GaAs nanowire and crystallite growth on amorphous substrate from metalorganic precursors

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GaAs nanowires and crystallites were grown by metalorganic chemical vapour deposition from the metalorganic precursors on amorphous silica obtained by thermal oxidation of 111 plane Si. The samples were characterized by scanning electron microscope, transmission electron microscope and energy dispersive X-ray spectroscopy. It was found that crystalline GaAs structures form without mechanism of crystal lattice copying from metalorganic precursors.

KEYWORDS: GaAs, nanowire, MOCVD

Nanowires (or nanowhiskers) have been grown already for five decades. Interest in fundamental properties of one dimensional material systems and industrial efforts to miniaturize optics and electronics devices have been driving this field forward. GaAs nanowires have been grown by different methods such as molecular beam epitaxy (MBE),1 metalorganic vapor phase epitaxy (MOVPE),2,3 chemical beam epitaxy (CBE),4 magnetron sputtering deposition,5,6 laser ablation,7 plasma ablation,8 and reactive ion etching.9 In the case of MOVPE metal catalyst (Au, Cu or Ag),10 self-catalyst,1 template (Al pattern for Au evaporation),11 and selective area12–14 growth techniques have been used. GaAs nanowires have been grown on various substrates like GaAs,13 Si,14 Si coated with SiO2.1,15 It has been believed (except the paper of Verheijen et al.15) that crystalline lattice of the substrate is copied by the nanowire during growth, even in the case when the crystal lattice was several nanometers under SiO2 layer.1 Here we describe nanowire growth on amorphous SiO2 films (thermal SiO2 and SiO2 coated TEM grids).

The substrates were thermally oxidized SiO2 of thickness of 378nm on 111 Si wafer and SiO2 coated Ni mesh TEM grid on which nanocrystallites and GaAs nanowires were grown in a lamp heated reactor by MOCVD method. In most cases both words MOCVD and MOVPE mean the same. In epitaxy (i.e. vapour phase epitaxy (VPE)) according to the definition the crystal lattice of substrate is copied. The deposition (i.e. chemical vapour deposition (CVD)) is not restricted to crystalline substrate by definition and was chosen as a name of growth in this article. Initially Ga was condensed on the substrate by introducing a flow of 8 - 30 sccm of trimethylgallium (TMG) to the reactor for 5 - 15 s at the temperature of 500 - 700 °C. GaAs nanowires were grown at the growth temperature of 480 °C and the time of growth was 2-3 min. During growth the flows were 8 sccm for TMG and 70 sccm for tertiarybutylarsine (TBA) with 5000 sccm H2 as the carrier gas.

Transmission electron microscopy (TEM) characterization confirmed the crystalline structure of the nanowires (Figs. 1,2). By changed growth conditions because of thinness of TEM grids, large ratio of diameters between nanowire and crystallite were achieved (several hundreds nanometers of crystallite to 7nm of nanowire) providing flexibility of nanowire with respect to crystallite. Movements of the nanowire relatively to the crystallite were observed during TEM characterization. Chemical analysis with energy dispersive X-ray spectroscopy (EDX) confirmed two compositions: one close to 1:1 of

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GaAs in atomic percent ratio and As-rich composition with an atomic ratio close to 1:5 of Ga:As. It can be assumed that former is related to crystalline structures and latter to amorphous coating formed due to TBA excess during the growth.

Scanning electron microscopy (SEM) characterization revealed crystallites with nanowires. The size of crystallites depends proportionally on the TMG flow, temperature and time given for droplet formation. GaAs nanowire growth was performed after changing flows and growth temperature as described in the experimental part. A droplet was formed on top of the nanowire. At certain growth conditions bulky layer forms instead of thin rare nanowires (Fig. 3).

Usually nanowire growth is explained accordingly to the theory of vapor phase epitaxy starting from proposed vapor-liquid-solid mechanism published already in 1964 for growth temperatures above the melting point of the catalyst. Later vapor-solid-solid mechanism was proposed for nanowire formation with catalyst particles below their melting temperatures. The same theories were also used for explaining metal catalyzed GaAs nanowire growth by laser ablation and MBE. Nevertheless the term ‘self-assembled’ growth appeared in scientific literature despite the use of crystalline substrates. Most valuable are the results when TEM is used to observe nanowire formation. E.g., Stach et al. observed GaN nanowire growth in situ with TEM. Nevertheless the details of crystalline material formation directly from organic precursors on non-crystalline surfaces have not been published yet. Stach et al. used crystalline c-plane sapphire as a substrate instead of amorphous material.

Growth of GaAs nanowires has been investigated thoroughly by many authors previously. Possibility of ‘self-catalysis’ from metalorganic precursors was mentioned already in the first article on the growth of nanowires by Wagner and Ellis, eliminating other possibilities of nanowire formation and making reference to metal catalyst particles. GaAs nanowires were grown by ‘self-catalyst’ on GaAs substrates for several decades. Recently 5nm of SiO$_2$ deposited on 111B GaAs was used as a substrate. Growth was explained by the VLS mechanism in which GaAs crystal lattice is copied through SiO$_2$. Verheijen et al. used a 500 nm thick SiO$_2$ layer as a substrate for the GaAs nanowire growth and Au catalyst particles, which are crystalline. The possibility to form a nanowires with continuous growth from metal surfaces was shown by us previously, thus it was not pure growth on amorphous material. Besides they did not comment the role of the substrate and treat Au as catalyst particles.

Our results obviously imply that nanowire formation mechanism is more fundamental than copying crystal lattice of the substrate. Catalyst VLS or VSS explanation also is not applicable here. ‘Self-assembly’ can be used as a definition of the growth mechanism. Obviously this fascinating formation of ‘order’ and ‘bonds’ formation can be explained only by fundamental theoretical studies. In VLS/VSS mechanism it was stated that one dimensional growth is more preferable thermodynamically and controlled by catalyst particle. Preferability of one directional growth of nanowire over the two dimensional (2D) growth has not been solved for oxide substrate.

In addition other methods and materials were used to make crystalline nanowires without presence of crystalline substrate. CdS nanowires were deposited from solution by solvothermal method. Oxide nanowires can be grown on amorphous substrates by heating and evaporation of precursor oxide powders, i.e. work by Oh et al. Our studies on thermally oxidized silica show nanowires with exceptional diameter and shape. At certain growth conditions the nanowires can be as large as several hundreds of nanometers in diameter and could be extended to 2D growth.

To conclude GaAs crystallizes from metalorganic precursors as GaAs nanocrystallites and consequently nanowires without any crystalline substrate in vicinity. Results have potential application for easy nanowire scratching from substrate without damage after the growth, instead of ‘contact printing’. From technological point of view it saves expensive substrates, can be used for 2D layer formation on oxides or other amorphous substrates by MOCVD.

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