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1. **ABSTRACT (Maximum 200 words)**

The growth of lattice mismatched epitaxial layers on a binary compound semiconductor interface can lead to a high density of defects, such as dislocations, that can degrade subsequent device performance. For the direct growth of lattice-mismatched materials, defects continue to dominate the properties and function of heteroepitaxial structures. The development of compliant and wafer-bonded structures has provided an alternative approach to the generation substrates for lattice mismatched epitaxial growth. The nature of the interface between bonded layers has not been extensively explored at present. This interface, consisting of a network of dislocations, can however eventually affect or even dictate the properties of the subsequent devices as well as its reliability. We propose to determine the detailed chemical and physical nature of this interface through the application of both conventional and nanoscale characterization tools. The physical and chemical structure of these interfaces was investigated by FTIR and high-resolution spectroscopies. The impact of thermal stress on these structures, as a measure of their long-term stability, will be assessed in the context of device reliability.

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Final Report

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Statement of the Research Problem

The growth of lattice mismatched epitaxial layers on a binary compound semiconductor interface can lead to a high density of defects, such as dislocations, that can degrade subsequent device performance. For the direct growth of lattice-mismatched materials, defects continue to dominate the properties and function of heteroepitaxial structures. The development of compliant and wafer-bonded structures has provided an alternative approach to the generation substrates for lattice mismatched epitaxial growth. The nature of the interface between bonded layers has not been extensively explored at present. This interface, consisting of a network of dislocations, can however eventually affect or even dictate the properties of the subsequent devices as well as its reliability. We have determined the detailed chemical and physical nature of this interface through the application of both conventional and nanoscale characterization tools of key bonding interfaces. The physical and chemical structure of these interfaces was investigated by FTIR and high-resolution spectroscopies. The impact of thermal stress on these structures, as a measure of their long-term stability, will be assessed in the context of device reliability.

Results: Short discussions are reported for several studies already published and longer descriptions are presented for those studies in preparation for publication


High frequency integrated circuit applications of GaSb-based materials are hampered by the lack of a suitable lattice matched insulating substrate. Wafer bonding was used to fabricate InAs/AlSb/GaSb-based heterojunction bipolar transistors (HBTs) on an insulating sapphire substrate through a low temperature bonding process that results in a high bond strength and permitted the mechanical and chemomechanical removal of the initial GaSb substrate. The use of selective etches allows for the retaining the epitaxial device layers over virtually the entire wafer area. Minimal degradation of the transferred layers occurred in the HRXD (004) rocking curves from the unbonded inverted device structure (top trace) and the bond-and-transferred structure on the sapphire substrate (bottom) show that absolute peak positions of the device layers were unchanged. The diffraction peaks are broadened in the bond-and-transferred scan. This broadening is attributed to bending of the device layers as they conform to the slight deviations from planarity of the sapphire substrate surface.
bonding and substrate removal process. The resulting transferred structures were fabricated into functional HBTs exhibiting a DC current gain of ∼5.


Highly-mismatched films (In_{0.44}Ga_{0.56}As, 3% mismatch) grown well beyond their critical thickness (to 3 μm) on GaAs glass-bonded compliant substrates exhibit surfaces four times smoother and strain distributions twice as narrow as films grown simultaneously on conventional GaAs substrates. The compliant substrates consist of a thin (~10nm) GaAs template layer bonded via a borosilicate glass to a mechanical handle wafer. The improvement of highly mismatched films grown well beyond their critical thickness on compliant substrate structures is commonly modeled in terms of an elastic partitioning of strain from the film to the thin (~10nm) single-crystal template layer. This study directly tested for this mechanism of elastic compliance. A comparison is reported of the strain in 92 nm In_{0.09}Ga_{0.91}As films and 76 nm In_{0.03}Ga_{0.97}As films grown simultaneously on conventional GaAs substrates and the compliant substrates responsible for the improved structural quality of In_{0.44}Ga_{0.56}As films. Elastic partitioning of strain from the mismatched film to the 10nm template layer prior to the onset of misfit dislocations is not observed for films grown on these glass-bonded compliant substrates.

