THE ROLE OF ATOMIC HYDROGEN FOR SUBSTRATE CLEANING FOR GROWTH OF CdTe BUFFER LAYERS AT REDUCED TEMPERATURES ON SILICON, CdTe, AND HgCdTe

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ABSTRACT

Atomic hydrogen is shown to be efficacious for cleaning CdTe and HgCdTe substrates for subsequent CdTe growth by molecular beam epitaxy. While single crystal ZnTe and CdTe growth was obtained on Si substrates that underwent an *ex-situ* HF-based etch, only polycrystalline CdTe or ZnTe could be obtained on surfaces cleaned using an atomic hydrogen source. This result is possibly related to gas-phase transport of Te to the Si surface.

INTRODUCTION

Atomic hydrogen has been demonstrated to be effective for cleaning many types of substrates prior to epilayer growth. Low temperature oxide removal from HgCdTe is of technological importance. 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.*[1] have demonstrated that atomic hydrogen can be used for low temperature oxide removal and cleaning of CdTe while preserving surface stoichiometry.

Since the first study of the growth of CdTe on Si by molecular beam epitaxy (MBE),[2] high temperature (>800 °C) thermal desorption has been the primary technique for oxide removal.[3] Recently, techniques have been developed [4] for *ex-situ* oxide removal from Si using etchants based on HF. These procedures result in a hydrogen-terminated surface which is remarkably resistant to further oxidation. The hydrogen can be subsequently desorbed in the MBE system at temperatures between 550 to 600 °C [5], leaving a clean, ordered Si surface for subsequent epilayer growth. This technique has been successfully used for the subsequent growth of ZnTe and CdTe on Si.[6, 7] An alternate, low temperature approach would be to use atomic hydrogen to remove the oxide, as has been demonstrated for GaAs/Si heteroepitaxy.[8]

In this paper, we demonstrate that atomic hydrogen can be used for low temperature *in-situ* cleaning of CdTe and HgCdTe. In addition, we present the results of an investigation of the cleaning of Si substrates using atomic hydrogen.

EXPERIMENT

The oxide-removal experiments and epilayer growths were performed in a custom MBE system at West Virginia University. [9-11] Substrate preparation is discussed in the individual sections. 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 H_2. The hydrogen flow used for substrate cleaning typically resulted in a system pressure of 2×10^{-6} Torr. After considering the ion gauge sensitivity for H_2, this represents a flux of about 8.6×10^{14} sec^{-1} cm^{-2} for atomic hydrogen at the above pressure. Assuming a unity accommodation coefficient, the time for a monolayer equivalent impingement is ~ 1.5 sec.

RESULTS - CdTe AND HgCdTe

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.[1] We show that atomic hydrogen cleaning also results in smooth, 2-D surfaces for subsequent growth.

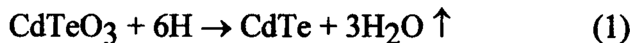
II-VI, Inc. (Saxonburg, PA) provided both (100) and (211)B-oriented substrates for this study. AFM investigation of the as-received substrates indicated an atomically smooth surface with an rms. surface roughness of less than 0.5 nm. However, we believe that this surface was actually a microscopically-thin 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 reflection high energy electron diffraction (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 LEED studies indicating a thin disordered surface on as-received substrates.[1]

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 minutes 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 H_20 for 5 minutes. The next step in this procedure was a 30 s dip in 1:9 HCl:deionized water followed by a 5-minute rinse in deionized water, and immediate blow-drying with N_2. AFM examination of a typical (100) CdTe surface from substrates provided at the start of this study after the above procedure indicated a highly textured surface at the microscopic level, with features 50 nm in height and an rms. roughness of 4 nm. Similar roughness was observed for (211)B-oriented substrates. We want to note that II-VI, Inc. has been actively working to improve their polishing process, and have recently achieved much smoother surfaces after this etch procedure (rms. roughness ~ 0.6 nm) indicating significantly less residual damage. 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 indicated by disappearance of the diffraction rings. However, the surface remained 3-D in nature, as the diffraction pattern exhibited only spots indicative of the textured surface. This pattern became two-dimensional only after the entire typical thermal treatment, which involved heating up to 300 ° C for 10 minutes.

