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Effect of thermal annealing on the surface, optical, and structural properties of *p*-type ZnSe thin films grown on GaAs (100) substrates

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II–VI/III–V heterostructures based on wide-energy band-gap II–VI compound semiconductors have been very attractive because of their potential applications in short-wavelength optoelectronic devices [1–5]. Among these II–VI/III–V mixed heterostructures, ZnSe/GaAs heterostructures have been particularly interesting due to their promising applications for the fabrication of laser diodes and light-emitting diodes operating in the blue-green region of the spectrum [6–10]. However, relatively little work has been performed on II–VI/III–V heterostructures in comparison with III–V/III–V heterostructures due to cross-doping problems resulting from interdiffusion or intermixing during growth and fabrication [11]. Since thermal treatment is necessary for the fabrication processes of several kinds of optoelectronic devices utilizing ZnSe/GaAs heterostructures, the role of the thermal annealing processes is very important in achieving high-performance devices [12]. Therefore, studies of the annealing effects on the surface, the structural, and the optical properties play a very important role in enhancing device efficiency.

This letter reports the effect of annealing of *p*-type ZnSe epilayers grown on *n*-type GaAs (100) substrates by using molecular beam epitaxy (MBE). Atomic force microscopy (AFM), photoluminescence (PL), and transmission electron microscopy (TEM) measurements were performed in order to investigate the surface, the optical, and the structural properties of as-grown and annealed ZnSe/GaAs heterostructures.

The samples used in this study were *p*-type ZnSe epitaxial layers grown on *n*-type GaAs (100) substrates in a Riber 32 P system by using MBE. Elemental Zn and Se with purities of 99.9999% were used as the source materials, and the flux ratio, Zn/Se, was approximately 0.5 during ZnSe epilayer growth. The *p*-type doping was carried out using an rf plasma source to excite nitrogen gas at a pressure of 10^{-8} Torr in the growth chamber. The deposition was 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. Using a capacitively coupled rf plasma system with a 13.56-MHz frequency, the as-grown samples were placed downstream in a hydrogen plasma with a power density of 0.078 W/cm^2 at a pressure of 0.9 Torr for 30 min at 80 °C. The rapid thermal annealing (RTA) process was performed in a nitrogen atmosphere with a tungsten-halogen lamp as the thermal source, and it was carried out at a temperature of 550 °C.

Capacitance-voltage (C-V) measurements were performed using a capacitance meter, which was automated using an IBM PC computer. The PL spectra were measured using a 65-cm monochromator equipped with an RCA 31034 photomultiplier tube. The excitation source was the 3250-Å line of a He-Cd laser operating with an excitation power density of approximately 10 kW/cm^2. The TEM observations were performed in a Jeol 200CX transmission electron microscope operating at 400 kV. The samples for the TEM measurements were prepared by cutting and polishing to an approximately 30-μm thickness by using diamond paper and then by argon-ion milling at liquid-nitrogen temperature to electron transparency.

The *p*-type ZnSe films grown by MBE had mirrorlike surface without any indication of pinholes and microcracks, which was confirmed by using Nomarski optical microscopy. The typical thickness of the *p*-type ZnSe layer was approximately 1 μm, which was estimated from the scanning electron microscopy measurements. The double-crystal rocking curves showed that the as-grown *p*-type 1-μm-thick ZnSe films were high-quality films with a full width at half maximum (FWHM) of 72.2 s. When the *p*-ZnSe films were annealed

