Defect reduction in ZnSe grown by molecular beam epitaxy on GaAs substrates cleaned using atomic hydrogen

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(Received 26 February 1996; accepted for publication 28 April 1996)

Atomic hydrogen is demonstrated to effectively clean GaAs substrates for subsequent growth of ZnSe by molecular beam epitaxy. Optical fluorescence microscopy is shown to be a useful technique to image nonradiative defects related to stacking faults. While the density of stacking faults in ZnSe films grown using conventional thermal cleaning is greater than 10^7 cm^{-2}, stacking fault densities lower than 10^4 cm^{-2} are obtained using atomic hydrogen cleaning. Low-temperature photoluminescence spectra of undoped ZnSe are dominated by excitonic transitions for the low defect density samples in contrast to the high level of defect-related emission from high defect density samples. © *1996 American Institute of Physics.* [S0003-6951(96)03427-4]

Since the first demonstration of a room-temperature green diode laser based on II–VI semiconductors by Haase *et al.*,[1] progress has been consistently impeded by materials quality. A major problem is a high density of defects related to stacking faults in ZnSe-based epilayers on GaAs substrates. The defects lead to degradation and device failure in an unacceptably short time.[2–4] The stacking faults originate at the substrate surface during initial layer growth[2,5] either due to incomplete oxide removal or poor surface preparation. For molecular beam epitaxy (MBE) growth of ZnSe on GaAs substrates, the final step prior to the growth is often a thermal cleaning to remove the native oxides.[6,7] The resulting GaAs surface exhibits a Ga-rich surface reconstruction which can lead to the formation of Ga_2Se_3 at the interface[8] to serve as nucleation sites for stacking faults. Either heating the substrate under an As flux or the growth of GaAs epilayers prior to ZnSe growth improves the interface quality.[9,10] Kuo *et al.* indicate that stacking fault densities less than 10^4 cm^{-2} can be obtained through a combination of GaAs epilayer growth followed by Zn treatment prior to ZnSe growth.[5] A disadvantage of this approach is that a separate growth chamber is required for the GaAs epilayer deposition to minimize the potential for cross contamination.

Atomic hydrogen is effective for cleaning substrates prior to epilayer growth.[11–18] Several studies achieved an As-stabilized GaAs surface after atomic hydrogen cleaning at temperatures between 360 and 400 °C[11–13] which is crucial to a high quality ZnSe/GaAs interface.[9] In this letter, we report that low defect density ZnSe layers can be achieved by atomic hydrogen cleaning of GaAs substrates prior to the growth of ZnSe films without any additional surface treatment. In addition, we demonstrate that optical fluorescence microscopy is useful for evaluating the density of macroscopic nonradiative defects.

ZnSe thin films were grown at West Virginia University on semi-insulating (100) GaAs substrates. Nitrogen doping was achieved using a cryogenically cooled rf plasma source (Oxford Applied Research CARS-25). Atomic hydrogen was produced using a thermal cracker (EPI) with an efficiency of about 5%. The 2-μm thick layers were grown at 250 and 300 °C with Zn to Se beam equivalent pressure (BEP) ratios ranging from 0.5 to 1.5. Doped layers were grown on an undoped 0.4 μm buffer layer.

The substrates were initially degreased, etched in $H_2SO_4:H_2O_2:H_2O(8:1:1)$ for 5 min at room temperature, and rinsed in flowing de-ionized water for 5 min. The substrates were then thermally treated. The more conventional treatment involved heating to 580 °C for 20 min prior to growth. Under the other treatment, the substrate was heated to 360 °C under atomic hydrogen at 1×10^{-6} Torr BEP for 20 min.

