Fabrication and Characterization of Self- and Artificially-Assembled ZnO Nanodots

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Self-assembled ZnO nanodots on SiO$_2$/Si with low-dimensional quantum characteristics were realized by metalorganic chemical vapor deposition (MOCVD). Transmission electron microscope results showed that the self-assembled ZnO nanodots on the SiO$_2$/Si substrates have a single crystal structure without any kinds of defects. In order to control the fabrication of functionalized ZnO nanodots (e.g., with controlled morphology and dimension) artificially we introduced a combination of “bottom-up” “top-down” approach based on the MOCVD deposition on functionalized substrates prepared by focused ion beam (FIB). Highly ordered two-dimensional ZnO-nanodot arrays with a 750-nm or 190-nm periodicity on SiO$_2$/Si substrates were fabricated in this study. Free exciton emission from a position-controlled single ZnO nanodot at room temperature was clearly observed in CL measurements.

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I. INTRODUCTION

The fundamental problem to “where to move and how to assemble” is crucial to open new renaissance of nanotechnology. “How can we freely control novel nanostructures?” Namely, an important issue in the novel nanotechnology is how to assemble individual atoms into nanostructures in an effective and controllable way. The fabrication of well-defined and well-controlled nanostructures and elucidation of their properties are crucial to efforts towards the realization of novel nanodevices as well as the understanding of the fundamental properties of the nanomaterials. A novel method for realization of well-controlled nanostructures possibly can allow us to pave a new way to realize semiconductor building blocks for novel multi-functional nanodevices.

Recently, ZnO has attracted attention as a promising material for short-wavelength optical device applications due to the great advantage of having the large binding energies of excitons (60 meV) [1] and biexcitons (15 meV) [2], which are quite larger than those of other semiconductor materials with wide band gaps such as GaN (24 meV and 5.7 meV, respectively) and ZnSe (21 meV and 3.4 meV, respectively) [3-6]. The strong exciton effects such as room temperature (RT) stimulated emission by inelastic exciton-exciton scattering have been reported [7-9]. Furthermore, many significant exciton effects promising for achieving large oscillator strength, significant nonlinear optical properties, and multie exciton interaction are expected in low-dimensional ZnO nanostructures because of enhancing exciton/biexciton binding energy [10,11], resulting in radiative recombination with fast decay of carriers and observation of strong excitonic recombination even at RT. In these regards, recently, studies on ZnO nanostructures have been extensively underway [12-14].

Our group has reported self-organized ZnO quantum dots on SiO$_2$/Si substrates by metalorganic chemical vapor deposition (MOCVD) [15]. However, in spite of many promising properties of self-organization, a number of problems such as randomness of size and position distribution have prohibited the real application to novel nanoscale optoelectronic devices. In this regard, we have demonstrated highly ordered ZnO nanodots on artificial nanopatterns which were prepared by focused ion beam (FIB). In this study, we propose a combination of ”bottom-up” ”top-down” approach based on the MOCVD growth of functionalized ZnO nanodots (e.g., with controlled morphology and dimension) on FIB-functionalized substrates to prepare highly ordered ZnO-nanodot arrays.

II. EXPERIMENT

The self-assembled ZnO nanodots in this study were prepared by MOCVD on thermally formed SiO$_2$ lay-
In order to grow self-assembled ZnO nanodots with low-dimensional quantum characteristics on SiO$_2$/Si substrates, we varied the flow rate of N$_2$O gas from 5000 to 10000 µmol/min at the fixed DEZn flow rate as 3 µmol/min. Under these growth conditions, the density of ZnO nanodots was steeply increased up to the order of $10^{11}$ cm$^{-2}$ with decreasing the flow rate of N$_2$O as shown in Fig. 1. This result shows that the increment of DEZn/N$_2$O ratio can give a distinct enhancement of the dot density by acceleration of the Volmer-Weber (V-W) type three-dimensional growth mode, which might be due to the increased sticking probability of Zn atoms on SiO$_2$/Si substrates by the suppressed pre-reaction between Zn and O atoms in the MOCVD reactor. The crystal structure of ZnO nanodots was confirmed by transmission electron microscope (TEM) [16]. In spite of the amorphous nature of SiO$_2$, the ZnO nanodots on the SiO$_2$ substrate have a single crystal structure without any kinds of defects. Moreover, the absence of a wetting layer was confirmed by the TEM result, indicating the V-W type nucleation of the ZnO nanodots.

