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Special Issue Paper

The Effect of High Energy Electrons During the Growth of ZnSe and ZnMgSe by Molecular Beam Epitaxy

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Electron irradiation during reflection high-energy electron diffraction is shown to affect the growth of ZnSe and ZnMgSe by molecular beam epitaxy. The high-energy electrons produce an electron stimulated desorption effect during growth of ZnSe which primarily affects adsorbed Se. Se desorption rates under electron irradiation are shown to be significantly larger than thermal desorption rates. Electron irradiation also decreases ZnSe growth rates under Zn-rich conditions. The decrease in growth rate can be suppressed by either growth under Se-rich conditions or by using high-index substrate orientations, in this case (211)B. High-energy electron irradiation does not alter composition during the growth of ZnMgSe.

Key words: ZnSe, ZnMgSe, reflection high energy electron diffraction, electron stimulated desorption

INTRODUCTION

Reflection high-energy electron diffraction (RHEED) is one of the most useful and undoubtedly the most widespread of the various techniques used for in-situ monitoring during molecular beam epitaxy (MBE) growth.[1–4] While it was recognized early that RHEED could affect growing material, it has proven to be fairly benign for growth of GaAs and related III-V materials. There have been few investigations of how RHEED actually influences growth kinetics, impurity incorporation, or point defect formation. Farrell et al.[5] and Wu et al.[6] have reported that the high-energy electron irradiation occurring during RHEED affects the stoichiometry of static ZnSe and CdTe surfaces, respectively. Electron irradiation was also shown to influence surface reconstruction during the growth of CdTe.[6]

We have recently observed that RHEED can have a dramatic effect on the growth kinetics in ZnSe. A "stripe" associated with the position of the RHEED beam can be seen on many samples, while the effect of electron irradiation can be seen on other samples only by careful analysis using techniques such as spatial/spectral reflectance imaging. This special issue paper details the preliminary results of our investigation of how high energy electron irradiation affects the growth of ZnSe and ZnMgSe.

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EXPERIMENTAL

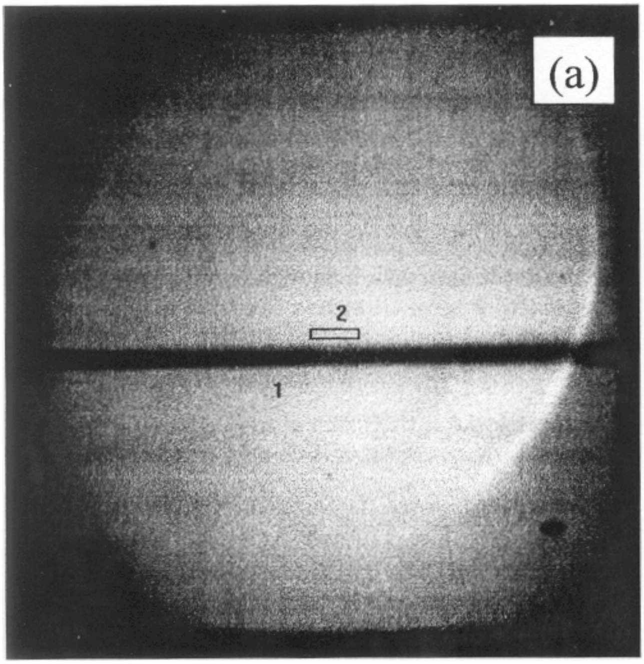
ZnSe and ZnMgSe were grown by MBE at West Virginia University. Details of the growth have been described elsewhere.[7] High-energy electron diffraction and irradiation studies were performed using a VE-026 electron gun from Vieetech Japan Co. Ltd. operating between 10 and 13 keV, with an electron current of ~25 μA. Studies were done in a typical RHEED geometry. RHEED images were captured and analyzed using a Si charge-coupled device (CCD) camera under the control of software from k-Space Associates, Inc. (Ann Arbor, MI). Film growth rates were monitored in-situ using the interference pattern observed in reflected light from a 680-nm diode laser. A Janis Super-Varitemp Dewar was used to obtain photoluminescence data using 325 nm excitation from a helium-cadmium laser with emitted light collected in a near-backscattering geometry using a 0.64 m grating spectrometer and a GaAs photomultiplier.

