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Priority communication

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Abstract

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 as demonstrated by the growth of single-crystal CdTe with atomically smooth surfaces. Preliminary device results demonstrate that atomic hydrogen cleaning may be viable for low-temperature HgCdTe processing. © 1998 Elsevier Science B.V. All rights reserved.

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Atomic hydrogen has been demonstrated to be an effective method 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 ex-situ cleaning procedures. 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. 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 a 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. In this communication, we report that atomic hydrogen can be used for low-temperature in-situ cleaning of HgCdTe and

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provide further insight into both the nature of the chemically etched HgCdTe surface and the effects of atomic H etching on surface stoichiometry.

Epitaxial growth and reflection high-energy electron diffraction (RHEED) results were obtained in a molecular-beam epitaxy system (MBE) which has been described elsewhere [2]. X-ray photoelectron spectroscopy (XPS) characterization was performed in a system where one chamber allowed omic hydrogen etching and sample heating, while a second contained the facilities for XPS analyses [3]. Atomic force microscopy (AFM) measurements were made in air using a Digital Instruments Nanoscope II, and reflectance measurements were performed using computerized Cary 14 spectrophotometer.

XPS analysis used the Mg anode (1253.6 eV X-ray line) of a Fisons twin-anode X-ray source operating at 300 W and a VG100AX hemispherical analyzer in a $1:1$ lens mode. Spectra were taken in constant analyzer energy mode at a 20 eV pass energy. 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. Following standard methods described by Moulder et al. [4], surface composition was determined using peak areas and elemental sensitivity factors established by Nitz et al. [5]. Although a range of sensitivity factors for Hg, Cd, and Te have been published, the values of Nitz et al. most closely match the results obtained in our system for samples of known composition. The sampling depth is approximately 10–15 Å based on data from Seah and Dench [6].

A commercial atomic hydrogen source (EPI-AHS-L) was used to generate atomic hydrogen [7]. The hydrogen flow used resulted in a beam flux monitor reading of about 3×10^{-6} Torr. After considering the ion gauge sensitivity for H_2 and the reported cracking efficiency [7] this results in an atomic hydrogen flux of $\sim 8.6 \times 10^{14} \, s^{-1} \, cm^{-2}$. The liquid-phase epitaxy (LPE) $Hg_{0.2}Cd_{0.8}Te$ substrates ($\sim 1 \, cm^2$) were provided by II–VI Inc. (Saxonburg, PA) and had been chemi-mechanically polished. The LPE layers were: degreased in trichloroethylene, acetone, and methanol; etched for 5 s in 0.5% Br : methanol; rinsed in methanol; and then immediately blown dry with nitrogen.

Atomic hydrogen cleaning was investigated at both room-temperature and at elevated temperatures. Initial studies were performed in the MBE system using RHEED. The chemically etched surface exhibited a very diffuse RHEED pattern 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 near room temperature, a brief (~ 5 min) 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. The pattern evolved into an ordered array of spots, indicative of a single-crystal 3-D surface after 60 min of total exposure. Raising the sample temperature to 80°C dramatically changed the process. Again, a brief exposure removed an initial layer. After a 20 min exposure, a well-defined 2-D pattern exhibiting sharp streaks was observed, as shown in Fig. 1. Continued exposure led to evolution of the streak patterns into a spotty 3-D pattern, indicative of surface roughening.

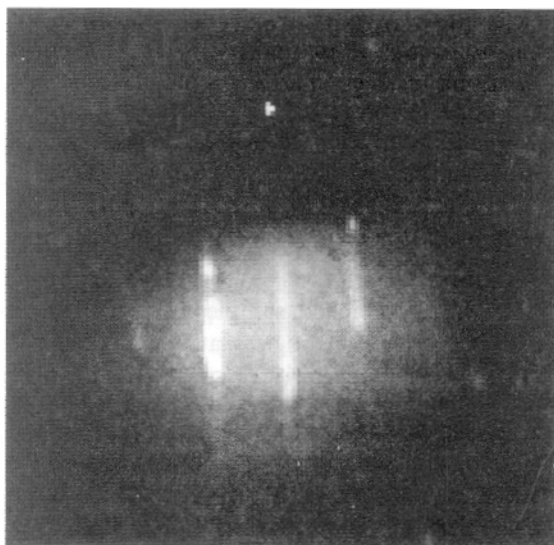AFM examination of a HgCdTe surface exhibiting a RHEED pattern similar to that shown in

