaks, such as (222), (400), (332), (431), and (440), appeared thereby confirming the oxidization of In NDs because of air-breaking (condition 2). A schematic illustration of the oxidized In ND is presented in Fig. 1c. To reduce the oxide layer, H_2 plasma treatments were performed at T_S = 200°C for 30 min (condition 3) in the sputtering chamber and stronger crystalline peaks of In (101), (002), (110), (112), and (200) appeared again. H-radicals generated during H_2 plasma treatment were found to be effective for reactions with the metal oxide film

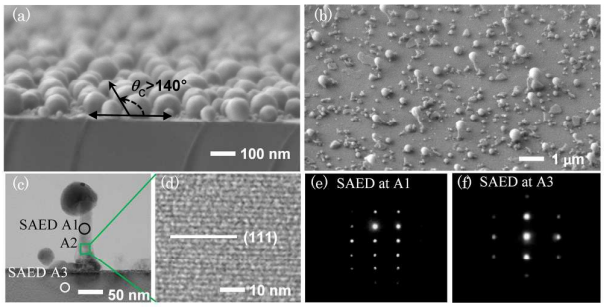

Fig. 2 (a) SEM image In NDs (by thermal evaporation), (b) SEM image of Si NWs grown at T_S = 630°C for 60 min, (c) TEM micrograph of Si NWs fabricated by In NDs, (d) HR-TEM micrograph of as-grown (111) oriented Si NWs at point "A2" of Fig. 2c, and (e)–(f) show SAED at points "A1" and "A3", respectively, of Fig. 2c.

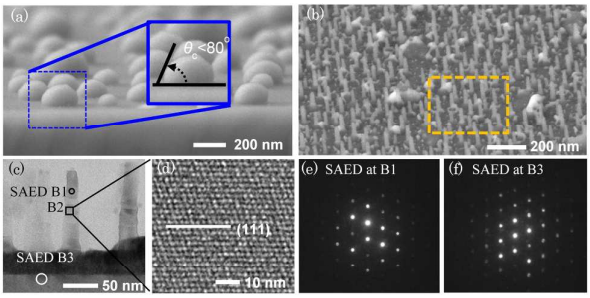

Fig. 3 (a) SEM images of In NDs grown by In sputtering, (b) SEM image of Si NWs grown at T_S = 600°C for 60 min. The magnified image in the dotted rectangular area is shown in Fig. 4b. (c) TEM micrograph of the vertically aligned Si NWs fabricated by In NDs, (d) HR-TEM micrograph of the as-grown (111) oriented Si NW taken at point "B1" of Fig. 3c, and (e)–(f) show the SAED patterns taken at points "B1" and "B3", respectively, of

on the substrate surface that form catalytic In NDs and reduce the In_2O_3 contents.[17] However, a thin In_2O_3 layer around the In NDs and an ultra-thin-oxide layer on the Si substrate may both be present, which possibly restricts the high density of the Si NWs growth as a result of the air-breaking and unavailability of a clean environment because of the presence of carbon and other impurities. The thin oxide layer around the In ND and on the substrate caused by air-breaking conditions can hinder the precipitation of Si atoms toward the Si substrate via In NDs at eutectic conditions because of the sticking coefficient of the In_2O_3 layer is smaller than that of the pure In NDs.

The interface between the In NDs and the Si substrate prior to the growth of Si NWs was investigated by HR-SEM. Fig. 2a shows that the In NDs deposited by thermal evaporation of pure In wire were spherically shaped with different sizes in the 30–100 nm range. To understand the origin of the spherical shape of In NDs (i.e., low wettability) on the Si substrate, we focused on the interactions mechanism of oxidized In NDs (In_2O_3) on the Si substrate in the context of surface free energy (E_f) and θ_C in a qualitative manner. Ricci *et al.* measured the E_f for pure In droplet and In_2O_3 at 850 K obtaining 525 mN/m and 500–520 mN/m, respectively.[17] Due to the presence of the thin oxide layer around the In ND and on the substrate caused by the air-breaking conditions, the E_f of In NDs on Si is reduced, as shown in Fig. 2a. Subsequently, the value of θ_C on Si substrate increased to 140°, as observed by HR-SEM (Fig. 2a). In this scenario, very low density and vertically aligned (111) oriented Si NWs at the supersaturation phase were grown, as shown in Fig. 2b. The TEM and SEM observations obtain variations in the diameter and length of Si NWs for 30–100 nm and 150–200 nm, respectively, as shown in Figs. 2b