Imaging reflectance experiments were performed at ChemIcon, Inc. (Pittsburgh, PA).

THE EFFECT OF ELECTRON IRRADIATION ON STATIC ZnSe SURFACES

During our studies of the growth of ZnSe, we often observe features on the grown layers that correlate with the location of the electron beam during RHEED measurements. We typically grow on small samples, 1.5 cm × 1.5 cm, and have sacrificed sample rotation for better knowledge and control of the sample temperature during growth. If RHEED is performed during growth, the samples contain a discoloration in the form of a stripe visible to the eye. Such a stripe is readily apparent for the sample shown in Fig. 1a, which is a reflectance micrograph taken at a wavelength of 900 nm. Figure 1b shows the spectral reflectance taken both inside and outside the RHEED stripe. Analysis of the interference pattern indicates a slight decrease in growth rate with electron irradiation. This leads to a phase difference in the interference of the reflected light in the two regions, and provides the contrast making the stripe apparent.

Electron-stimulated desorption (ESD) effects have been previously reported by Farrell et al. for ZnSe,[5] and for CdTe by Wu et al.[6] Electron irradiation was shown to increase Se-desorption from ZnSe, and Te-desorption from CdTe static surfaces. In particular, the Se-stabilized (100) ZnSe surface exhibits either a (2×1) or a (1×1) reconstruction with an additional two-fold reconstruction along the [011] direction. The Zn-stabilized surface always exhibits a c(2×2) reconstruction.[8] Thus, either the disappearance of the reconstruction along [011] or the emergence of the two-fold reconstruction diffraction along the [010] direction can be used to monitor Se desorption. We chose to monitor the emergence of the [010] reconstruction to indicate the attainment of a Zn-stable surface. Approximately 0.3 μm of ZnSe was grown under conditions known to produce high quality material. The growth was interrupted and the static surface exposed to a Se-flux for about 5 sec. The Se shutter was closed and the RHEED pattern was monitored using a CCD camera. Figure 2 indicates the times required after the Se shutter was closed for the emergence of the [010] reconstruction pattern for several substrate temperatures for surfaces under electron irradiation. Each point represents the average of five measurements. The temperature-depen-



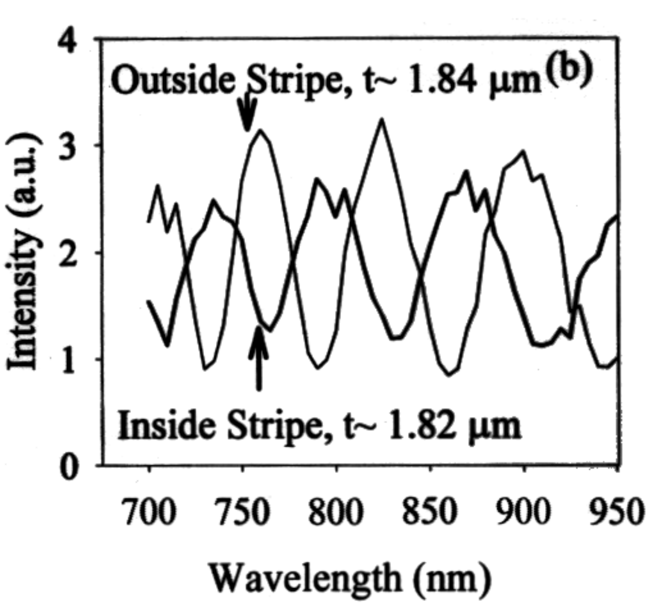


Fig. 1. (a) Reflectance image of a ZnSe layer at a wavelength of 900 nm, (b) spectral reflectance from the locations indicated by the rectangles.