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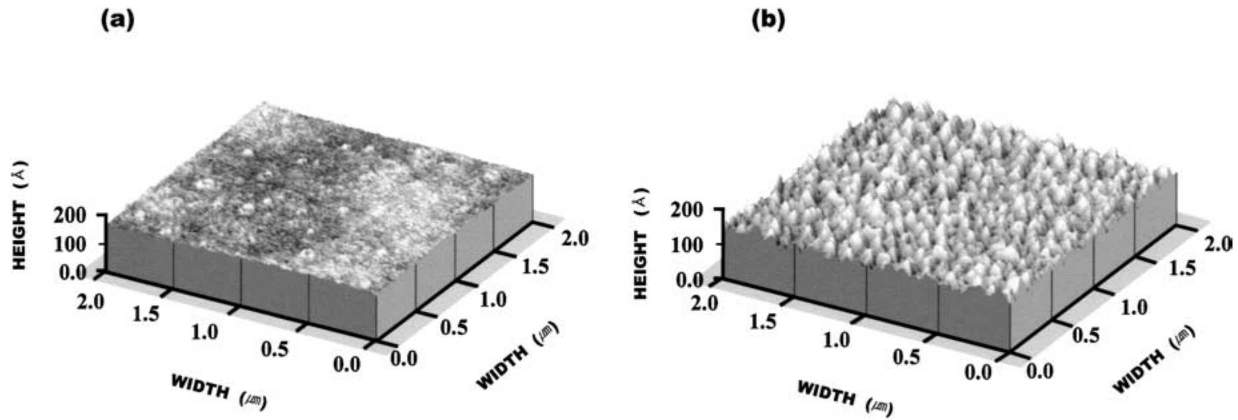

Figure 1 Atomic force microscopy images of (a) as-grown and (b) annealed (550 °C) *p*-type ZnSe epilayers grown on GaAs substrates.

at 550 °C, the FWHMs of the surfaces of the annealed ZnSe epitaxial layers increased to 101.2 s, indicative of a deterioration of the ZnSe films.

Fig. 1 shows the AFM images of (a) as-grown and (b) annealed *p*-type ZnSe epilayers grown on GaAs substrates. The root-mean-square surface roughness of the as-grown and the annealed *p*-type ZnSe epitaxial layers, as determined from the AFM measurements, were 4.20 and 12.2 Å, respectively. While the surface of the as-grown *p*-ZnSe epilayer grown on the *n*-GaAs substrate is very smooth, that of the annealed *p*-ZnSe epilayer was rougher. The deterioration of the surface of the annealed *p*-ZnSe epilayer originates from evaporation of elemental Se atoms in the ZnSe epilayer.

Fig. 2 shows that the PL spectra at 20 K for (a) the as-grown and (b) the annealed 550 °C *p*-type epilayers grown on GaAs substrates. The carrier densities ($N_a - N_d$) of the as-grown and the annealed *p*-type ZnSe layers, as determined from the capacitance-voltage measurements at 300 K, were approximately 3×10^{17} cm^{-3} and 3.5×10^{17} cm^{-3}, respectively. The increase in the carrier density for the annealed *p*-type ZnSe thin film in comparison with that for the as-grown *p*-type ZnSe epilayer originated from an increase in the number of Se vacancies and the dissociation of the nitrogen complex in *p*-type ZnSe. The PL spectrum for the as-grown *p*-type ZnSe shows a dominant deep donor-acceptor pair (DAP_d) emission, residual shallow donor-acceptor pair (DAP_s) peaks at 2.655 and 2.684 eV [13] and their phonon replicas, a deep acceptor bound exciton (I_1) peak at 2.785 eV [14], and a weak-intensity free exciton line (E_x) at 2.802 eV. The DAP_d emission is related to the transition between deep donors and nitrogen acceptors, and the DAP_s emission is considered to be a transition between residual shallow donors and nitrogen acceptors [15]. When the ZnSe/GaAs heterostructure is annealed at 550 °C, while the PL intensities of the DAP_d and DAP_s peaks together with their phonon replicas slightly decrease, that of the I_1 peak in Fig. 1b remarkably increases in comparison with that for the as-grown sample. This result indicates that the number of Se vacancies and the amount complex dissociation were increased due to thermal annealing treatment, which was confirmed by the C-V measurements.

