The Use of Atomic Hydrogen for Substrate Cleaning for Subsequent Growth of II-VI Semiconductors

L.S. HIRSCH, ZHONGHAI YU, S.L. BUCZKOWSKI, and T.H. MYERS*
Department of Physics, West Virginia University Morgantown, WV 26506-6045
M.R. RICHARDS-BABB
Department of Chemistry, West Virginia University Morgantown, WV 26506-6045

Atomic hydrogen is shown to be particularly efficacious for the preparation of substrates for subsequent growth of II-VI compounds by molecular beam epitaxy. A commercial thermal cracker was used to produce atomic hydrogen in the molecular beam epitaxy growth chamber for in-situ cleaning. This paper discusses the use of atomic hydrogen for both oxide removal from GaAs prior to ZnSe and CdTe growth, and for low-temperature oxide removal from CdTe and HgCdTe. Reflection high energy electron diffraction, ultra violet fluorescence microscopy, Nomarski interference contrast microscopy, and atomic force microscopy were used to characterize the growths.

**Key words:** II-VI semiconductors, atomic hydrogen, CdTe, HgCdTe, molecular beam epitaxy, surface cleaning, ZnSe

INTRODUCTION

Atomic hydrogen has been demonstrated to be effective for cleaning many types of substrates prior to epilayer growth.\(^1\)\(^-\)\(^8\) Progress in II-VI semiconductor devices has been consistently impeded by material quality. An ongoing problem has been a high density of defects related to stacking faults originating at the substrate-epilayer interface. The defects serve as nucleation sites for dislocation generation during device operation, leading to degradation and ultimate device failure in an unacceptably short time.\(^9\)\(^-\)\(^11\) It is believed that the stacking faults occur during initial layer growth.\(^9\)\(^,\)\(^12\) The stacking faults are either due to incomplete oxide removal or poor surface preparation that induces the formation of stoichiometry-related defects. For molecular beam epitaxy (MBE) growth of ZnSe on GaAs substrates, the final step prior to growth is often a thermal cleaning at temperatures ranging from 580 to 650°C to remove the native oxides.\(^13\)\(^,\)\(^14\) However, the resulting GaAs surface after this treatment exhibits a Ga-rich surface reconstruction. This gallium-rich surface can lead to the formation of GaSe\(_2\) at the interface,\(^15\) which can then 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 has been shown to improve the interface quality.\(^16\)\(^,\)\(^17\) A recent study by Kuo et al. indicates that stacking fault densities less than 10\(^4\) cm\(^{-2}\) can be obtained through a combination of GaAs epilayer growth followed by Zn treatment of the surface prior to ZnSe growth.\(^12\) 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.

Another area of interest is low temperature oxide removal from HgCdTe. CdTe has been shown to be an effective surface passivation layer for HgCdTe. Unless the CdTe layer is grown as part of a heterostructure, however, it must be deposited after the HgCdTe surface has undergone exposure to air and/or chemical etching of the surface. This allows the formation of an oxide layer, and possibly an amorphous
Te layer, which must be removed prior to CdTe growth. Typical thermal oxide removal requires temperatures above 180°C in vacuum. Such temperatures can degrade the surface of the HgCdTe. Luo et al. have demonstrated that atomic hydrogen can be used for low temperature oxide removal and cleaning of CdTe while preserving surface stoichiometry.

In this paper, we report that low defect density ZnSe layers can be achieved through the use of atomic-hydrogen cleaning of GaAs substrates prior to the growth of ZnSe films without any additional surface treatment. In addition, we demonstrate that atomic hydrogen can be used for low temperature in-situ cleaning of CdTe and HgCdTe.

**GENERAL EXPERIMENTAL DETAILS**

The oxide-removal experiments and epilayer growths reported here were performed in a custom MBE system at West Virginia University which has a base pressure of $5 \times 10^{-11}$ Torr. Substrate preparation is discussed in the individual sections. Nomarski microscopy and ultra violet (UV) fluorescence microscopy were performed using an Olympus BX60M microscope, with a 100 W Hg lamp used to excite the fluorescence. Atomic force microscopy (AFM) measurements were made in air using a Digital Instruments Nanoscope II.

