Extended Abstracts of the 2008 International Conference on Solid State Devices and Materials, Tsukuba, 2008, pp. 562-563

P-8-6

Growth mechanism of one-dimensional Nickel-Silicide Nanowires

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1. Introduction

Nickel mono-silicide (NiSi) is widely used in advanced semiconductor devices, and NiSi nanowires (NiSiNWs), as potential replacement of copper interconnect, have attracted many research interests [1-2]. NiSiNWs have been synthesized by siliciding Si nanowires or Ni-catalyzed growth with silicon source [3-5]. However, the growth mechanism of NiSiNWs is not comprehensively understood yet. In this work, we employed chemical-vapor-deposition (CVD) method to obtain single crystal NiSiNWs on nickel films with SiH_4/H_2 gases and studied the possible involvement of vapor-liquid-solid (VLS) mechanism in the early stage of nanowire growth and further growth by Ni diffusion. The effects of various process conditions on the growth of NiSiNWs are also investigated.

2. Experiment

Two types of samples were prepared to grow NiSiNWs: 20-nm-thick electron-beam-evaporated Ni films on silicon substrate (Ni/Si system) or 200-nm-thick tantalum nitride/400-nm-thick thermal oxidization SiO_2/silicon substrate (Ni/TaN system). Nanowires were synthesized in a thermal heated CVD chamber at 550°C with 3 consequent steps: heating for 3min, treatment in the flow of 1000 SCCM H_2 at 25T for 1 min, and growth with SiH_4/H_2 in the flow rate of 200:200 SCCM at 25T for 10 min. Oxygen plasma treatment on as-deposited film prior synthesis, and different synthesis temperature were also employed in our experiments.

3. Results and Discussion

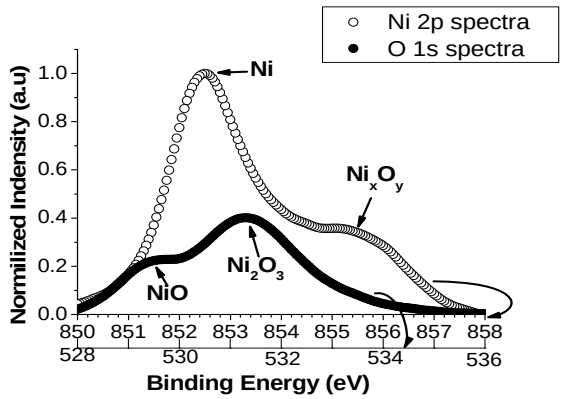

Fig. 1 XPS results of Ni 2p and O 1s spectra of Ni film deposited on silicon substrate. Secondary peak at 855.4 eV in Ni 2p spectra is traced to Ni-O binds, and O 1s spectra indicates the formation of Ni2O3 and NiO phases at 531.3 eV and 529.3 eV, respectively.

XPS analysis (Fig. 1) shows a thin layer of natural Ni-O compounds exist on the surface of as-deposited nickel film with the coexistence of Ni_2O_3 and NiO phases [6]. The low melting point of nickel sesquioxide Ni_2O_3 at ~600°C, is close to the optimum NiSiNW growth temperature at 550-600°C [4], also implies VLS mechanism may involve in nanowire synthesis since Ni_2O_3 melts, grooves to droplets, enhances Si diffusion and triggers NiSiNW growth [7].

Neither of Ni/Si systems obtains nanowires (Fig. 2(a) and (b)) after synthesis. TaN layer prevents Ni diffusing into silicon substrate and reaction between Ni and SiO_2, straight nanowires are synthesized on Ni/TaN system with SiH_4/H_2 gas (Fig. 2(c)) in the diameter of 18-28 nm. TEM shows the uniform nanowire diameter along the stem and spear-shape tip, in-situ EDS measurement presents the Ni:Si atom ratio is 0.96:1 at the tip and 0.90:1 at the stem, which agrees well with single-crystal NiSi composition. However, synthesis with H_2 only, discrete ball-like clusters agglomerate among small grains on the surface of Ni/Si systems (Fig. 2(b)), dense island-shape blisters spread over the surface of Ni/TaN systems (Fig. 2(d)) with large variation in size. O 1s XPS spectra (Fig. 3) indicate heavy concentration of NiO remains after deoxidization of Ni_2O_3 instead of $NiSi_xO_y$ (corresponding to Ni_2SiO_4 and $NiSiO_3$) compounds.