The effect of atomic hydrogen cleaning was investigated at both room temperature and at elevated temperatures. At room temperature, both the diffuse scattering and the rings related to oxides and/or a Te-overlayer disappear after about a 20 minute exposure to atomic hydrogen. A bright, three-dimensional spot pattern is obtained after a total exposure of about 30 minutes,

similar to that observed for the 200 °C thermal pretreatment. For temperatures above about 80 °C, however, the oxide/Te overlayer was rapidly removed and a sharp 2-D pattern with well-defined steaks was observed. 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 TeO_2 or $CdTeO_3$. [12-14] Removal of these oxides may proceed by reactions of the form:



$$CdTeO_3 + 6H \rightarrow CdTe + 3H_2O \uparrow \quad (1)$$

$$TeO_2 + 4H \rightarrow Te + 2H_2O \uparrow \quad (2)$$

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

$$Te + 2H \rightarrow TeH_2 \uparrow \quad (3)$$

To test this hypothesis, 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 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 2×10^{-6} Torr exhibited a consistent decrease in growth rate of about 0.1 Å/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 investigate 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 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 obtained for HgCdTe at room temperature and 80 °C were similar to that observed for CdTe. As-prepared HgCdTe exhibited a diffuse pattern with superimposed rings indicative of an oxide/amorphous Te overlayer. Only after 60 minutes at room temperature did distinct RHEED patterns emerge, indicating removal of the oxide overlayer. The patterns remained spotty, indicative of a rough surface, and there was 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 minute exposure to atomic hydrogen, a well-defined two-dimensional pattern exhibiting

sharp streaks was observed, as shown in Fig. 1. 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. 1 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. The resulting epilayer exhibited the same atomic-level smoothness as the HgCdTe surface when examined by AFM, again with an rms. surface roughness less than 0.5 nm, as shown in Fig. 2.

RESULTS - Si

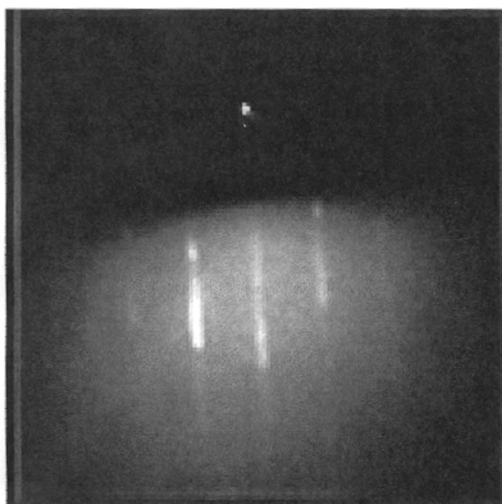


Figure 1. RHEED pattern from HgCdTe cleaned at 80 °C for 20 minutes using atomic hydrogen.

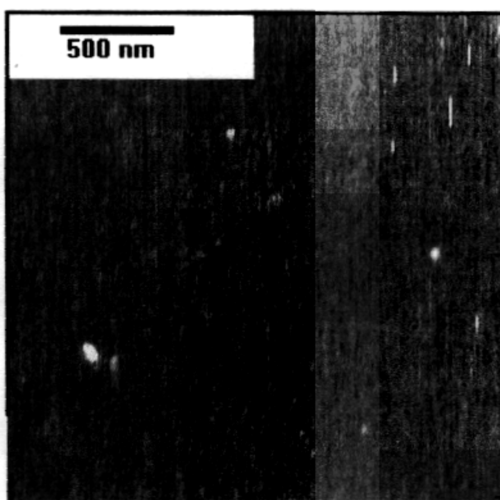


Figure 2. AFM micrograph of an 0.25 μm thick layer of CdTe grown on a HgCdTe surface cleaned using atomic hydrogen. The height scale is 10 nm

Based on prior work by Dhar *et al.*[6] and Lyon *et al.*,[7] we decided to first try growths on (211)-oriented Si substrates cleaned following the procedure outlined by Fenner *et al.* [4] The as-prepared Si substrates gave a RHEED pattern exhibiting diffuse scattering and rings. However, these features disappeared upon heating the substrate above 200 °C, leaving only the sharp, streaky RHEED pattern shown in Figure 3(a). Note the presence of strong Kikuchi lines. The disappearance of the rings may correspond to a desorption of residual carbon from the etch, as reported in a prior study.[15] For comparison, we also investigated the use of atomic hydrogen for cleaning the Si surface. In particular, we found that about a 20 minute exposure of atomic hydrogen at 600 °C removed the oxide layer from a Si substrate etched in a HF:H_2O solution. We also exposed a Si substrate cleaned using the Fenner etch to atomic hydrogen for an equivalent amount of time. Either procedure resulted in a RHEED pattern similar to that obtained by the Fenner etch alone, as shown in Figure 3(b). The only discernible difference was that the samples exposed to atomic hydrogen had a larger amount of diffuse scattering, often indicative of a sub-monolayer thick disordered surface layer. Samples were heated to temperatures as high as 700 °C, well above the desorption temperature for hydrogen on Si,[5] without any observation of change

