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Formation mechanisms of self-assembled ZnSe nanostructures on Cl-doped ZnSe thin films grown on (100) GaAs substrates

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Bright-field transmission electron microscopy images, high-resolution transmission electron microscopy images, energy dispersive spectroscopy profiles, and high-resolution x-ray diffraction curves showed that a high density of ZnSe nanostructures with a small size was formed on the Cl-doped ZnSe thin films grown on GaAs substrates. The formation of the ZnSe nanostructures was attributed to the strain energy resulting from the existence of the compressive strain generated by the accumulation of Cl impurities on the surface of the ZnSe thin film and from the residual strain existing in the ZnSe thin film with a thin thickness. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2795081]

Among the many kinds of nanostructures,[1–5] semiconductor quantum dots (QDs) have become particularly attractive because of their promising applications in electronic and optoelectronic devices, such as single electron transistors,[6,7] light emitting diodes,[8,9] lasers,[10,11] and biological devices,[12] and their potential applications in quantum computing.[13] II-VI semiconductor QDs, such as CdSe, ZnSe, and ZnO,[14–17] in comparison with III-V materials, have attracted more attention due to their higher exciton binding energies and stronger exciton-photon interactions. After laser diodes fabricated utilizing ZnSe-based semiconductors operating at room temperature were demonstrated,[18,19] the formation of ZnSe QDs has been extensively studied.[14,20–24] Self-assembled QDs have been typically formed from materials grown under compressive stress in the Stranski-Krastanov (SK) growth mode or the Volmer-Weber (VW) growth mode due to the self-organizing mechanism.[14,20–22] SK and VW QD growths require a large lattice mismatch between the wetting layer and the barrier layers to achieve elastic relaxation through the formation of QDs.[25,26] Even though the surface nanostructures have been formed on the same materials without lattice mismatch by using droplet epitaxy,[27–29] one type of VW growth, very few studies on the formation of self-assembled ZnSe surface nanostructures on Cl-doped ZnSe thin films grown on (100) GaAs substrates.

This letter reports the microstructural properties and the formation mechanisms of self-assembled ZnSe nanostructures on Cl-doped ZnSe thin films grown on (100) GaAs substrates. High-resolution x-ray diffraction (HRXRD) measurements were performed to investigate the misfit between the ZnSe thin films and the GaAs substrates. Transmission electron microscopy (TEM) measurements were carried out in order to investigate the microstructural properties of the ZnSe nanostructures, the ZnSe thin films, and the heterointerfaces between the ZnSe thin films and the GaAs substrates. Energy dispersive spectroscopy (EDS) measurements were performed to characterize elemental composition variations between the ZnSe nanostructures and the ZnSe thin films. A formation mechanism is described on the basis of the HRXRD curve, the TEM and the high resolution TEM (HRTEM) images, and the EDS profiles.

The samples used in this study were *n*-type ZnSe epitaxial layers grown on n-type GaAs (100) substrates by using molecular beam epitaxy (MBE) with a Riber 32 P MBE system. Elemental Zn and Se with purities of 99.9999% were used as the source materials, and the Zn/Se flux ratio was approximately 0.5 during ZnSe epilayer growth. The growth of *n*-type ZnSe epilayers was carried out using Cl impurity doping in a growth chamber at a pressure of 10^8 Torr. The depositions of the ZnSe epilayers were done at a substrate temperature of 280 °C, and the typical growth rate was 0.7 μm/h. Prior to ZnSe growth, the chemically cleaned GaAs substrates were thermally etched to desorb any GaAs-oxide layer. The TEM measurements were performed using a JEM-ARM1300S transmission electron microscope operating at 1.25 MeV.

Figure 1(a) presents a cross-sectional bright-field TEM image showing a ZnSe thin film with a thickness of approximately 30 nm grown on a GaAs substrate. A high density of ZnSe nanostructures exists on the ZnSe thin film. Figure 1(b) shows a HRTEM image of the ZnSe nanostructures consisting of the {111} planes and the (100) plane, which are the most stable planes in the zinc-blende structure. The width and the height of the ZnSe nanostructures formed on the ZnSe thin film are approximately 5.5 and 2 nm, respectively.