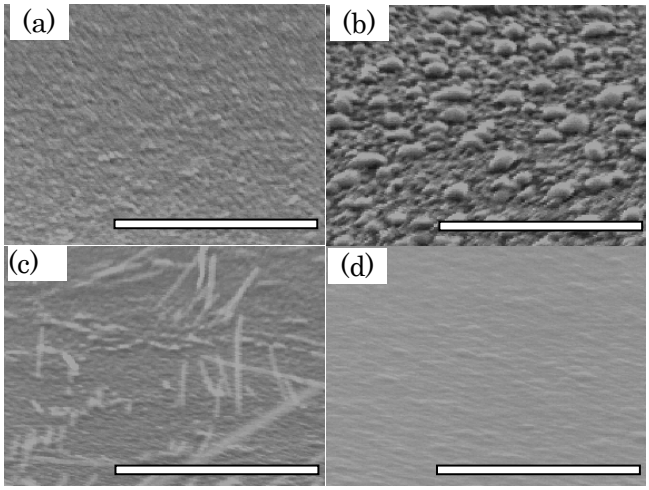

Fig. 2 SEM images (scale bar: 1 μm) of Ni film on silicon after synthesis process with (a) SiH_4 and H_2 gases, and (b) H_2 gas only, and Ni film deposited on $TaN/SiO_2/Si$ substrate after synthesis process with (c) SiH_4 and H_2 gases, and (d) H_2 gas only.

Oxygen plasma treatment is introduced to create thick layer of nickel oxide; oxygen plasma also increase surface temperature due to ion bombardment, and clear agglomeration phenomenon are exhibited (Fig. 4(a)). Subsequently, massive clusters formed greatly influence NiSiNW growth (Fig. 4(b)) and degrade the clearness of SEM image. None

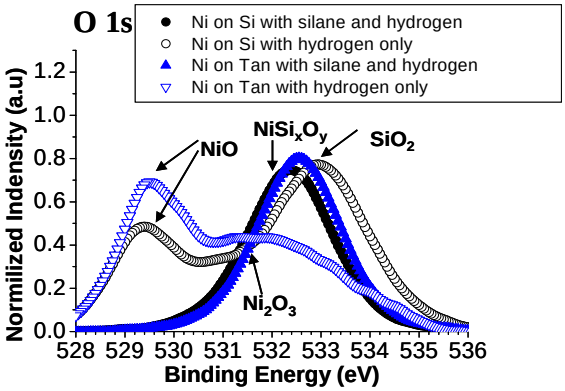

Fig. 3 XPS of O 1s spectra after synthesis nickel films on Si or TaN. With H_2 gas only, heavy NiO phases exist on surface layer, Ni_2O_3 remains with reduced concentration, and without $NiSi_xO_y$ compounds for Ni/TaN system.

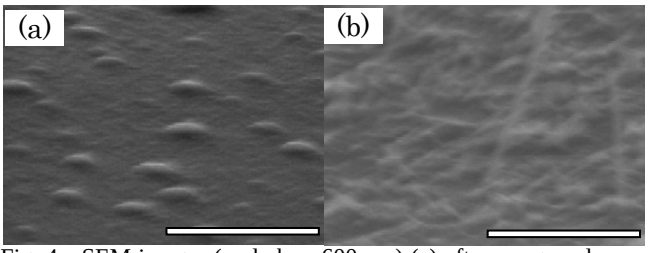

Fig. 4 SEM images (scale bar: 600 nm) (a) after oxygen plasma treatment on Ni film deposited on $TaN/SiO_2/Si$ substrate, and (b) after synthesis process with SiH_4 and H_2 gases on Ni film deposited on $TaN/SiO_2/Si$ substrate with oxygen plasma treatment.

