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研究課題名（和文）Multi-functional Al-catalyzed Si nanowires: self-assembled zero and one-dimensional hybrid nanostructure formations

研究課題名（英文）Multi-functional Al-catalyzed Si nanowires: self-assembled zero and one-dimensional hybrid nanostructure formations

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研究成果の概要（和文）：表面処理を施した基板上への多機能Al触媒SiNW成長に成功したので報告する。まず、VLS法を用いたSiNW形成について、成長パラメータの影響を調査した。Al触媒SiNWによるソーラーセル形成では、変換効率が9%を超えた。ケミカルエッチングとポストメカニカルポリッシングを施したフレキシブル基板上に形成された薄膜SiNWソーラーセルの変換効率は5.0%以上を達成した。続いて、i-Ge/p-Siコアシェルとコアダブルシェル、それぞれのNW構造による、NWトランジスタ形成を調査した。薄膜B-doped Si中間層の形成と最外層p-SiシェルへのBドーピングにより、キャリア生成性能の向上を達成した。

研究成果の学術的意義や社会的意義
All functionalized SiNW formations together with device demonstration encourage the increased ability to widespread SiNW-based applications with low-cost materials and high throughput techniques as new alternative SiNWs and nanostructures providing for future technology.

研究成果の概要（英文）：The multi-functional aluminium (Al)-catalyzed silicon nanowire (SiNW) growths on the controlling of surface transformation were successfully performed. The effects of growth parameters on SiNW formation using a vapor-liquid-solid (VLS) mechanism were studied. The SiNW properties for photovoltaic applications were obtained extremely low light reflectance below 10 % and the Al doping concentration of less than 1019 cm-3 range. The Al-catalyzed SiNW-based solar cell fabrication was realized with an efficiency higher than 9% with complete Al catalyst removal. Thin SiNW solar cells provided by pre-chemical etch and post-mechanical polish for developing into the flexible devices were achieved the efficiency upon 5.0%. The core-shell and core-double-shell NW structures of p-Si and i-Ge were studied for NW transistor applications. The thin B-doped Si intermediate layer and B doping in the p-Si shell outermost layer successfully improved the ability of carrier generation.

研究分野：Nanomaterials science and engineering

キーワード：Nanostructures　Nanowires　Silicon　Germanium

１．研究開始当初の背景

Silicon nanowires (SiNWs) have significantly attracted attention during the last decade as building blocks for many advanced technology applications, including photovoltaics, field-effect transistors, lithium-ion batteries, and gas sensing. Vapor-liquid-solid (VLS) mechanism is well known that it can form SiNWs using the vapor phase diffusion through the liquid droplet of metal catalyst and crystalizing as solid wire when the Si concentration in the metal-Si droplet reaches a critical point. Gold (Au) has been previously used as a metal catalyst. However, applying Au-catalyzed SiNWs to electronic applications is difficult owing to the high Au concentration level which degrades the device performance. Therefore, supplying of other metal catalysts is mandatory to overcome this problem. Al is an inexpensive material, availability by various methods, suitable for VLS growth and electronic properties, etc., proposing it a great choice for using as a new catalyst to grow SiNWs in this research.

２．研究の目的

The purposes of this research are applying new challenging catalyst and low-cost materials of Al and Si with high throughput techniques of VLS growth, nanoimprinting, and colloidal lithography for hybrid nanostructure SiNWs formation. The research results are expected to not only be greatly beneficial for fundamental studies but also favorable for technology transfer to industrial manufacturing as a new alternative nanostructure providing. Utilizing of Al-catalyzed SiNW and Si/Si, Si/germanium (Ge) core-shell NW formations for electronic applications are targeted to promote from this research to solve the problematic issues of deep-level-trap from metal catalysts and increase the possibility for multi-functional device fabrications.

３．研究の方法

The mechanisms of each Al-catalyzed hybrid-nanostructure SiNW formation by the VLS process using chemical vapor deposition (CVD) relating to various growth parameters were observed. Critical catalyst thickness, substrate temperature, growth time, and gas flow rate on various NW formations were controlled. Al catalyst removal before device fabrications by chemical etching and Al concentration in SiNWs were examined. Al-catalyzed SiNW-based devices of SiNWs-based solar cells were fabricated and optimized. Research topics on doping concentration controls using B_2H_6 for Al-catalyzed SiNWs and core-shell NW structures of Si/Ge heterojunction were performed to study and enhance the core-shell NW performances for transistor application.

４．研究成果

The main results and new findings obtained from this research are described below:

(1) The vapor-liquid-solid growth using Al catalysts could successfully create array shaping single-crystalline silicon nanowires (SiNWs) as shown in Fig. 1. The SiNW solar cells fabricated by an optimized condition of the NW growth time with the resolving of metal catalyst contamination problems showed the highest power conversion efficiencies of thin SiNW solar cells upon 9.0%.

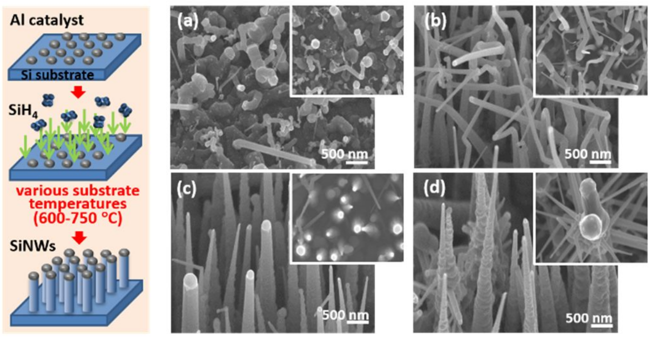

Figure 1. Schematic and 30°-tilted SEM images of Al-catalyzed SiNWs formed at various substrate temperatures of (a) 600 °C, (b) 650 °C, (c) 700 °C, and (d) 750 °C. Insets are the top view SEM images.

