ELSEVIER

Journal of Crystal Growth 225 (2001) 420–425

JOURNAL OF CRYSTAL GROWTH

www.elsevier.nl/locate/jcrysgro

In-situ reflectance monitoring of GaSb substrate oxide desorption

C.J. Vineis[a,b], C.A. Wang[a,*], K.F. Jensen[b,c]

[a] *Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02420-9108, USA*
[b] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA*
[c] *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA*

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°C, 550°C, or 575°C. Features observed in the in-situ reflectance associated with the oxide desorption process are 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.

PACS: 68.55.A; 73.61.Ey; 81.15.Kk

Keywords: A1. In-situ reflectance monitoring; A3. Epi-ready; A3. Organometallic vapor phase epitaxy; A3. Oxide desorption; A3. Substrate etch; B1. GaSb

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

*Corresponding author. Tel.: +1-781-981-4466; fax: +1-781-981-0122.

E-mail addresses: cjv@ll.mit.edu (C.J. Vineis), wang@ll.mit.edu (C.A. Wang).

0022-0248/01/$ - see front matter
PII: S0022-0248(01)00904-6

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 wavelengths that are most sensitive to the oxide desorption process, with minimal additional complexity to the experimental set-up.

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. This angle was chosen due to its easy accessibility in the organometallic vapor phase epitaxy (OMVPE) growth system. Optical fibers and lenses direct randomly-polarized white light from a 5 W tungsten-halogen lamp through the quartz wall of the OMVPE reactor to the GaSb substrate. 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 1 s integration time.

The GaSb substrates were Te-doped n-type greater than $1 \times 10^{17}\,cm^{-3}$, and were (0 0 1) misoriented 2° toward (1 0 1). Substrates were used either as-received epi-ready, or were degreased in solvents, etched in acid and rinsed before loading into the reactor. All substrates not used epi-ready were degreased. The solvent degrease consisted of hot trichloroethylene, followed by acetone and then 2-propanol. The etch procedure was 5 min of agitation in HCl. This was followed by an additional 30 s etch in Br_2–HCl–HNO_3–CH_3COOH in certain cases for comparison [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°C, 550°C, 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 and 1800 s. In some experiments, GaSb was deposited with a triethylgallium (TEGa) flow rate of 1 sccm and trimethylantimony (TMSb) flow rate of 1.5 sccm.

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/s with 512 points per line.

3. Results

In-situ reflectance at 500 nm during heating of three different GaSb substrates is shown in Fig. 1. The epi-ready substrate in Fig. 1 was loaded into the reactor and heated with no pre-growth surface treatment (i.e. as-received), while the HCl-etched

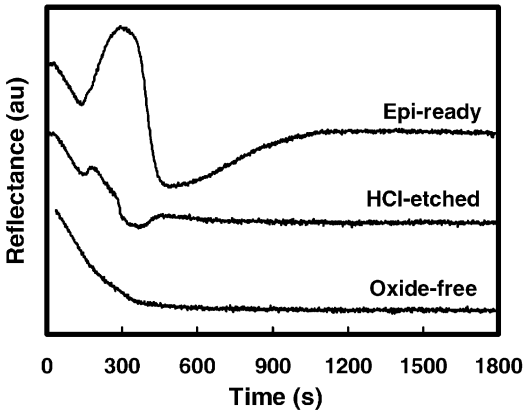

Fig. 1. In-situ reflectance at 500 nm during heating of an epi-ready substrate, an etched substrate, and an oxide-free substrate. The temperature is stable at 550°C by 460 s. The curves have been intentionally offset for clarity.

substrate was degreased in solvents, etched in HCl and rinsed in 2-propanol before loading into the reactor. Heating began at 25 s, and the temperature was stable at 550°C by 460 s. To obtain the oxide-free curve, a substrate was heated to 550°C, cooled to 30°C, and re-heated to 550°C. Since the substrate remained in the reactor in a H_2 ambient during cooling and subsequent re-heating, it is expected that the surface was oxide-free during re-heating.

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. In addition, the reflectance of the epi-ready substrate takes a longer time (1200 s) to equilibrate than the HCl-etched substrate (600 s). These differences are due to different substrate oxide thicknesses. Ex-situ ellipsometry indicated that the approximate oxide thickness on the epi-ready substrate was 5–6 nm, while it was 1–2 nm on the etched one.

Fig. 2 shows AFM images of two GaSb surfaces annealed at 550°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 also heated for 1200 s. The epi-ready surface exhibits a random texture (root-mean-square (RMS) roughness ~0.33 nm), while the etched substrate (RMS roughness ~0.20 nm) is mainly vicinal with mono- and bi-layer steps.

