THE USE OF ATOMIC HYDROGEN FOR LOW TEMPERATURE OXIDE REMOVAL FROM HgCdTe

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ABSTRACT

Reflection high energy electron diffraction (RHEED) patterns of HgCdTe surfaces etched with bromine methanol have a diffuse pattern with a faint ring pattern indicative of an overlayer consisting of a mixture of oxides and amorphous Te. Exposure to an atomic hydrogen flux results in a RHEED pattern indicative of a high quality, two-dimensional surface. Atomic force microscopy (AFM) measurements indicate a rms. surface roughness less than 1 nm. CdTe grown on this surface at 80 °C maintains the streaky RHEED pattern and smooth surface as indicated by AFM. X-ray photoelectron spectroscopy measurements indicate that the etched surfaces contain both an oxide layer and a metallic Te overlayer which were removed by continued exposure to atomic hydrogen. Further exposure results in significant HgTe depletion, which appears to be a near-surface phenomenon. Preliminary device results indicate that use of atomic hydrogen is a viable approach for low temperature clean-up of etched HgCdTe surfaces.

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INTRODUCTION

Atomic hydrogen has been demonstrated to be effective for cleaning many types of substrates prior to epilayer growth. In many cases, the use of atomic hydrogen dramatically reduces process temperatures for the removal of oxides and other overlayers typically left by etching procedures. Luo et al. have demonstrated that atomic hydrogen can be used for low temperature oxide removal and cleaning of CdTe while preserving surface stoichiometry. CdTe has been shown to be an effective surface passivation layer for HgCdTe. Therefore, an area of great interest in processing advanced infrared detectors is low temperature oxide removal from HgCdTe followed by deposition of CdTe. Unless the CdTe layer is grown as part of a heterostructure, it must be deposited after the HgCdTe surface has undergone exposure to air and/or chemical etching of the surface. Such exposure allows the formation of an oxide layer, and possibly an amorphous Te layer, which must be removed prior to CdTe growth. Typical thermal oxide and Te overlayer removal requires temperatures above 180°C in vacuum. Such temperatures can degrade the surface of the HgCdTe.

In this paper, we report that atomic hydrogen can be used for low temperature in-situ cleaning of HgCdTe and provide further insight into both the nature of the chemically etched HgCdTe surface and the effects of atomic H etching on surface stoichiometry.

GENERAL EXPERIMENTAL DETAILS

Two different experimental facilities were used to obtain the results presented here. Epitaxial growth and reflection high energy electron diffraction (RHEED) results were obtained in a molecular beam epitaxy system (MBE) which has been described elsewhere. X-ray photoelectron spectroscopy (XPS) characterization experiments were performed in a two-chamber ultrahigh vacuum (UHV) system used for semiconductor processing studies. One chamber allowed atomic hydrogen etching with controlled sample heating, while the second contained the facilities for XPS. XPS analysis was performed using the Mg anode (1253.6 eV x-ray line) of a Fisons twin anode x-ray source operating at 300 watts. Emitted electrons were analyzed using a VG100AX hemispherical analyzer in 1:1 lens mode resulting in a sampling area slightly more than 4
Spectra were taken in constant analyzer energy mode at a 20 eV pass energy with the work function determined by calibration on argon-etched silver foil. Data acquisition and analysis was performed with VGX900 board and software. The composition and chemical state of the surface were determined by monitoring the Te 3d_{5/2}, Cd 3d_{5/2}, and Hg 4f_{7/2} photoelectron peaks. Surface composition was determined in a standard manner\(^{14}\) using peak areas and elemental sensitivity factors established by Nitz et al.\(^{15}\) and subsequently discussed by Christie et al.\(^{16}\)

In both systems, samples were mounted on a molybdenum transfer block using colloidal graphite in water (Aquadag). The block was radiatively heated from behind with the temperature monitored using a type K thermocouple in contact with the back of the block. Atomic force microscopy (AFM) measurements were made in air using a Digital Instruments Nanoscope II. Reflectance measurements were made using a computerized Cary-14 spectrophotometer.