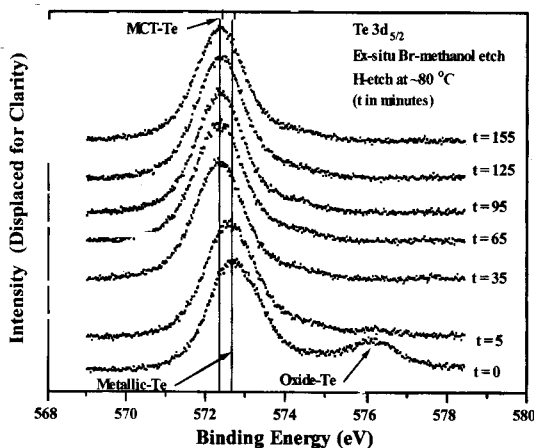Fig. 1. RHEED pattern of HgCdTe exposed to atomic hydrogen at 80°C for 20 min.

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

Fig. 1 indicated a microscopically smooth surface with an RMS surface roughness less than 5 Å. 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. The resulting epilayer exhibited the same atomic-level smoothness when examined by AFM, again with an RMS surface roughness less than 5 Å [8]. This demonstrates that atomic hydrogen can be used to obtain a HgCdTe surface suitable for low-temperature epitaxial growth of CdTe.

To better understand the processes occurring during atomic hydrogen etching, experiments were performed in the etch/XPS analysis apparatus. Fig. 2 shows a series of Te $3d_{5/2}$ photoelectron spectra for increasing exposures to atomic hydrogen. These spectra were obtained from a substrate etched at 80°C, but are similar to those obtained at 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 a representative of metallic Te [9]. As the etch proceeds, the latter peak shifts to a lower binding energy of 572.3 eV which is a representative of Te in CdTe and HgCdTe [10,11]. The corresponding Cd $3d_{5/2}$ and the Hg $4f_{7/2}$ photoelectron spectra did not exhibit a characteristic oxide peak, and their binding ener-

gies were consistent with values reported for CdTe and HgCdTe [10–12]. Combined with the RHEED analyses, these results suggest the Br-methanol etch leaves an amorphous-Te overlayer which is oxidized in transit to the analysis 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 [6]. For all the Br-methanol etched samples analyzed here, this was found to be on the order of 3–5 Å thick. That is, the oxide appears to be on the order of a monolayer or less in thickness. This result applies to samples left at atmosphere for several days before being loaded into the UHV system as well as samples transferred as rapidly as possible (~20 min) into the system. This suggests that oxide formation is 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 time determined from both RHEED and XPS, we estimate an oxide etch rate of 1.0 Å/min.

There is evidence of more than one type of oxide. One sample was briefly re-exposed (~3 h) to atmosphere after the oxide-Te peak was removed (i.e. after 5 min of atomic hydrogen). This resulted in a more intense XPS oxide-Te peak indicating an oxide twice as thick as on the Br-etched samples. The increased oxide thickness may be due to surface roughening which is consistent with spotty/diffuse RHEED patterns obtained during the initial stages of atomic hydrogen etching. Alternatively, this increase may be caused by exposure of more of the underlying HgCdTe matrix for oxidation. The Te peak binding energy for the re-exposed sample was consistent with a mixture of metallic Te and Te in a HgCdTe matrix. This oxide was also more resistant to atomic hydrogen etching. The initial removal rate, 0.52 Å/min, was a factor of two less than for the oxide on the Br-methanol etched surfaces, and decreased with time to a rate of 0.30 Å/min. Both results suggest that more than one type of oxide can be formed on a HgCdTe surface, depending intimately upon prior surface treatment.

