A Technique for the Preparation of Cross-Sectional TEM Samples of ZnSe/GaAs Heterostructures Which Eliminates Process-Induced Defects

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ABSTRACT Cross-sectional transmission electron microscopy (TEM) sample preparation of ZnSe/GaAs epitaxial films is investigated. Conventional argon ion milling is shown to produce a high density (~5-8 x 10^11/cm^2) of small (diameter ~60-80 Å) extended defects (stacking faults, microtwins, double positioning twins, etc.). In addition, transmission electron diffraction results indicate a thin ZnO layer can also occasionally form upon ion milling or electron-beam irradiation although the exact conditions for ZnO formation are not well understood. Conventional TEM (amplitude contrast) and high-resolution TEM (phase contrast) imaging in combination with transmission electron diffraction studies were performed to determine the optimum method of removing the ion milling related damage and ZnO layers during sample preparation. HF/HCl, NaOH/H_2O, H_2SO_4/H_2O_2/H_2O and Br_2/CH_3OH etching mixtures as well as low voltage argon or iodine ion milling were studied. A low energy (2 keV) iodine or argon ion milling step was shown to remove the ZnO layer and reduced the density of the extended defects associated with Ar^+ ion milling, but was unsuccessful in removing all of the defects. Auger electron spectroscopy results indicate residual iodine was either left on the surface or implanted beneath the surface during iodine ion milling. Etching the XTEM samples in HF/HCl was shown to be effective in removing the ZnO layer but had little or no effect on the ion milling induced defects. Etching the samples in a 0.5% Br_2/CH_3OH solution resulted in complete elimination of the ion milling induced extended defects including the residual defects associated with iodine ion milling. In addition the Br_2/CH_3OH etch produced the best surface morphology. Thus a brief (1–2 seconds) Br_2/CH_3OH etch after conventional preparation (argon ion milling) of cross-sectional ZnSe/GaAs TEM samples appears to be an inexpensive and superior alternative to iodine ion milling.

INTRODUCTION

Recently, many investigations have been devoted to developing visible light-emitting devices (LEDs) in the green to near-ultraviolet (UV) region of the spectrum using wide bandgap II-VI compound semiconductors. ZnSe having a direct bandgap of 2.7 eV is especially important for blue electroluminescent devices such as LEDs and diode lasers. However, it is difficult to make p-type ZnSe films having low resistivity at the present time. It has been reported that crystal defects, such as microtwins, may play an important role in this problem (Fitzpatrick et al., 1983; Neumark, 1989). In the studies of the crystal defects within the ZnSe epitaxial film, transmission electron microscopy (TEM) is a powerful instrument. For TEM sample preparation of compound semiconductors, Ar^+ ion milling is widely used (Abrahams and Bucicchi, 1974) to obtain electron transparent foils for testing materials because of the uniform thinning rate. However, it is well known now that Ar^+ ion milling induces surface defects during TEM sample preparation of many III-V and II-VI compound semiconductors. Cullis and Chew (1985, 1987, 1988), for example, have shown that ion milling damage will result in "black dot" contrast under strong reflection conditions in some III-VI compound semiconductors (CdTe, ZnSe, and ZnS). This is also observed in III-V compound semiconductors (InP and InSb) (Chew et al., 1984, 1987, 1988). The induced surface defects must be eliminated if accurate image interpretation of defects arising from epitaxial growth is to be realized in the TEM. For example, in some high-resolution TEM investigations of ZnSe epitaxial films (Cockayne et al., 1985; Werthen et al., 1983; Williams et al., 1984, 1987), the Ar^+ ion milling induced defects may have obscured the features intrinsic to the film growth process. Recent studies have acknowledged these defects may influence their TEM results (Petruzello et al., 1988).

In addition to extended defects formation it has been noted that image artifacts may also arise from surface contamination or oxide formation during sample preparation (Thompson-Russell and Edington, 1977). Elec-
electron irradiation upon TEM examination (Feldman et al., 1985; Lu and Smith, 1989; Petford-Long and Smith, 1986) has also been shown to produce defects, such as oxides or an induced wurtzite phase. This problem usually can be circumvented by decreasing the time a region of sample is exposed to the electron beam.

Cullis and Chew (1985) modified an Ar\textsuperscript{+} ion milling apparatus using some alternative ion species, such as Xe\textsuperscript{+}, I\textsuperscript{−}, and N\textsuperscript{+}, to remove the Ar\textsuperscript{+} ion milling induced defects. They concluded low voltage I\textsuperscript{−} ion milling could be the best alternative process though it cannot eliminate the induced defects completely.

