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Diffusion suppression in vapor–liquid–solid Si nanowire growth by a barrier layer between the Au catalyst and substrate

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ABSTRACT

Nanowires have attracted significant interest because of their unique characteristics. Vapor–liquid–solid (VLS) growth is the standard method for fabricating nanowires and Au is the most commonly used catalyst. However, Au catalyst droplets diffuse over the Si substrate surface with a high migration velocity and agglomerate at relatively low temperatures. In our previous work, we reported a significant improvement in the positioning and diameter distribution of VLS-grown Si nanowires by inserting a diffusion barrier layer and concluded that the barrier layer suppressed the formation of AuSi eutectic droplets and prevented the droplets diffusing on the substrate surface during nucleation. In the present study, we analyzed the nucleation of the Au catalyst and examined its behavior during nucleation. Detailed multidirectional analysis and in situ observations confirmed that the formation and agglomeration of AuSi eutectic droplets was suppressed by the formation of a silicide layer. This because of the higher reaction temperatures between the diffusion barrier and the substrate silicon, and between the catalyst and the diffusion barrier, compared with the reaction between the Au catalyst and substrate silicon.

1. Introduction

Nanowires have unique characteristics that are expected to enable advances in scaled-down electronics and thus are promising building blocks for next-generation devices. Vapor–liquid–solid (VLS)-growth is a standard method for fabricating nanowires [1] and its growth kinetics, physical properties [2–7], and applications [8–10] have been extensively investigated.

In conventional VLS, the growth conditions are limited by the growth material and catalyst and the method by which the growth material is supplied. A temperature above the eutectic temperature, which is determined from the phase diagram of the catalyst and growth material, is required. Furthermore, for CVD growth, a higher temperature is needed to crack the precursor, depending on the precursor type. The catalyst and substrate can form a eutectic phase, even during the nucleation step, depending on the choice of material. The formation of a eutectic phase before growth begins can hinder uniform nanowire growth through the agglomeration of the catalyst.

Au is a widely used catalyst for the VLS growth of Si and Ge nanowires because it forms eutectic droplets at relatively low temperatures over a wide range of semiconductor compositions [11]. Nanowires can be grown in a chosen direction by placing an Au catalyst directly on the Si substrate [3–7]. The driving force of the growth depends on the difference in chemical potential between the eutectic droplet and substrate, and the chemical potential of substrate varies with its orientation. This directed growth is desirable for shape control; however, Au diffuses over the Si surface and agglomerates [12], which can reduce the uniformity of the eutectic droplets. Generally, the diameter of the eutectic droplets determines that of the nanowires. Thus, reducing the uniformity of the eutectic droplet size distribution may make the nanowire diameters non-uniform, which is undesirable for practical applications. Furthermore, the direct contact between Au and the Si substrate may degrade the electrical device performance because of an increase in electrical noise arising from deep-level traps formed in depletion regions [13,14].

We have previously investigated improving the control of nanowire growth and the spatial separation of Au from the Si substrate by inserting a Ti or Ni diffusion barrier layer between the Au catalyst and Si substrate [15]. Our method substantially improved the positioning and diameter distribution of the VLS-grown nanowires.

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We confirmed that a silicide layer was formed between the nanowire and substrate, and suggested that the silicide layer suppressed the agglomeration of Au on the Si surface by spatial separation. Furthermore, we proposed that the silicide layer functioned as a crystalloid seed layer and produced vertical nanowire growth, even though the Au catalyst was initially separated from the Si substrate by the diffusion barrier layer. Our experimental results agreed well with this explanation; however, we did not obtain direct evidence of the mechanism.

In this study, we investigated the nucleation step during nanowire growth and the nucleation step on its own. Furthermore, we used in situ scanning electron microscopy (SEM) while increasing the temperature to examine the behavior of the catalyst and diffusion barrier layer during nucleation.

2. Experimental

Electron-beam patterned samples and unpatterned samples were prepared. In the electron-beam patterned samples, hole-shaped electron-beam resist patterns (diameter: 40–70 nm; pitch: 150–300 nm) were formed by electron-beam lithography (ELS-7700, Elionix Inc.) on an RCA-cleaned Si(1 1 1) substrate. The samples were placed in an electron-beam evaporation deposition system (EBX-2000C, ULVAC). A Ti or Ni diffusion barrier layer (3 nm) was deposited, and then the Au catalyst layer (7 nm) was deposited. For the reference sample, there was no diffusion barrier layer and the catalyst was deposited directly on the Si substrate. The electron-beam resist was removed by the conventional lift-off process to form a disk-shaped catalyst pattern on the diffusion barrier layer (on the Si substrate in the reference sample).

To evaluate nanowire growth, the electron-beam patterned samples were placed in a conventional low-pressure chemical vapor deposition (LPCVD) reactor (LPD-1200, SUMCO). Nanowires were grown by the VLS method. The growth conditions in the nucleation step were 500 °C, 13 min, and 2 Torr He; and in the growth step they were 500 °C, 40 min, and 2 Torr SiH_4/He with a partial SiH_4 pressure of 0.066 Torr. To evaluate nucleation, the electron-beam patterned samples were placed in an LPCVD reactor and annealed at 500 °C and 2 Torr He for 13 min.

