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Selective formation of ZnO nanodots on nanopatterned substrates by metalorganic chemical vapor deposition

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Selective formation of ZnO nanodots was accomplished by metalorganic chemical vapor deposition on nanopatterned SiO$_2$/Si substrates. Self-organized ZnO nanodots were selectively formed in nanopatterned lines of Si created by etching of SiO$_2$ with focused ion beam (FIB), whereas any nanodots were hardly observed on the SiO$_2$ surface in the vicinity of the FIB-sputtered Si areas. The mechanism of the selective formation of ZnO nanodots on FIB-nanopatterned lines is mainly attributed to the effective migration of Zn adatoms diffusing on the SiO$_2$ surface into the Si lines followed by the nucleation at surface atomic steps and kinks created by Ga$^+$ ion sputtering. Cathodoluminescence measurements confirmed that the emission originated from the selectively grown ZnO nanodots. © 2003 American Institute of Physics. [DOI: 10.1063/1.1622795]

Nanoscale semiconductor structures such as quantum wells, wires, and dots have stimulated great interest due to the predicted improvement in device performance. Many unique and fascinating properties have been demonstrated in semiconductor nanostructures. ZnO is of interest for electrical and optical devices with its multifunctionality as well as excitonic effects. In these regards, the realization of low-dimensional ZnO nanostructures is strongly demanded, resulting in a lot of nanoscale, nanophotonic, and nanomagnetic devices. Even though the realization of self-assembled low-dimensional ZnO nanostructures such as nanowires and quantum dots has been reported, the ZnO nanostructures grown on substrates are randomly distributed with fluctuations on their size and their position. One of the major bottlenecks of the nanoscale devices relies on the lack of reproducibility of naturally formed nanostructures, which indicates that a better control of the periodicity, shape, and size of nanostructures should be developed in order to realize nanoscale multifunctional devices.

Focused ion beam (FIB) has been regarded as an important tool for maskless patterning, which is the outstanding capability of FIB compared with other lithographic techniques. In this letter, we report the selective formation of ZnO nanodots on FIB-nanopatterned SiO$_2$/Si substrates by metalorganic chemical vapor deposition (MOCVD).

The SiO$_2$ layer with a thickness of 50 nm was thermally formed in a furnace in oxygen atmosphere at 1100 °C. The SiO$_2$/Si samples were immediately transferred into the FIB chamber (SEIKO SMI-2050). Nanopatterned lines in 8×8 $\mu$m$^2$ fields were patterned by FIB on SiO$_2$ (50 nm)/Si (111) substrates using 30 keV Ga$^+$ ions at a beam current of 48 pA with an ion dose of $3.4 \times 10^{17}$ cm$^{-2}$ as shown in Fig. 1(a). The estimated diameter of the beam was 23 nm.

An atomic force microscope (AFM), (SEIKO SPA-400) image of the lines patterned by FIB is shown in Fig. 1(b) together with the cross-sectional image [Fig. 1(c)] obtained by a line scan of the AFM profile. The SiO$_2$ layer (50 nm) on Si (111) was successfully removed by the energetic Ga$^+$ ion sputtering. The etched depth of SiO$_2$/Si substrates was about 100 nm. The width of individual nanopatterned lines was 390 nm at the SiO$_2$ surface.

The ZnO nanodots on nanopatterned SiO$_2$/Si (111) sub-

FIG. 1. (a) A schematic image of FIB-nanopatterning of a SiO$_2$/Si substrate with 30 keV Ga$^+$ ions at a beam current of 48 pA. The beam diameter was 23 nm. (b) An AFM image of FIB-nanopatterned lines. (c) A cross-section image of a single nanopatterned line, which was obtained by a line scan of the AFM profile.
The total pressure of the reactor was fixed at 200 Torr. The wafer was grown in the temperature range of 500–650 °C for 22 s. Typical flow rate of DEZn source at different temperatures with intervals of 50 °C in the gas as an oxygen source and diethylzinc (DEZn) vapors and consumes adsorbed species transported by surface diffusion. In addition, the selective formation of ZnO nanodots in nanopatterned lines can be quite associated with the generation of surface atomic steps created by Ga⁺ ion sputtering. Surface atomic step generated by sputtering has been shown to strongly increase the growth rate of InP on FIB-patterned GaAs, which suggests that introducing surface steps and kinks enhances the nucleation probability of depositing material. The nucleation on the steps and kinks in the sputtered areas acts as a sink for migrating surface adatoms and consumes adsorbed species transported by surface diffusion. Namely, Zn adatoms near the patterned boundary during the growth of ZnO can easily migrate from SiO₂ to Si and form stable nucleation on Si, resulting in the selective formation of ZnO nanodots on nanopatterned Si.