In this paper, the nature of the ion milling damage is discussed and another approach beside iodine ion milling is introduced which completely removes the ion milling induced surface defects in cross-sectional TEM (XTEM) specimens of ZnSe/GaAs epitaxial layers. After Ar\textsuperscript{+} ion thinning a perforation, the sample is briefly chemically etched to remove the ion milling damages. This appears to produce superior results to the iodine milling. We have studied several etchants and these results are compared with low voltage argon or iodine ion milling. Etching XTEM samples appears to be a quick, inexpensive method of removing ion milling damage.

**MATERIALS AND METHODS**

**Thin Film Growth of ZnSe**

ZnSe epilayers were grown to various thicknesses under a standard set of growth conditions by the molecular beam epitaxy (MBE) technique. A Zn to Se beam equivalent pressure ratio of 1:2 and a substrate temperature of 275°C were employed throughout this study. GaAs, oriented 2° off (100) toward (110), was used as the substrate material. Ex situ substrate preparation involved a UV-ozone treatment process to create a carbon-free oxide surface while thermal treatment in situ was used to desorb the oxide and provide an atomically-clean GaAs surface. Finally, the ZnSe hetero-epitaxial layers were deposited in a custom-designed (non-commercial) MBE system which has previously been used to grow ultra-high-purity, homoepitaxial ZnSe layers (Park et al., 1990).

**TEM Sample Preparation**

The XTEM sample preparation has been previously reported (Jones, 1988) and involves the cutting, gluing, and lapping of thin strips prior to ion milling. The sample was mounted onto a copper ring. Ar\textsuperscript{+} ion milling thinning was performed on a Gatan dual stage ion mill without liquid nitrogen cooling apparatus. The chamber pressure was kept below 5 × 10\textsuperscript{−}5 Torr. A voltage of 5 keV with beam current of 0.5 mA/gun and an angle of 15° was used. After perforation, a low voltage (2−3 keV), shallow angle (10°), low beam current (0.3 mA/gun) ion milling treatment is typically done to remove the higher voltage ion milling damage. For this final mill, both argon and iodine plasma gases were investigated. The time required to remove most of the surface damage ranged from 3 to 20 minutes depending on the specimens. As an alternative to the final milling, immersing the perforated cross-sectional sample in one of four different etchants to remove the ion milling damage was also investigated. These etchants have been previously reported to be effective for substrate cleaning prior to ZnSe homoepitaxial growth or removing surface oxides. The composition and etching time are listed below:

1. A HF/HCl solution in a volume ratio of 1:1 (Yeh and Holloway, 1990) for 20 seconds.
2. A hot 30% (wt) NaOH solution in D.I. water (Ohishi et al., 1988) for 5 seconds.
3. A H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{4}(35%)/H\textsubscript{2}O solution in a volume ratio of 5:1:1 (Stitius, 1981) for 10 seconds.
4. A 0.5% Br\textsubscript{2}/CH\textsubscript{3}OH solution (Yodo et al., 1988, 1989) for 1−2 seconds then solution (1) for 20 seconds.

The entire etching process is as follows: 1) clean in a boiling Freon bath; 2) dip in etching solution; 3) rinse in D.I. water; and 4) drying.

**Electron Microscopy**

Bright-field (BF) 2-beam (g\textsubscript{220}) images as well as the selected area diffraction patterns (SADPs) at [011] and [111] poles are used to characterize the structural defects. These observations were made at 200 keV in a JEOL 200CX STEM. The phase contrast images were taken by a JOEL 4000FX high-resolution (point-to-point resolution of 2.0 Å at Schertzer defocus) TEM at 400 keV acceleration voltage. Scanning auger electron spectroscopy (Perkin Elmer PHI 660 SAM) was used to characterize the surface impurity concentration and stoichiometry.

**RESULTS**

The following is a summary of the damage observed in ZnSe after Ar\textsuperscript{+} ion milling at high voltage (5 keV).

Under a strong 2-beam (g\textsubscript{220}) reflection condition, the XTEM samples which were thinned by Ar\textsuperscript{+} ion milling present a black dot contrast in the ZnSe epitaxial layer but not in the GaAs substrate as shown in Figure 1. The black dot contrast is associated with the ion milling process which indicates a high concentration of faulted (b = a/3[111]) interstitial loops in the near surface region (Petruzello, 1988). The formation of surface defects on ZnSe during Ar\textsuperscript{+} ion milling is not dependent upon whether or not sample cooling is applied (Cullis, 1985, 1988).

To understand the Ar\textsuperscript{+} ion milling defects further, we also examined the SADPs from ZnSe films. After intensive studies of the SADPs at many crystallographic poles (essentially mapping the damage in the reciprocal space), we concluded that the ion milling process results in three distinctly different features in the electron diffraction patterns. They are: 1) Streaks along four <111> directions observable at the [011] pole (Fig. 2A,B); 2) satellite spots around the ZnSe fundamental reflections at both [011] and [111] poles (Fig. 2C,D); 3) 1/3 [224] extra spots at the [111], [123] poles, etc. (Fig. 2E,F).

