Nucleation-limited composition of Al$_{1-x}$In$_x$As nanowires

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Abstract. Despite the great advances in synthesis of III-V ternary nanowires over the past decade, there is a lack of understanding and detailed information about Al$_{1-x}$In$_x$As nanowire growth. Recently, we have developed an analytical approach for understanding the composition of ternary nanowires nucleating from a quaternary liquid melt. Herein, we use our model to describe the formation of Al$_{1-x}$In$_x$As nanowires and tuning their composition within the nucleation-limited regime of nanowire growth via the vapor-liquid-solid mechanism. In particular, we examine the influence of growth temperature and the total concentrations of group III elements on the liquid–solid composition dependence. The obtained results may be useful for Al$_{1-x}$In$_x$As nanowire growth.

1. Introduction

III-V semiconductor nanowires are an exciting class of nanoscale objects whose properties are of considerable interest: they have high crystalline quality and exhibit high optical absorption, superior carrier mobility, a tunable narrow bandgap and flexibility of band alignments. A combination of unique properties provides promising prospects for use in nanotechnology with a variety of potential applications including optoelectronic, biotechnology and energy harvesting applications. However, commercialization of nanowire-based devices requires tuning of the chemical composition, since it determines the physical properties of the structure. A method for precisely controlling the composition of ternary nanowires could enable almost unlimited bandgap engineering. Among nanowires of different III$_x$V$_{1-x}$ semiconductor materials, only a few investigations have been carried out on Al$_{1-x}$In$_x$As nanowires [1,2]. Nanowires were grown via the so-called vapor-liquid-solid mechanism [3,4]. In such a case, catalyst droplets (Au droplets [1]) collect semiconductor material from the surrounding vapor and play the role of favorable nucleation sites by lowering supersaturation required for nanowire growth. Thus, the process involves nucleation and growth of a ternary compound from a quaternary (Al-In-As-Au) liquid melt. Composition control of ternary nanowires remains challenging due to the complexity of the growth process and the fact that interactions take place in heterogeneous catalysts. In this contribution we present a theoretical investigation of Al$_{1-x}$In$_x$As nanowire synthesis based on our previous model [5], with the aim to provide avenues for accelerating the development and implementation of applications based on Al$_{1-x}$In$_x$As nanowires.

2. Theoretical model

Within the analytical model, we consider the formation of a ternary nucleus of Al$_{1-x}$In$_x$As from a quaternary liquid drop consisting of Al, In, As, Au. We calculate the chemical potential difference, which is the driving force for nanowire growth. The resulting model is derived from thermodynamic...
considerations and based on the two-component nucleation theory, and it allows us to describe the nucleation- limited vapor-liquid-solid growth of ternary nanowires. Ternary and composition-dependent binary interactions are taken into account during the calculations. Finally, we find the solid composition as a function of the liquid composition for the Al-In-As-Au system. All details can be found in [5].

3. Results and discussion
We start the investigation of the nucleation of Al\textsubscript{1-x}In\textsubscript{x}As nanowires from a quaternary Al–In–As–Au alloy with the analysis of liquid-solid composition dependencies \( y(x) \) for different growth temperatures. The values of binary and ternary interaction parameters and Gibbs free energies can be found in [5]. The pseudobinary interaction parameter equals \( \theta_{\text{AlAs-InAs}} = 9171.2 \) Joule [1]. Figure 1 shows the liquid droplet composition versus the Al\textsubscript{1-x}In\textsubscript{x}As solid composition for growth temperatures from 350°C to 700°C at fixed total concentrations of group III elements \( c_{\text{In}} + c_{\text{Al}} = 0.5 \) and an As concentration \( c_{\text{As}} = 0.02 \). It is seen that the compositional control of Al\textsubscript{1-x}In\textsubscript{x}As nanowires over the entire range is possible at all presented growth temperatures. This can be explained by the fact that temperatures which are relevant for Al\textsubscript{1-x}In\textsubscript{x}As nanowire growth are higher than the critical temperature of the system under which the miscibility gap appears (\( T = 278°C \) [6]). However, the slope of the \( y(x) \) curve changes only for \( y > 0.995 \), which indicates that very high \( y \) values are needed in order to tune the composition of Al\textsubscript{1-x}In\textsubscript{x}As NWs. Moreover, this effect is amplified with decreasing temperature.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Analytical calculations for the liquid–solid composition dependence for different temperatures at \( c_{\text{In}} + c_{\text{Al}} = 0.5 \) and \( c_{\text{As}} = 0.02 \).}
\end{figure}