The reflection high-energy electron diffraction (RHEED) pattern evolves from a ring or dot pattern prior to the preheat (indicative of an oxide layer) to a spotty and then streaky pattern at the end of cleaning. The conventional preheat led to a Ga-rich surface, indicated by a (4×2) reconstruction, which became rough if the heating continued too long. ZnSe growth on this surface became two dimensional (2D) within 10 s after growth initiation. Atomic hydrogen cleaning resulted in an As-stabilized surface with a (2×4) surface reconstruction. ZnSe layers grown on this surface resulted in a 2D growth mode immediately after growth initiation. We also tried thermal cleaning under a molecular hydrogen flux with the cracker turned off, which yielded results similar to the conventional preheat and required a temperature of 580 °C to obtain oxide removal.

Two types of stacking fault defects are observed in ZnSe films grown on GaAs substrates.[5,19] Frank-type stacking faults appear as triangular-shaped twin faults, while Schockley-type stacking faults are more line shaped. The radiative efficiency is lower in the region of the stacking fault, allowing the use of cathodoluminescence (CL) to image the defects.[5,20,21] Here, we report that optical fluorescence microscopy can also image these stacking faults. An Olympus BX60M microscope with a standard fluorescence attachment utilizing a 100 W Hg lamp resulted in a simpler system than that required for CL.

Figure 1(a) is the fluorescence micrograph of an undoped ZnSe film grown on GaAs substrate with conventional thermal cleaning. The dark features are nonradiative regions due to stacking faults, with short line-shaped features ascribed to Shockley-type stacking faults and the larger

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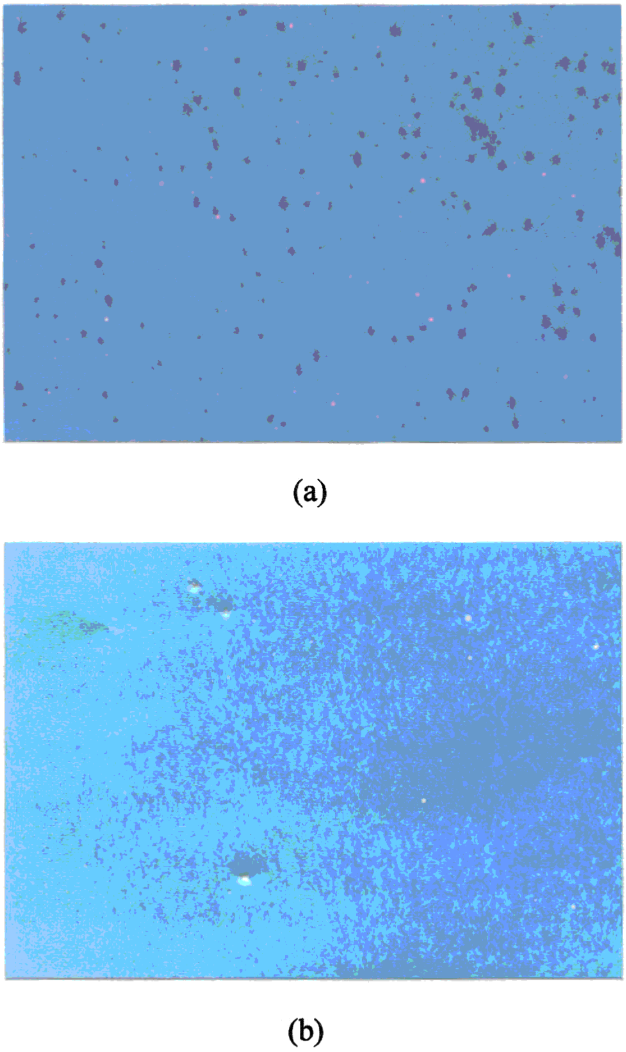


FIG. 1. Optical fluorescence micrograph of undoped ZnSe/GaAs grown (a) with conventional thermal cleaning, (b) with atomic hydrogen cleaning. The micrographs represent an area of 125 by 88 μm.