A commercial atomic hydrogen source (EPI-AHS-L) was used to generate atomic hydrogen by thermal cracking of molecular hydrogen on a heated tungsten filament. The filament is heated using a current-regulated power supply, which we typically operate at 9.5 amps to produce a filament temperature of about 2200°C resulting in a 5% cracking efficiency for H₂. The hydrogen flow used for substrate cleaning typically resulted in a system pressure of $2 \times 10^{-4}$ Torr and a reading at our beam flux monitor of about $3 \times 10^{-6}$ Torr. After considering the ion gauge sensitivity for H₂, this represents a flux of about $8.6 \times 10^{14}$ s⁻¹ cm⁻² for atomic hydrogen at the above pressure. Assuming a unity accommodation coefficient, the time for a monolayer equivalent impingement is $\approx 1.5$ s.

**ZnSe AND CdTe GROWTH ON GaAs**

Of interest here is that several studies have demonstrated an As-stabilized GaAs surface after atomic hydrogen cleaning at substrate temperatures between 360 and 400°C. Prior studies have indicated that such an As-stabilized surface is crucial to a high quality ZnSe/GaAs interface. ZnSe films were grown on semi-insulating, (100)-oriented GaAs substrates using high purity (7N) elemental Zn and Se from conventional MBE furnaces (EPI). The 2 μm thick layers were grown at 250 and 300°C with corrected 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 thick buffer layer.

The substrates were initially degreased using organic solvents (trichloroethane, acetone, and methanol), etched in a \( \text{H}_2\text{SO}_4: \text{H}_2\text{O}_2: \text{H}_2\text{O} \) (8:1:1) solution for 5 min at room temperature and rinsed in flowing deionized water for 5 min. Prior to growth, the substrates were thermally treated in vacuum in one of two ways. The more conventional treatment involved heating to 580°C for between ten to twenty minutes followed by cooling to the growth temperature. Under the other treatment, the substrate was heated to 360°C and exposed to atomic hydrogen at a pressure of 2 × 10⁻⁶ Torr BEP for 20 min at which point the hydrogen flow is cut off and the substrate is cooled to the growth temperature.

The sample surface was monitored by reflection high energy electron diffraction (RHEED) during cleaning and growth. Figure 1a is a typical RHEED pattern of a (100) GaAs substrate without in-situ cleaning. The RHEED pattern exhibits rings and a spotty pattern indicative of an oxide overlayer. The conventional preheat led to a Ga-rich surface which became rough if the heating continued too long. As shown in Fig. 1b, the diffraction pattern intensity was not strong, and remained spotty, indicating a rough surface. Subsequent ZnSe growth on this surface only became two-dimensional (2D) 10 s after growth initiation. The atomic hydrogen cleaning step resulted in an As-stabilized surface, indicated by observation of a weak (2 × 4) surface reconstruction pattern. A typical bright, streaky RHEED pattern of such a surface is shown in Fig. 1c. Note also the presence of the Kikuchi lines. ZnSe layers grown on this surface resulted in a 2D growth mode immediately after growth initiation. We note in passing that 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.

The mechanism for the removal of the oxide layer has been reported by Yamada et al. There are typically three major components of the oxide layer: \( \text{Ga}_2\text{O}_3 \), \( \text{Ga}_2\text{O} \), and As oxides. It is known that the latter two desorb at lower temperatures (300–400°C) than the \( \text{Ga}_2\text{O}_3 \). Therefore, it is the \( \text{Ga}_2\text{O} \) component that requires the high temperatures in the thermal cleaning. The reason this compound can be removed at lower temperatures under atomic hydrogen is that the hydrogen reacts with the \( \text{Ga}_2\text{O} \) to create the more volatile compound \( \text{Ga}_2\text{O}_3 \) through the following mechanism:

\[
\text{Ga}_2\text{O} + 4\text{H} \rightarrow \text{Ga}_2\text{O}_3 \uparrow + 2\text{H}_2\text{O} \uparrow
\]

The \( \text{Ga}_2\text{O} \) desorption then leaves the surface devoid of the oxides, as well as removing Ga to produce an As-rich surface. Note that it takes about 20 min to remove the oxide layer although the arrival rate of atomic hydrogen is large enough to provide sufficient atomic hydrogen in less than 10 s. The need for four hydrogen atoms to reduce the \( \text{Ga}_2\text{O} \) may be the factor producing a kinetic limit, resulting in this low efficiency. Even with the low efficiency, however, this process produces a high quality surface for subsequent growth as detailed below.