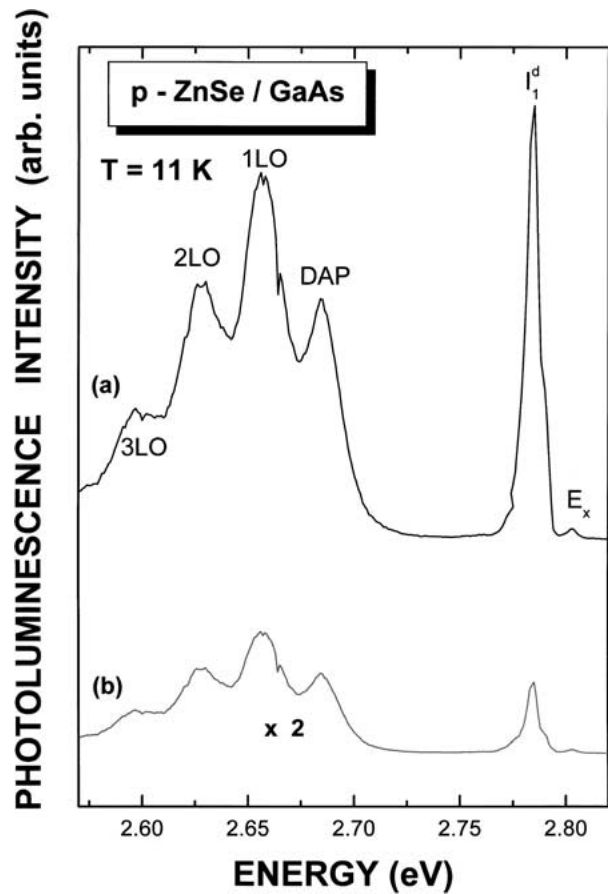

Figure 2 Photoluminescence spectra at 11 K for (a) as-grown and (b) annealed (550 °C) *p*-type ZnSe epilayers grown on GaAs substrates.

Fig. 3 shows bright-field TEM images of (a) the as-grown and (b) the annealed (550 °C) *p*-type ZnSe epilayers. There are no significant problems at the heterointerfaces of the ZnSe/GaAs grown at 280 °C, and the interface between the ZnSe epilayer and the GaAs substrate is relatively flat. When the ZnSe/GaAs heterostructure is annealed at 550 °C, a relaxation behavior occurs at the interface.

Cross-sectional high-resolution TEM images of the (a) as-grown and the (b) annealed (550 °C) *p*-type ZnSe epilayers are shown in Fig. 4. Both images show the top ZnSe layer and the bottom GaAs substrate as well as the lattice structures on both sides of the heteroepitaxial interface. The image of the as-grown

