A statistical model for synthesis of bandgap graded nanostructure

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Abstract. Bandgap graded nanostructure has lots of potential applications in fields such as multicolor display, nanoscale light source and photovoltaic devices. Thus, their productivity improvement has always been a critical problem. Here we proposed a statistic model to describe the bandgap graded CdSSe nanostructure growth process, which would enable the prediction and control of the yield. The model investigated the relation between the productivity of CdSSe nanostructure and the vapor-liquid-solid (VLS) growth conditions, including temperature, pressure and distance from the heating zoom. The model would help to reduce the uncertainty in nanostructure growth process and realize robust synthesis of bandgap graded nanostructure.

1. Introduction

Bandgap graded nanomaterial has promising applications in multicolor nanolaser, high-efficiency photovoltaic devices and wearable display devices. In this work, we proposed a statistical model for the growth ratio of bandgap graded CdS\textsubscript{1-x}Se\textsubscript{x} nanostructure. As x continuously increase from 0 (pure CdS) to 1 (pure CdSe), the bandgap of nanostructure will change from 2.44 eV to 1.74 eV [1], while the corresponding fluorescent spectrum changes from 509 nm to 714 nm, covering a wide range of visible spectrum.

Owing to lattice mismatch, the bandgap graded nanostructure suffers from a much lower production than traditional semiconductor nanostructures. Besides, two types of source material are needed for synthesis of bandgap graded nanostructure, inducing more uncertainties in the growth process. Thus, it’s necessary to propose a growth model to precisely control and increase the production of the growth process of bandgap graded nanostructures.

A lot of modeling work has been done about growth of traditional nanostructure, but there is still no report on bandgap graded nanomaterial. Three methods are commonly used for modeling of nanoscience, that is, physical model, statistical model and physical-statistical model [2-6]. As there are still no relative research on the growth mechanism of bandgap graded nanostructure, physical or physical-statistical modeling method is not appropriate for its growth process [7-10]. In recent years, some statistical model has been proposed to predict the synthesis process of traditional single composition nanostructure [11-15]. Shafiei S (2007) applied the method of DoE and polynomial fitting...
in analyzing the effect of six variables on the diameter of ZnO nanowire [16]. Dasgupta T(2008) used generalized linear model (GLM) to fit the relationship between the proportion of three nanostructures and three growth conditions [17]. Similar work was done by Ebrahimi N (2012) using Bayesian method [18].

We precisely controlled the growth temperature, pressure and distance of the substrates as variables, and designed a series of experiments to investigate the bandgap graded nanostructure growth process. We applied a GLM to fit the data, then built a statistical model to predict the proportion of each bandgap graded nanostructure (nanobelt, nanowire) in the total nanostructure under certain circumstance. The probability of obtaining each nanostructure is expressed as a function of those three variables.

2. Experiment

We used source-moving vapor-liquid-solid (VLS) method to synthesis the CdSSe bandgap graded nanostructure [19]. The experimental setup is schematically shown in figure 1.

1.0 g CdS powder and 0.2 g CdSe powder were used for the experiment series. As is shown in figure 1, CdS and CdSe were separately placed in two boats. Boat with CdS was placed in the middle of heating zoom of furnace inside the quartz tube. Boat with CdSe was placed in the upstream of the quartz tube without being heated. 10 silicon substrate coated with gold of 2 nm were put on a quartz sheet in line, and the distance between each substrate was 8 mm. The quartz sheet was placed in the downstream of the tube.

We precisely controlled the pressure in the quartz tube to the preset parameter, and pumped nitrogen as protect gas with flux of 180 sccm. Then we heated the furnace to the preset temperature in 18 minutes, and held it for 40 minutes to synthesis the CdS nanostructure. After that, we use a step motor to push the CdSe boat into the heating zoom with speed of 1 cm/min to fabricate the bandgap graded nanostructure. As the CdSe boat was pushed into the center heating area, the CdSe composition continuously increased in the vapor. We held this process for 20 minutes. The vapor would cool down and crystallize on the silicon substrate, forming the bandgap graded nanostructure. Then we waited for the free cooling of the device.

We observed the nanostructure under optical microscope. When emitted with laser of 405 nm, fluorescence wavelength of CdS$_{1-x}$Se$_x$ will change from ~500 nm to ~700 nm as x increases. Thus we could distinguish bandgap graded nanostructure directly by its fluorescence color, as shown in figure 2a. Figure 2b is the SEM image of the substrate. Figure 2c and 2d are lattice diffraction image on the CdS and CdSe side of a single nanowire, respectively. Figure 2e and 2g are florescence images of a
single bandgap nanowire and nanobelt, respectively, and figure 2f and 2h are corresponding SEM images.