To investigate optical properties of the self-assembled ZnO nanodots presented at Fig. 1, we carried out photoluminescence (PL) measurements. In the PL spectra excited by 325-nm line of a He-Cd laser (10 mW) as an excitation source at 10 K from two ZnO-dot samples grown with the flow rate of N$_2$O gas as 7000 and 10000 µmol/min, the broad emission band with a tail up to about 3.65 eV over the ZnO band gap was observed in addition to a peak labeled “D$_0^X$” which is attributed to the well-known neutral donor-bound exciton emission. This is an indication that the experimentally observed band-gap enhancement results from low-dimensional quantum confinement characteristics. However, we could not observe the band-tail emission over the ZnO band gap from the sample grown with the flow rate of N$_2$O as 5000 µmol/min, which might be attributed to the deteriorated stoichiometry of ZnO nanodots due to the excessive supply of Zn atoms compared to that of the other two samples.

The high-resolution (minimum diameter of ion beam : 5 nm) FIB instrument (SEIKO SMI-2050) was used for realization of artificially-assembled ZnO nanodots on functionalized SiO$_2$/Si substrates. Figure 2 shows AFM images of two-dimensional (2D) ZnO-nanodot arrays formed with growth temperature of 700 °C in FIB-engraved nanoholes, where typical flow rates of DEZn were 1 and 3 µmol/min with that of N$_2$O 7000 µmol/min. Individual nanodots, with the average heights [16 nm and 10 nm] and widths [100 nm and 130 nm] in Figs. 2(a) and 2(b) respectively, were selectively formed in the 2D nanohole arrays with a 750-nm periodicity. A
few number of random ZnO dots on the planar SiO$_2$ surface as well as the selectively formed ZnO dots in the well-ordered 2D nanohole arrays can be seen in the Fig. 2(a), while the periodical 2D arrays of ZnO nanodots are successful achieved without any precipitates on the planar SiO$_2$ surface as shown in Fig. 2(b). The 2D ZnO-nanodot arrays were formed over the nanopatterned area of $100 \times 100 \mu m^2$. This result shows that the dependence of source flow rates for selective formation of ZnO nanodots into FIB-engraved nanopatterns, which indicates that the key condition in the preparation of well-organized 2D ZnO-nanodot arrays on the same FIB-functionalized substrates is the easy diffusion of adsorbed adatoms on a SiO$_2$ surface.

The adatoms (probably Zn atoms) adsorbed on SiO$_2$ during growth diffuse into the nanoholes and preferably form ZnO nanodots in the nanoholes rather than on the planar SiO$_2$ surface. In other words, although a number of Zn adatoms may be evaporated during diffusion along the planar SiO$_2$ surface due to relatively high growth temperature of 700 $^\circ$C, Zn adatoms reaching at the nanoholes acting as artificial traps for diffusing Zn adatoms are nucleated and form nanosize dots. The existence of a few ZnO precipitates on the planar SiO$_2$ surface as shown in Fig. 2(a) indicates that a low flow rate of DEZn is required for the complete diffusion of Zn adatoms adsorbed on the planar SiO$_2$ surface to the FIB-patterned nanohole arrays. To enhance the surface diffusion length of Zn adatoms, the growth condition was optimized as the DEZn flow rate of 1 $\mu$mol/min with N$_2$O that of 7000 $\mu$mol/min. As shown in Fig. 3, dimension of the dots selectively formed in the same patterns by the same flow rate of DEZn (1 $\mu$mol/min) is a function of MOCVD-growth time, indicating that the enlargement of the dot dimension as well as no nucleation of ZnO dots on the planar SiO$_2$ surface are due to not only adsorption of growth species on ZnO seeds formed in the nanoholes but also accumulation of Zn and O adatoms on the ZnO seeds by surface diffusion.

The average height and width of the selectively grown ZnO nanodots in Fig. 2(a) is larger and narrower than those of the nanodots in Fig. 2(b), respectively. Our previous study showed that a c-axis growth mode of ZnO thin films on Si and SiO$_2$ is enhanced by increment of DEZn flow rates [17]. Namely, ZnO nanodots with a c-axis preferred orientation are grown in the nanoholes by a large amount of DEZn (3 $\mu$mol/min), resulting in the formation of nanodots with larger heights and narrower widths compared to the dots grown by the DEZn flow rate of 1 $\mu$mol/min in nanoholes.