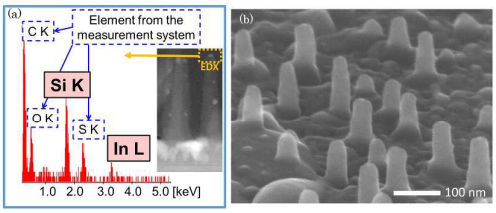

Fig. 4 (a) EDX spectra obtained from the top of Si NWs, (b) HR-SEM image of the vertically aligned and (111) oriented Si NWs.

and 2c. At the eutectic phase, the precipitation of Si atomic migration through the liquid phase of In NDs to the Si substrate is hindered by the thin oxide layer that exists around the majority of In NDs and on the Si substrate. This could not support the growth of Si NWs, and only a few Si NWs were grown, where the θ_C may be small and wettable surface contact area of the In NDs on the Si substrate may not be symmetric. The (111) oriented crystallinity at point "A2" (in Fig. 2c) was confirmed by the HR-TEM image, as shown in Fig. 2d. The SAED at points "A1" and "A3" (in Fig. 2c) corresponding to Si NWs and Si substrate, respectively, exhibit a spotty pattern, as shown in Figs. 2e and 2f, respectively, indicating that VLS growth occurred successfully for few Si NWs with a density of 2.5 μm^{-2}.

In the second experiment, we optimized the growth conditions to obtain good conditions for the interface between In NDs and the Si substrate by eliminating the oxide layer as well as further decrease the θ_C. We performed all the growth steps from In NDs growth until Si NWs growth in a relatively clean and high vacuum chamber without air-breaking. Previously, Mattila *et al.* reported that the θ_C of In on Si (111) is approximately 125° at 350°C.[18] In our second experiment, the θ_C of In NDs was found to be drastically decreased from 140° to 80°, as shown in the inset of Fig. 3a. Due to the optimized growth conditions, the In NDs on the Si substrate were hemispherically shaped with sizes in the 70–100 nm range. The increase of the E_f of In NDs because of the combined action of the H_2 plasma treatment at T_S of 600°C is confirmed, and clean growth is achieved by performing the entire growth process in the same chamber (without air-breaking). Both SEM and TEM observations confirm that the verticality of (111) oriented Si NWs was nicely controlled with a uniform top diameter and length of approximately 18 nm and 100 nm, respectively, as shown in Fig. 3b, 3c, and 4b.

The symmetric distribution of the In NDs liquid contact points on the Si substrate shown in Fig. 3a confirms that the E_f of In NDs increased because of the combined action of H_2 plasma treatment with T_S as high as 600°C and use of a clean chamber without air-breaking at 10 Pa. The cylindrically symmetric flow of the precipitated Si atoms toward the Si substrate via symmetrical In NDs contact points at a very low θ_C may cause control of the verticality of (111) oriented Si NWs, as shown in Fig. 3b. The top diameter of the vertically aligned Si NWs of approximately 18 nm is the smallest value ever achieved for the case of In-catalyzed Si NWs grown in the VLS mode. The density of the Si NWs grown at T_S = 600°C was also improved reaching to 70 μm^{-2}. The Si NWs were found to be cone shaped, as shown in Fig. 3c and 4b. This can be explained by an analogy with the similar tapering of the NWs grown by Au catalyst in the VLS mode.[19] According to Sharma *et al.*, as the NWs elongate from the In droplets, the base of the NWs remains exposed to the reactive radicals for a longer time than the newly grown upper part of NWs.[20] Further explanation about the morphological shape of In NDs and Si NWs are shown in the supplemental information. Fig. S1 explains the Neman quadrilateral relation which gives surface morphology of In NDs in term of θ_C. Fig. S2 shows the migrated In NPs from the tip of Si NWs toward the sidewall of Si NWs. The In catalyst loss can lead to a gradual reduction in the In NDs diameter during the Si NWs growth. The In-catalyst trapping by NWs could possibly give rise to the tapering of NWs[21,22] and restricted the height of NWs.