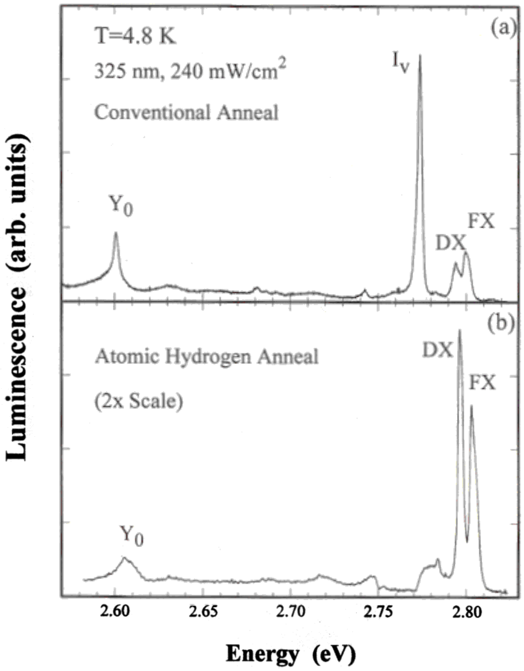


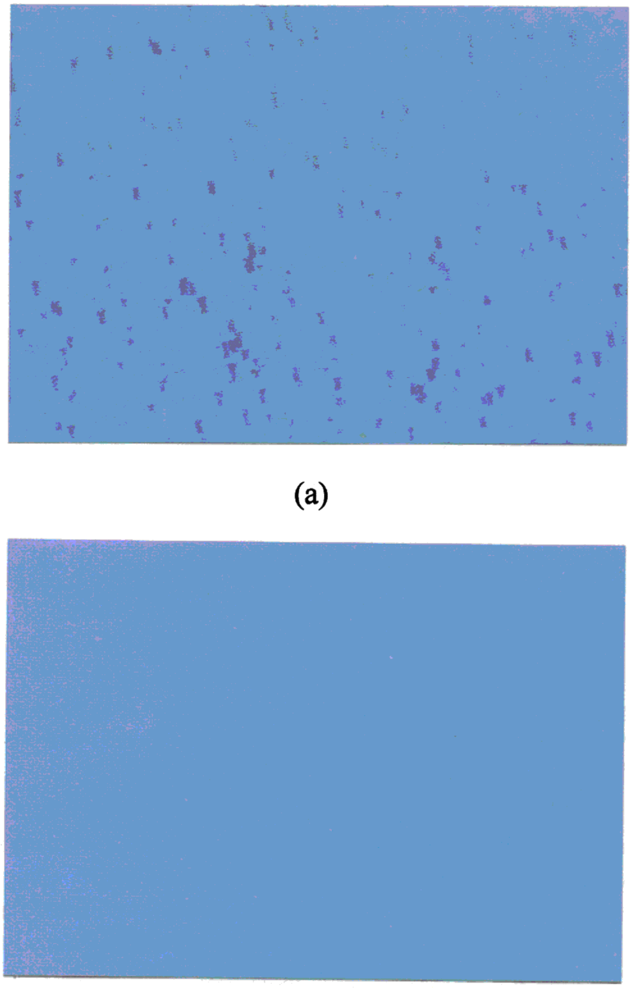
FIG. 2. Low-temperature photoluminescence spectra of undoped ZnSe/GaAs grown (a) with conventional thermal cleaning, (b) with atomic hydrogen cleaning (intensities shown are enhanced by a factor of 2).

triangular-shaped features to Frank-type stacking faults. The density of both types of defects was determined to be greater than 10^7 cm^{-2}. Figure 1(b) shows a typical fluorescence micrograph of undoped ZnSe grown on a GaAs substrate cleaned with atomic hydrogen. A significant reduction in defect density is observed. The dark features associated with the stacking faults were isolated and difficult to find on these layers. The density of both types of stacking faults was conservatively estimated to be less than 10^4 cm^{-2}. We did not observe a significant difference for the two different substrate temperatures or growth-flux ratios investigated.

