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Abstract

The use of specular reflectance to monitor GaSb substrate oxide desorption in-situ is reported. Substrates were loaded into the organometallic vapor phase epitaxy reactor either as-received (epi-ready) or after receiving a solvent degrease, acid etch and rinse. A variety of surface preparations and anneal conditions were investigated. HCl was used as the etchant, and in certain cases was followed by an additional etch in Br_2-HCl-HNO_3-CH_3COOH for comparison. Rinse comparisons included 2-propanol, methanol, and deionized water. Substrates were heated to either 525, 550, or 575 °C. Features observed in the in-situ reflectance associated with the oxide desorption process were interpreted based on the starting oxide chemistry and thickness. Based on in-situ reflectance and ex-situ atomic force microscopy data, a recommendation on a reproducible GaSb substrate preparation technique suitable for high-quality epitaxial growth is suggested.

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Keywords: GaSb; Oxide desorption; In-situ reflectance monitoring; OMVPE; Epi-ready; Substrate etch

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1. Introduction

High-quality epitaxial crystal growth requires a clean, oxide-free starting substrate surface. Oxide desorption is routinely monitored using reflection high-energy electron diffraction (RHEED) in molecular beam epitaxy. However, RHEED and other electron-based in-situ probes require a high vacuum environment, and therefore cannot be utilized in atmospheric- or low-pressure epitaxial systems. Recent studies in these systems have reported the use of optical- or x-ray-based in-situ probes, and have focused more on the epitaxial growth process than on substrate oxide desorption [1-10]. It is of particular interest to monitor oxide desorption from GaSb substrates because they provide a lattice-matched template for mid-infrared III-V materials [11,12], and these substrates have been difficult to prepare for epitaxy.

A variety of in-situ optical probes have been discussed in the literature, including reflectance [4-6], ellipsometry [7,13], reflectance difference spectroscopy [8], diffuse scattering [9,14], and surface photoabsorption [10,15]. Reflectance is an attractive technique for monitoring oxide desorption because it is relatively easy and inexpensive to implement, and it is sensitive to the presence of a few monolayers of oxide. Use of a broadband light source and spectrometer to enable spectral reflectance monitoring provides the flexibility to select the wavelengths that are most sensitive to the oxide desorption process, with minimal additional complexity to the experimental setup.

This paper reports the use of spectral reflectance as an in-situ monitor of GaSb substrate oxide desorption. A variety of pre-growth surface preparations and anneal conditions were investigated. Recommendations for a reproducible GaSb substrate

preparation technique for high-quality epitaxial growth are suggested based on in-situ reflectance and ex-situ atomic force microscopy (AFM) results.

2. Experimental procedure

The in-situ reflectance monitoring system is similar to that described previously [1], although a 55° incidence angle is used in this work. Optical fibers and lenses direct randomly polarized white light from a 5 W tungsten-halogen lamp through the quartz wall of the organometallic vapor phase epitaxy (OMVPE) reactor to the GaSb substrate at a 55° incidence angle. The reflected beam is collected by another lens and fiber and transmitted to the silicon photodiode array (Si PDA) spectrometer. The Si PDA is a commercial 512-element-array unit with a wavelength range of 380-1100 nm that has all its optics and electronics mounted directly on a PC plug-in board. Data were acquired with a one second integration time.

The GaSb substrates were Te-doped n-type greater than $1x10^{17}$ cm^{-3}, and were (001) misoriented 2° toward (101). Substrates were used either as-received epi-ready, or were degreased in solvents, etched in acid and rinsed before loading into the reactor. The solvent degrease consisted of hot trichloroethylene, followed by acetone and then 2-propanol. The etch procedure was 3 min of agitation in HCl, or HCl followed by an additional 30 s etch in Br_2-HCl-HNO_3-CH_3COOH [16]. Substrates were then rinsed in one of three different solutions: 2-propanol, methanol, or deionized water (DI H_2O), and blown dry with N_2. After the substrates were loaded into the reactor, they were heated to 525, 550, or 575 °C in a H_2 carrier gas at a flow rate of 10 slpm at 150 Torr. The heating

rate during the initial part of the heat-up was 1.8 °C/s. Total time for heat-up and anneal was varied between 600 s and 1800 s.

The surface morphology was measured by ex-situ AFM operated in tapping mode. Etched Si cantilevers with a nominal tip radius of 5 to 10 nm and a sidewall angle of 10° were used. Samples were typically scanned at 2 lines per second with 512 points per line.