GaSb epilayers were grown on epi-ready and HCl-etched substrates. AFM images (not shown here) indicate that the 0.18 μm-thick epilayer grown on the epi-ready substrate is rougher (RMS roughness ~0.60 nm) than the underlying substrate itself. This suggests that growth on the epi-ready substrate has occurred in an undesirable growth mode which causes continual surface roughening during deposition. However, epitaxial growth on the HCl-etched substrate remained vicinal with the same RMS roughness as the underlying substrate, indicating that growth occurred in the preferred step-flow mode. The etched surface is clearly more suitable for subsequent epitaxial growth by step-flow mode.

GaSb substrates that received an additional 30 s etch in Br_2–HCl–HNO_3–CH_3COOH to remove GaSb after the 5 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 oxide removal.

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

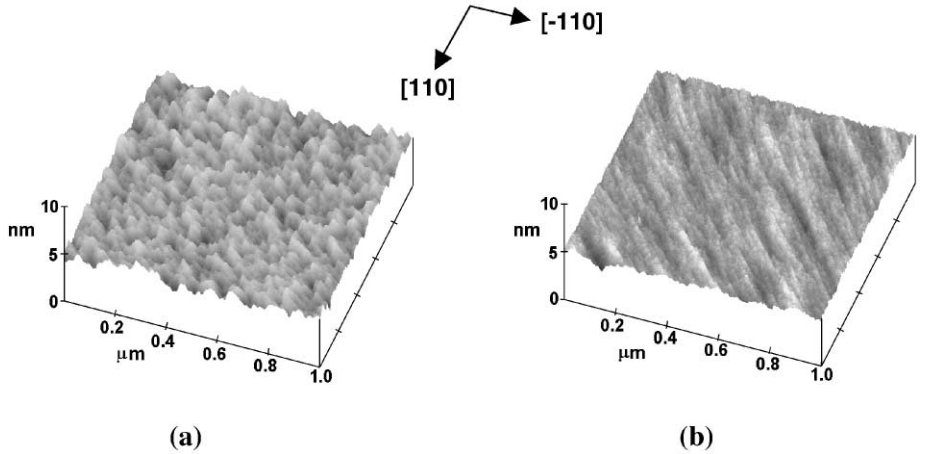

Fig. 2. AFM images of (a) epi-ready and (b) HCl-etched surfaces annealed at 550°C. Note that the annealed etched surface appears vicinal, while the epi-ready surface is rough.

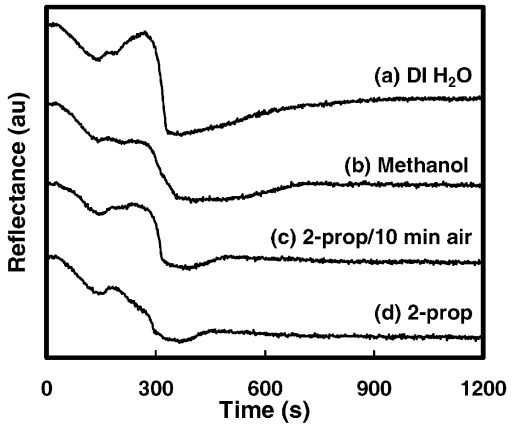

Fig. 3. In-situ reflectance at 500 nm illustrating the effect of post-etch rinse. Substrates were rinsed in solvents, etched in HCl, and then rinsed in either: (a) DI H_2O, (b) methanol, (c) 2-propanol and subsequent 10 min air exposure, or (d) 2-propanol. Note that the 2-propanol rinse and quick reactor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

2-propanol followed by a 10 min exposure to atmosphere under a clean hood, or (d) 2-propanol. The substrates were typically in the rinse liquid for about 120 s, and were subsequently loaded into a N_2-purged glove box. Substrates were then transferred into the reactor within 150 s (except for curve (c)). Since curve (d) exhibits the least deviation from the reflectance measured for an oxide-free substrate (see Fig. 1), these results suggest that a 2-propanol rinse and minimal exposure to air 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. While all four surfaces are essentially vicinal, those rinsed in DI H_2O or methanol exhibit slight pitting and take longer to equilibrate (1800 s) than the surface rinsed in 2-propanol (600 s).

The effect of anneal temperature on oxide desorption and surface morphology was also studied. HCl-etched substrates were rinsed in 2-propanol and then heated for 720 s to either 525 or 575°C. The surface morphology of these samples is similar to that of the sample heated to 550°C (shown in Fig. 2(b)), indicating that under these preparation conditions, the annealed substrate surface is relatively insensitive to anneal temperature.