Based on the above results, nanohole arrays with a 190-nm periodicity were engraved by FIB on SiO$_2$/Si substrates in order to realize compact 2D ZnO-nanodot arrays. In addition, to realize complete 2D ZnO-nanodot arrays without formation of ZnO precipitates on the planar SiO$_2$ area, the MOCVD-growth condition of Fig. 2(b) was applied. Figure 4(a) is a plan-view AFM image of artificial 2D ZnO-nanodot arrays with a period of 190 nm. Here, highly ordered ZnO nanodots with a 190-nm periodicity are clearly confirmed, giving an average height and width of the nanodots of 4 and 45 nm, respectively. As shown in Fig. 4, it is very hard to find any site having defects in this $3 \times 3 \mu m^2$ areas measured by AFM with 225-dot sites, corresponding to almost perfect nucleation into the nanoholes. This result indicates that every nanohole engraved by FIB acted as an artificial trap for a nucleation site to form a ZnO nanodot. Successful formation of one nanodot per one nanohole means complete position control of nanodots.

The reliable formation of highly ordered 2D ZnO-nanodot arrays is due to formation mechanisms responsible for initial nucleation. Considering amorphous nature of SiO$_2$, the selective formation of ZnO nanodots in FIB-nanopatterned SiO$_2$ areas is not discussed in terms of the change of the surface structure such as the generation of surface atomic steps and kinks. In energy-dispersive X-ray measurements the Ga-related peaks, though it appeared at a shoulder of the Zn-related peak, were observed from the selectively grown 2D ZnO-nanodot arrays on FIB-patterned SiO$_2$ (not shown). This result suggests that Ga atoms are incorporated into the patterned area during the FIB-nanoengraving. From the experimental result, it could be concluded that the reliable formation of self-ordered ZnO-nanodot arrays on...
functionalized substrates is mainly due to incorporated Ga ions which act as artificial traps for Zn adatoms. It can be expected in this study that the incorporated Ga atoms become preferred nucleation centers themselves, followed by the formation of highly ordered ZnO-nanodot arrays in the FIB-patterned areas. Another possibility that cannot be ruled out is the generation of Ga$^+$ ion-induced defects on the SiO$_2$ surface such as dangling bonds, allowing the preferred nucleation to be enhanced. Zn adatoms introduced into the MOCVD reactor move on the SiO$_2$ surface and in the nanopatterns in order to form stable nuclei. Zn adatoms diffuse from the SiO$_2$ surface to the Ga-introduced surface areas and/or Ga$^+$ ion-induced defects on SiO$_2$, which act as preferential nucleation centers. Thus the nanopattermes become artificial traps for diffusing Zn adatoms, and ZnO nuclei are formed by the reaction with oxygen adatoms.

Free exciton (EX) emission from a position-controlled single ZnO nanodot shown in Fig. 2(b) and Fig. 4 at RT was clearly observed in cathodoluminescence (CL) measurements as shown in Fig. 5. Although the emission intensity is so weak and the emission band is broad, observation of EX emission from the single nanodot at RT indicates that the optical property of the ZnO nanodot is prominent. However, it is very difficult to discuss quantum size effects from the broad emission in this stage. More concrete optical properties of position-controlled ZnO-nanodot arrays will be reported elsewhere.

IV. CONCLUSIONS

Self-assembled ZnO nanodots with low-dimensional quantum characteristics have been fabricated on SiO$_2$/Si substrates by MOCVD, which has been confirmed by AFM and PL studies. In PL results measured at 10 K, we observed the broad spectra with band tails, which were located at the higher energy with respect to band-edge emission of ZnO thin films. This is the indication of the quantum confinement effects in the nanodots. Highly ordered 2D ZnO-nanodot arrays with a 750-nm or 190-nm periodicity on SiO$_2$/Si substrates functionalized by FIB were realized in this study. A EX emission band from a position-controlled single ZnO nanodot at RT was clearly observed in CL measurements, indicating that the optical property of the artificially controlled ZnO dot is prominent. The selective formation phenomena of 2D nanodot arrays on FIB-functionalized substrates would be satisfied in other material systems and can be a useful tool for nanoscale photonic applications such as photonic band gaps, nano-sized optical circuits, and nanoscale laser arrays without the selection limit of material systems.

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