3. Results

In-situ reflectance at 500 nm during heating of two different GaSb substrates is shown in Fig. 1. The substrate in Fig. 1(a) was loaded into the reactor and heated with no pre-growth surface treatment (i.e. as-received epi-ready), while that in Fig. 1(b) was degreased in solvents, etched in HCl and rinsed in 2-propanol before loading into the reactor. Heating begins at 25 s, and the temperature is stable at 575 °C by 500 s. Two heating curves are displayed in each figure – one with the oxide, and one without the oxide. To obtain the "oxide-free" curves the substrates were heated to 575 °C, cooled to 30 °C, and re-heated to 575 °C. Since the GaSb substrate remained in the reactor in a H_2 ambient during cooling and subsequent re-heating, it is expected that the GaSb surface was oxide-free during re-heating.

Figure 1 shows that the reflectance of the surface with the oxide is lower than that without the oxide at the beginning of heating. (The reflectance curves have not been offset or shifted.) In addition, the reflectance of the epi-ready substrate displays a much larger deviation from the oxide-free substrate during heating than does the HCl-etched substrate. Quantitative analysis of the in-situ reflectance data is in agreement with ex-situ

ellipsometry that the approximate oxide thickness on the epi-ready substrate is 5-6 nm, while it is 1-2 nm on the etched surface.

Figure 2 shows AFM images of two GaSb surfaces annealed at 575 °C. The substrate in Fig. 2(a) was loaded into the reactor and heated for 1200 s with no pre-growth surface treatment (i.e. epi-ready), while that in Fig. 2(b) was degreased in solvents, etched in HCl, rinsed in 2-propanol and heated for 600 s. The epi-ready surface appears rough, while the etched substrate displays uniform vicinal behavior. This difference in morphology is not due to different anneal times, as is discussed below. The etched surface is clearly more suitable for subsequent epitaxial growth by step-flow mode. AFM images (not shown here) of 0.18 μm thick epitaxial GaSb on GaSb indicate that the epitaxial GaSb grown on the epi-ready substrate is rougher than the underlying substrate itself, suggesting that growth on the epi-ready substrate has occurred in an undesirable 3-D growth mode. However, epitaxial growth on the HCl-etched substrate remained vicinal with the same roughness as the underlying substrate, indicating that growth occurred in the preferred step-flow mode.

GaSb substrates that received an additional 30 s etch in Br_2-HCl-HNO_3-CH_3COOH after the 3 min HCl etch displayed very similar in-situ reflectance heating curves and surface morphologies to those that were etched only in the HCl. This suggests that the additional 30 s etch in Br_2-HCl-HNO_3-CH_3COOH is an unnecessary step.

For substrates that were solvent degreased and etched only in HCl, the effect of the post-etch rinse on the reflectance during heating was also investigated. Figure 3 shows the reflectance at 500 nm from substrates that were rinsed ten times in: (a) DI H_2O, (b)

methanol, (c) 2-propanol followed by a 10 min exposure to atmosphere under a clean hood, or (d) 2-propanol. The curves have been intentionally offset for clarity. The substrates were typically in the rinse liquid for a total of 120 s, and were loaded into the reactor within 150 s (except for curve (c)) of being rinsed. The in-situ reflectance suggests that a 2-propanol rinse and quick reactor load develops the least oxide formation. AFM images (not shown here) confirm that the substrate rinsed in 2-propanol (bottom curve of Fig. 3) is the most suitable for subsequent epitaxial growth by step flow. While all four surfaces are essentially vicinal, those rinsed in DI H_2O or methanol exhibit some pitting and take far longer to equilibrate (1800 s) than the surface rinsed in 2-propanol (600 s).

To investigate the effect of anneal temperature, substrates were degreased in solvents, etched in HCl, rinsed in 2-propanol and then heated for 720 s to 525, 550, or 575 °C. Surface morphologies for all three anneal temperatures are like that shown in Fig. 2(b), indicating that under these conditions the etched and annealed substrate surface is relatively insensitive to anneal temperature. Total anneal time also has no significant effect on the surface morphology of etched GaSb substrates rinsed in 2-propanol. AFM images of substrates prepared that way and annealed for 720, 1020, or 1800 s are also like that shown in Fig 2(b). This is in agreement with the in-situ reflectance signal, which equilibrates after 600 s for etched surfaces rinsed in 2-propanol. However, this is not the case for epi-ready substrates or etched substrates rinsed in DI H_2O or methanol. In those cases, it can be seen in Figs. 1(a) and 3 that the reflectance signal takes longer to equilibrate, and therefore longer anneal times are necessary. AFM indicates that epi-

ready surfaces heated for 1200 s or longer are smoother than those annealed for 900 s. This is also observed in the in-situ reflectance plotted in Fig. 1(a). The reflectance of the epi-ready substrate is still increasing at 900 s, and does not equilibrate until 1200 s. However, it should be pointed out that even with total anneal times of 1800 s, the epi-ready surface never achieved the vicinal nature of annealed etched substrates. As a result, high quality epitaxial growth on epi-ready substrates could not be achieved.

