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Analysis of Structure and Orientation of Vertical Germanium Single Crystal Nanowires on Silicon Substrates

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1. Introduction

The science of one dimensional single crystal growth has made tremendous improvements since its first demonstration in 1964 [1-4]. There exist many techniques to synthesize nanowires, some of which are the solvo-thermal process [5], laser ablation [6] and chemical vapor deposition [3, 4] (CVD). We have used the CVD technique of growth in our work, which is prevalent in semiconductor manufacturing. Our CVD chamber used for synthesizing germanium nanowires is a cold-wall reactor with lamp heating for rapid thermal cycles. We employ the Vapor-Liquid-Solid (VLS) mechanism of growth in the synthesis of our nanowires using germane (GeH_4) diluted in hydrogen (H_2) as the precursor. In this paper, we report on the orientation and crystallographic quality of vertical germanium nanowires grown epitaxially on <111> silicon substrates. These properties are important for nanowires so that they can be implemented with high density in advanced electronic and photonic integrated circuits.

2. Orientation control of nanowires

Orientation control of the nanowires was obtained by catalyst deposition on hydrogen terminated silicon substrates followed by nanowire growth at 315°C. To obtain epitaxial growth of nanowires, the samples were cleaned with 4:1 H_2SO_4:H_2O_2 to remove the organic contamination, 5:1:1 H_2O:H_2O_2:HCl to remove any metal contamination and then treated with 50:1 HF to remove the oxide resulting in a hydrogen terminated surface. The H-terminated surface was immediately deposited with 3 nm of gold by e-beam evaporation.

The nanowires obtained from this process on <111> silicon are shown in the plan view SEM picture in Fig. 1a which shows a strong degree of order, significantly better than prior samples grown on thermal oxide. The ordering of the nanowires was also confirmed by a cross section SEM shown in Fig. 1b, which shows a high yield ordered vertical nanowire growth. Some slanted nanowires were also observed and are due to the growth of the nanowires from the silicon <111> facets that get exposed during the treatment of the silicon surface with hydrofluoric acid. Some samples have shown more slanted nanowire growth than vertical growth and we believe that by obtaining atomically flat surfaces we can control growth along the preferred <111> direction. Significant amount of taper is visible for the wires, which we attribute to coherent sidewall deposition of germanium during simultaneous axial VLS growth. For this method of catalyst deposition, the nanowire diameter also varies from wire-to-wire because the catalyst diameter is dictated by wetting of the deposited gold film on the HF-last silicon substrate. On increasing the partial pressure of germane to 1.8 torr long slender vertical wires were obtained as shown in Fig. 2a. Fig. 2b shows the heteroepitaxial growth of germanium nanowires obtained on silicon <100> substrates which also shows a strong degree of ordering. The epitaxial nanowire growth relationships in the <100> silicon substrate case are obviously complex and will be discussed at length elsewhere.

3. TEM Analysis

The TEM images of the vertical nanowires shown in Fig. 3 confirm that these nanowires grow epitaxially in the <111> direction, consistent with the orientation of the underlying silicon <111> substrate. Interplanar spacings observed in the re-solidified metal catalyst particles are consistent with those of pure Au. The interfaces between the re-solidified catalyst and nanowire tip appear atomically abrupt and relatively flat. The catalyst particle size is often observed to be larger than the nanowire diameter at the tip. By measuring the lattice spacing from high resolution TEM pictures in Fig. 3a and 3d it is concluded that the vertical nanowires were growing epitaxially in the <111> direction. A schematic illustration of the atomic positions in a local region of the high resolution image is shown in Fig. 3c. Also, the selected area electron diffraction pattern obtained from an isolated vertical nanowire (Fig. 3b) is consistent with the <111> growth direction. Because of limited contrast difference between germanium oxide and the glue in which the nanowires were surrounded during TEM specimen preparation, we are not able to estimate the thickness of the native oxide present on the nanowires from these images.

Weak beam dark field images were taken from the vertical <111> wires in an attempt to search for possible dislocations. Except under special tilt conditions, dislocation imaging is difficult in high resolution TEM. Weak beam dark field contrast is particularly sensitive to the strain field in the vicinity of a dislocation core. Dark field images were formed using weak beams corresponding to several different diffraction vectors. Representative images are shown in Fig. 4. If dislocations are present in a cubic crystal such as germanium it should produce a weak beam contrast if the dot product of the diffraction vector and the Burgers vector is non-zero. None of our results obtained to date from these vertical epitaxial nanowires suggest the presence of dislocations. Particular effort was made to find evidence of per-

fect dislocations with ½ <110>, and none were found. These results are encouraging from the perspective of device applications of vertical germanium <111> nanowires. However, due to specimen preparation difficulties, we have not yet performed a systematic study of nanowire regions near the silicon substrate surface. Therefore, we cannot yet conclude that the entire nanowire length is dislocation-free.