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.\(^{17}\) The filament is heated using a current-regulated power supply, which we operate at 9.5 amps to produce a filament temperature of about 2200 °C for a 5% cracking efficiency for H\(_2\). The hydrogen flow used for substrate cleaning in the growth system typically resulted in a system pressure of 2×10\(^{-6}\) Torr and a reading at our beam flux monitor of about 3×10\(^{-6}\) Torr. This represents a flux of about 8.6×10\(^{14}\) sec\(^{-1}\) cm\(^{-2}\) for atomic hydrogen at the above pressure after considering the ion gauge sensitivity for H\(_2\). The time for a monolayer equivalent impingement is \(\sim 3\) s, assuming a unity accommodation coefficient. The source-to-substrate distance was about 35 cm in the growth system, and 15 cm in the analysis system. The hydrogen flow was adjusted to give equivalent flux at the sample surface.

The filament used to dissociate hydrogen operates at an elevated temperature and produces a significant amount of heat and light and so surface heating should be considered. For example, it was observed that the temperature of substrates etched near room temperature in the analysis system actually increased to 50 °C during the etch (no power to the heater). Since heating occurred from the front surface in this case, the
HgCdTe surface could be significantly warmer. This, in part, may underlie the similarity in the XPS spectra resulting from near room temperature and 80 °C etching discussed later. Radiant heating due to the filament was not as much an issue for the MBE system due to the longer source-to-sample distance as well as the presence of a liquid nitrogen cooling shroud. In the growth chamber, the thermocouple only indicated a temperature rise of 1 to 2°C for near-room temperature (no power to heater). In addition, the melting point of In on the front surface of a HgCdTe wafer was used to probe the surface temperature near 160 °C, both with and without power to the hydrogen source. A relative decrease in temperature, as measured by the thermocouple, was observed with the hydrogen source on indicating a surface temperature rise of about 10 °C.

The liquid phase epitaxy (LPE) Hg$_{1-x}$Cd$_x$Te samples (with x~0.2) used throughout these studies were provided by II-VI, Inc. (Saxonburg, PA) and had been chemomechanically polished to remove surface features related to the LPE process. Prior to insertion into the MBE system, the LPE layers 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.

**RHEED AND CdTe GROWTH**

The effect of atomic hydrogen cleaning was investigated at both room temperature and at elevated temperatures. Initial studies performed in the MBE system using RHEED were reported at the 1996 workshop. In brief, the chemically etched surface exhibited a RHEED pattern with a diffuse background superimposed with occasional rings characteristic of an amorphous or polycrystalline overlayer. Attempts to grow CdTe on this surface always resulted in polycrystalline material. With the HgCdTe at about 1 °C, due to the cooling of our liquid nitrogen shroud, a brief (~ 5 minute) exposure to atomic hydrogen eliminated most of the diffuse scattering and rings. The RHEED then consisted of a highly irregular spot pattern, indicative of a rough surface with a possible partially polycrystalline overlayer. After a total of 60 minutes of exposure to atomic hydrogen, the pattern began to resolve into an ordered array of spots, indicative of a single-crystal three-dimensional (3-D) surface. Raising the sample temperature to 80°C dramatically changed the process. Again, a brief exposure appeared to remove an initial layer. In contrast to
the 1 °C etch, a well-defined two-dimensional (2-D) pattern exhibiting sharp streaks was observed after a 20 minute exposure, as shown in Fig. 1(a). Continued exposure to atomic hydrogen eventually resulted in the evolution of the streak patterns into the ordered 3-D spot pattern similar to extended exposure at 1 °C.

AFM examination of a HgCdTe surface both cleaned with atomic hydrogen and exhibiting a RHEED pattern similar to that shown in Fig. 1(a) indicated a microscopically-smooth surface with an rms. surface roughness less than 0.5 nm, with a suggestion of monolayer steps. CdTe grown at 80 °C on such a surface at a rate of 0.1 μm/hr (using a single effusion cell) maintained the sharp, streaky RHEED pattern, as indicated by Fig. 1(b). The resulting CdTe epilayer surface exhibited the same atomic-level smoothness when examined by AFM, again with an rms. surface roughness less than 0.5 nm. This demonstrates that atomic hydrogen can be used to obtain a HgCdTe surface suitable for low-temperature epitaxial growth of CdTe.