(2) Thin Si substrates were provided by pre-chemical etch and post-mechanical polish for decreasing low Si material consumption and developing into the flexible devices. With the SiNW formation on these wafers, the vertical Al-catalyzed SiNWs were better controlled on post-polished Si substrate and the higher NW density and smaller NW diameter were also observed. The light reflectance of both SiNWs could reduce to lower than 20% as shown in Fig. 2. The light absorbance could reach higher than 80% and the power conversion efficiencies of thin SiNW solar cells were achieved upon 5.0%.

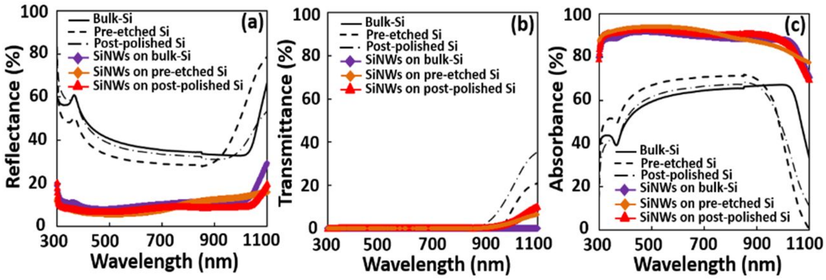

Figure. 2 (a) Light reflectance, (b) transmittance, and (c) absorbance of SiNWs on pre-etched and post-polished thin Si substrates

(3) The p-Si/i-Ge core-shell NW structures were studied for NW transistor applications. The hole gas accumulation in the i-Ge shell region induced by unintentional Al-doped p-Si core was found the limitation and difficult to further increase by adding B doping, resulting in the limit of hole gas density. Therefore, the effects of various B doping in the p-Si shell outermost layer in the p-Si/i-Ge/p-Si core-double shell NW structure on the hole gas generation were investigated as shown in Fig. 3. From the Raman measurement, the Ge optical phonon peaks of core-double shell NWs were downshifted from that of bulk-Ge to a lower value with higher B_2H_6 flow rates, indicating the Fano effect in i-Ge regions. The improvement of hole gas generation by adding of B doping in the p-Si shell outermost layer was proofed in this research.

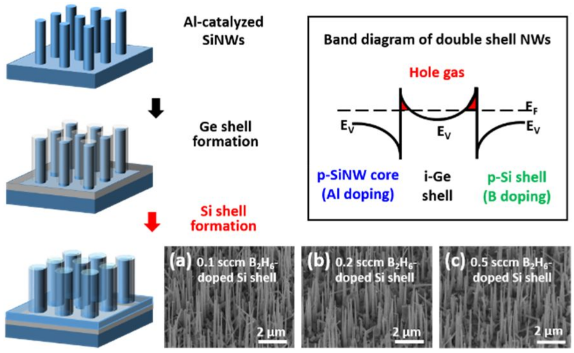

Figure. 3 Schematic, band diagram, and SEM images of Al-catalyzed SiNW/Ge/B-doped Si core-double shell formation with various B_2H_6 flow rates of (a) 0.1, (b) 0.3, and (c) 0.5 sccm in outermost Si shell.

(4) The effect of the thin B-doped Si intermediate layer with various boron (B) concentrations in this core-shell NW structure was also successfully improved the hole gas generation. The asymmetrical broadening (the Fano effect) confirmed the induced hole gas accumulation in the i-Ge shell region by Al-doped p-SiNW core and an additional B-doped Si thin layer. All Si optical phonon peaks showed a larger downshift from the value of bulk Si, corresponding to the impurity doping of Al in p-SiNW core and increase B in the thin Si intermediate layer. The improvement of hole gas density in the i-Ge shell region by adding of B doping p-Si interposition layer was demonstrated in this research.

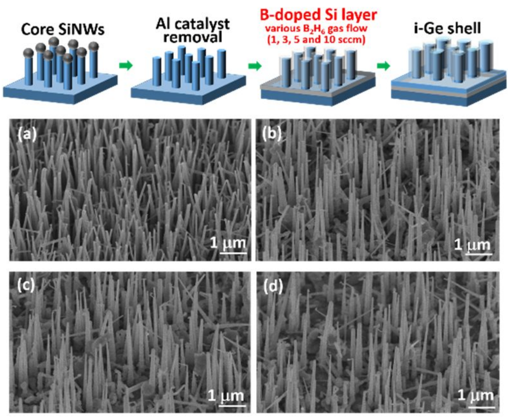

Figure. 4 Schematic of Al-catalyzed p-SiNW/i-Ge core-shell structural formation with a B-doped p-Si intermediate layer. SEM images of core-shell NWs with B-doped Si layer insertion formed various B_2H_6 flow rates of (a) 1, (b) 3, (c) 5, and (d) 10 sccm.

The results of the ex-situ Al catalyst preparation for VLS-SiNW formation using CVD technique, high-efficiency photovoltaic devices, and Al-catalyzed Si/Ge heterostructure in this research are novel, unique, and beneficial for the NW research filed. All functionalized SiNW formations together with device demonstration encourage the increased ability to widespread SiNW-based applications with low-cost materials and high throughput techniques as new alternative SiNWs and nanostructures providing for future technology.

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計10件（うち招待講演　0件／うち国際学会　6件）

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３．学会等名 MANA International Symposium 2020（国際学会）
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

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