Next, we analyze liquid-solid composition dependencies \( y(x) \) for different total concentrations of group III elements at fixed growth temperatures. In particular, such analysis makes it possible to compare Au-catalyzed and self-catalyzed growth of ternary nanowires [5]. The relationship between the solid and liquid compositions at \( T = 500 \) °C and \( c_{\text{As}} = 0.02 \) for total concentrations of group III elements \( c_{\text{In}} + c_{\text{Al}} \) from 0.3 to 0.7 is presented in figure 2. It can be seen that an increase in the total
concentrations of group III elements shifts the liquid-solid dependence up, hampering compositional tuning of Al$_{1-x}$In$_x$As nanowires. In other words, a small variation in the liquid composition leads to a significant change in the solid composition.

![Analytical calculations for the liquid–solid composition dependence](image)

**Figure 2.** Analytical calculations for the liquid–solid composition dependence for different total concentrations of group III elements at $T = 500^\circ$C and $c_{As} = 0.02$.

The curve that separates the homogeneous solid solution from the miscibility gap region is presented in figure 3. We use expression (1) to calculate the binodal line corresponding to the boundary at which two distinct phases may coexist. The spinodal line, in turn, is defined by the condition that the second derivative of Gibbs free energy is zero can be found from expression (2). It should be noted that we use only the first Redlich-Kister polynomial parameter and ignore the composition-dependent parameters. Accounting for the second Redlich-Kister polynomial parameter leads to an asymmetrical shape of binodal and spinodal. However, the composition-dependent pseudobinary interaction parameter has a small value, so expressions (1) and (2) can be used. Thus, according to our model, the miscibility gap region disappears at $T = 553^\circ$C, while the experimental value equals $T = 554^\circ$C [6]. Moreover, the critical composition where the binodal and spinodal meet is in the center [6].

$$T_b = \frac{2\omega_x(1-2x)}{R \ln(x/(1-x))},$$

$$T_s = \frac{2\omega_x(1-x)}{R}.$$  \hspace{1cm} (1)

Here, $T$ is the growth temperature ($b$ for binodal and $s$ for spinodal), $R$ is the gas constant and $x$ is the solid composition.
Figure 3. Binodal and spinodal lines calculated for ternary Al$_{1-x}$In$_x$As compounds.

4. Conclusion
In summary, we have calculated the nucleation-limited compositions of ternary Al$_{1-x}$In$_x$As nanowires that form from quaternary alloys with gold. The results of this study show that the composition of Al$_{1-x}$In$_x$As nanowires can be controlled over a wide range by tuning the composition of the catalyst droplet and temperature because of a low value of the pseudobinary interaction parameter. Special attention is paid to the influence of the growth temperature and the total concentrations of group III elements on the liquid-solid composition dependence. The obtained results may be useful for Al$_{1-x}$In$_x$As nanowire growth.

Acknowledgement
EDL and JJ gratefully acknowledge the financial support from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant 722176 (project acronym INDEED). VGD thanks the Ministry of Education and Science of the Russian Federation for financial support under grant 14.587.21.0040 (project ID RFMEFI58717X0040).

References
[1] Pentin I V, Schon J C and Jansen M 2010 Phys. Chem. Chem. Phys. 12 8491-8499
[2] Haapamaki C M, Baugh J and LaPierre R R 2012 J. of Cryst. Growth 354 11-15
[3] Jabeen F, Grillo V, Rubini S and Martelli F 2008 Nanotechnology 19 275711
[4] Colombo C, Spirkoska D, Frimmer M, Abstreiter G and A Fontcuberta i Morral 2008 Phys. Rev. B 77 155326
[5] Leshchenko E D, Ghasemi M, Dubrovskii V G and Johansson J 2018 CrystEngComm 20 1649
[6] Panish M B and Ilegems M 1972 Prog. Solid State Chem. 7 39-83