X-RAY PHOTOELECTRON SPECTROSCOPY MEASUREMENTS

In order to better understand the processes occurring during atomic hydrogen etching, a series of etch experiments were performed in the analysis system which allowed XPS measurements as a function of etch time. Fig. 2 shows a series of Te 3d₅/₂ photoelectron spectra for increasing exposures to atomic hydrogen. These spectra were obtained from a substrate etched at 80 °C, but they are similar to those obtained for near room temperature. The t = 0 spectrum is typical of all Br-methanol etched samples analyzed in this study. The photoelectron peak at 576.1 eV has been previously associated with Te in the oxide state, while the peak at 572.7 eV is representative of metallic Te. As the etch proceeds, this latter peak shifts to lower binding energies and ultimately attains a binding energy of 572.5 eV which is representative of Te in CdTe and HgCdTe. The corresponding Cd 3d₅/₂ and the Hg 4f₇/₂ photoelectron spectra did not exhibit a characteristic oxide peak, and indicated binding energies consistent with values reported for CdTe and HgCdTe. Combined with the prior discussion of RHEED, these results suggest that the Br-methanol etch leaves behind a thin amorphous-Te overlayer which is oxidized in transit to the XPS system.
An estimate of the oxide thickness can be obtained from the ratio of the oxide-Te and amorphous-Te peaks from the t = 0 spectrum in Fig. 2. For all the Br-methanol etched samples analyzed here, this was found to be on the order of 0.2 nm thick. That is, the oxide appears to be on the order of only a monolayer or less in thickness. This result applies to samples which had been exposed to atmosphere for several days before being loaded into the UHV system as well as samples transferred as rapidly as possible (~20 minutes) into the system. Oxide formation appears to be self-limited due to the low mobility of the oxide constituents in the near surface layers and to a relatively low number of reactive surface sites on a Br-methanol etched surface. Using this thickness and etch times determined from both RHEED and XPS, we estimate an oxide etch rate of 0.4 Å/min.

There is always concern that the use of atomic hydrogen may lead to non-stoichiometric etching of CdTe. We performed ex-situ reflectance measurements to look for gross shifts in stoichiometry due to hydrogen etching. The E₁ reflectance peak probes a region approximately 100 to 200 nm thick. Measurements of the E₁ reflectance peak before and after atomic hydrogen cleaning were identical within instrumental resolution indicating that any stoichiometry change over the depth probed by this measurement is less than Δx=0.01.

The near-surface case, however, is quite different. Fig. 3 shows typical changes in the surface composition indicated by XPS as the atomic hydrogen etch proceeds. In all cases, an increase in the concentration of Hg, Cd and Te was observed following the removal of the oxide overlayer. With continued etching, the Te decreased slightly to a relatively constant value which was typically within a few per cent of its initial concentration, while the Hg decreased to a value significantly lower than either its initial or nominal bulk concentration. The Cd concentration, on the other hand, increased. The relative atomic concentrations approximately indicated one Te for each remaining Hg and Cd, implying Te removal as well as Hg removal. In all cases, the steady state composition of the atomic hydrogen-etched HgCdTe surface was HgTe depleted.

The data shown in Fig. 3 were obtained for a substrate etched at 80 °C. Analyses for substrates etched near room temperature produced similar results with any differences
being traceable to differences in bulk composition or the initial composition of the oxide/Te overlayers. This is not surprising recalling the substrate block temperature was observed to rise to 50 °C during “room-temperature” etching.