There is always concern that the use of atomic hydrogen may lead to nonstoichiometric etching of
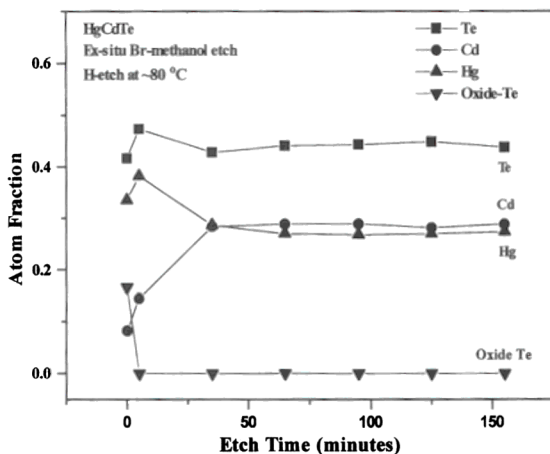
Fig. 3. HgCdTe surface composition as a function of atomic hydrogen etch time.

CdTe [13]. We performed ex-situ reflectance measurements to look for gross shifts in stoichiometry [14]. Measurements of the E_1 reflectance peak probes a layer approximately 100 nm thick. Measurements before and after atomic hydrogen cleaning were identical within instrumental resolution indicating that any stoichiometry change probed by this measurement is less than $\Delta x = 0.01$.

Fig. 3 shows typical changes in the surface composition as the atomic hydrogen etch proceeds at both room-temperature and 80°C. As discussed previously, surface composition was determined using peak areas and elemental sensitivity factors [4]. 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 to a relatively constant value which was typically within a few percent of its initial concentration, while the Hg decreased significantly. The Cd concentration, on the other hand, increased. The relative atomic concentrations approximately indicated a 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. Both composition and XPS peak binding energies attained steady state at the same point in the etch process. We note that the near-surface HgTe depletion may actually be advantageous for

device fabrication because of the beneficial band-bending this would create near the surface.

Surface oxides on CdTe have been reported to contain TeO_2 or $CdTeO_3$ [15–17]. It is believed that similar oxides are present on HgCdTe, in addition to a Te overlayer. Removal of these layers may proceed by the formation of volatile TeH_2 and H_2O. To evaluate the former mechanism, a polycrystalline 30 Å thick Te layer on a silicon substrate was removed using atomic hydrogen irradiation at 80°C in about 300 s, indicating an etch rate of 0.1 Å/s. A reaction involving the breaking the relatively weak HgTe bond must also occur since HgTe depletion is observed. 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. Extended atomic hydrogen exposure may extract the Te bound primarily to Hg with steady state attained as the etch produces a composition resistant to further HgTe bond breaking. We have no direct evidence for Cd extraction. One possible measure for the removal of Cd in conjunction with the above mechanism would be the total etch rate. The fairly rapid smoothing of the HgCdTe surface at 80°C may indicate that atomic hydrogen can etch HgCdTe.

To determine an etch rate for HgCdTe, three HgCdTe layers grown by MBE with x-values of 0.24, 0.32, 0.48 were patterned with a dense array of small photoresist dots. The samples were exposed to an atomic hydrogen flux for 60 min at 80°C and examined using AFM after stripping the photoresist. The only discernible features were infrequent photoresist remnants that marked the position of the dots. A measurable step height was not apparent above the background RMS surface roughness of 2.5 nm, indicating a step height of less than 5 nm and HgCdTe etch rate less than 0.05 Å/s. The lack of detectable etching indicates that HgTe depletion is a near-surface phenomenon.

A set of three LPE HgCdTe layers underwent atomic hydrogen etching resulting in a streaky 2-D pattern followed by deposition of 0.25 μm of CdTe at 80°C. The samples were processed into Hg-diffused devices at Lockheed Martin Microelectronics Center (Nashua, NH) and resulted in >99% yield

of working devices. The resulting average R_0A values were low, 8, 18, and 678 $\Omega\,cm^2$, for cut-off wavelengths of 9.9, 8.3, and 8.1 μm, respectively and it is not clear if this was due to bulk material quality or surface-related effects. However, the high yield of devices demonstrated that the use of atomic hydrogen did not have an egregious effect on the passivation process such as compensation of the dopants. Thus, the results are viewed as encouraging and additional samples cleaned with atomic hydrogen will be processed in the near future. These latter samples will involve direct comparison between passivation with and without atomic hydrogen cleaning, and will include variable-area diode test structures to allow isolation of surface related dark-current contributions.

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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