Two types of stacking fault defects are observed in ZnSe films grown on GaAs substrates and are typically studied using transmission electron microscopy (TEM). These are the same type of defects that have also plagued growth of CdTe and HgCdTe on the (100) orientation. Frank-type stacking faults, which are bound by Frank partial dislocations, appear as triangular-shaped twin faults. Shockley-type stacking faults, which are bound by Shockley partial dislocations, are more line-shaped. The radiative efficiency is lower in the region of the stacking fault, allowing the use of techniques such as cathodoluminescence (CL) to image the defects. Here, we demonstrate that optical fluorescence microscopy can also be used to image these stacking faults. An Olympus BX60M microscope was used with a standard biological fluorescence attachment utilizing a 100W Hg lamp as the excitation source, resulting in a much simpler system than that required for CL.

Figure 2a is the fluorescence micrograph of a ZnSe film grown on GaAs substrate with conventional thermal cleaning. The dark features are nonradiative regions due to stacking faults, with the short line-shaped features ascribed to Shockley-type stacking faults and the larger triangular-shaped features to Frank-type stacking faults. These images are very similar to those observed under transmission electron microscopy. The density of both types of defects was determined to be greater than 10⁷ cm⁻² by simply counting the number of stacking faults in the field of view. Figure 2b shows a typical fluorescence micrograph of a ZnSe grown on GaAs substrate cleaned.
this is comparable to samples grown after the more complex approach of growing a GaAs buffer layer followed by a Zn pre-treatment. We did not observe a significant difference for the two different substrate temperatures (250 and 300°C), the presence of nitrogen-doping, or the growth-flux ratios investigated.

The growth of CdTe is also susceptible to twin-related defects, resulting in a surface feature often referred to as a “pyramidal hillock.” Thus, CdTe was also grown on GaAs cleaned using atomic hydrogen to investigate if atomic hydrogen cleaning led to a significant reduction of those features. The CdTe thickness was nominally 2.0 µm. The resulting pyramidal hillock density was \(1 \times 10^4\) cm\(^{-2}\), comparable to the lowest that one of us (THM) has ever obtained on (100)-oriented CdTe substrates, and a factor-of-ten lower than what was obtained previously by us on GaAs substrates using conventional thermal cleaning. This indicates that the atomic hydrogen cleaning leaves a surface appropriate for CdTe growth as well. This density, \(10^4\) cm\(^{-2}\), may represent an intrinsic lower limit for twin-related features for CdTe growth as this is continually seen for (100)-oriented substrates. Indeed, lower densities are only obtained by using CdTe or GaAs tilted off (100) by as much as 10°,25–27 or other orientations such as (211)B.24,30 An interesting followup to the present study would be an investigation of atomic hydrogen cleaning on such off-axis substrates. We also note in passing that, to our knowledge, a detailed study of the effect of off-axis growth on twin-related defects in ZnSe has not yet been performed.

There are advantages in using atomic hydrogen for cleaning of GaAs over other types of substrate preparation. The first is the low substrate temperature needed to perform the cleaning. For GaAs surfaces, the atomic hydrogen cleaning can be accomplished at a temperature less than 400°C, while thermal cleaning must be carried out around 600°C. The lower temperature can result in less cross-contamination from heated surfaces. The atomic hydrogen cleaning also results in an appropriate As-stabilized GaAs surface for subsequent ZnSe or CdTe growth, 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, resulting in a cleaner surface.2,11 The primary advantage, however, is that this approach may eliminate the need for the growth of a GaAs epilayer, resulting in a less complicated growth process for subsequent manufacture of layers for light-emitter fabrication.

**CdTe AND HgCdTe SURFACE CLEANING**

This section discusses the use of atomic hydrogen to clean CdTe and HgCdTe surfaces. A prior study by Luo et al. has shown that atomic hydrogen is very effective at removing oxygen, chlorine, sulfur, and carbon from CdTe surfaces while preserving stoichiometry.18 We show that atomic hydrogen cleaning also results in smooth, 2-D surfaces for subsequent growth.
II–VI, Inc. provided both (100) and (211)B-oriented substrates for this study. AFM investigation of the as-received substrates indicated an atomically smooth surface with a root mean square (rms) surface roughness of less than 0.5 nm. However, we believe that this surface was actually a disordered layer resulting from residual polishing damage. The surface tended to "smear" under the AFM probe tip, resulting in movement of material. By comparison, this effect was never seen on epitaxial CdTe or etched CdTe or HgCdTe surfaces. When inserted into the MBE system and examined by RHEED, as-received substrates exhibited only diffuse scattering, even for substrates that were etched in HCl prior to insertion to strip surface oxides. This is consistent with previous low energy electron diffraction (LEED) studies indicating a disordered surface on as-received substrates.18 CdTe substrates were then examined after undergoing a chemical etching procedure typical of that used for MBE growth. The substrates were degreased sequentially in trichloroethane, acetone, and methanol. The CdTe was then etched for 5 min in a 0.5% Br:methanol solution, followed by two methanol dips. The substrates were then blown dry with high purity nitrogen gas, and rinsed in deionized H2O for 5 min. The next step in this procedure was a 30 s dip in 1:9 HCl:deionized water followed by a 5-min rinse in deionized water, and immediate blow-drying with N2.