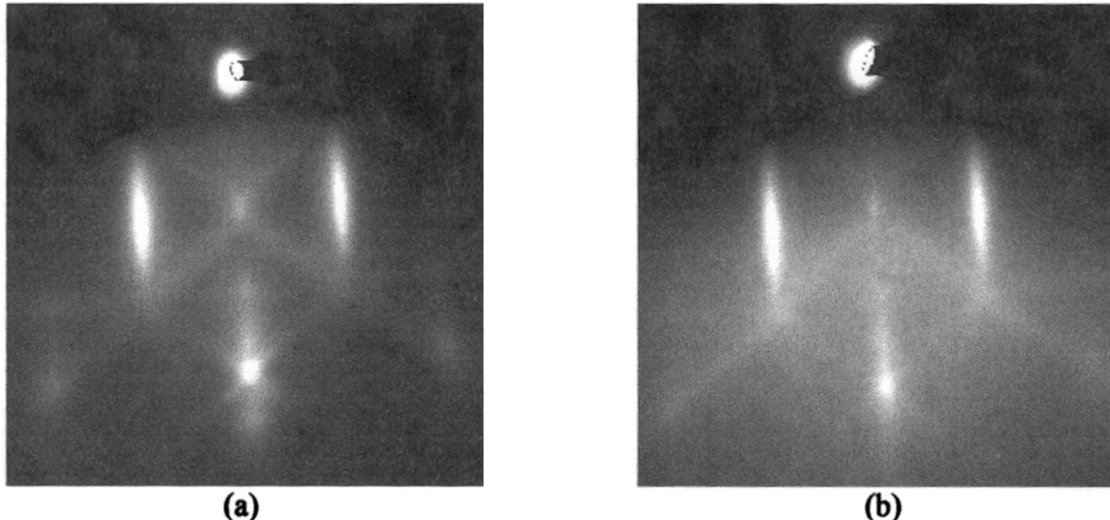


Figure 3. RHEED patterns along the (110) azimuth of (211)-oriented Silicon cleaned using (a) the Fenner procedure and (b) atomic hydrogen

from the bulk-like (1x1) RHEED patterns shown in Figure 3 indicating an absence of surface reconstruction.

We obtained only polycrystalline ZnTe and CdTe on a Si surface prepared by either of the three techniques described. It is well known that bare silicon surfaces are highly reactive with the Column VI elements O, S, Se and Te, reacting with similar chemistries. For example, one of the difficulties encountered with the growth of ZnSe on Si [16] was the formation of an amorphous $SiSe_2$ layer at the interface, analogous to SiO_2. We believe that the polycrystalline growth observed was due to the formation of an amorphous $SiTe_2$ layer upon exposure to flux containing Te, analogous to the results observed with Se. Following the lead of Romano [16] *et al.* and Dhar *et al.* [6], we passivated the Si surface by exposure to an As flux during heating to about 550 °C. With the As passivation, we were able to obtain single crystal growth on substrates cleaned by the Fenner process, but growth on substrates exposed to atomic hydrogen continued to result in polycrystalline material. Further investigation indicated that the problem always occurred if the substrate was exposed to atomic hydrogen prior to As-passivation. After As-passivation, atomic hydrogen exposure did not present any deleterious effects.

We believe this effect is not directly related to exposure to atomic hydrogen. As discussed earlier, atomic hydrogen can etch Te (and presumably CdTe and ZnTe) at low temperatures with H_2Te as an etch bi-product. We had a significant coating of Te-bearing compounds in the growth chamber which would see exposure to atomic hydrogen, resulting in a background of H_2Te. Any H_2Te striking the heated Si surface would decompose, allowing Te to react with the surface. Exposure of a Si substrate cleaned with the Fenner process directly to Te did not lead to structural rearrangement in the RHEED pattern. The background diffuse scattering increased, however, consistent with the observations of Fig. 3. Thus, we believe the atomic hydrogen in the system is transporting Te to the Si surface, resulting in a disordered $SiTe_x$ overlayer. Since we do not have the analytical capabilities on our growth chamber to investigate surface contamination, we could not directly confirm this speculation. However, it is consistent with the above results. Thus, our study may indicate that atomic hydrogen cannot be used for oxide removal from Si substrates inside a II-VI MBE chamber. Cleaning in an external preparation chamber may still be feasible.

CONCLUSIONS

We have shown that atomic hydrogen can be used to clean CdTe and HgCdTe for subsequent CdTe growth, removing both oxides and Te overlayers from the surface. However in the case of silicon, hydrogen may transport Te from the walls of the chamber onto the reactive substrate, resulting in an amorphous layer hindering growth. Therefore, hydrogen cleaning can be an effective *in-situ* cleaning method, as long as the environmental contamination does not form a volatile compound with the hydrogen which is subsequently reactive with the substrate.

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