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Investigation of Au and In as solvents for the growth of silicon nanowires on Si(1 1 1)

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Abstract

This paper reports on the bahavior of Au and In as solvents for the growth of silicon nanowires on a Si(1 1 1) substrate via vapor–liquid–solid (VLS) mechanism. Gold is the mostly used solvent for growing silicon nanowires but in the present work indium was also applied, as it may bring some advantages for later electronic application of the wires.

The main focus of this work is the behavior of gold and indium on a silicon substrate but also the different morphologies and distributions of the grown wires are compared.

Individual metal droplets have been located in pre-structured nanopores to serve as starting points for wire growth. The method used to exactly position the metal droplets and thus obtain a regular arrangement of nanowires is also presented.

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1. Introduction

Nanowire-based devices are of great interest in diverse areas ranging from electronics, optoelectronics and sensor components to biotechnology [1–3]. Among different fabrication methods for nanowires, chemical vapor deposition (CVD) and physical vapor deposition (PVD) are the most widely applied. The experimental conditions depend not only on the growth method but also on the chosen nanowire material [4–6]. Common aim of all approaches is a perfect control of wire growth by experimental parameters and a possibility to position the nanowires which is essential for most of the applications.

In this work, the investigation of Au and In as solvents for the growth of silicon nanowires on Si(1 1 1) via PVD by means of the well-known vapor–liquid–solid (VLS) mechanism will be presented. Silicon nanowires are mostly grown from gold droplets. It is still a controversial issue how gold is incorporated into the wire and thus how it influences the electronic properties of the wire. Gold is a deep-level defect in bulk silicon and if this is also true for nanowires grown from gold droplets, an alternative metal for the growth would be necessary. For this reason, apart from gold we also tried indium as solvent for the growth.

2. Experimental

In all our experiments, Si(1 1 1) substrates were initially cleaned by an RCA standard process [7] in order to remove organic contaminations. The substrate was dipped into an HF (40%, w/v):H_2O solution at a ratio of 1:5 to remove the native oxide from the silicon surface before inserting it into the ultra-high vacuum (UHV) chamber where the growth process took place. The nanowire growth procedure consisted of three steps: the first one was the desorption of residual oxide at a substrate temperature of 850 °C, the second one was metal evaporation from an effusion cell at a substrate temperature of 550 °C in order to form droplets on the substrate, and the last step was the evaporation of silicon at the same substrate temperature and at a rate of

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about 0.5 Å/s which was accomplished by means of an electron beam evaporator.

The pre-structuring of substrates was performed by focused ion beam (FIB) treatment with 30 kV Ga$^+$ ions. Distances, widths and depths of nanopores could be set up by adjusting blank time, current and dwell time of the ion beam.

3. Results and discussion

The indium droplet distribution on the substrate before silicon evaporation appeared to be very inhomogeneous when a desorption step had been carried out (Fig. 1). Large droplets with diameters of about 10–20 μm and with density of about 600 mm^{-2}, as well as many tiny indium deposits of sizes below 100 nm, located in the free space between the larger droplets, were observed. When the desorption step was omitted, the distribution was seen to be much more homogeneous with droplet diameters of about 200 nm and density of about 7.7×10^6 mm^{-2} (Fig. 2).

The gold distribution after a desorption step was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements (Fig. 3). Again, different sizes of droplets were detected. The larger ones had diameters of about 100 nm and a density of about 1.5×10^6 mm^{-2}, which can be seen in the SEM image.

But in contrast to the indium experiments, the distribution of gold droplets did not change when skipping the desorption step.

Zakharov et al. [8] also found an inhomogeneous distribution of gold droplets in the range between 10 and 300 nm under comparable experimental conditions.

To explain differences in droplet formation between indium and gold, we will consider in the following the effects of different diffusion coefficients of gold and indium on silicon, the solubility of substrate atoms in the two metals, the surface tension of gold and indium and the surface energy of silicon and silicon oxide.

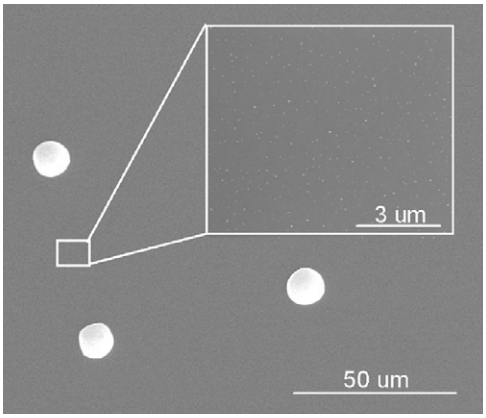

Fig. 1. SEM image of the indium droplet distribution after a desorption step had been carried out.

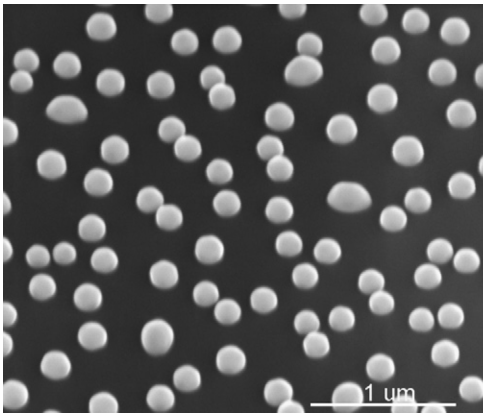

Fig. 2. SEM image of the indium droplet distribution when the desorption step had been skipped.

The diffusion coefficients at temperatures around 550 °C for indium and gold on a clean Si(1 1 1) surface are 0.30 and 0.12 m^2/s, respectively [9,10]. They are of the same order of magnitude and thus cannot account for our very different experimental results.

We believe that a thin oxide layer forms during insertion of the sample into the UHV chamber in spite of the preceding HF-dip. There are hints in the literature [11] that deposition of gold onto a thin layer of SiO_2 on Si(1 1 1) favors the decomposition of SiO_2, i.e. that gold contributes to cleaning the surface. This could explain why the gold distribution is the same with or without desorption step.

Unfortunately, no literature data about the enhancement of decomposition of a silicon oxide layer by indium were found. From the phase diagrams In–Si and Au–Si (Fig. 4), it can be seen that the solubilities of silicon in gold and indium at our growth temperatures are >20 and <1 mol%, respectively. It could be argued that also the solubilities of SiO_x in gold and indium are significantly different and thus that indium does not enhance the decomposition of an oxide layer. If this is actually the case, the indium distribution will then depend on whether a desorption step has been applied or not.

Let us consider now the role of surface tension and surface energy of the different components of our experiment. From the phase diagram Au–Si, we expect to have a liquid Au–Si alloy at our growth temperatures with a silicon concentration of about 25 mol%. For this concentration, Naidich et al. [12] found a surface tension of about 1.0 J/m^2 at 1500 °C. No data could be found in the literature for the surface tension of indium–silicon alloys. However, as the solubility of silicon in indium at our growth temperature is less than 1 mol%, we take the surface tension of pure indium as an approximation which is 0.6 J/m^2 at its melting point (157 °C) [13]. As the surface tension of most liquids decreases in a nearly linear fashion with increasing temperature [14], there is a wide difference between the surface tension of the Au–Si alloy and the In–Si alloy at our growth temperatures.