Figure 3 shows an AFM micrograph of a typical (100) CdTe surface after the above procedure. The surface was highly textured at the microscopic level, with features 50 nm in height and a rms roughness of 4 nm. Similar roughness was observed for (211)B-oriented substrates. RHEED measurements on the as-etched substrates gave irregular, spotty patterns with superimposed rings indicative of a residual Te overlayer, probably from the Br:methanol etch. The substrate had to be heated to temperatures above 200°C to remove the Te as evidence by disappearance of diffraction rings. However, the surface remained 3D in nature, as the diffraction pattern exhibited only spots indicative of the textured surface. This pattern remained during the entire typical thermal treatment, which involved heating up to 300°C for 10 min. AFM examination approximately two days after the thermal treatment indicated surface structure similar to that shown in Fig. 3. With this surface texture in mind, it is easy to see the requirement for the growth of a CdTe buffer layer to obtain a flat, 2-D surface.

The effect of atomic hydrogen cleaning was investigated at both room temperature and at elevated temperatures. A RHEED pattern observed for an etched (211)B-oriented substrate prior to in situ treatment, is shown in Fig. 4a. At room temperature, both the diffuse scattering and the rings related to oxides and/or a Te-overlayer disappear after about a 20 min exposure to atomic hydrogen. A bright, three-dimen-
Fig. 6. (a) AFM micrograph of an atomic hydrogen cleaned LPE HgCdTe layer. (b) RHEED pattern of CdTe grown on a similar LPE HgCdTe layer. (c) AFM micrograph of the CdTe layer whose RHEED pattern was shown in (b). The AFM micrographs represent an area of 2 μm x 3 μm and have a z-scale of 10 nm.

Spectral spot pattern is obtained after a total exposure of about 30 min, similar to that observed for the thermal pretreatment. For temperatures above about 80°C, however, the oxide/Te overlay was rapidly removed and a sharp 2-D pattern with well-defined streaks was observed, as shown in Fig. 4b. AFM examination of the surface of substrates cleaned above 80°C indicated a microscopically flat, featureless surface with an rms surface roughness of less than 0.5 nm.

Surface oxides on CdTe are probably TeO₂ or CdTeO₅. Removal of these oxides may proceed by reactions of the form:

\[ \text{CdTeO}_x + 6\text{H} \rightarrow \text{CdTe} + 3\text{H}_2\text{O} \uparrow \]  
\[ \text{TeO}_2 + 4\text{H} \rightarrow \text{Te} + 2\text{H}_2\text{O} \uparrow \]

Reaction (3) has the potential to leave behind a Te overlay, and RHEED also indicates the presence of a Te overlay after chemical etching. We believe that the following mechanism is also important for atomic hydrogen cleaning of CdTe:

\[ \text{Te} + 2\text{H} \rightarrow \text{TeH}_2 \uparrow \]

To test this hypothesis, we deposited a polycrystalline Te layer of about 30Å thickness on a silicon substrate. At 80°C, this layer was removed by atomic hydrogen irradiation in about 300 s, indicating a Te etch rate of 0.1Å/s. Compared to the previously calculated arrival rate for atomic hydrogen, this corresponds to about a 10% efficiency in the use of atomic hydrogen, possibly limited by a kinetic barrier due to the need for two hydrogens to be available at a given Te atom for removal.