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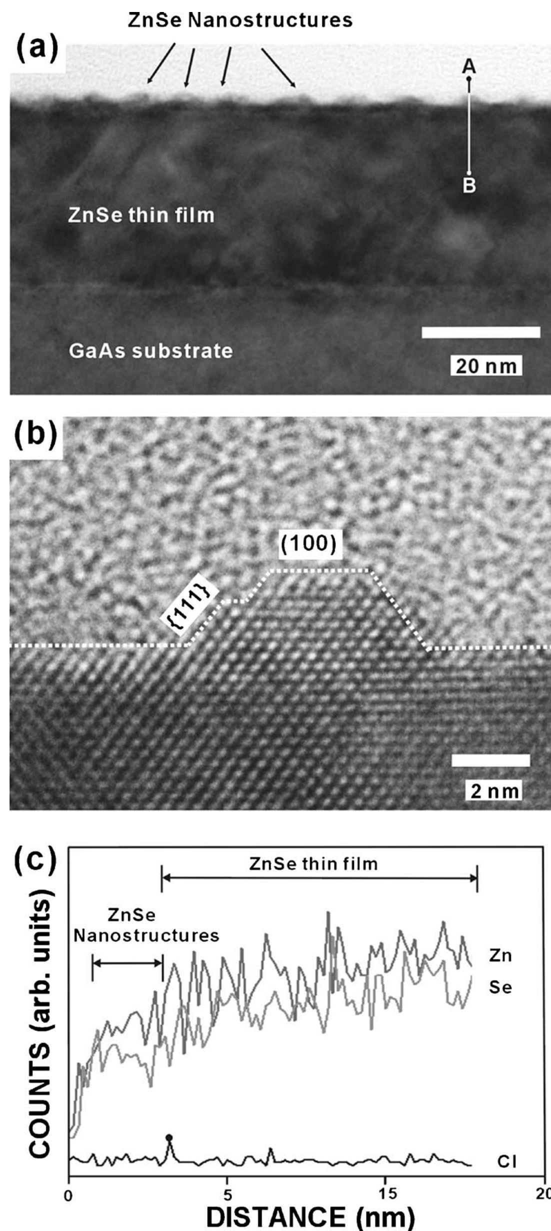

FIG. 1. (a) Cross-sectional bright-field transmission electron microscopy image showing ZnSe nanostructures on ZnSe thin film with a thickness of approximately 30 nm grown on a GaAs substrate. (b) High-resolution transmission electron microscopy image of ZnSe nanostructures with a width and a height of approximately 5.5 and 2 nm on the ZnSe thin film. (c) Energy dispersive spectroscopy line profiles for the elemental composition variation from A to B shown in (a).

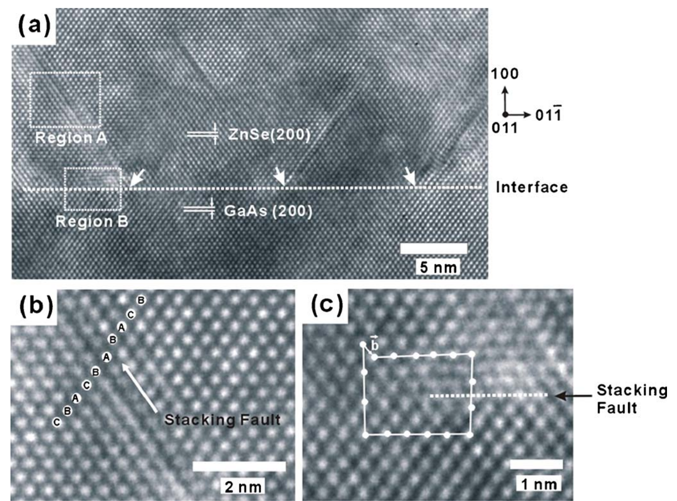

FIG. 2. (Color online) (a) Cross-sectional high-resolution transmission electron microscopy image along the [011] beam direction at the heterointerface between the ZnSe thin film and the GaAs substrate. (b) A magnification of region A in the high-resolution transmission electron microscopy image shown in (a), and (c) a magnification of region B in the high-resolution transmission electron microscopy image shown in (a).

The formed ZnSe nanostructures with a high density are much smaller than those of ZnSe self-assembled QDs grown in the SK and the VW modes.[14,20–22] A EDS spectral analysis between regions A and B shown in Fig. 1(a) was carried out in order to clarify the existence of Cl impurities on the surface of the ZnSe thin film. The EDS line profile indicates that an accumulation of the Cl impurities occurs on the surface of the ZnSe thin film during the growth of the ZnSe thin film. The lattice mismatch between the ZnSe thin film and the GaAs substrate ($\Delta d/d$), determined by the angular distance in the HRXRD curve, is approximately 0.155%. The HRXRD peak corresponding to the ZnSe epilayer is broadened due to the defects generated by the ZnSe/GaAs misfit strain relaxation. The value of the angular distance for the ZnSe thin films with a large thickness is lower, and the full width at half maximum of the peak is smaller, indicative of full relaxation of the lattice constant for the ZnSe thin film with a large thickness.[30] However, the misfit strain in the ZnSe thin film with a thickness of approximately 30 nm studied in this work is not fully relaxed.

