Point defect modification in wide band gap semiconductors through interaction with high-energy electrons: Is reflection high-energy electron diffraction truly benign?

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Electron irradiation during reflection high-energy electron diffraction is shown to affect the materials properties of ZnSe and GaN during growth 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 can be suppressed by either growth under Se-rich conditions or by using high index substrate orientations, in this case (211)B. Electron irradiation also influences growth rates for GaN grown by rf plasma-assisted molecular beam. Characterization using Raman and photoluminescence spectroscopy along with secondary ion mass spectrometry indicate electron irradiation can have a dramatic impact on point defect and impurity content of GaN. © *2000 American Vacuum Society.* [S0734-211X(00)06904-3]

I. 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 and on the incorporation of impurities/generation of point defects in ZnSe and GaN. A ''stripe'' associated with the position of the RHEED beam can be seen on many materials, while the effect of electron irradiation can only be seen by careful analysis on other samples, using techniques such as UV fluorescence microscopy. This article details the preliminary results of our current investigation of how high-energy electron irradiation affects the growth of ZnSe and GaN.

II. EXPERIMENT

ZnSe and GaN were grown by MBE in two separate systems at West Virginia University, one dedicated to the growth of III–nitride compound semiconductors and the other for the growth of II–VI materials. Details of the growth have been described elsewhere.[7,8] 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 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. UV fluorescence measurements were made on an Olympus Model BX60M Metallurgical System Microscope with a BX-FLA reflected light fluorescence attachment. A Janis SuperVaritemp 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 and Raman scattering experiments were performed at ChemIcon, Inc. (Pittsburgh, PA). Secondary ion mass spectrometry (SIMS) measurements were performed at Charles Evans and Associates (Redwood City, CA).

III. MACROSCOPIC EFFECTS OF HIGH ENERGY ELECTRON IRRADIATION: ZnSe

During our studies of the growth of ZnSe, we often observe the presence of 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 by 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

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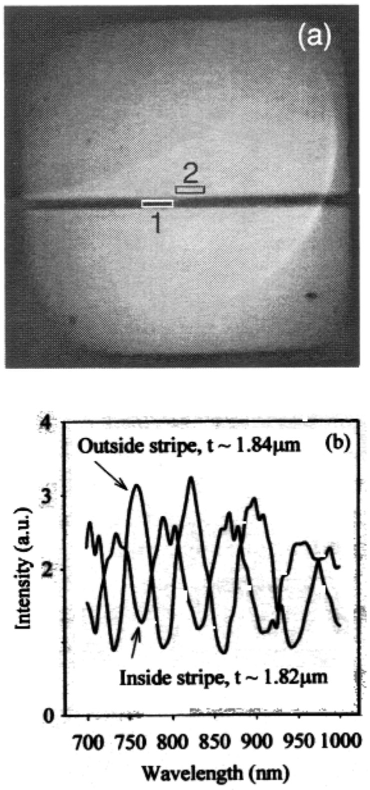

FIG. 1. (a) Reflectance image of a ZnSe layer at a wavelength of 900 nm; (b) spectral reflectance from the locations indicated by the rectangles.

Fig. 1(a), which is a reflectance micrograph taken at a wavelength of 900 nm. Figure 1(b) 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, and for CdTe by Wu *et al.* 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 twofold reconstruction along the $[01\bar{1}]$ direction. The Zn-stabilized surface always exhibits a $c(2\times2)$ reconstruction.[9] Thus, either the disappearance of the reconstruction along $[01\bar{1}]$ or the emergence of the twofold reconstruction diffraction along the [010] direction can be used to monitor Se desorption. We chose to monitor 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 s. 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. Each point represents the average of five measurements. The temperature dependence is

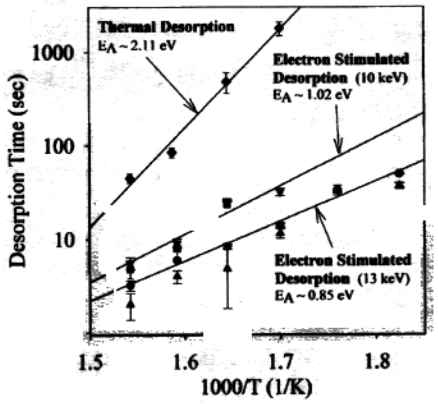

FIG. 2. Time intervals required for a Se-stable surface to evolve to a Zn-stable surface at various temperatures, with and without electron irradiation.

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, 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 vs ~1.0 eV indicates that a large electron stimulated desorption effect is present.