It was also found that the anneal time, which ranged from 600–1800 s, had no significant effect on the reflectance and surface morphology of HCl-etched, 2-propanol-rinsed substrates. Epi-ready substrates, however, were more sensitive to anneal time. AFM images (not shown here) indicate that epi-ready surfaces heated for 1200 s or longer are smoother than those annealed for only 900 s. This surface smoothing might explain the continually increasing reflectance from 900 to 1200 s shown in Fig. 1. 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.

The effect of TMSb flow during substrate heating was investigated for epi-ready and HCl-etched substrates. TMSb at a flow rate of 1.5 sccm was introduced into the reactor when the substrate temperature reached 330°C (200 s). Features related to the oxide desorption process seen in the in-situ reflectance data occurred at lower temperatures with TMSb flow, suggesting that oxide desorption kinetics may have increased with TMSb flow. The effect was more noticeable for epi-ready substrates than for etched substrates. However, for both substrates, 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

The differences observed in the reflectance spectra from the various GaSb substrate preparation methods can be explained by considering previously reported studies [17–21] on the native oxide of GaSb. The oxide is primarily composed of Ga_2O_3 and Sb_2O_3, with respective free energies of formation at 25°C of –239 kcal/mol and –150 kcal/

mol [18]. Since Sb_2O_3 is metastable in contact with GaSb, the following reaction takes place:

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

with a free energy change of –68.5 kcal/mol [19,21]. It has been reported that this reaction takes place significantly at temperatures above 200°C [22]. It has also been reported that Sb_2O_3 and Ga_2O_3 begin to desorb at approximately 340°C and 500°C, respectively [22–24]. Therefore, the following reactions are likely to occur 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.

These previously reported temperatures correlate well with features observed in the in-situ reflectance shown in Fig. 4. In this figure, the reflectance of the sample in Fig. 3(c) is shown at 633 nm along with the reflectance of an oxide-free substrate. (This wavelength was chosen because it most clearly displays the onset of various features in the oxide desorption process.) Note that the two reflectance curves have not been offset; therefore, their relative reflectance contains valuable information. In particular, the starting reflectances indicate that the presence of an oxide reduces the reflectance of a GaSb substrate, in agreement with theoretical calculations using randomly-polarized light at a 55° incidence angle. Therefore, 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, at 220°C the reflectance of the substrate with the oxide increases above that of the oxide-free surface, which implies that a third phase must be present on the surface, in addition to the GaSb and oxides. This third phase might be the elemental Sb produced by reaction (1) above.

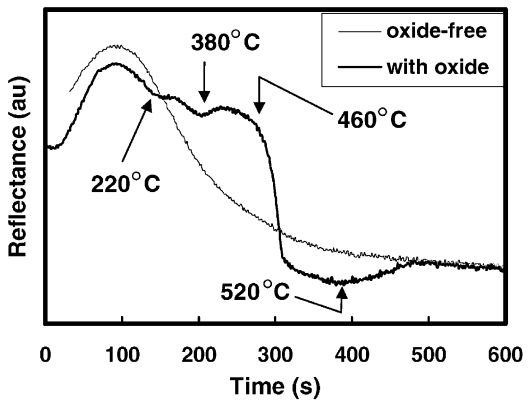

Fig. 4. In-situ reflectance at 633 nm highlighting the various features that occur in the reflectance during substrate heat-up and oxide desorption. Note that these two curves have not been intentionally offset.

At 380°C, the reflectance of the surface with the oxide increases again, which is probably due to desorption of Sb_2O_3. This increase is more prominent than the increase shown for the HCl-etched substrate in Fig. 3(d). This difference can be explained by the relative amount of Sb_2O_3 present on these two substrates. Since HCl etches Sb_2O_3 [25], it is expected that an etched GaSb substrate loaded directly into the reactor will contain less Sb_2O_3 than one that has been etched and intentionally exposed to air. For substrates that are etched and loaded directly into the reactor, all of the Sb_2O_3 probably reacts with the GaSb before the sample reaches 380°C. Therefore, no Sb_2O_3 is left on these surfaces to desorb at 380°C, and no peak is seen at 380°C in the reflectance of such a substrate. However, the substrate associated with the reflectance in Fig. 4 was exposed to atmosphere for 10 min before loading into the reactor, and therefore would have more Sb_2O_3 present on the surface.

The next feature seen in the reflectance in Fig. 4 is a sudden drop at 460°C (280 s). This sharp drop continues until about 315 s, at which point the reflectance is below that of the oxide-free surface. The lower reflectance is due to the remaining Ga_2O_3. The magnitude of the reflectance drop is proportional to the expected amount of elemental Sb produced by reaction (1). Therefore, this drop is possibly due to desorption of the elemental Sb. At 520°C (380 s), the reflectance increases again, which is probably due to desorption of Ga_2O_3. Once the oxide is completely removed (485 s), the reflectance matches that of the oxide-free surface.