**Figure 2.** Features of bandgap graded nanostructure. (a) Fluorescence image. The fluorescent color changes from green to red. (b) SEM image of the substrate. (c)(d) The lattice diffraction images of (c) CdS and (d) CdSe. The crystal orientation is [110] and [201] respectively. (e)(f) The (e) fluorescent image and (f) SEM image of single CdSSe nanowire. (g)(h) The (g) fluorescent image and (h) SEM image of single CdSSe nanowire.

After fabricating the bandgap graded nanostructure, we used sampling method to calculate the proportion of each nanostructure. According to the experimental result, the bandgap graded nanostructure could only be synthesized on the edge of the silicon substrates. Also, in our experiment, bandgap graded nanostructure could only be observed on the last three substrates, due to the temperature distribution. We brushed a piece of glass over the edge of the substrates and count the proportion of bandgap graded nanostructure under optical microscopy with 405 nm lasing. Figure 3 are the images of samples on glass pieces.

**Figure 3.** Samples on glass pieces.
We designed a series of experiments to investigate the influence of temperature, pressure, and distance from the heating zoom on the growth ratio of bandgap-graded nanostructures separately. We selected 9 groups of pressure (400 mBar, 430 mBar, 500 mBar, 550 mBar, 600 mBar, 650 mBar, 700 mBar, 750 mBar, and 800 mBar) and 7 groups of temperature (860 °C, 870 °C, 880 °C, 890 °C, 900 °C, 920 °C, and 940 °C). The distance of the substrate from the heating zoom were 6.4 cm, 7.2 cm, and 8.0 cm, respectively. Here in Table 1, we exhibit partial data. Note that we stop calculating if there is still no bandgap-graded nanostructure in 100 nanostructures.

| Pressure (mBar) | Temperature (°C) | Distance (cm) | Bandgap graded nanobelt | Bandgap graded nanowire | Other nanostructures |
|-----------------|------------------|---------------|-------------------------|------------------------|---------------------|
| 400             | 880              | 6.4           | 3                       | 6                      | 139                 |
|                 |                  | 7.2           | 0                       | 0                      | 100                 |
|                 |                  | 8.0           | 0                       | 0                      | 100                 |
|                 |                  | 6.4           | 0                       | 0                      | 100                 |
| 500             | 880              | 7.2           | 0                       | 0                      | 100                 |
|                 |                  | 8.0           | 4                       | 6                      | 196                 |
|                 |                  | 6.4           | 0                       | 0                      | 100                 |
| 550             | 880              | 7.2           | 4                       | 9                      | 151                 |
|                 |                  | 8.0           | 8                       | 6                      | 179                 |
|                 |                  | 6.4           | 0                       | 0                      | 100                 |
| 600             | 880              | 7.2           | 5                       | 5                      | 59                  |
|                 |                  | 8.0           | 4                       | 5                      | 34                  |
|                 |                  | 6.4           | 2                       | 6                      | 265                 |
| 430             | 860              | 7.2           | 10                      | 15                     | 182                 |
|                 |                  | 8.0           | 0                       | 0                      | 100                 |
|                 |                  | 6.4           | 2                       | 6                      | 89                  |
| 430             | 900              | 7.2           | 14                      | 14                     | 278                 |
|                 |                  | 8.0           | 0                       | 0                      | 100                 |
|                 |                  | 6.4           | 0                       | 0                      | 100                 |
| 430             | 940              | 7.2           | 0                       | 0                      | 100                 |
|                 |                  | 8.0           | 9                       | 9                      | 87                  |
|                 |                  | 6.4           | 0                       | 0                      | 100                 |
| 600             | 860              | 7.2           | 0                       | 0                      | 100                 |
|                 |                  | 8.0           | 0                       | 0                      | 100                 |
|                 |                  | 6.4           | 3                       | 3                      | 118                 |
| 600             | 920              | 7.2           | 4                       | 8                      | 151                 |
|                 |                  | 8.0           | 0                       | 0                      | 0                   |

Then, we used Minitab to analyze the data. Figure 4 are the surface plot of the percentage of bandgap-graded nanostructure. Figure 4a-c represent for proportion of bandgap-graded nanowire and figure 4d-f represent for proportion of bandgap-graded nanobelt. From left to right, the figures represent for substrates with distance of 6.4 cm, 7.2 cm, and 8.0 cm, respectively. Through the figure, we can see that there is no extremely unusual data point.
3. Statistical analyse and modelling

