Selective growth of ZnO nanorods by the hydrothermal technique

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Abstract
Zinc oxide nanorods were selectively grown on engineered substrates, Ag-patterned and photoresist-patterned substrates, by the hydrothermal technique using zinc nitrate (Zn(NO₃)₂) and hexamethylenetetramine ((CH₂)₆N₄). The nanorod growth was affected by the substrate to be used. The nanorods were vertically grown on a GaN substrate but not on a Si substrate because of lattice mismatch. However, since the nanorods were grown on a thick Ag film no matter what substrate was used, a thick Ag film was deposited on a Si substrate to prepare the Ag-patterned substrate. Accordingly, the nanorods were grown only on the Ag pads. When the sizes of Ag pads were small such as 100 nm × 100 nm, one single nanorod was grown on an Ag pad. As another engineered substrate, the photoresist was patterned to prepare an array of holes on a GaN-on-sapphire substrate by e-beam lithography. When the hole size was 10 nm × 10 nm and higher, concentrations of Zn(NO₃)₂ and ((CH₂)₆N₄) were employed, all holes were successfully filled with a single nanorod.

Keywords: ZnO, hydrothermal, selective growth, nanorod, patterned substrate

Classification numbers: 4.06, 5.01

1. Introduction
Zinc oxide ZnO nanorods have attracted increasing attention because of their wide variety of electronic and photonic device applications as a wide band gap semiconductor. One of the interesting applications is an ultraviolet (UV) light-emitting diode (LED) fabricated from n-ZnO and p-ZnO. Since it is difficult to form p-ZnO, it may be replaced by p-NiO as a p-type material in the pn diode. NiO is known to be a p-type wide band gap semiconductor [1], and an ultraviolet-detector was made of a p-NiO/n-ZnO [2]. However, improvement of the diode characteristic is expected by using ZnO nanorods, which usually have crystallinity better than ZnO thin films because of the 1D growth. The position-controlled growth of ZnO nanorods is highly desirable for practical applications.

We earlier reported ZnO nanorods grown on various substrates by the hydrothermal technique and the effects of a substrate to be used on the growth of ZnO nanorods [3]. ZnO nanorods could grow vertically on a GaN substrate but not on a Si substrate. Utilizing the effect of substrate, ZnO nanorods can be formed selectively on the engineered substrate. Various techniques for the selective growth of ZnO nanorods have been well reviewed [4]. The most successful results were obtained by the vapor–liquid–solid (VLS) process, and the solution-based growth technique, however, provided little control over the area density. In this study, we ‘engineer’ a substrate for selective growth over a large area.

2. Experimental
As described later, Ag-patterned Si and photoresist-patterned GaN-on-sapphire substrates were used to study selective growth of ZnO nanorods. The details of the hydrothermal...
Figure 1. SEM micrographs of ZnO nanorods grown: (a) on a thick Ag film on Si, (b) on a thin Ag film on Si, (c) on a thick Ag film on GaN-on-sapphire and (d) on a thin Ag film on GaN-on-sapphire.

growth of ZnO nanorods were described elsewhere [3]. The substrate was suspended face down in an aqueous solution mixture of zinc nitrate (Zn(NO₃)₂) and hexamethylenetetramine ((CH₂)₆N₄) enclosed in a stainless steel bottle with a screw cap. The concentrations of both solutions were the same and optimized for the selective growth on each type of substrate. The stainless steel bottle was heated from the bottom in an oil bath, and the temperature of the solution was adjusted to 90 °C. The substrate was removed from the bottle after 3 h and rinsed in deionized (DI) water. The scanning electron microscopy (SEM) micrographs of the grown nanorods were obtained using a JEOL JSM-6340. Photoluminescence (PL) spectra were collected at room temperature using an excitation wavelength of 325 nm of a He–Cd laser.

3. Results and discussion

Two types of substrates were used as ‘engineered’ substrates. One is Ag-patterned Si and the other photoresist-patterned substrate. Thin (5 nm thick) and thick (50 nm thick) Ag films were deposited by vacuum evaporation of Ag on Si through a shadow mask to prepare Ag-patterned substrates, while the photoresist on GaN-on-sapphire substrates was patterned with an array of 100 nm holes by e-beam lithography to prepare the photoresist-patterned substrates.