First, the <111> streaks indicate planar defects, probably Frank loops (Cockayne, 1984; Ponce, 1983),...
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Ar$^+$ Ion Milling at Low Voltage (2 keV). Lowering the ion energy of the Ar$^+$ ion beam to 2 keV dramatically reduced the black dot contrast. However, many of the small defects still remained (Fig. 4A).

$I$’+ Ion Milling at Low Voltage (2 keV). For this condition, I$^+$ ion milling is able to eliminate most of the defects induced by the high voltage Ar$^+$ ion milling. Figure 5 shows a series of micrographs of the same region in which the black dot clusters are removed gradually upon low voltage I$^+$ ion milling. All extra features on the corresponding SADPs also disappear as shown in Figure 6. Note, the “ZnO” reflections disappear rapidly, while the <111> streaks vanish gradually on [011] SADPs. This is consistent with the model of a thin ZnO layer on the surface and a deeper layer of extended defects. Monte Carlo TRIM simulations indicate the damage may be as deep as 100 Å for the high voltage (5 keV) Ar$^+$ ion milling process while for low voltage (2 keV) I$^+$ ion milling the defects may be only 40 Å deep. After I$^+$ ion milling, no strong ZnO reflection was seen on these [111] SADPs. This confirms that this extra feature in the SADP is related to Ar$^+$ ion milling and not intrinsic to the ZnSe. However, some small defects could still be seen on the surface of ZnSe film. Despite these few residual defects the misfit dislocations in the ZnSe film can now be successfully identified (Fig. 4B). Our results are consistent with previous studies (Cullis, 1985, 1988).

Chemical Etching of XTEM Samples. An alternative sample preparation procedure is to chemically etch the Ar$^+$ thinning related defects. This is done by dipping the perforated cross-sectional sample to the etching solution for only several seconds such that the supporting copper ring does not etch significantly but the surface defects do.

HF/HCl is not effective in etching ZnSe and thus had very little effect on the extended defects on the ZnSe surface. However, it is useful in removing any surface oxide layers. In Figure 4C, the etched sample still presents the black dot contrast under 2-beam condition (g=220), but the extra spots believed to arise from ZnO disappear and only <111> streaks and the fundamental spots remain in the corresponding SADPs. This also suggests that the first type of extra spots may be associated with a surface oxide layer and not an intrinsic hexagonal ZnSe phase as was previously suggested (Jones, 1989). The observation that a HF/HCl etchant removed these extra spots without etching ZnSe also implies that these first extra reflections are not associated with an internal defect such as a double positioning twins.

After hot NaOH/H$_2$O solution etching, the sample surface is very rough and many Moire fringes were observed (Fig. 4D). An example of the SADPs after NaOH/H$_2$O etch indicates formation of an unknown phase on the surface.

The H$_2$SO$_4$/H$_2$O$_2$/H$_2$O solution behaves as a Zn-preferential etchant (McGee, 1988). The surface morphology (Fig. 4E) is better than that of the NaOH/H$_2$O etched sample and no significant black dot contrast was observed. There is still some residual contrast arising from small defects although it is less than low voltage I$^+$ or Ar$^+$ ion milling. No extra features exist on

Fig. 1. The black dot contrast induced by 5 keV Ar$^+$ ion milling on a XTEM sample of ZnSe (thickness = 1 μm) grown on GaAs substrate. This black dot contrast arises principally from the (111) Frank’s loops under the g=220 reflection condition.
Fig. 2. A, B: streaks along four <111> directions in the [011] SADPs of ZnSe films indicating there are planar defects lying on four [111] planes. C, D: the first set of extra spots: satellite spots around the ZnSe fundamental reflections on the [011] and [111] SADPs. E, F: the second set of extra spots: 1/3 (224) extra reflections on [111] and [123] SADPs.
the corresponding SADP indicating most of the Ar+ ion milling defects have been removed. However, the etch rate of this solution appears to be nonuniform making it difficult to produce large areas that are transparent to electron beam.

The sample etched by Br2/CH3OH presented the best surface morphology as shown in Figure 4F. The black dot contrast is no longer observed and the misfit dislocations can be clearly imaged using 2-beam conditions. Note, compared with the low voltage Ar+ (Fig. 4A) or I+ (Fig. 4B) samples using the same strong reflection condition (g220, S > 0), the residual defects are not observed after Br2/CH3OH etching. Figure 3B is a high-resolution TEM micrograph taken from the same sample and shows a perfect [011] phase contrast image of the ZnSe film. Comparison of Figure 3A,B confirms that the microtwins and stacking faults associated with the black dot contrast are effectively removed by the Br2/CH3OH etch. The result in Figure 3B also shows that the density of stacking faults in the epitaxial layer is low, indicating the MBE conditions are producing high quality epitaxial layers. A summary of the different sample preparation processes is listed in Table 1.