4. Conclusions

In conclusion we have reported and demonstrated our ability to control the orientation and crystal growth direction of nanowires. The vertical nanowires are found to be defect free and hetero-epitaxial in nature through TEM analysis. We believe that low temperature, vertical epitaxial nanowire growth has advantages for realizing nanowire based circuitry and devices and in harnessing the high packing density of these semiconducting nanostructures for 3D integration, ultra high density memory or computing.

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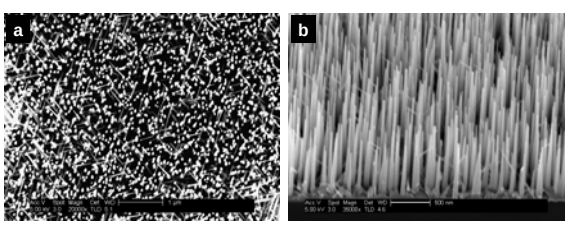


Fig. 1: a) Cross-section and b) Plan view SEM of epitaxial nanowires grown at 315°C, 30 torr total pressure and 0.27 torr of GeH_4 showing highly degree of order.

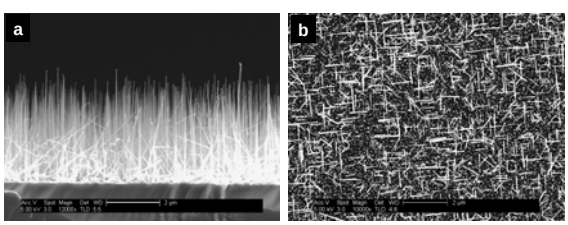


Fig. 2: Nanowires grown at 315°C, 18 torr total pressure and 1.8 torr of GeH_4. a) Cross-section SEM of vertical heteroepitaxial nanowire growth on Si <111> b) Plan view SEM of heteroepitaxial growth on Si <100>.

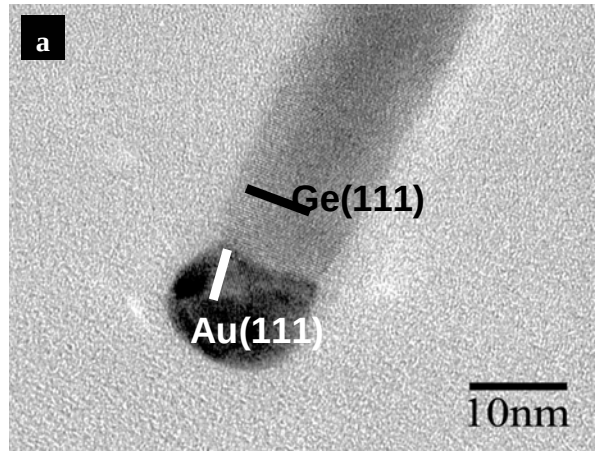


Fig. 3a: High resolution TEM of nanowires in Fig. 1. a)

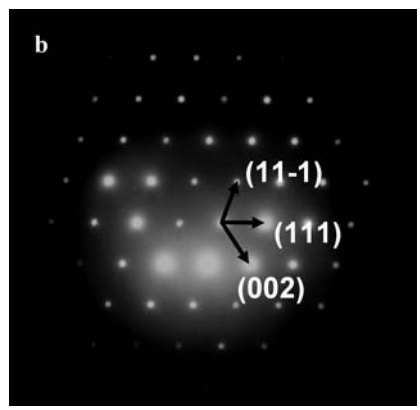


Fig. 3b: Selected area electron diffraction pattern.

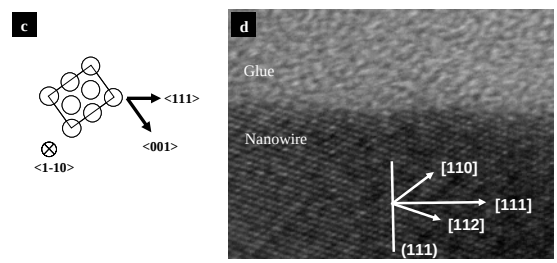
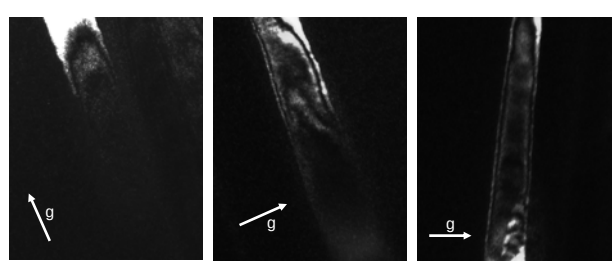


Fig. 3: c) Schematic illustration of atomic positions
d) High resolution TEM image



g=(111) reflection g=(110) reflection g=(110) reflection

Fig. 4: Weak beam Dark Field TEM images of vertical epitaxial germanium nanowires showing absence of screw dislocation and defects.