The (111) orientation of Si NWs at point "B2" (in Fig. 3c) was confirmed by the examination of HR-TEM (Fig. 3d). The SAED at point "B1" and "B3" (in Fig. 3c) of Si NWs and Si substrate, respectively, both show the spotty pattern (Figs. 3e and 3f). Fig. 4a shows the results of a compositional investigation by energy dispersive X-ray spectroscopy (EDX) taken at the top of the Si NWs shown in the inset. The Si NWs only contained a Si peak, while In was detected for the spheres. The magnified SEM image of Si NWs with a top diameter of approximately 18 nm is shown in Fig. 4b. This diameter value is quite small compared with the previously obtained vertically aligned Si NWs grown with In catalyst in the VLS mode. Although the need to decrease the tapering and increase the length of the In-catalyzed Si NWs is still an open challenge, it can be speculated that the control of the diameter of In NDs the removal of In NPs from the top of the Si NWs, and a further reduction of θ_C can further enhance the length of NWs. Because of their shallow acceptor levels and vertical alignment, In-catalyzed Si NWs may be a potential candidate material for nanoscale devices.

Conclusions

We have controlled the verticality and (111) orientation of Si NWs as well as scaled down the diameter of Si NWs to 18 nm using In-catalyzed VLS mode growth. The density of vertically aligned Si NWs was enhanced from 2.5 μm^{-2} to 70 μm^{-2}.

Notes and references

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Table of Contents Use Only

Control of verticality and (111) orientation of In-catalyzed silicon nanowires grown by vapor-liquid-solid mode for nanoscale device applications

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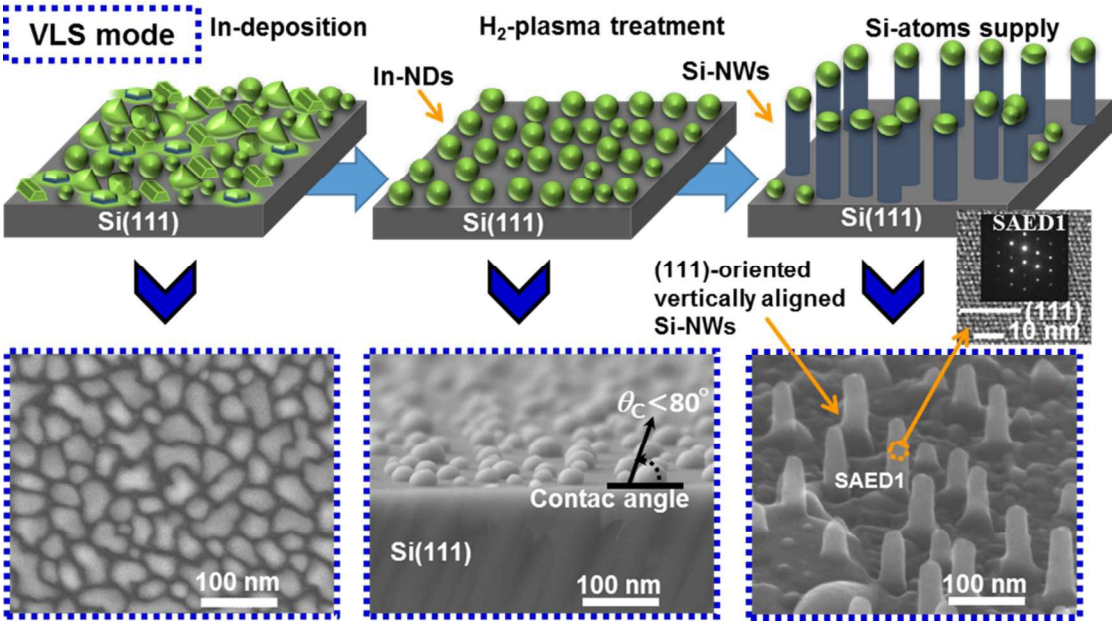

Synopsis: Decreasing of the contact angle helps to grow a vertically-aligned Si NW with a diameter of 18 nm.