

Synopsis

Si nanowires have potential applications in a variety of technologies such as micro and nanoelectronics, sensors, electrodes and photovoltaic applications due to their size and specific surface area. Au particle-assisted vapour-liquid-solid or VLS growth method remains the dominant process for Si nanowire growth. A comprehensive kinetic model that addresses all experimental observations and provides a physico-chemical model of the VLS growth method is thus essential. The work done as part of this research is divided into two sections.

A steady state kinetic model was first developed for the steady state growth rate of Si nanowires using SiCl_4 and SiH_4 as precursors. The steady state refers to a balance between the rates of injection and ejection of Si into the Au droplet. This balance results in a steady state supersaturation under which wire growth proceeds. In particular evaporation and reverse reaction of Si from the Au droplet and modes of crystal growth for wire growth have been considered in detail for the first time. The model is able to account for both, the radius independent and radius dependent growth rates reported in the literature. It also shows that the radius dependence previously attributed to purely thermodynamic considerations could also as well be explained just by steady state kinetics alone. Expressions have been derived for the steady state growth rate that require the desolvation energy, activation energy for precursor dissociation and supersaturation prevalent in the particle as inputs for calculation.

In order to evaluate this model the incubation and growth of Si nanowires were studied on sapphire substrates in an indigenously built automated MOCVD reactor. Sapphire was chosen as the substrate, as opposed to Si which is commonly used, so as to ensure that the vapour phase is the only source of Si. A classical incubation period for nucleation, of the order of 4-8 minutes, was experimentally observed for the first time.

Using the change in this incubation period with temperature a value of $15kT$ was determined to be the desolvation energy for growth using SiH_4 . The steady state growth rate of Si nanowires were measured and compared with the predictions of the model using the values of activation energies so determined.

The thesis based on the current research work is organized as follows:

Chapter 1 introduces the research area followed by a brief outline of the overall work

Chapter 2 provides a summary of current literature, and puts the research described in this thesis in perspective. The diameter dependent growth rate of NWs which was initially solely attributed to the Gibbs-Thomson effect is first summarized. Experimental observations to the contrary are then highlighted. These contradictions provided the incentive for the research described in this thesis. Following a summary of the growth rate theories, the experimental observations on incubation available in the literature are summarized. All the other variants of the VLS method are also discussed.

Chapter 3 describes the design, construction and working of an indigenously built semi- automated CVD reactor. This CVD reactor was used to conduct the Si NW growth experiments over sapphire substrates.

Chapter 4 develops the physical chemistry model for Au catalyzed Si nanowire growth using SiCl_4 and SiH_4 precursors. The model originated from the contradictions present in the literature over the rate limiting step of the VLS growth mechanism and the steady state growth rate dependence on wire diameter. The development starts with explaining the thermodynamics of the steady state VLS process. The significance of the model lies in the detailed analysis of the all the atomistic process occurring during the VLS growth. In particular the evaporation and reverse reaction of Si from Au-Si droplet is explained in detail and possibly for the first time. Expressions for steady state growth rate by various modes, such as layer by layer growth (LL), by multilayer growth (ML) and growth by movement of a rough interface at the L-S growth interface are derived and presented.

Chapter 5 discusses the results which emerge out the kinetic model from the previous chapter. Under a single framework of equations, the model is successful in explaining both the diameter independent and diameter dependent growth of NWs. As one of the major outcomes of the model, the growth rates of Si NWs are predicted and trends in growth rate are found to agree with those experimentally observed. Growth rate dependencies on pressure and temperature are implicitly included in the equations derived. An estimate of supersaturation has been extracted for the first time using the framework of equations.

Chapter 6 contains the experimental results of the Si NW growth over sapphire substrates. An incubation period in the order of 3-8 minutes has been observed for Si NW growth on sapphire. The data has been compared with existing literature data and interpreted using classical transient nucleation theory. The incubation period data has been utilized to extract the kinetic parameter, Q_D , which is the desolvation energy. These parameters and the measured steady state growth rates have been used to estimate the supersaturation existing in the droplet using the framework developed in chapters 4 and 5.

Chapter 7 summarizes the outcome of the current research and highlights the future directions for the research problem addressed in this thesis.