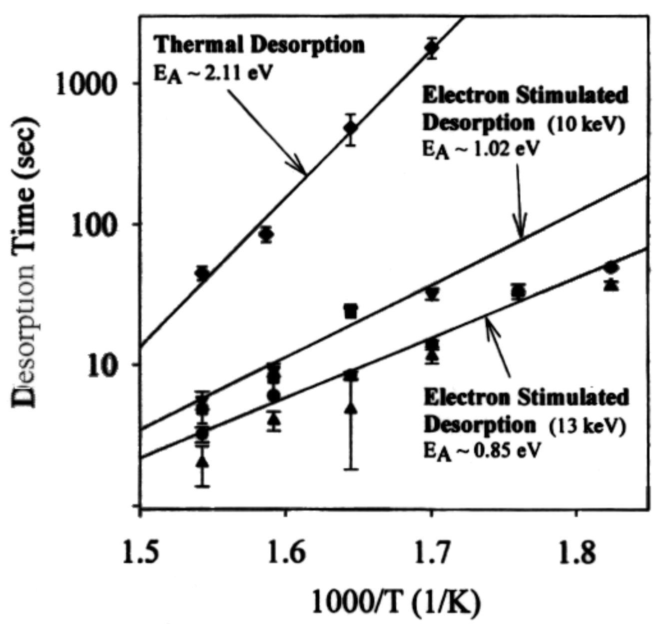


Fig. 2. Time intervals required for a Se-stable surface to evolve to a Zn-stable surface at various temperatures, with and without electron irradiation.

dence is indicative of a thermally-activated process, with an activation energy between 0.8 and 1.0 eV, possibly depending on electron energy. The desorption times for a strictly thermal process, one without electron irradiation, are also shown. For the latter case, the ZnSe surface was exposed to excess Se as before at the various substrate temperatures, but without the presence of electron irradiation. After a time, the sample was probed with the electron beam to see if a Zn-stable surface had emerged. The surface was then exposed to Se once again to produce a Se-stable surface. The process was repeated for various waiting times prior to electron beam exposure to bracket the Se thermal desorption time. The significant difference in activation energy between the two cases, 2.1 eV vs. ~1.0 eV indicates a large electron stimulated desorption effect is present.

THE EFFECT OF ELECTRON IRRADIATION DURING GROWTH OF ZnSe

The electron-stimulated desorption (ESD) of Se could lead to a decrease in growth rate. To investigate this, the RHEED beam was defocused to give a stripe approximately 3 mm wide. The laser used for growth rate measurements was focused to coincide with this stripe. By turning the electron beam on and off while monitoring the film thickness evolution, the effect on growth rate could be determined at various substrate temperatures as indicated in Fig. 3a for growth on a (100) surface. While increasing the substrate temperature lowers the growth rate for both Zn- and Se-