Low-temperature photoluminescence (PL) spectra also showed a dramatic difference between samples cleaned with atomic hydrogen and those grown after the conventional thermal anneal. The PL was measured at 4.8 K using the 325 nm line from a He–Cd laser (focused to a power density of 240 mW/cm^2). Spectra were corrected for system response. PL of high quality undoped layers will be dominated by excitonic features while defect-related features will dominate the PL spectra in layers with high defect densities.[19] The Y_0 line at 2.60 eV line has been related to dislocation loops.[21,22] The I_v line at 2.774 eV has been attributed to an extended defect complex[23] and depends on the density of defects.[19,21] Figure 2 shows the PL spectra corresponding to the samples in Fig. 1. Figure 2(a) exhibits prominent I_v and Y_0 lines which can be attributed to the high defect density in the film. Exciton-related emissions were quite weak. In contrast, as shown in Fig. 2(b), features due to donor-bound excitons (DX) and free excitons (FX) were dominant in the undoped samples grown on substrates cleaned with atomic hydrogen. While possible to obtain PL spectra similar to Fig. 2(b) using a thermal anneal and different growth conditions, the only change between the layers whose PL is shown in Fig. 2 was the substrate cleaning process. This underscores the importance of substrate preparation in determining overall layer quality.

Heavy nitrogen doping ($>10^{18}$ cm^{-3}) enhances the formation of stacking faults.[24] In this study, ZnSe with nitrogen-incorporation levels greater than 10^{19} cm^{-3} (determined at Charles Evans and Associates, Rosewood, CA) were grown on substrates cleaned by both techniques. Figure 3(a) is a fluorescence micrograph of a sample grown with the conventional thermal cleaning. Stacking faults were observed at densities of about 10^8 cm^{-2}. In contrast, the micrograph displayed in Fig. 3(b) indicates a defect density of about 10^4 cm^{-2} for a sample cleaned with atomic hydrogen prior to growth. Low-temperature PL spectra of the doped films were dominated by the broad donor–acceptor pair (DAP) peaks in the range of 2.50–2.65 eV, typical of such heavily nitrogen-doped layers.[24–27] The peak intensity was about twice as large for atomic hydrogen cleaning, a direct reflection of the decrease in nonradiative defects.

There are advantages in using atomic hydrogen cleaning. The first is the low substrate temperature needed to perform the cleaning. For GaAs surfaces, the atomic hydrogen clean-



(a)

(b)

FIG. 3. Optical fluorescence micrograph of nitrogen doped ZnSe/GaAs grown (a) with conventional thermal cleaning, (b) with atomic hydrogen cleaning. The micrographs represent an area of 125 by 88 μm.

ing can be accomplished at a temperature less than 400 °C, while thermal cleaning must be carried out around 600 °C. The atomic hydrogen cleaning also results in an appropriate As-stabilized GaAs surface, eliminating the need for an As flux. Additionally, atomic hydrogen has been shown to be effective at removing carbon and other surface impurities as well as oxides.[12,28] This approach may eliminate the need for the growth of a GaAs epilayer, resulting in a less complicated growth process.

In conclusion, we have demonstrated that the density of defects related to stacking faults in MBE-grown ZnSe layers on GaAs substrates are reduced by using atomic hydrogen cleaning prior to growth. Both Frank- and Shockley-type stacking faults are easily observed using an optical fluorescence microscope. The defect density is greater than 10^7 cm^{-2} for both doped and undoped ZnSe films grown with conventional thermal cleaning. In contrast, the density is less than 10^4 cm^{-2} for those films grown with atomic hydrogen cleaning of the GaAs substrate. Low-temperature PL measurements of undoped ZnSe films indicate that the PL spectra are dominated by defect-related transitions (both I_v and Y_0 lines) for samples grown with thermal cleaning, while for atomic hydrogen cleaned samples the PL features are primarily excitonic. Thus, we believe that the use of atomic hydrogen to clean GaAs is an efficacious, yet simple, approach for producing ZnSe layers with low stacking fault densities.

We want to thank M. C. Petcu for assisting with the PL measurements. This work was supported by the West Virginia/National Science Foundation EPSCoR program and two NSF instrumentation Grants, No. DMR92-08130 and No. DMR92-14350.

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