Finally, the effect of trimethylantimony (TMSb) flow during substrate heating was investigated. TMSb at a flow rate of 1.5 sccm was introduced into the reactor during heating of some epi-ready and etched substrates at 200 s (330 °C). In-situ reflectance data suggest that oxide desorption kinetics may have increased with TMSb flow, particularly at temperatures above 400 °C (240 s). The effect was more noticeable for epi-ready substrates than for etched substrates. However, AFM images were similar for substrates annealed with and without TMSb flow, with substrates annealed under TMSb flow having a tendency to be slightly rougher than those annealed without TMSb flow. This roughness might be associated with excess antimony on the surface, and it is possible that under different TMSb flow rates results could differ.

4. Discussion

Previous studies have reported that the native oxide present on GaSb is primarily composed of Ga_2O_3 and Sb_2O_3 [17-21]. Sb_2O_3 is metastable in contact with GaSb, so at elevated temperatures the following reaction takes place:

$$Sb_2O_3 + 2GaSb \rightarrow Ga_2O_3 + 4Sb \qquad (1)$$

with a free energy change of –68.5 kcal/mol [19,21]. In addition, Sb_2O_3 and Ga_2O_3 will desorb at elevated temperatures. The free energy of formation at 25 °C for Sb_2O_3 is –150 kcal/mol, while it is –239 kcal/mol for Ga_2O_3 [18]. The following reactions are likely to take place during heating of a GaSb substrate with a native oxide: reaction of Sb_2O_3 and GaSb to form Ga_2O_3 and elemental Sb; desorption of Sb_2O_3; and desorption of Ga_2O_3. Results from x-ray photoelectron spectroscopy, RHEED, and Auger electron spectroscopy indicate that in vacuum, reaction (1) begins to take place around 200 °C, Sb_2O_3 begins to desorb around 340 °C, and Ga_2O_3 begins to desorb between 480 and 510 °C [21-24]. Examination of curve (c) in Fig. 3 (2-propanol rinse/10 min air exposure) and Fig. 1(b) reveals that the reflectance begins to increase at 220 °C, which is likely due to the formation of elemental Sb from reaction (1). The presence of this Sb might also explain why the reflectance from a sample with an oxide increases above that of an oxide-free sample during substrate heating (see Fig. 1(a)). Since the existence of an oxide reduces the reflectance of a GaSb substrate (see the starting reflectances in Fig. 1), if the oxide simply desorbed during substrate heating with no other reactions taking place, then the reflectance of the surface with the oxide could never be higher than that without the oxide. However, the formation of a 3rd phase (the elemental Sb) could cause the reflectance of the oxidized substrate to increase above that of the oxide-free surface.

Curve (c) in Fig. 3 shows that the reflectance increases again around 380 °C, probably due to desorption of Sb_2O_3. This increase is not present in the heating curve of the etched substrate in Fig. 1(b) or the bottom curve of Fig. 3. Since HCl etches Sb_2O_3 [25], it is expected that an etched GaSb substrate will contain only the small amount of

Sb_2O_3 that can form in the 150 s it takes to load the sample into the reactor. All of this Sb_2O_3 probably reacts with the GaSb before the sample reaches 380 °C; therefore, no Sb_2O_3 is left on the surface to desorb at 380 °C on a well-etched substrate, and no peak is seen at 380 °C in the reflectance of such a substrate. However, the substrate associated with the reflectance in Fig. 3(c) was exposed to atmosphere for 10 min before loading into the reactor, and therefore would have more Sb_2O_3 present on the surface. Any unreacted Sb_2O_3 remaining on the surface by 380 °C desorbs at that point, causing the reflectance to increase.

Around 440 °C (265 s) the reflectance suddenly drops, possibly due to desorption of the elemental Sb produced by reaction (1) above. Finally, the reflectance of the surface with the oxide is still below that of the oxide-free surface until about 520 °C (325 s). At this temperature the gap between the two signals starts to decrease, which might be due to desorption of Ga_2O_3.