The shape and morphology of the nanowire samples were observed by SEM (S-5500, Hitachi). Elemental analysis was performed by energy-dispersive X-ray spectroscopy (EDS; Helios Nanolab 600, FEI). The cross-sectional structure was observed by transmission electron microscopy (TEM; Tecnai F30ST, FEI) with an accelerating voltage of 300 kV. The cross sections for TEM were prepared with a focused ion beam system (Helios Nanolab 600, FEI).

Real-time observation was performed by in situ SEM (Quanta, FEI) with unpatterned samples under a controlled temperature and atmosphere. A high vacuum of 1×10^{-6} Torr or less was used instead of 2 Torr He, which was the actual atmosphere during the nucleation step due to equipment limitations.

3. Results and discussion

3.1. Configuration evaluation

Representative SEM images of the electron-beam patterned (diameter, 50 nm; pitch, 150 nm) samples after VLS nanowire growth are shown in Fig. 1. As we previously reported [15], the nanowire distributions are narrower for Au/Ti (average, 50.26 nm; standard deviation (SD), 3.26 nm) and Au/Ni (average, 47.99 nm; SD, 4.56 nm) compared with Au (average, 52.77 nm; SD, 8.15 nm). This indicates that the surface diffusion of Au and the ensuing agglomeration are suppressed by the Ti or Ni diffusion barrier.

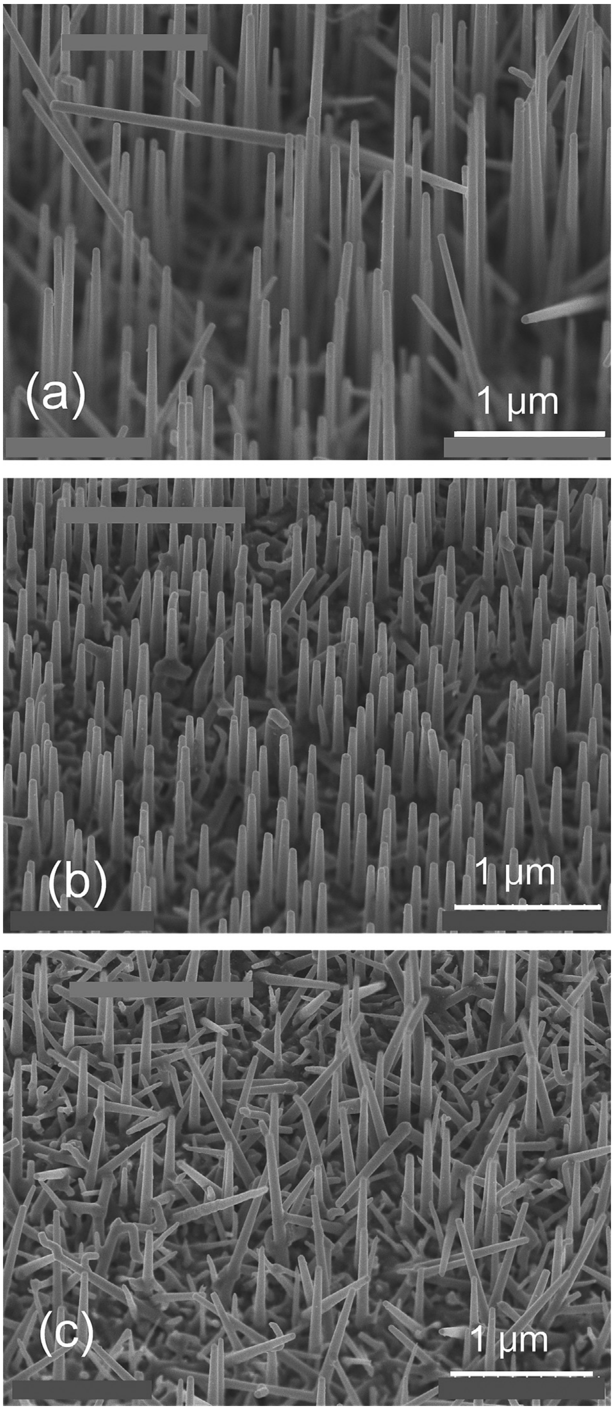

Fig. 1. SEM observation image at a 30° tilt of nanowires grown by VLS from (a) Au only, (b) Au/Ti, (c) Au/Ni patterns with a diameter of 50 nm and a pitch of 150 nm.

Fig. 2 shows the low magnification SEM images of the Au, Au/Ti, and Au/Ni samples after VLS nanowire growth. In the Au-only sample, agglomerated particles were visible outside the electron-beam patterned region (lower right, 4 × 4 rectangle, Fig. 2(a)), whereas they were not in the Au/Ti and Au/Ni samples (Fig. 2(b) and (c), respectively). The EDS spectra confirmed that the agglomerated particles consisted of Au (data not shown). These results indicate that Au in direct contact with the Si substrate may diffuse and move around the surface at a speed of several micrometers per minute.