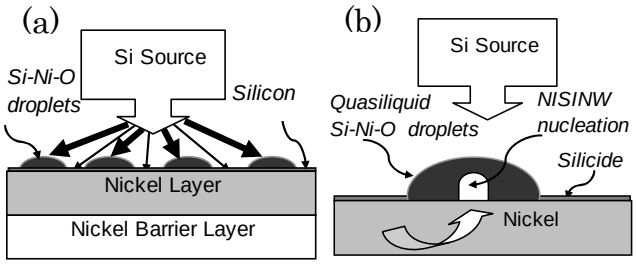

Fig. 5 Schematic illustrations of (a) Si-Ni-O droplet agglomeration, and (b) NiSiNWs initial growth.

of nanowire is found at open area without any clusters covered, the longer nanowires are observed at relatively small clusters, while short and thick nanowires or sprouts are located at relatively large clusters. It should be noted that the diameters of NiSi nanowires are ranging between 17-27 nm, similar to those without oxygen treatment, as shown in Fig. 2(c). As depicted in Fig. 5(a), surface nickel oxides forms Si-Ni-O droplets after heating and provide rich silicon to nickel cubic structure, initial nucleation sites of NiSiNWs [3], and trigger nanowire growth with the aid of nickel diffusion (Fig. 5(b)) [4].

Ni-catalyzed NiSiNWs exhibit relatively consistent diameters regardless of the size of particular cluster or process conditions at a fixed temperature. While, as temperature increase to 575ºC and 600ºC, the diameters apparently increase to 35-55 nm and 93 nm, respectively. The Arrhenius plot exhibits the natural logarithm of diameter is linearly proportional to the reciprocal of synthesis temperature, and the NiSiNW formation activation energy is calculated to be 1.72 eV. Thus the diameters of nanowires are tunable within temperature window.

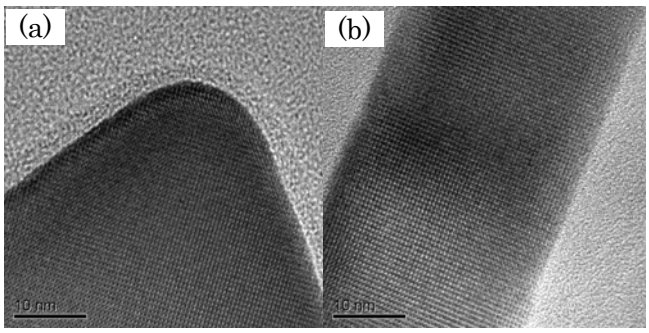

Fig. 6 TEM results of NiSiNW grown at 575 °C: (a) tip of nanowire, and (b) stem of the nanowire.

As shown in Fig. 6, tip and stem of nanowires grown at 575°C possess single crystal structures, and EDS analysis on a stem indicates a SiO_2 shell surrounding the single crystal NiSi core. One of lattice spacing is measured at 0.57nm along growing axis with 0.53nm of lattice spacing at the direction perpendicular to growing axis. These lattice spacing are very close to the parameters (a=0.5233nm, b=0.3258nm, c=0.5659nm) of NiSi orthorhombic unit cell under normal conditions [8].

4. Conclusions

We synthesized NiSiNWs on electro-beam-evaporated Ni films with SiH_4/H_2 gases in a CVD chamber, and studied the growth mechanism of NiSiNWs. Results show that NiO and Ni_2O_3 phases coexist on nickel surface and agglomerate after heating, and the initial growth of NiSiNWs is triggered by the Ni_2O_3 with the aid of nickel diffusion is proposed. It is also found that the diameter of NiSiNWs is mainly controlled by the synthesis temperature with activation energy of 1.72 eV.

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