3.1. Selective growth on Ag-patterned substrates

Figures 1(a)–(d) show SEM micrographs of the ZnO nanorods grown on thin and thick Ag films deposited on Si and GaN-on-sapphire substrates. The concentrations of Zn(NO₃)₂ and (CH₂)₆N₄ mixed in the stainless steel bottle were both 10 mM. The substrate underneath the Ag film does not affect the growth of ZnO nanorods if the Ag film is thick, while the substrate does affect the growth of ZnO nanorods if the Ag film is thin. The SEM micrographs of ZnO nanorods grown on Si and GaN without the Ag films [3] are similar to those shown in figures 1(b) and (d), respectively.

It is clear from figure 1 that for the selective growth on the Ag-patterned substrate, thick Ag films must be deposited on Si but not on GaN so that the ZnO nanorods can be grown only on Ag. Figure 2(a) shows a low-magnification SEM micrograph of the ZnO nanorods grown on the Ag-patterned Si substrate. The edge of the Ag pad is magnified in figures 2(b) and (c). The ZnO nanorods are grown only on the Ag pads. The edge of ZnO-nanorod area is sharp. The ZnO nanorods grown on a Ag pad in figure 2(c) are similar to those grown on the Ag film shown in figures 1(a) and (c). We challenged ourselves to grow one single ZnO nanorod on a Ag pad by preparing a pad size of 100 nm × 100 nm using e-beam lithography. One single ZnO with a diameter of 100 nm was grown on the Ag pad, as shown in figure 1(d). The photoluminescence excited with a He–Cd laser was imaged from the Ag-patterned Si substrate after the growth of ZnO nanorods for further confirmation of the
selectively grown ZnO nanorods on the Ag pads. The yellow luminescence associated with point defects [3] is imaged only on the Ag pads, as shown in figure 3. The luminescence pattern is similar to that of the Ag pads.

3.2. Selective growth on photoresist-patterned substrates

As seen in figure 1(d), a single nanorod is grown on only a few Ag pads. The Ag film is polycrystalline and contains randomly oriented grains. If there are many grains, the (002) plane of ZnO may match with a crystal orientation of some grains. The preferred growth direction of ZnO nanorods is the c-axis direction of the hexagonal lattice [3]. If the Ag pad area is extremely small, only a few pads may have grains whose crystal orientation is suitable for the growth of ZnO nanorods.

The increased density of ZnO nanorods which are separated from each other in an array can be obtained by the growth on the photoresist-patterned single-crystal substrate which has a good lattice match with ZnO. E-beam lithography was applied to obtain Au nanodot arrays for the nanorod growth using VLS [5]. However, to the best of our knowledge, the direct chemical growth of a single ZnO nanorod in each open area of the photoresist-patterned substrate has never been reported.

The photoresist was patterned to make an array of holes on a GaN-on-sapphire substrate by e-beam lithography, and then the hydrothermal growth of ZnO nanorods was carried out. When the hole size was 500 nm × 500 nm, more than one nanorod was grown as shown in figure 4(a). When the hole size was decreased to 100 nm × 100 nm, only one single nanorod was grown in a hole but not grown in all holes, as seen in figure 4(b). Almost all holes were filled with a single nanorod with the increased molar concentrations of Zn(NO$_3$)$_2$ and (CH$_3$)$_3$N$_4$ to 100 mM, as shown in figure 4(c). Although a single nanorod was successfully grown in each hole, the aspect ratio of nanorods decreased because of higher solution concentrations, as observed in the nanorods grown on GaN-on-sapphire without the pattern for higher solution concentrations.

4. Conclusion

We engineered the substrates for the selective hydrothermal growth of ZnO nanorods. Two types of engineered substrates were used: one was Ag-patterned, and the other was photoresist-patterned substrate. The ZnO nanorods were grown selectively on the Ag pads if the Ag film was thick and Si substrate was used. If the Ag film was thin, the growth was controlled more by the substrate underneath the Ag film. One single nanorod could be successfully grown on some Ag pads with a size of 100 nm × 100 nm, but nothing was grown on the other Ag pads. In order to increase the density of well separated ZnO nanorods in the array, the hydrothermal growth was carried out on the photoresist-patterned GaN substrate.
When the hole size was decreased to 100 nm × 100 nm by e-beam lithography, one single nanorod was successfully grown in each hole of the array. Almost all holes were filled with ZnO nanorods in the case of higher concentrations of Zn(NO$_3$)$_2$ and (CH$_2$)$_6$N$_4$.

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