Based on the above interpretation, a possible explanation for the observation of the rough surface of the annealed epi-ready substrate is that it is roughened by consumption of GaSb from reaction (1). Since an epi-ready substrate contains far more Sb_2O_3 than an HCl-etched substrate, it is not surprising that reaction (1) would cause a more dramatic effect on the surface morphology of an epi-ready substrate than an etched substrate. The roughness of the epi-ready substrate is not due to incomplete oxide desorption, since the substrate reheat (shown in Fig. 1) indicates a perfectly clean, oxide-free surface.

5. Conclusions

In-situ reflectance has been used as a valuable tool for observing oxide desorption from GaSb substrates. Information in the literature about the native oxide on GaSb was used to interpret features seen in the reflectance during substrate heating. Based on in-situ reflectance and ex-situ AFM of annealed surfaces and subsequent epitaxial growth, the following substrate preparation procedure is recommended for reproducible, high quality epitaxial growth on GaSb:

1. Solvent rinse (hot trichloroethylene, acetone, methanol)
2. Etch/agitate for 3 min in concentrated HCl
3. Rinse ten times in 2-propanol; blow dry with N_2
4. Heat to any temperature from 525-575 °C for at least 600 s in a H_2 ambient

This procedure yields extremely reproducible vicinal GaSb substrate surfaces suitable for step-flow epitaxial growth.

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FIGURES

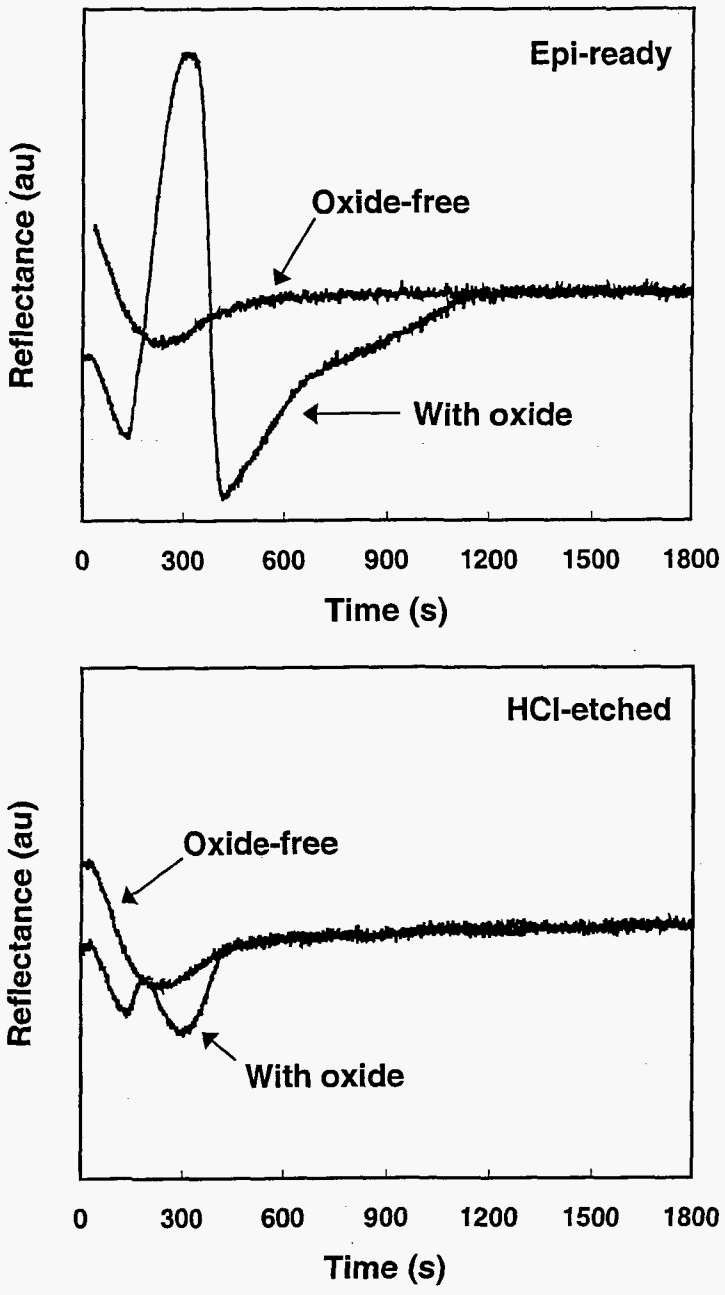

Fig. 1. In-situ reflectance at 500 nm of the heat-up of (a) an epi-ready substrate and (b) an HCl-etched substrate. Each graph also displays oxide-free data from re-heating the substrate. The baseline of the curves has not been shifted or offset.