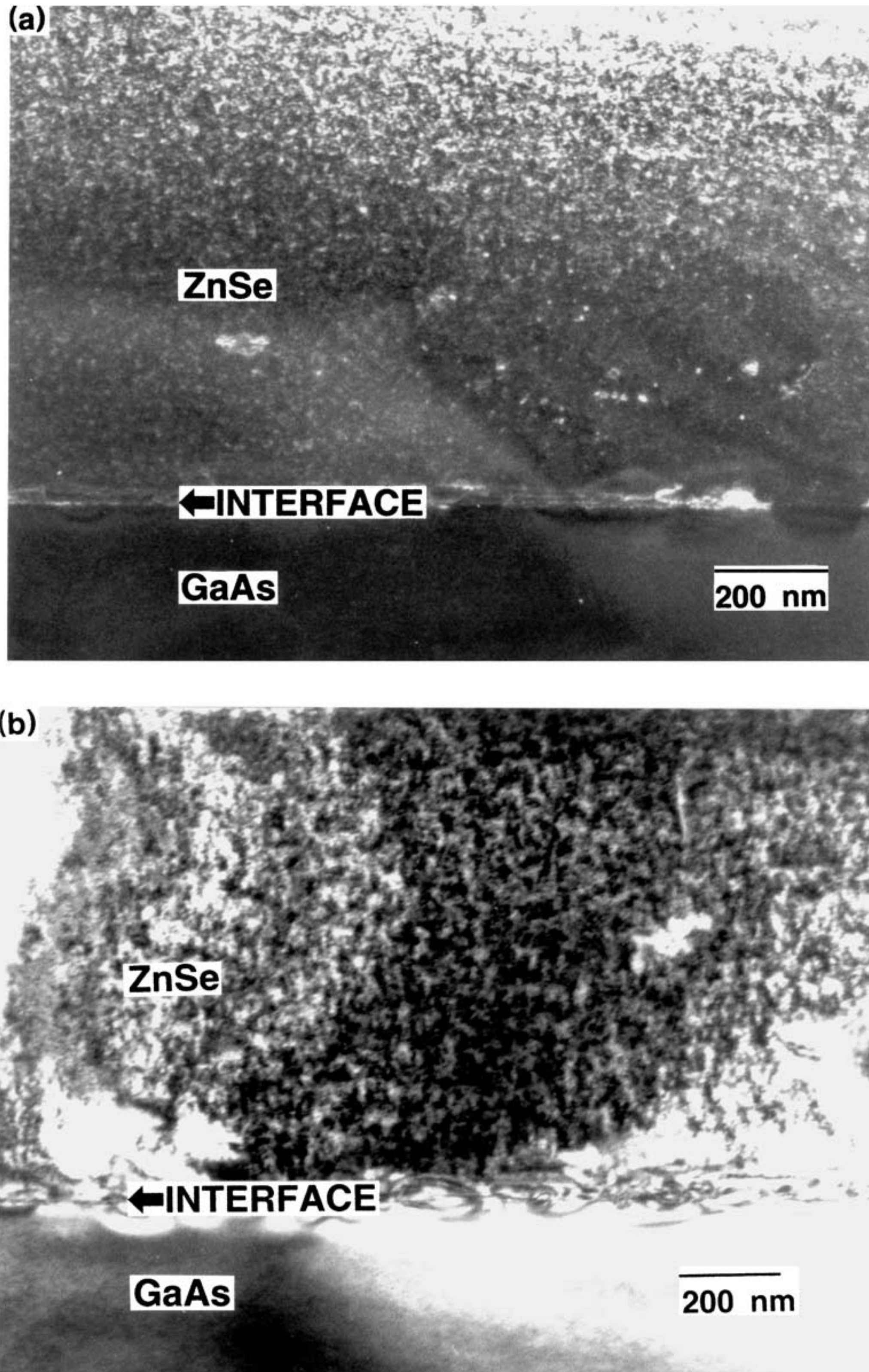

Figure 3 Bright-field transmission electron microscopy images of the (a) as-grown and (b) annealed (550 °C) *p*-type ZnSe epilayers.

ZnSe/GaAs structure indicates the presence of misfit dislocations and Frank partial dislocations resulting from the lattice mismatch between the ZnSe epilayer and the GaAs substrate. Since the Frank partial dislocations act as nucleation sites for misfit dislocations [16], the number of misfit dislocations in the annealed ZnSe is much larger than that in the as-grown undoped ZnSe. The bright-field and the high-resolution TEM images indicate that the qualities of the ZnSe epilayer and the ZnSe/GaAs interface are deteriorated by thermal annealing.

In summary, AFM, PL, and TEM measurements were performed on as-grown and annealed *p*-type ZnSe epitaxial films grown on *n*-type GaAs substrates by using MBE. When the ZnSe epilayers were annealed at 550 °C, the root-mean-square surface roughness, as indicated by the AFM images, became larger, and the PL intensity of the I_1 peak increased due to an