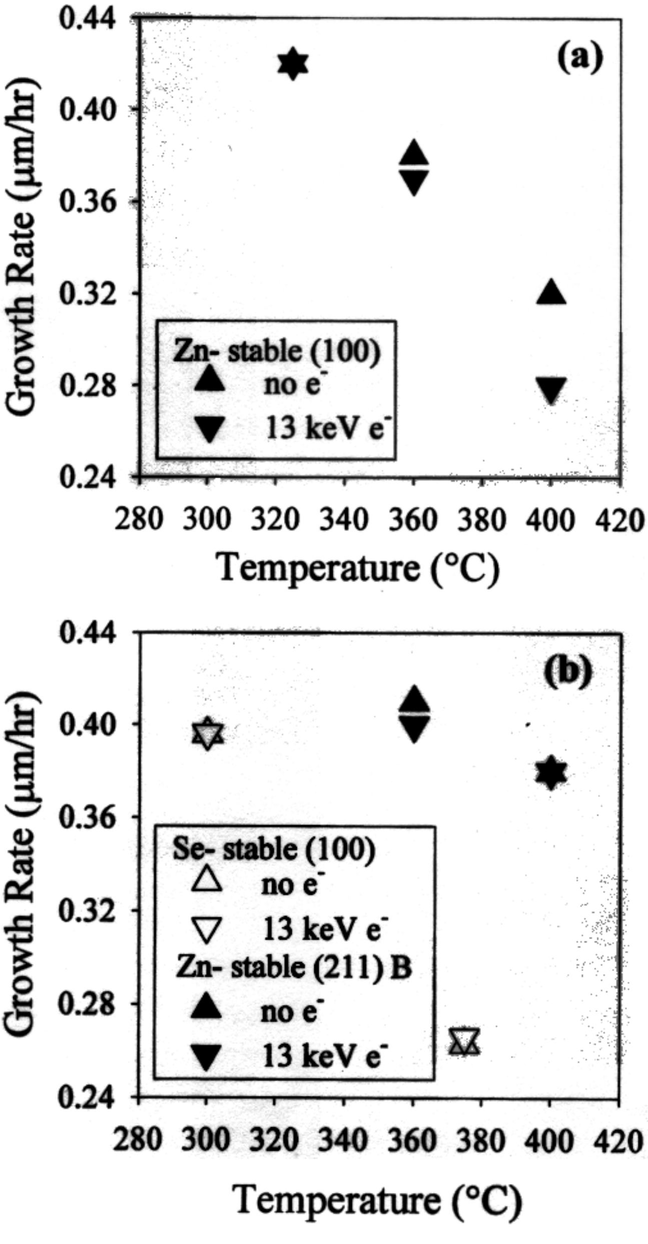


Fig. 3. ZnSe growth rates with and without electron irradiation for (a) Zn-stable (100) growth, (b) Se-stable (100) growth and Zn-stable (211)B growth.

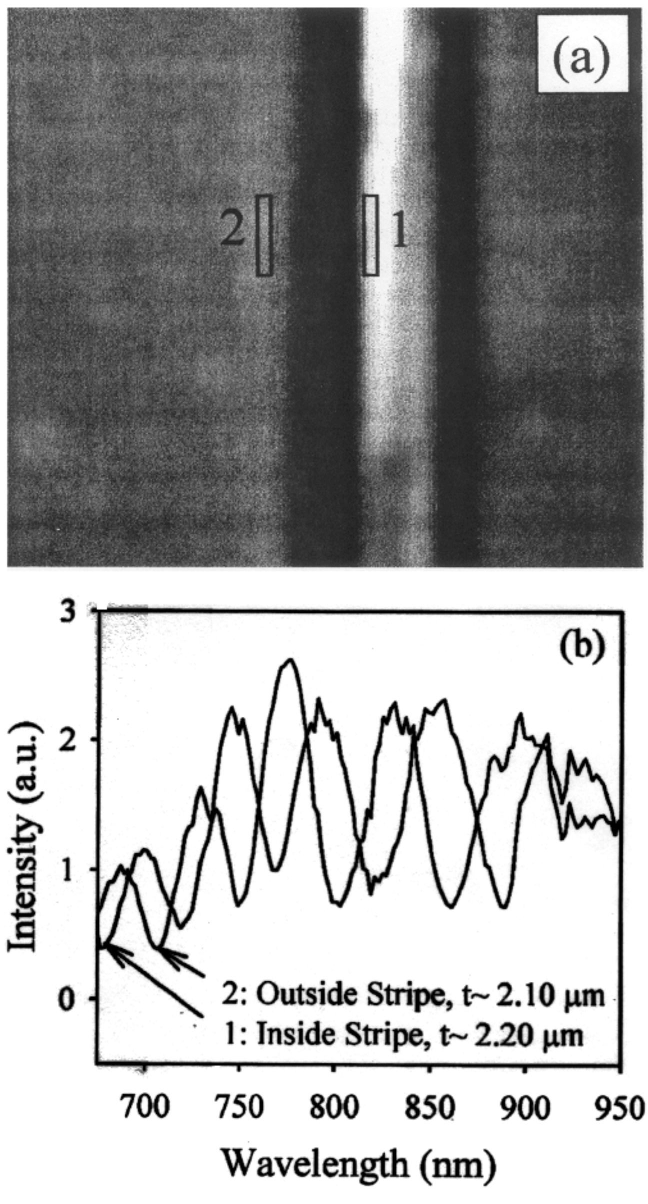


Fig. 4. (a) Reflectance image of a ZnMgSe layer at a wavelength of 900 nm, (b) spectral reflectance from the locations indicated by the rectangles.

stable growth, the presence of high energy electrons leads to a much more pronounced decrease in growth rate at higher temperatures for Zn-stable growth. A similar effect was not observed for Se-stable growth, as shown in Fig. 3b, consistent with the belief that the ESD process is primarily affecting Se adatoms.