Figure 2(a) shows a cross-sectional HRTEM image along the [011] beam direction at a heterointerface between the ZnSe thin film and the GaAs substrates. ZnSe epilayers are pseudomorphically grown with relative orientations of the ZnSe$\langle 011\rangle \| $GaAs$\langle 011\rangle$ and ZnSe$\{200\} \|$GaAs$\{200\}$, and stacking faults, indicated by the arrows, are generated at the ZnSe/GaAs heterointerface to accommodate the misfit strain. Figure 2(b), which is a magnification of region A in the HRTEM image shown in Fig. 2(a), shows a stacking fault transformation from the perfect-crystal layer sequence of *ABCABC* into to the imperfect-crystal layer sequence of the *ABCABABC*, resulting from the removement of the layer *C* from a perfect-crystal layer with a displacement of $R = -1/3\langle 111\rangle$. This type of the stacking fault is typically observed in the ZnSe/GaAs heteroepitaxial system.[31,32]

Figure 2(c), which is a magnification of region B in the HRTEM image shown in Fig. 2(a), shows that a misfit dislocation at the heterointerface between the ZnSe thin film and the GaAs substrate is caused by inserting or removing a (001) plane with a displacement of **b**. The schematic diagrams of Fig. 3 explain the generation of the misfit dislocation due to the insertion or removal of the (001) plane at the ZnSe/GaAs heterointerface for strain accommodation due to a GaAs surface miscut. Because an elastic energy is generated by the substrate surface step,[33] the atomic arrangement of the ZnSe thin film is tilted, as shown in Fig. 3(a). The generated strain due to the existence of a surface miscut might be accommodated by the dislocations existing at the heterointerface in the heterostructures.[34] Since the elastic energy due to the GaAs surface miscut can be accommodated by the insertion of a (001) layer, the strained ZnSe thin film shown in Fig. 3(a) changes into a strain-accommodated ZnSe thin film, as shown in Fig. 3(b), which is in reasonable agreement with the HRTEM image in Fig. 2(c).

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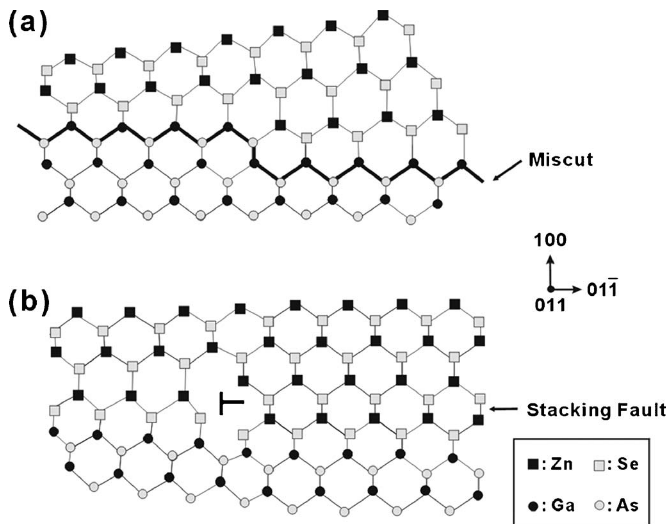

FIG. 3. (a) Schematic diagram of the tilted ZnSe thin film due to the elastic energy generated by the GaAs substrate surface step. (b) The strained ZnSe thin film accommodated by inserting the (001) layer shown in Fig. 2(c). T represents the dislocation core of the ZnSe film.

The strain generated not only from the misfit between the ZnSe thin film and the GaAs substrate but also from the surface miscut should be considered to describe a formation mechanism for the ZnSe nanostructures on the ZnSe thin film grown on a GaAs substrate. Even though the strain for the thicker ZnSe film can be effectively accommodated by the misfit dislocation, a small amount of residual strain still remains in a very thin ZnSe film with a thickness of 30 nm, as identified in the HRXRD curve. Cl impurities accumulated on the surface of the ZnSe thin film shown in Fig. 1(c) induce a compressive strain, acting as nucleation sites for the formation of ZnSe nanostructures, in the surface of the ZnSe thin film. The strain created in the surface can decrease the surface energy resulting from the formation of the isolated islands, resulting in the strain relaxation in the surface. Therefore, the compressive strain generated due to the accumulation of Cl impurities on the surface of the ZnSe thin film and the residual strain existing in the ZnSe thin film with a thin thickness provide the strain energy for the formation of the ZnSe nanostructures on Cl-doped ZnSe thin films grown on GaAs substrates.

In summary, ZnSe nanostructures were formed on the Cl-doped ZnSe thin film grown on a GaAs substrate by using MBE. The bright-field TEM images and the HRTEM images showed that a high density of ZnSe nanostructures was formed on the ZnSe thin films grown on GaAs substrates. The width and the height of the ZnSe nanostructures were approximately 5.5 and 2 nm, which are very small size. The formation of the ZnSe nanostructures on Cl-doped ZnSe thin films grown on (100) GaAs substrates was attributed to the strain energy resulting from the existence of the compressive strain generated by the accumulation of Cl impurities on the surface of the ZnSe thin film and from the residual strain existing in the ZnSe thin film with a thin thickness.

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