We have not been able to directly measure an etch rate for CdTe (or ZnTe) due to atomic hydrogen by either direct exposure of thin layers deposited on silicon substrates or by observation of RHEED oscillations. However, etching must be possible as indicated by the smoothing of textured surfaces. An upper bound for the CdTe etch rate can be inferred from the difference in the CdTe growth rate observed when grown with and without the presence of atomic hydrogen. CdTe grown under an atomic hydrogen flux of 2 x 10⁻⁶ Torr exhibited a consistent decrease in growth rate of about 0.1Å/s, which is comparable to the Te removal rate. The fairly rapid smoothing of the rough, as-etched CdTe surfaces may indicate that atomic hydrogen is more effective at etching three-dimensional structures since edge sites will be more reactive. Temperatures of 80°C or above may be required to thermally desorb residual Cd, as there are no stable, volatile hydrides of Cd. Exposing thin ZnTe/Si epilayers to atomic hydrogen also indicated etch rates less than 0.1Å/s.

While low-temperature oxide removal resulting in a sharp, well-ordered interface is of interest for CdTe, it is crucial for CdTe-passivation of HgCdTe for infrared detector fabrication. II–VI, Inc. also provided liquid phase epitaxy (LPE) HgCdTe samples to allow an investigation of the applicability of atomic hydrogen cleaning to HgCdTe. The as-received LPE samples had been chemo-mechanically polished to remove surface features related to the LPE process. Prior to insertion into the MBE system, the LPE layers were cleaned and etched as follows. The substrates were degreased in trichloroethylene, acetone, and methanol. They were then etched for 5 s in 0.5% Br: methanol, followed by a methanol rinse and then immediately blown dry.

Results were similar to that observed for CdTe. Figure 5 contains the time-evolution of RHEED patterns observed for cleaning at 1°C (below room temperature due to our liquid N₂ shroud) and 80°C. Figure 5a shows the diffuse pattern characteristic of as-prepared HgCdTe. Only after 60 min did distinct
RHEED patterns emerge, indicating removal of the oxide overlayer. As shown in Fig. 5c, the patterns remain spotty, indicative of a rough surface, and there is still diffuse scattering. We believe that the etching process which can lead to a smooth surface is inhibited by Hg and Cd remaining on the surface. Raising the sample temperature to 80°C dramatically increased the speed of the process. After a 20 min exposure to atomic hydrogen, a well-defined two-dimensional pattern exhibiting sharp streaks was observed, as shown in Fig. 5d. Continuing exposure to atomic hydrogen eventually resulted in the evolution of the streak patterns into spotty 3-D patterns, indicative of surface roughening.

AFM examination of a HgCdTe surface both cleaned with atomic hydrogen and exhibiting a RHEED pattern similar to that shown in Fig. 5d indicated a microscopically smooth surface with an rms surface roughness less than 0.5 nm, with a suggestion of monolayer steps. A representative AFM micrograph is shown in Fig. 6a. CdTe grown at 80°C on such a surface at a rate of 0.1 μm/h (using a single effusion cell) maintained the sharp, streaky RHEED pattern as indicated by Fig. 6b. The resulting epilayer exhibited the same atomic-level smoothness when examined by AFM, again with an rms surface roughness less than 0.5 nm, as shown in Fig. 6c.

There has been some concern that the use of atomic hydrogen may lead to nonstoichiometric etching of CdTe. However, such nonstoichiometry is typically found for ECR-type plasma etching where vastly different etch rates can occur for the various metal-radical and atomic hydrogen chemistries. Here, we believe the CdTe and HgCdTe etching is primarily due to hydrogen removal of Te with subsequent thermal desorption of "excess" Cd or Hg. At 80°C, significant changes in surface stoichiometry should not take place. While we did not have the in-situ analytical capabilities to check this assertion, we could perform ex-situ reflectance measurements to look for gross shifts in stoichiometry. Measurements of the E, reflectance peaks probes a layer approximately 100 nm thick. Measurements of the E, reflectance peak before and after atomic hydrogen cleaning were identical within instrumental resolution. This indicates that any stoichiometry change probed by this measurement is less than Δx = 0.01.

SUMMARY AND CONCLUSIONS

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 density of both types of defects 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. 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.

It is also shown that atomic hydrogen is an effective method for cleaning CdTe and HgCdTe. At 80°C, we were able to remove the oxides as well as excess Te, leaving the substrate relatively flat. There was no evidence for any gross changes in stoichiometry for the HgCdTe layers due to atomic hydrogen cleaning. Hence, we have demonstrated that atomic hydrogen irradiation is an acceptable method of cleaning CdTe and HgCdTe for subsequent layer growth.

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