Based on the above interpretation, a proposed explanation for the rougher surface of the annealed epi-ready substrate compared to the etched substrate is that the epi-ready substrate is

roughened by consumption of GaSb from reaction (1). Since an epi-ready substrate contains approximately five times more Sb_2O_3 than an HCl-etched substrate, reaction (1) suggests that more GaSb is consumed during the heating 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 (not shown) indicated a 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, 2-propanol),
2. Etch/agitate for 5 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 in a H_2 ambient for at least 600 s.

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

Acknowledgements

The authors gratefully acknowledge D.C. Oakley for assistance in substrate preparation, and P. Nitishin and E. Shaw for helpful discussions. This work was sponsored by the Department of Energy under AF Contract No. F19628-00-C-0002. The opinions, interpretations, conclusions and recommendations are those of the author and are not necessarily endorsed by the United States Air Force.

References

[1] C.J. Vineis, C.A. Wang, K.F. Jensen, W.G. Breiland, J. Crystal Growth 195 (1998) 181.
[2] I.P. Herman, Optical Diagnostics for Thin Film Processing, Academic Press, New York, 1996.
[3] D.W. Kisker, G.B. Stephenson, P.H. Fuoss, S. Brennan, J. Crystal Growth 146 (1995) 104.
[4] K.P. Killeen, W.G. Breiland, J. Electron. Mater. 23 (1994) 179.
[5] R.M. Lum, M.L. McDonald, J.C. Bean, J. Vandenberg, T.L. Pernell, S.N.G. Chu, A. Robertson, A. Karp, Appl. Phys. Lett. 69 (1996) 928.
[6] T. Farrell, J.V. Armstrong, P. Kightley, Appl. Phys. Lett. 59 (1991) 1203.
[7] C. Herzinger, B. Johs, P. Chow, D. Reich, G. Carpenter, D. Croswell, J. Van Hove, Mat. Res. Soc. Symp. Proc. 406 (1996) 347.
[8] J.P. Harbison, D.E. Aspnes, A.A. Studna, L.T. Florez, M.K. Kelly, Appl. Phys. Lett. 52 (1988) 2046.
[9] J.M. Olson, A. Kibbler, J. Crystal Growth 77 (1986) 182.
[10] N. Kobayashi, J. Crystal Growth 195 (1998) 228.
[11] C.A. Wang, H.K. Choi, S.L. Ransom, G.W. Charache, L.R. Danielson, D.M. DePoy, Appl. Phys. Lett. 75 (1999) 1305.
[12] H.K. Choi, J.N. Walpole, G.W. Turner, M.K. Conners, L.J. Missaggia, M.J. Manfra, IEEE Photonics Tech. Lett. 10 (1998) 938.
[13] E.A. Irene, Thin Solid Films 233 (1993) 96.
[14] D.J. Robbins, A.J. Pidduck, A.G. Cullis, N.G. Chew, R.W. Hardeman, D.B. Gasson, C. Pickering, A.C. Daw, M. Johnson, R. Jones, J. Crystal Growth 81 (1987) 421.
[15] D.A. Allwood, N.J. Mason, P.J. Walker, J. Crystal Growth 195 (1998) 163.
[16] F.W.O. Da Silva, C. Raisin, M. Silga, M. Nouaoura, L. Lassabatere, Semicond. Sci. Technol. 4 (1989) 565.
[17] Y. Mizokawa, O. Komoda, S. Miyase, Thin Solid Films 156 (1988) 127.
[18] P. Barman, S. Basu, Appl. Surf. Sci. 55 (1992) 173.
[19] Y. Mizokawa, O. Komoda, H. Iwasaki, S. Nakamura, Jpn. J. Appl. Phys. 23 (1984) L257.
[20] C.W. Wilmsen in Physics and Chemistry of III–V Compound Semiconductor Surfaces, in: C.W. Wilmsen (Ed.), Plenum Press, New York, 1985, Chapter. 7.
[21] G.P. Schwartz, G.J. Gualtieri, J.E. Griffiths, C.D. Thurmond, B. Schwartz, J. Electrochem. Soc. 127 (1980) 2488.
[22] L.J. Gomez Zazo, M.T. Montojo, L.J. Castano, J. Piqueras, J. Electrochem Soc. 136 (1989) 1480.
[23] M. Kodama, Adv. Mater. Optics Electron. 4 (1994) 319.
[24] Z. Lu, Y. Jiang, W.I. Wang, M.C. Teich, R.M. Osgood Jr., J. Vac. Sci. Technol. B 10 (1992) 1856.
[25] D.R. Lide, CRC Handbook of Chemistry and Physics, 73rd Edition, CRC Press, Boca Raton, 1992 pp. 4–41.