MECHANISMS AND ETCH RATES

Surface oxides on CdTe have been reported to contain TeO$_2$ or CdTeO$_3$.$^{27-29}$ It is believed that similar oxides are present on HgCdTe. Removal of these oxides may proceed by reactions of the form:

\[
\text{CdTeO}_3 + 6\text{H} \rightarrow \text{CdTe} + 3\text{H}_2\text{O} \uparrow \\
\text{TeO}_2 + 4\text{H} \rightarrow \text{Te} + 2\text{H}_2\text{O} \uparrow
\]

(1)  

(2)

Reaction (2) has the potential to leave behind a Te overlayer, and both XPS and RHEED indicate the presence of a Te-overlayer after chemical etching. We believe that the following mechanism is also important for atomic hydrogen cleaning of CdTe:

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

(3)

To evaluate the efficacy of this latter mechanism, we deposited a polycrystalline Te layer of about 30 Å 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 0.1 Å/sec. 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 hydrogen atoms to be available at a given Te atom for removal.

A reaction involving breaking the relatively weak HgTe bond must also occur since HgTe depletion is observed in the near-surface region. Schematically, we could write:

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

(4)

where the Hg is thermally desorbed. Since the Te is actually in a HgCdTe matrix and is potentially bonded to a Cd, this mechanism should be quite sensitive to alloy composition and depth. Indeed, the steady-state composition we observe after extended atomic hydrogen exposure may be due to the extraction of all the Te bound primarily to Hg.
That is, steady state is attained as the etch produces a composition that is resistant to further HgTe bond breaking and removal. We have no evidence for Cd extraction. One possible measure for the removal of Cd in conjunction with mechanism (4) would be the total etch rate.

Previously we were unable 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, some etching must be possible as indicated by the smoothing of textured surfaces at temperatures above 80 °C. An upper bound for the CdTe etch rate was be inferred to be about 0.1 Å/s from the difference in the CdTe growth rate observed when grown with and without the presence of atomic hydrogen. The fairly rapid smoothing of the HgCdTe surface at 80 °C may indicate that atomic hydrogen can etch HgCdTe. Temperatures of 80 °C or above may be required to thermally-desorb residual Hg or Cd, as there are no stable, volatile hydrides of either, yet both have a fairly high vapor pressure at this temperature.

We attempted to measure an etch rate for HgCdTe as follows. The Norwegian Defense Research Establishment provided three HgCdTe layers grown by MBE with x-values of 0.24, 0.32 and 0.48. The layers had been etched in a Br-based solution, and then patterned with a dense array of small photoresist dots. The samples were introduced into the MBE system, and exposed to an atomic hydrogen flux for 60 minutes at 80 °C. After stripping the photoresist, the patterns could still be observed using a differential interference-contrast (DIC) microscope. If steps were present, however, they were too small to be measured optically or with a surface profilometer. The samples were then examined using AFM. The only discernible features were infrequent photoresist remnants that marked the position of the dots, as shown in Fig. 4. We could not detect a measurable step height above the background rms. surface roughness of 2.5 to 2.9 nm. This indicates a step height of less than 5 nm, and a resulting HgCdTe etch rate of less than 0.05 Å/sec. The pattern observed with the DIC microscope was probably due to due surface stoichiometry changes occurring with atomic hydrogen cleaning.

Several experiments performed in this study indicated that the oxide present after the Br-methanol etch is relatively unstable. In one experiment, the sample was exposed to
the hydrogen source filament without hydrogen gas being introduced into the chamber. This alone was sufficient to remove the oxide overlayer as determined with both XPS and RHEED. However, continued exposure for up to 60 min did not remove the Te overlayer (XPS and RHEED) or result in an ordered surface (RHEED). On another occasion, the substrate was allowed to remain in the analysis chamber for approximately 48 hours without heating after the as-etched surface had been analyzed. Subsequent analysis revealed that the oxide was desorbed during this period.

The desorption mechanism could involve thermal, photon, or electron stimulated processes. Alternatively, oxide removal may occur simply as the result of etching by atomic hydrogen produced from the residual gases of the system. Several of these possibilities were eliminated on the basis of relatively simple experiments. Thermal desorption was ruled out by annealing an oxide-containing surface at temperatures of 80 °C, 100 °C, and 120 °C without removing the oxide. Electron stimulated desorption was ruled out by observing that the filament-to-substrate current was a factor of 40 lower that the photo-emission current produced during XPS analysis (under which condition the oxide overlayer was stable).

