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Hierarchical ZnO/Si nanowire arrays as an effective substrate for surface-enhanced Raman scattering application

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ABSTRACT

Hierarchical arrays of ZnO/Si nanowires were prepared through very convenient two-step solution method on silicon substrates. The tree-like nanowire structures showed high crystal quality, where well aligned Si nanowires were grown vertical to the substrate surface, whereas uniform assembly of branched ZnO nanowires was grown normal to the Si nanowires (backbones). Raman analysis indicated that among all the specimens having identical chemical compositions and dimensions but different forms (thin films or nanowires), Ag-decorated hierarchical arrays of ZnO/Si nanowires possessed the highest intensity peak in surface enhanced Raman scattering spectra. Such arrays demonstrated exceptional ability of detecting Rhodamine 6 G, limiting to a value as low as 1×10^{-8} mol/L and an enhancement factor up to 1.5×10^{4}. Both, experimental designing and band structure analysis indicated that electromagnetic effect of the localized surface plasmon resonance of Ag nanoparticles caused eight times enhancement, whereas chemical effect of hierarchical arrays of ZnO/Si nanowires played a more critical role in the high Raman sensitivity. Our results would be helpful to better understand the enhancement mechanisms and meanwhile, could be extended for further potential applications of hierarchical semiconducting nanowires.

1. Introduction

Surface-enhanced Raman scattering (SERS) has attracted worldwide research interest based on its powerful analytical abilities to trace chemicals and detect biological species, as well as instantaneous response and free of damage [1–4]. Generally, optical enhancement by localized surface plasmon resonance (LSPR) of rough metallic substrates is associated with electromagnetic enhancement, while enhancement by charge transfer between detected agents and substrates, that enhances the molecular polarizability tensor is described as chemical enhancement [5,6]. This means that the most critical issue in performing SERS experiments is either to choose or fabricate an ideal substrate [7,8]. Over the past few decades, much effort has been put forward to develop metallic (primarily Ag, Au and Pt) nanostructured substrates for SERS. The electromagnetic field, originating from such metallic nanostructures shows enhancement factor up to 10^{16}, whereas charge transfer between detected agents and substrates demonstrates chemical enhancement factor up to 10^{3} [9–11]. Nevertheless, only rough metallic surfaces or nano-particles (NPs) demonstrate well LSPR. To fabricate a substrate, which could generate such a strong electromagnetic field, is still rare. In some cases, chemical enhancement may be superior to electromagnetic enhancement. Therefore, a substrate, demonstrating both the enhancements, is highly desirable. This can be achieved via depositing noble metal NPs onto the surface of other substrates (materials), which can violently improve the sensitivity, selectivity and durability of the SERS substrates.

On the basis of charge transfer process, substrates of 3-dimensional (3D) hybrid semiconducting nanowires (NWs) could be the best candidate for SERS. Integrated junctions of two or more semiconducting NWs would maximize interfacial area and provide a suitable band gap for electron-hole separation under excitation of Raman laser. The high surface to volume ratio of NWs would supply large surface area to decorate metallic particles as hot spots and adsorb molecules. Obviously, overlapping of several bands in a hybrid substrate resulted by multiple (2 or more) 1-dimensional (1D) semiconducting NW structures would facilitate the charge transfer between substrate and