Farrell et al. determined a thermal activation energy of ~0.6 eV for the ESD process from 10 keV electrons in ZnSe, considerably lower than our measured value of ~1.0 eV at the same energy. This difference in activation energy may be related to the fact that we used (100) substrates off-cut 2° towards [011] with a higher step density that may have caused the Se to be more tightly bound to the surface. To further test this idea, we investigated growth of ZnSe on (211)B-oriented GaAs substrates. This orientation does not exhibit differing reconstruction depending on Zn or Se-stable conditions, precluding RHEED desorption studies. However, as illustrated by the data in Fig. 3b, there was not a measurable difference in growth rate with and without electron irradiation on the (211)B orientation up to 375°C under Zn-stable conditions, indicating the effects of ESD were much less pronounced for this highly-vicinal orientation.

Farrell et al.[5] attribute the ESD process to the generation of holes in the ZnSe, which, according to Marfaing,[9] will affect the more electronegative surface specie, in this case Se. Simpson et al.[10] argue that this same process is the underlying origin of photon-stimulated effects also observed for above bandgap light illumination during growth. The observations reported here do not contradict this proposed mechanism, but also do not unambiguously resolve the underlying processes. In addition, there is little discussion in the literature on how the ESD process affects point defect formation, which is important for doping of ZnSe. We are extending the studies of the work on ZnSe reported in this special issue paper to address these two issues, with particular emphasis to see if RHEED affects the generation of point defects in II-VI semiconductors.

THE EFFECT OF ELECTRON IRRADIATION DURING GROWTH OF ZnMgSe

RHEED stripes have also been observed on ZnMgSe grown by MBE under Se-stable conditions which should suppress ESD effects. Figure 4 illustrates such a stripe imaged using spatial/spectral imaging. The presence of a RHEED stripe in the alloy provides a possible test to see if ESD effects primarily Se. If there are ESD effects for the Group II specie, it should not be the same magnitude for both Zn and Mg. Thus, a compositional change with high-energy electron irradiation would indicate an ESD effect for the group II adatoms.

A series of $Zn_{1-x}Mg_xSe$ samples were grown at temperatures ranging from 250°C to 400°C with composition, x, ranging from 0 to 0.45. The samples were grown under the excess Se flux that was shown to minimize the effects of electron irradiation for ZnSe. RHEED stripes were observed on each sample.

Spatial/spectral reflectance imaging allowed measurement of the thickness both inside and outside the RHEED stripe on each sample. Typically thickness changes were less than 2%, with the largest measured change around 8%. The magnitude of the thickness changes ranged around 30 nm to 150 nm for ~2 μm thick epilayers. Since this is an optical measurement, the apparent thickness change could also be due to a change in the index of refraction and thus composition. To check this latter point, measurements were made using a surface profilometer that indicated thickness variations of this order, but instrumental resolution limited quantitative comparison. Low-temperature photoluminescence measurements were made on the RHEED stripes and surrounding area. The resulting spectra were indistinguishable for each sample, presenting strong evidence that no change in composition occurred from electron irradiation. The photoluminescence result is consistent with adsorbed Se being the primary surface specie affected by high energy electron irradiation.

SUMMARY

The results reported here clearly show that high-energy electron irradiation can affect the growth of compound semiconductors. A significant electron stimulated desorption effect is observed for Se during the growth of ZnSe. While the effects on growth rate can be minimized either by growing under Se-stable conditions or on high index orientations, this may not give the best conditions for all types of structures. In addition, it is not yet clear how electron irradiation affects point defect formation. Since high-energy electrons can distinctly alter surface reconstruction and surface chemistry, RHEED measurements must be carefully considered on a case-by-case basis in order to not misinterpret the observations.

ACKNOWLEDGEMENTS

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