**Surface Composition**

Auger electron spectroscopy was done on ZnSe after each of the ion milling and etching treatment. These results confirmed that a higher oxygen concentration (compared with that of the as-grown sample) can exist on the surface after Ar+ ion milling which is consistent with the TEM observation. In addition, iodine was detected on the surface after I+ ion milling that could be either residual iodine on the surface or iodine implanted in the near surface region. The details of these surface science studies will be presented elsewhere.

**CONCLUSION**

In this paper, we have shown that high voltage (5 keV) Ar+ ion milling could induce three distinct types of defects, namely, [111] planar defects, possibly a thin oxide layer, and double positioning twins (or microscopic hexagonal layers). Low voltage (2–3 keV) Ar+ or I+ ion milling is able to reduce the density of those induced defects, however, some small defects still remained. An alternative approach is demonstrated in

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**TABLE 1. The characteristics of ZnSe after different treatments**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Ar+</th>
<th>Ar+−I+</th>
<th>HF/HCl</th>
<th>NaOH/H2O</th>
<th>H2SO4/H2O2/H2O</th>
<th>Br2/CH3OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF images (g220)</td>
<td>Black dots</td>
<td>Small dots</td>
<td>Black dots</td>
<td>Moire fringe</td>
<td>Rough surface</td>
<td>Clean</td>
</tr>
<tr>
<td>SADPs &lt;111&gt; streaks</td>
<td>Strong</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>ZnO spots</td>
<td>Strong</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Other extra spots</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>[213]$<em>{1}$/[110]$</em>{c}$</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td>Surface morphology</td>
<td>Bad</td>
<td>Fair</td>
<td>Bad</td>
<td>Slow</td>
<td>Slow</td>
<td>Slow</td>
</tr>
<tr>
<td>Surface stoichiometry</td>
<td>Higher oxygen</td>
<td>Residual iodine</td>
<td>—</td>
<td>—</td>
<td>Se-rich</td>
<td>—</td>
</tr>
<tr>
<td>Etching rate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Fast</td>
</tr>
</tbody>
</table>
Fig. 4 A–C.
TEM SAMPLES OF ZnSe/GaAs

Fig. 4. A comparison ZnSe XTEM specimens after high voltage (5 keV) Ar⁺ thinning followed by the following finishing processes. All images were taken using a 2-beam $g_{xyz}$ (s > 0) BF condition. A: A 2 keV Ar⁺ ion mill at 10° with a gun current of 0.3 mA/gun. Note the residual contrast. The corresponding SADP at the [011] and [111] pole. Note the <111> streaks. B: A 2 keV Ar⁺ ion mill at 10° for 20 minutes at a gun current of 10 mA/gun. The black dot contrast was reduced but some small defects remain. The corresponding [011] and [111] SADPs. Note no significant extra spots or streaks were observed. C: A HF/HCl etch for 20 seconds. Note the sample still shows the black dot contrast. The corresponding [011] and [111] SADPs. Note the first type of satellite spots (see Figure 2C) disappear and only the <111> streaks remain. D: A NaOH/H₂O etch for 5 seconds. Note a new etching induced artifact (Moire fringe) appears such that the detail feature cannot be resolved. The corresponding [011] and [111] SADPs exhibit some additional reflections (arrows) which were not identified. E: A H₂SO₄/H₂O/H₂O etch for 10 seconds. Note the better surface condition than the NaOH/H₂O etch and that the black dot contrast disappears but the surface is still rough. The corresponding [011] and [111] SADPs. Note no extra features can be seen in the corresponding SADPs. F: A Br⁻/CH₃OH etch for 1 second. Note all ion milling related defects were removed. The corresponding [011] and [111] SADPs. Note they only show the fundamental reflections of ZnSe.
Fig. 5. Removal of the high voltage $\text{Ar}^+$ ion milling damages upon $\text{I}^+$ ion milling. Note the dislocation indicated by the arrows is the same for all micrographs.
Fig. 6. The SADPs corresponding to BF images in Figure 5. Note the satellite spots disappear rapidly, while the <111> streaks become gradually weaker and finally disappear. This indicates that the defects related to the satellite spots are closer to (or on) the surface whereas the defects associated with the <111> streaking are deeper.
which the perforated TEM sample was dipped briefly in an etching solution to eliminate the ion milling induced defects. Br₂CH₂OH solution appears to be the most promising etchant for preparation of high quality ZnSe/GaAs XTEM samples.

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