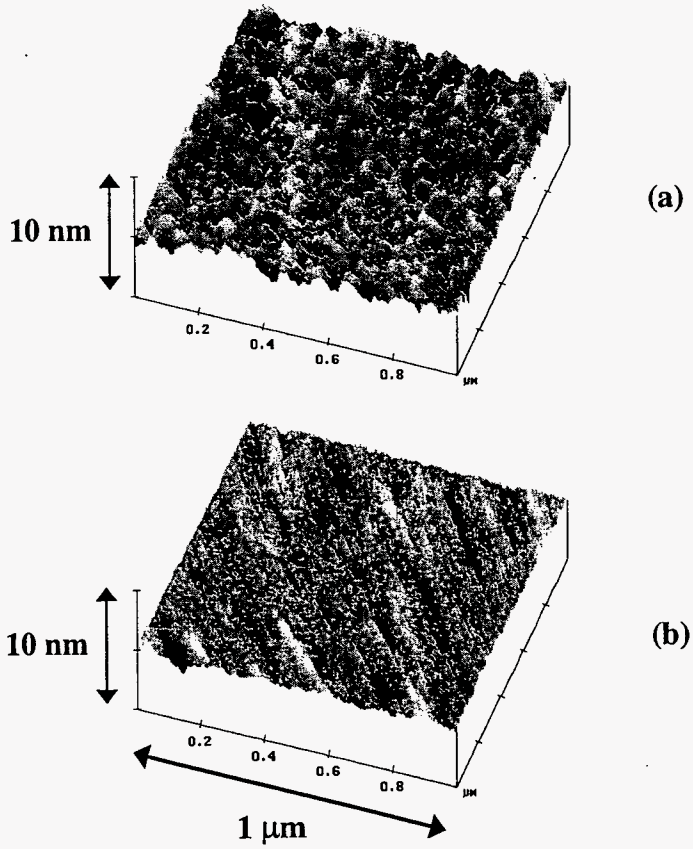

Fig. 2. AFM images of (a) epi-ready and (b) HCl-etched surfaces annealed at 575 °C. Note that the annealed etched surface appears vicinal, while the epi-ready surface is rough.

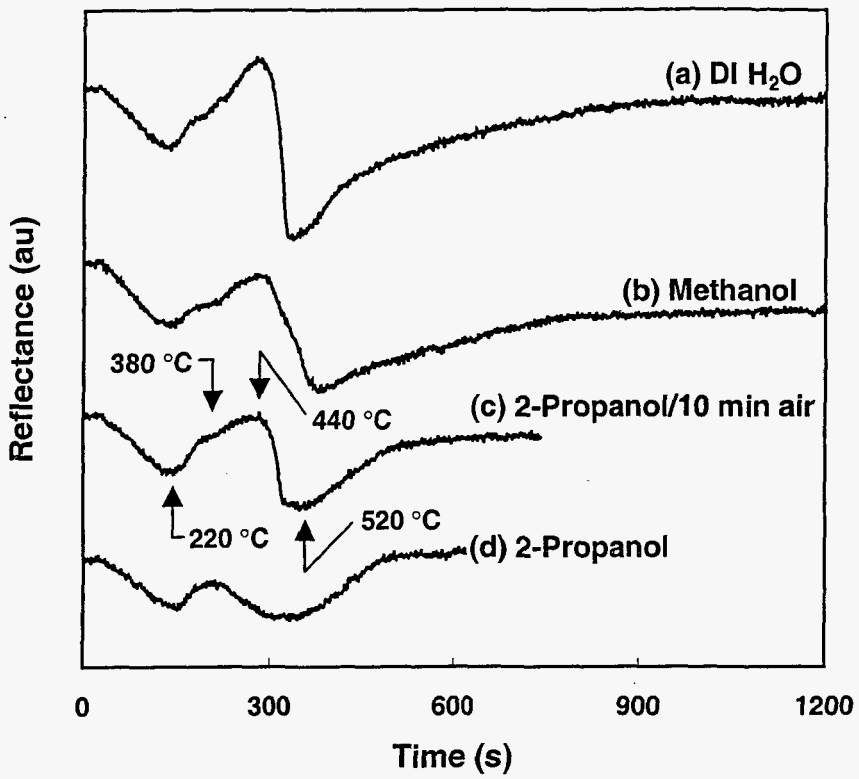

Fig. 3. In-situ reflectance at 500 nm illustrating the effect of post-etch rinse. Substrates were rinsed in solvents, etched in HCl, and then rinsed in either: (a) DI H_2O, (b) methanol, (c) 2-propanol and subsequent 10 min air exposure, or (d) 2-propanol. Note that the 2-propanol rinse and quick reactor load, curve (d), results in the least oxide formation. Curves have been intentionally offset for clarity.