As speculated by Farrell *et al.*, the 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. 3(a). While increasing the substrate temperature lowers the growth rate for both Zn- and Se-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. 3(b), 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 $[01\bar{1}]$ 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. As illustrated by the data in Fig. 3(b), there was not a measur-

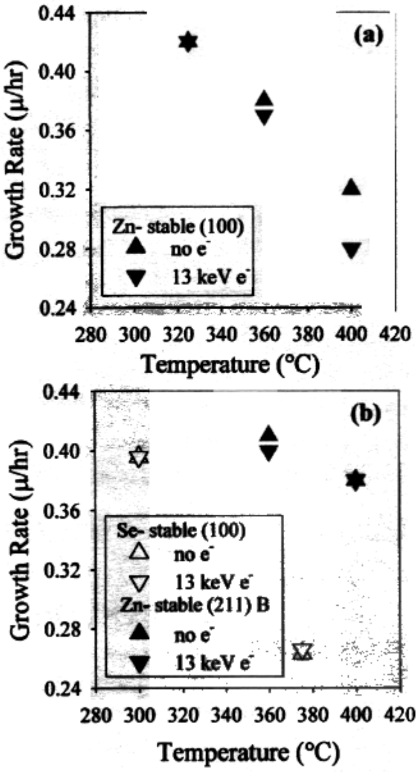

FIG. 3. ZnSe grown rates with and without electron irradiation, for various growth conditions.

able difference in growth rate with and without electron irradiation up to 400 °C under Zn-stable conditions, indicating the effects of ESD were less pronounced for this highly stepped orientation.

Farrell *et al.*[5] attribute the ESD process to the generation of holes in the ZnSe, which according to Marfaing[10] will affect the more electronegative surface species, in this case Se. Simpson *et al.*[11] argue that this same process is the underlying origin of photon-stimulated effects also observed for above band-gap 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 article to address these two issues, with particular emphasis to see if RHEED affects the generation of point defects in II–VI semiconductors.

IV. MICROSCOPIC EFFECTS OF HIGH ENERGY ELECTRON IRRADIATION: GaN

We have also observed RHEED stripes to occur during the growth of GaN. While we do not see a pronounced decrease in growth rate due to the presence of electron irradiation, we have observed cases where there is a variation on the order of 5%. Many times the presence of an electron stimulated process is more easily determined by measuring microscopic properties. Figure 4 is a gray-scale micrograph of the integrated visible room temperature luminescence of a GaN sample exhibiting a RHEED stripe. The micrograph was taken using our UV fluorescent microscope. The contrast is provided primarily by a significant change in intensity of the so-called yellow luminescence, a band centered around 2.2 eV.

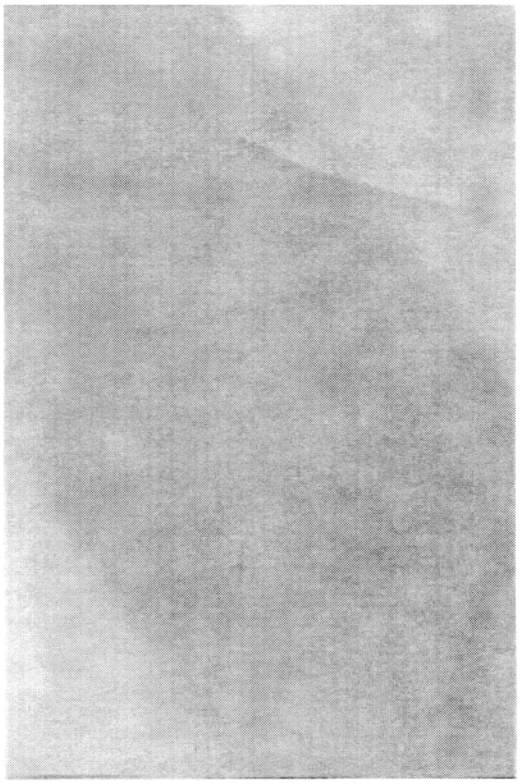

FIG. 4. Integrated visible fluorescence micrograph of a RHEED stripe on a GaN layer.

This particular sample was grown during a time when the GaN MBE system had a small air leak, resulting in the incorporation of significant amounts of carbon and oxygen, as indicated in the SIMS data plotted in Fig. 5. The scans labeled "outside stripe" were taken near the RHEED stripe, while the others were taken inside the stripe. There is a sig-

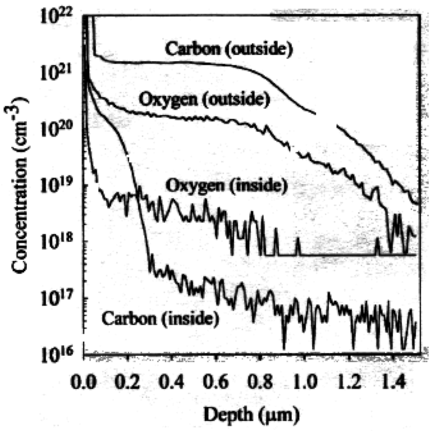

FIG. 5. SIMS of GaN indicating an ESD effect for oxygen and carbon.

