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Kyoto University
Catalyst-free synthesis of ZnO nanowall networks on Si₃N₄/Si substrates by metalorganic chemical vapor deposition

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ZnO nanowall networks were synthesized on Si₃N₄/Si (100) substrates at low growth temperature of 350 °C by metalorganic chemical vapor deposition (MOCVD) without any help of metal catalysts. Depending on MOCVD-growth conditions, a large number of nanowalls with extremely small wall thicknesses below 10 nm are formed into nanowalls with a thickness of about 20 nm, resulting in the formation of two-dimensional nanowall networks. The ZnO nanowall networks were found to have a preferred c-axis orientation with a hexagonal structure in synchrotron x-ray scattering experiments. Room-temperature hydrogen incorporation into ZnO nanowall networks has been observed in photoluminescence measurements. © 2006 American Institute of Physics.

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respectively, while the hexagonal insets of Figs. 1 respectively, show cross-sectional FE-SEM images of the ZnO nanowall networks on Si$_3$N$_4$/Si (100) substrates. A scale bar in the insets indicates 500 nm.

1(a) and 1(d), it is difficult to observe the extremely small nanowalls in the sample grown with the DEZn flow rate of 3 $\mu$mol/min. This fact indicates that zinc atoms play an important role in the formation of nanowall networks with high density. The average heights of ZnO nanowall networks are 950 nm, 1.1 $\mu$m, and 1.2 $\mu$m, respectively, as shown in the insets of Figs. 1(d)–1(f).

Figures 2(a) and 2(b) show the diffraction profiles of the ZnO nanowall samples grown with the DEZn flow rate of 3 and 5 $\mu$mol/min, respectively, along the substrate normal direction in reciprocal space measured by typical $\theta$–2$\theta$ scans [$Q=4\pi \sin(\theta/2)/\lambda$]. The diffraction peak of the ZnO nanowall networks grown with the DEZn flow rate of 5 $\mu$mol/min occurs only at 2.41 Å$^{-1}$ which is related with the ZnO (0002) Bragg reflection [Fig. 2(b)], while the ZnO nanowall networks grown with the DEZn flow rate of 3 $\mu$mol/min not only have the ZnO (0002) Bragg reflection but also the ZnO (1010) and ZnO (10$ar{1}$1) Bragg reflections [Fig. 2(a)]. The diffraction profile is measured in the $\langle 2.1 \, \bar{A}^{-1}\rangle$ direction in reciprocal space, keeping in-plane momentum transfer at the reciprocal of the in-plane lattice spacing to study the stacking order of the grown ZnO nanowall networks. The cubic (11$ar{1}$) and cubic (002) reflections would occur at (2.1, 0, 0.8 Å$^{-1}$) and (21.0, 1.6 Å$^{-1}$), respectively, while the hexagonal (10$ar{1}$1) reflection would occur at (2.1, 0, 1.2 Å$^{-1}$). Therefore, we could conclude that the crystal structure of both samples is hexagonal, as shown in Figs. 2(c) and 2(d).

Effects of the DEZn flow rate on the crystal quality and surface morphology of ZnO thin films on Si substrates have been investigated in a previous research (which will be published elsewhere). When the DEZn flow increases, the c-axis oriented crystallinity is improved, but the surface smoothness deteriorates, which indicates that ZnO grows three dimensionally in a high DEZn flow rate. In the growth condition of a high DEZn flow rate, a large number of zinc adatoms incorporate and effectively form ZnO nuclei on Si$_3$N$_4$/Si (100) substrates, resulting in the formation of nanowalls with an extremely small wall thickness and a high density as well as a preferred c-axis crystal orientation. Therefore, an average height of the nanowall networks increases with the increment of a DEZn flow rate, as shown in the insets of Fig. 1.

We measured the azimuth scan at the nonspecular ZnO (1011) Bragg peak position to study structural correlation between substrates and ZnO nanowall networks (not shown). From the experiment, it could be concluded that both samples have no epitaxial relationship between substrates and ZnO nanowall networks, but a preferred c-axis growth behavior of ZnO on Si$_3$N$_4$/Si substrates due to the amorphous Si$_3$N$_4$ layer on Si. Although the formation mechanism of catalyst-free MOCVD-grown nanowall networks on Si$_3$N$_4$/Si substrates is not described clearly in the present study, relaxation of the lattice mismatch strain induced by the absence of epitaxial relation between ZnO and the Si$_3$N$_4$ layer may play a key role in the formation of the ZnO nanowall networks.

The influence of the H$_2$ treatment to optical properties of the ZnO nanowall networks was investigated by photoluminescence (PL) measurements using excitation at the 325 nm line of a He–Cd laser as an excitation source. Figure 3 shows PL spectra of the as-grown nanowall-network samples [shown in Figs. 1(a) and 1(c)] and H$_2$-treated nanowall-network samples. Hydrogenation [H$_2$ flow rate: 1000 SCCM

![FIG. 1. FE-SEM images of MOCVD-grown ZnO nanowall networks on Si$_3$N$_4$/Si (100) substrates at 350 °C under different DEZn flow rates. ((a), (b), and (c)) Plan-view FE-SEM images of the ZnO nanowall networks with DEZn flow rates of 3, 4, and 5 $\mu$mol/min, respectively. (d), (e), and (f) Tilting-view FE-SEM images of (a), (b), and (c) samples, respectively. Insets show cross-sectional FE-SEM images of the ZnO nanowall networks on Si$_3$N$_4$/Si (100) substrates. A scale bar in the insets indicates 500 nm.](Image 66x457 to 282x739)

![FIG. 2. (a) and (b)] Powder diffraction profiles along the substrate normal direction in reciprocal space measured on the ZnO nanowall networks grown with the DEZn flow rate of 3 and 5 $\mu$mol/min, respectively. [(c) and (d)] Scattering profiles along the (2.1 Å$^{-1}$) direction from the samples of Figs. 2(a) and 2(b), respectively. They are sensitive to the stacking sequence of the atomic layers of ZnO nanowall networks.](Image 341x494 to 533x739)
In summary, catalyst-free synthesis of ZnO nanowall networks on Si$_3$N$_4$ (50 nm)/Si (100) substrates at low growth temperature of 350 °C by MOCVD without catalyst driving was reported in this work. In the MOCVD-growth condition with the DEZn flow rate of 5 μmol/min, a large number of nanowalls with extremely small wall thicknesses below 10 nm formed networks into nanowalls with a thickness of about 20 nm. The nanowall density, size, and crystal orientation are strong functions of the DEZn flow rate. Hydrogen-storage behavior of the ZnO nanowall networks hydrogenated at RT has been investigated by RT PL measurements, indicating that ZnO nanowall networks are promising in the application of hydrogen-energy devices.

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