The depletion zone width ($L_D$) was found to be below about 0.5, 0.8, and 0.9 μm at the growth temperature of 500, 550, and 600 °C, respectively. As mentioned before, the existence of the depletion zone indicates that Zn atoms prefer to form ZnO dots on the patterned area rather than on the SiO₂ surface. $L_D$ gives key information for the design of periodic nanopatterned lines for selective growth because random ZnO dots on SiO₂ cannot be formed when the distance between the nanopatterns is smaller than $2L_D$. The maximum lengths of 1 (500 °C), 1.6 (550 °C), and 1.8 μm (600 °C) for the diffusion of Zn adatoms from the SiO₂ surface to the nanopatterned Si area under the DEZn flow rate of 3 μmol/min are smaller than the interdistance of 2 μm between the nanopatterned lines. This fact explains why the several ZnO nanodots remain in the areas (C) in Fig. 2. In fact, the selective formation of ZnO nanodots was achieved without any depletion regions when the nanopatterns with narrower interdistance and the growth condition with the low DEZn flow rate were applied, as will be shown in Fig. 3.

FE–SEM images of the ZnO nanodots selectively grown by the DEZn flow rate of 1 μmol/min at different growth temperature in FIB-nanopatterned lines with an interdistance of 1 μm. Insets show ZnO nanodots in a single FIB-nanopatterned line. (a) 500, (b) 550, (c) 600, and (d) 650 °C.
on the FIB-nanopatterned SiO$_2$/Si substrates with an inter-
distance of 1 $\mu$m at different growth temperatures from 500 to 650 °C are presented in Fig. 3. The flow rate of DEZn was 1 
$\mu$mol/min. Compared to the results in Fig. 2, the selective
growth of ZnO nanodots was realized in this growth condi-
tion without the depletion region. Further, the average size of
the ZnO nanodots is enlarged and the size uniformity dete-
rmines with increasing the growth temperature. The average
diameters, estimated by the FE–SEM results, of the ZnO
nanodots grown at different growth temperature are about 12
nm (500 °C), 13 nm (550 °C), 17 nm (600 °C), and 22 nm
(650 °C).

As can be seen in the insets of Figs. 3(a) and 3(b), many
ZnO nanodots were concentrated on the center of the nano-
patterned lines. This fact can be explained by the shortened
surface diffusion length of adatoms during the growth, which
occurred due to a large number of surface atomic steps and
kinks produced at the bottom of nanopatterned lines by the
implantation of Ga$^+$ ions in accordance with the result of
InAs on FIB-patterned GaAs substrates. However, the in-
crement of growth temperature usually makes the surface
diffusion length of Zn adatoms longer. This fact means that
the adatoms can easily diffuse with jumping over the surface
atomics steps and kinks, resulting in the enlargement of dot
formation areas in the nanopatterned lines as shown in the
insets of Figs. 3(c) and 3(d). The inset of Fig. 3(d) shows
that ZnO grown at 650 °C has a dot- and layer-mixed structure,
which is attributed to the enhancement of a two-dimensional
growth mode at relatively high growth temperature.

CL spectra, recorded at RT, of selectively grown ZnO
nanodots at 550 and 650 °C on nanopatterned lines are
shown in Fig. 4. The CL spectra are from four nanopatterned
lines presented in the SEM images of Figs. 3(b) and 3(d) and
consist of a broad emission band around 3.34 eV with an
additional emission at about 2.7 eV. We could confirm the
presence of sufficient Zn atoms from the nanodots selec-
tively grown on FIB-nanopatterned areas by energy-
dispersive x-ray analysis. This result indicates that the emis-
sion band around 3.34 eV coincides with the free exciton
emission from ZnO (EX$_{ZnO}$) because free exciton emission
becomes dominant at RT due to the ionization of impurities
bounding exciton at low temperatures. The EX$_{ZnO}$ band of
around 3.34 eV from the selectively grown ZnO nanodots in
CL measurements is a little bit higher than that from a ZnO
thin film on SiO$_2$/Si measured by RT photoluminescence.
This result is attributed to a blue shift of the emission by a
band filling effect which were originated by high energy CL
excitation of 20 keV. Regarding the broad emission band
located at about 2.7 eV, we speculate that it comes from
defects or naturally formed Si nanocrystals in SiO$_2$ dur-
ing thermal oxidation, since the same emission band is om-
nipresent in our SiO$_2$/Si substrates by CL measurements.

In summary, we have accomplished the selective forma-
tion of ZnO nanodots by MOCVD on FIB-nanopatterned
SiO$_2$/Si substrates. The FE–SEM measurements clearly
showed the selective formation of ZnO nanodots on the
nanopatterned Si surface areas. The mechanism of the selec-
tive formation of ZnO nanodots on FIB-nanopatterned lines
is mainly attributed to the fact that nanoscale patterns of Si
act as efficient artificial traps for diffusing Zn adatoms on the
surface of SiO$_2$ during the MOCVD growth. CL measure-
ments recorded at RT confirmed that the emission originated
from the selectively grown ZnO nanodots.

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