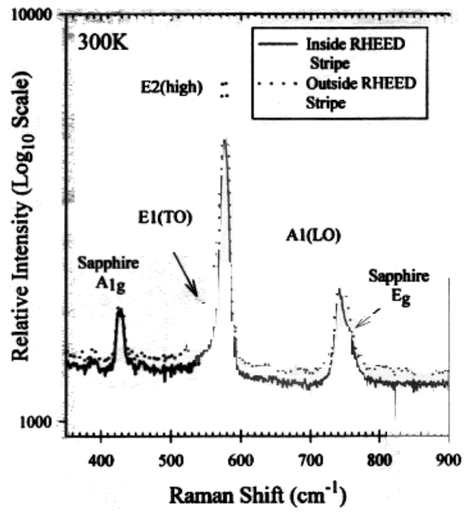

FIG. 6. Raman spectra indicating improved material quality inside the RHEED stripe.

nificant decrease in both the carbon and oxygen incorporated under electron irradiation, indicating that some type of ESD process is taking place for these impurities.

Figure 6 compares Raman spectra taken inside and outside the RHEED stripe. The presence of the $E1(\mathrm{TO})$ resonance feature is not allowed in the Raman configuration used, and its presence in this configuration is taken to imply structural disorder.[12] This indicates the somewhat surprising result that the GaN grown under electron irradiation during RHEED has improved structural properties. This is also supported by low temperature photoluminescence (PL) measurements, as illustrated by the spectra shown in Fig. 7. PL outside the stripe exhibited: a broad donor-acceptor pair luminescence peak near 3.455 eV; the I_1 line associated with high residual background n-type doping; a strong signal at 3.400 eV that may be related to carbon; and smaller features at 3.22 and 3.26 eV that may be related to cubic inclusions. In contrast, the PL from the GaN that is inside the RHEED stripe region is dominated by free excitonic PL at 3.482 eV and by acceptor-bound excitonic PL at 3.455 eV. Both the A and B excitons could be resolved in temperature-dependent PL measurements (not shown). While assignment of the PL transitions is important, of primary concern to this article is the observation that completely different PL spectra were obtained inside and outside the region undergoing high-energy electron irradiation. The presence of free-excitonic transitions in the PL measurements indicated improved materials quality in the electron irradiated GaN, consistent with the Raman results. It is clear based on all of the above results that high-energy electron irradiation can have a significant impact on microscopic properties during the growth of GaN. The most interesting implication is that high-energy electron irradiation during growth can improve the materials quality of GaN.

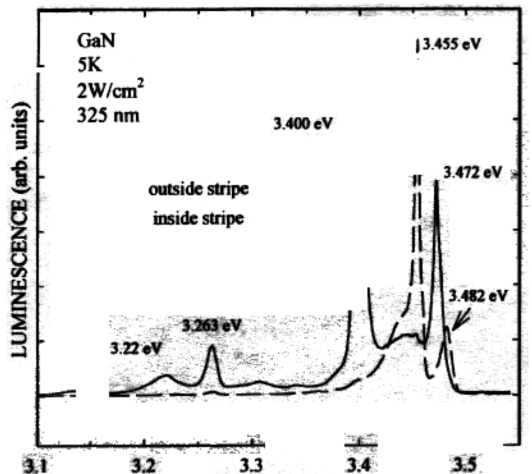

FIG. 7. PL spectra indicating improved material quality inside the RHEED stripe.

V. SUMMARY

From the results reported here there can be no doubt that high-energy electron irradiation can affect both macroscopic and microscopic materials properties in 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, and it may certainly modify alloy compositions.

GaN also exhibits effects related to high energy electron irradiation. An ESD effect is seen for oxygen and carbon, with small changes in growth rate occurring during electron irradiation. Raman and PL spectroscopy measurements indicate that, under certain conditions, electron irradiation during growth results in improve materials properties.

Since high energy electrons can distinctly alter surface reconstructions, surface chemistry, and epilayer materials properties, RHEED measurements must be carefully considered on a case-by-case basis to not misinterpret the observations. Indeed, if RHEED is performed during growth with sample rotation, the possibility exists to produce a periodic alloy or point defect "superlattice" structure within the material.

ACKNOWLEDGMENTS

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