In order to analyse the data, we firstly normalized the three variables to [0, 1] by the following transformation,

\[ P = \frac{(PRES - \min(PRES))}{(\max(PRES) - \min(PRES))} \]  
\[ T = \frac{(TEMP - \min(TEMP))}{(\max(TEMP) - \min(TEMP))} \]  
\[ D = \frac{(DIST - \min(DIST))}{(\max(DIST) - \min(DIST))} \]  

We used GLM to fit the data, and the order of GLM is set to be quadratic. Additionally we applied DOE analyse in Minitab to draw a Pareto chart of these parameters, and deleted the parameters with little effect. Then we had following variable vector,

\[ X = [1, P, T, D, D^2, PT, TD] \]  

Also we got the following GLM regression function, in which NW represents for the proportion of nanowire, and NB for proportion of nanobelt.

\[ NW = -187.5 + 6.15P - 20.2T + 429D - 241.3D^2 - 11.68PT + 24.9TD \]  
\[ NB = -63.8 + 1.47P - 10.6T + 149D - 84.5D^2 - 3.10PT + 13.5TD \]
Table 2 and table 3 are analysis of the GLM for nanowire and nanobelt, respectively. We can tell that for the model of bandgap graded nanowire, the P value shows an obvious relationship with the formation of bandgap graded nanostructures, for which most factor can reach a confidence level of around 0.1. For the model of nanobelt, though the P value is not sufficiently low, the fitting result shows relatively good match. Consider that there are lots of unknown variables and uncertainties in nanostructure growth process, we consider that this model accords with the data on the whole.

**Table 2. Analysis of GLM for nanowire.**

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|--------|----|--------|--------|---------|---------|
| Regression | 6 | 148.38 | 24.73 | 2.26 | 0.053 |
| P | 1 | 47.89 | 47.89 | 4.37 | 0.042 |
| T | 1 | 11.87 | 11.87 | 1.08 | 0.303 |
| D | 1 | 71.67 | 71.67 | 6.55 | 0.014 |
| D*D | 1 | 73.75 | 73.75 | 6.73 | 0.012 |
| P*T | 1 | 28.2 | 28.2 | 2.58 | 0.115 |
| T*D | 1 | 14.86 | 14.86 | 1.36 | 0.25 |
| Error | 50 | 547.53 | 10.95 |
| Total | 56 | 695.9 |

**Table 3. Analysis of GLM for nanobelt.**

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|--------|----|--------|--------|---------|---------|
| Regression | 6 | 18.955 | 3.159 | 0.53 | 0.78 |
| P | 1 | 2.738 | 2.738 | 0.46 | 0.499 |
| T | 1 | 3.247 | 3.247 | 0.55 | 0.462 |
| D | 1 | 8.635 | 8.635 | 1.46 | 0.233 |
| D*D | 1 | 9.047 | 9.047 | 1.53 | 0.222 |
| P*T | 1 | 1.986 | 1.986 | 0.34 | 0.565 |
| T*D | 1 | 4.377 | 4.377 | 0.74 | 0.394 |
| Error | 50 | 295.68 | 5.914 |
| Total | 56 | 314.635 |

The residual analysis for the data and model is shown in Figure 5. From the residual plot, we can see that the residual accords to normal distribution on the whole.

![Figure 5. Residual plots for the GLM for (a) nanowire and (b) nanobelt.](image-url)
Using the model we obtained, we can draw contour plots for the model to predict the growth of each nanostructure. The contour plots are shown in figure 6. Figure 6a, 6c and 6e represent for the bandgap graded nanowire proportion and figure 6b, 6d and 6f for the bandgap graded nanobelt proportion at distance of 6.4 cm, 7.2 cm and 8.0 cm respectively.

**Figure 6.** Predicted growth result for different temperature and pressure circumstances. (a)-(c) Prediction of bandgap graded nanowire at distance of (a) 6.4 cm, (b) 7.2 cm, (c) 8.0 cm. (d)-(f) Prediction of bandgap graded nanobelt at distance of (d) 6.4 cm, (e) 7.2 cm, (f) 8.0 cm.

4. Conclusion
Till now we obtain a GLM model for the growth of bandgap nanowire and nanobelt. The model shows good fit result for nanostructure growth. Using this model we can precisely design the synthesis condition and manage the growth of CdSSe bandgap graded nanowire.

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