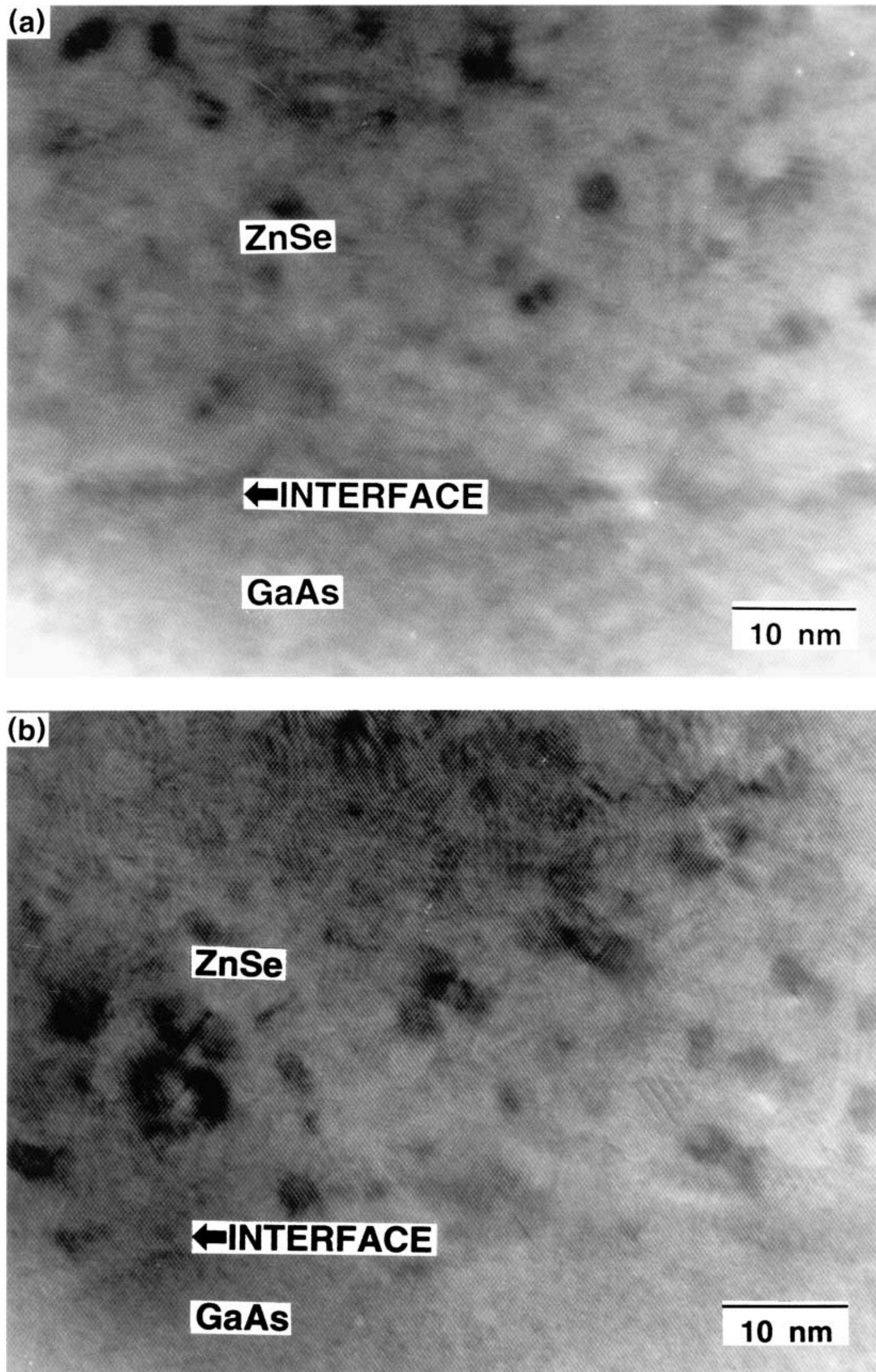

Figure 4 High-resolution transmission electron microscopy images of the (a) as-grown and (b) annealed (550 °C) *p*-type ZnSe epilayers.

increase in the number of Se vacancies and in the amount of complex dissociation resulting from thermal energy. The qualities of the ZnSe epilayer and the ZnSe/GaAs interface were deteriorated by thermal annealing. These results indicate that the crystalline qualities of the *p*-type ZnSe thin films and of the ZnSe/GaAs heterointerface deteriorate upon thermal annealing.

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