Preliminary investigations in the MBE system indicate that photo-stimulated desorption may be the underlying mechanism for oxide removal without atomic hydrogen. The output from a 100W tungsten-halogen lamp was filtered to pass only 400 to 700 nm light and focused on the HgCdTe layer. This cool illumination was found to eliminate the diffuse scattering observed with RHEED and associated with the oxide overlayer. This effect will be the subject of further study.

There is also evidence that more than one type of oxide can occur on HgCdTe. In one hydrogen etching experiment, it was necessary to re-expose the HgCdTe sample to atmosphere for 3 hours after the oxide-Te peak was removed (i.e. after a 5-minute atomic hydrogen etch at room temperature). When this surface was re-analyzed, a more intense oxide-Te peak was observed, indicating an oxide layer twice as thick as on the Br-methanol etched samples. This thicker layer may have been due to an increase in the number of reactive surface sites produced by surface roughening during this stage of the atomic hydrogen etch which is consistent with spotty / diffuse RHEED patterns obtained
during the initial stages of atomic hydrogen etching. Alternatively, this increase in oxide
formation may be caused by more of the underlying HgCdTe matrix being exposed for
oxidation. Interestingly, the Te photoelectron peak binding energy was consistent with a
mixture of metallic Te and Te in a HgCdTe matrix. This oxide was also more resistant to
atomic hydrogen etching, with an etch rate that varied with thickness. The initial removal
rate was 0.23 Å/min, close to a factor of two slower than typical for all Br-methanol
etched samples, slowing to a rate of 0.13 Å/min. Both results indicate that there may
indeed be more than one type of oxide formed on a HgCdTe surface, depending intimately
upon prior surface treatment.

PRELIMINARY DEVICE RESULTS

A set of three LPE HgCdTe layers were etched and exposed to atomic hydrogen
until a streaky 2-D pattern was obtained. Approximately 0.25 μm of CdTe was then
deposited at 80 °C at a rate of 0.1 μm/hr. The samples were sent for processing into Hg-
diffused devices at Lockheed Martin Microelectronics Center (Nashua, NH). The time
between the CdTe passivation step and further processing was longer than six months due
to corporate mergers and shifting of laboratory equipment from Syracuse, NY to Nashua,
NH. Even so, the processing resulted in >99% yield of working devices. The resulting
average R₀A values were 8, 18, and 678 Ω cm², for cut-off wavelengths of 9.9, 8.3, and
8.1 μm, respectively. This can be compared to the results for a control that underwent
standard processing in the same "lot", 55 Ω cm² and 9.7 μm. The lower values for the
devices fabricated using atomic hydrogen-cleaned HgCdTe may be due to the long
ambient exposure (including courier mail shipping) spent between CdTe deposition and
other processing, a major departure from the standard diffused diode process. The results
are encouraging and additional LPE samples cleaned with atomic hydrogen will be
processed in the near future. Importantly, the results of this first process lot indicate that
use of atomic hydrogen may indeed be a viable approach to low temperature
oxide/overlayer removal.
CONCLUSIONS

In conclusion, thermally produced atomic hydrogen is shown to remove both oxides and the Te overlayer left by Br-based etches. While near-surface HgTe depletion occurs, the surface is suitable for subsequent epitaxial growth. Importantly, preliminary device results indicate that use of atomic hydrogen may indeed be a viable approach to low temperature oxide/overlayer removal.

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REFERENCES

FIGURE CAPTIONS

Figure 1. **RHEED** images for (a) HgCdTe cleaned using atomic H and (b) CdTe epitaxy on such a surface.

Figure 2. Te 3d_{5/2} photoelectron spectra for series of increasing exposures to atomic hydrogen.

Figure 3. HgCdTe surface composition as a function of atomic hydrogen etch time.

Figure 4. Atomic force microscopy image and surface profile. A remnant of the photoresist dot is shown. No evidence of HgCdTe etching was observed.
Figure
Te 3d $^{5/2}$ ex-situ MeOH-Betch H-etch at ~80°C [t in minutes]

$\begin{array}{cccccc}
t = 155 & t = 125 & t = 95 & t = 65 & t = 35 & t = 5 \\
\end{array}$

Intensity (Displaced for Clarity)