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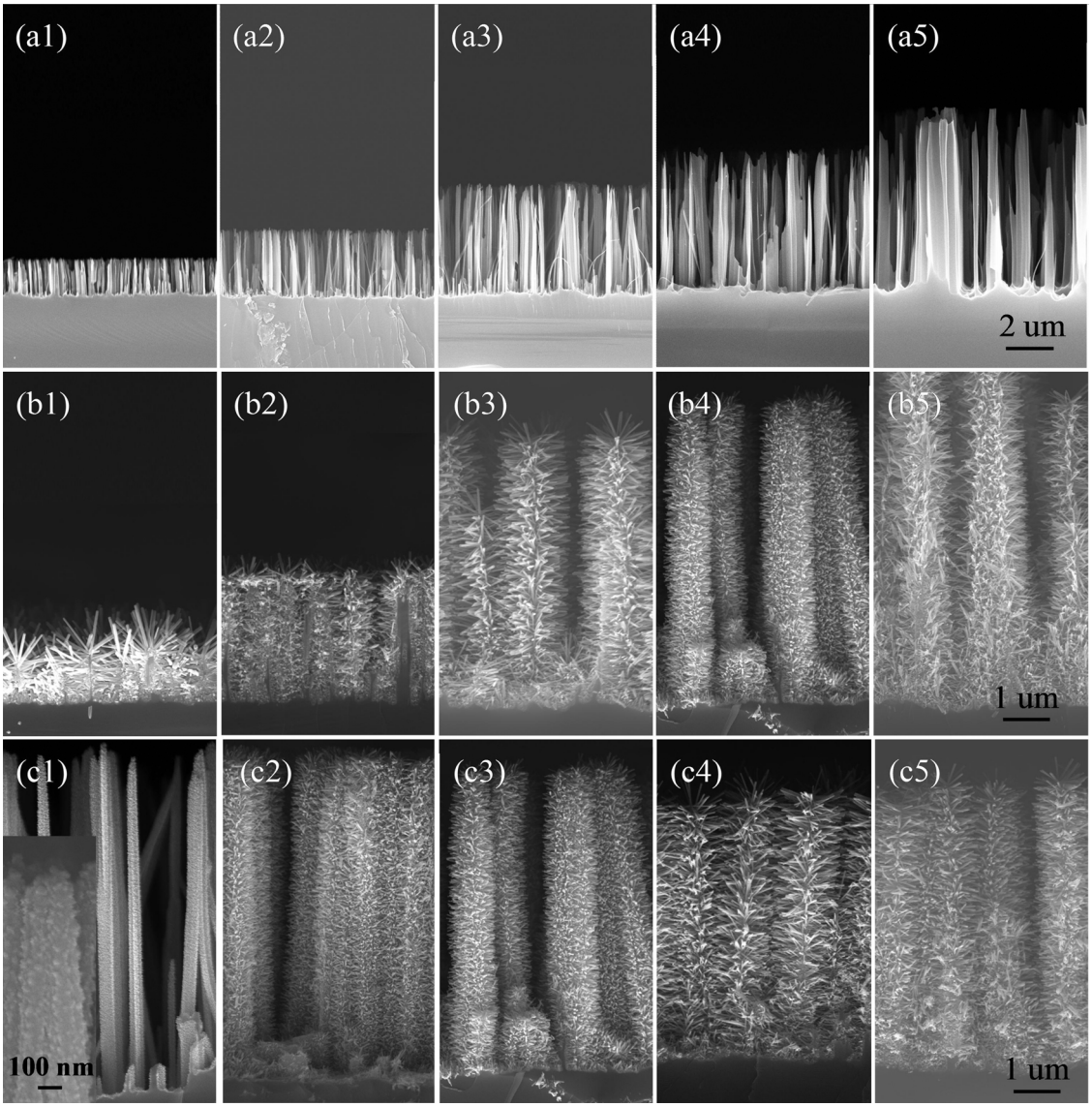

Fig. 1. Cross-sectional SEM images of Si and ZnO/Si NW arrays achieved via different growth periods: (a1–a5) Si substrates etched for 5, 10, 15, 20, and 25 min respectively; (b1–b5) Si substrates etched for 5, 10, 15, 20, and 25 min respectively thereafter hydrothermally grown for 40 min; (c1–c5) Si substrates etched for 20 min thereafter hydrothermally grown for 0, 20, 40, 60, and 80 min respectively. The inset in (c1) shows enlarged view of the seeded sample.

probing molecules. All these features together would leadenhanced SERS sensitivity and other photovoltaic applications.

By above considerations, a very convenient two-step solution method for synthesis of 3D hierarchical arrays of ZnO/Si NWs and spectroscopic detection of rhodamine 6 G (R6 G) by Raman, are presented herein. The Ag-decorated hierarchical arrays were found to be an effective substrate for SERS, which approached detection limit as low as 1×10^{-8} mol/L and showed enhancement factor up to 1.5×10^{4} in contrast to silicon substrate. The observed high Raman sensitivity was assigned to the specific features of metal decorated 3D hierarchical arrays of ZnO/Si NWs. The higher curvature effect and larger surface area of additional branched ZnO NWs with metal NPs (hot spots) and hetero-junction interfaces facilitated the separation and conduction of photo-induced charged carriers, where dominating chemical effect was observed in SERS enhancement.

2. Experimental

P-type boron-doped (100) Si wafers with a resistivity of 1–10 Ω.cm and a thickness of 450 μm were purchased from Guangwei Electronic Materials Co. Ltd (Shanghai, China). Silver nitrate ($AgNO_3$) 99.95% was ordered from the First Regent Factory (Shanghai, China). Silver (Ag) target 99.99% for magnetron sputtering was bought from Keda Coating Materials Co. Ltd (Suzhou, China). Diethyl Zinc ($Zn(C_2H_5)_2$) 99.999% for atomic layer deposition (ALD) was bought from Ke-Micro Company (Jiaxing, China). Rhodamine 6 G (R6 G) with dye content of ~95% was ordered from Sigma-Aldrich (No. R4127). Hydrofluoric acid (HF) 40%, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), and hexamethylenetetramin ($C_6H_{12}N_4$) were all bought from Xilong Chemical Co. Ltd (Guangdong, China). Distilled water (H_2O) with resistivity higher than 18.0 MΩ cm was purified by a hi-tech laboratory water purification system. All the solvents and chemicals used in the experiments were at least reagent grade and were used as received.

Hierarchical arrays of ZnO/Si NWs were fabricated by a very convenient, low-cost, and two-step solution method [12–14]. Briefly, the Si NWs were grown by metal-assisted chemical etching of Si wafers (substrates) with $HF/AgNO_3$ (4/0.02 mol/L) solution at 50 ℃, then 25 nm thick ZnO seed layer was deposited over the surfaces of Si NWs by a TALD-100-2H1R ALD from Ke-Micro Company (Jiaxing, China), finally ZnO NWs were developed by hydro-thermal growth in the