**Determination of the growth chemistry of Borosilicate Glasses as a bonding media**

SiO₂ deposition from TEOS is a well-studied system with a widely accepted reaction mechanism. We have studied the growth rate and detailed chemistry by mass spectrometry underlying the growth of SiO₂ deposition and (SiO₂)ₓ(B₂O₅)₁₋ₓ. BSGs have several useful physical properties, such as a composition-dependent viscosity, that are utilized in many integrated circuit applications. BSG films with boron concentrations exceeding ~3.5 atomic % are unstable. High B₂O₃ content layers react with water vapor to form boric acid. The glass composition and humidity determine the rate of reaction. As a result, BSG growth has generally been limited to low boron concentrations leading to limited understanding of the BSG reaction mechanism over a broad composition range compared to pure SiO₂ growth.
TEOS is a common SiO$_2$ precursor used in the semiconductor industry because it has low toxicity and flammability hazards compared to other SiO$_2$ sources, such as SiH$_4$ and O$_2$. In addition, TEOS-based films have excellent properties, for example film density and step coverage uniformity. SiO$_2$ growth from TEOS using thermal energy, such as LPCVD, is governed by the overall reaction, \( Si(OCH$_2$CH$_3$)$_4 \Rightarrow SiO$_2$ + 4C$_2$H$_4 + 2H_2O \). The SiO$_2$ growth mechanism involves contributions from a highly reactive TEOS intermediate and from direct surface decomposition of the TEOS parent molecule. The reactive intermediate contribution dominates the SiO$_2$ growth behavior for deposition on planar surfaces. SiO$_2$ deposition from TEOS on planar surfaces is reported to be a surface reaction rate limited process described by a Langmuir-Hinshelwood rate law, \( R_{SiO$_2$} = \frac{k_1P_{TEOS}^{0.5}}{1 + K_1P_{TEOS}^{0.5}} \), where \( k_1 \) is a kinetic rate constant and \( K_1 \) is adsorption equilibrium. The rate law parameters suggested the above equation were determined from experimental growth rate data by rearranging the equation into a linear expression, \( \frac{1}{R_{SiO$_2$}} = \frac{1}{k_1P_{TEOS}^{0.5}} + \frac{K_1}{k_1} \). A linear fit was made to the data plotted as the inverse of the measured deposition rate versus \( P_{TEOS}^{0.5} \). The slope and intercept relate to the kinetic rate constant and equilibrium constant. This rate law accurately describes the data, with \( k_1=14.1 \pm 1.1 \) nm min$^{-1}$ Torr$^{-0.5}$ and \( K_1=0.8 \pm 0.4 \) Torr$^{-0.5}$.

**BSG Growth from TEOS and TMB:** Doping of oxides is important since it leads to control over the oxide properties such as viscosity. The addition of B$_2$O$_3$ to the oxide layer was achieved using trimethyl borate (B(OCH$_3$)$_3$ or TMB) and O$_2$. TMB is proposed to react with O$_2$ to form B$_2$O$_3$ according to the following overall reaction, \( B(OCH$_3$)$_3 + \frac{3}{2}O_2 \Rightarrow \frac{1}{2}B_2O_3 + 3CO_2 + \frac{9}{2}H_2O \). The goal of the study was to develop a reaction mechanism for BSG growth from TEOS and TMB precursors.

Both the growth rate and the B$_2$O$_3$ concentration are non-linear functions of the TMB-to-TEOS gas phase ratio. Any composition of glass from 100 mole % SiO$_2$ to 100 mole % B$_2$O$_3$ can be deposited in the LPCVD reactor. While any composition above 10 mole % B$_2$O$_3$ will react with atmospheric water vapor to form boric acid, compositions greater than 50 mole % B$_2$O$_3$ will do so in less than 15 minutes in our laboratory environment. Practically, this means that storage in a vacuum and/or N$_2$-filled desiccator is required if high-boron composition glasses are to be used later for any application. The addition of TMB and O$_2$ to the reactor is known to catalyze the TEOS-derived SiO$_2$ deposition rate. The observed linear dependence of BSG growth rate on the TMB partial pressure suggests that the TMB molecule does not decompose to a reactive intermediate before depositing B$_2$O$_3$ or that any TMB-related intermediate formation is the rate-limiting step. The former is expected over the latter since the methoxy groups, -OCH$_3$, on the TMB molecule do not decompose as readily as the ethoxy groups, -OCH$_2$CH$_3$, on the TEOS molecule. Ethoxy groups can decompose through a $\beta$-elimination pathway. Unfortunately, this rate law could not be investigated in detail for pure B$_2$O$_3$ growth due to the extreme rapidity of the reaction with water vapor to form boric acid on the film surface preventing accurate ex situ film characterization.

The long-term stability of BSG films with respect to atmospheric H$_2$O absorption is a critical issue for the use of these films in a wide array of applications. A potential solution is to deposit a thin SiO$_2$ film, i.e. 10 nm, as a capping layer for high boron content layers preventing
exposure of the unstable layer to H\textsubscript{2}O. Films greater than 70 mole % B\textsubscript{2}O\textsubscript{3} BSG can not be capped and protected with thin SiO\textsubscript{2} layers at the growth temperatures greater than 675°C since 70 mole % B\textsubscript{2}O\textsubscript{3} BSGs are liquid at 675°C. During growth, therefore, SiO\textsubscript{2} is readily incorporated into the liquid BSG layer until the overall composition reaches a solid. This type of process is termed melt-through diffusion. A potential for success exists in capping film less than 70 mole % B\textsubscript{2}O\textsubscript{3} in our present system.

**BSG Film Characterization:** The morphology of the BSG films was investigated as a function of changing reactor conditions. The film roughness increases with increasing film thickness, reactor temperature, and boron content. Modeling of two-dimensional growth has been used to demonstrate that the r.m.s. roughness increases exponentially with growth time according to the expression, \( w(t) \propto t^\beta \), where \( w(t) \) is the r.m.s. roughness of the layer, \( t \) is the growth time and \( \beta \) is the growth exponent. For SiO\textsubscript{2} deposited at 675°C, \( \beta \) was determined to be 0.23± 0.03. For SiO\textsubscript{2} at a slightly increased temperature of 715°C, \( \beta \) was determined to be 0.30 ± 0.03. The growth rate at 675°C is 3.5 nm/min, increasing to 12 nm/min at 715°C. Within the context of a two-dimensional growth model, an increasing value of \( \beta \) was found for processes that reduced the importance of surface diffusion of adsorbed species. For example, based on theoretical modeling of the growth process, a growth exponent of 0.24 was determined for deposition that allowed limited surface diffusion, while \( \beta=0.5 \) was determined for completely random deposition with no surface diffusion. Therefore, an increasing value of \( \beta \) for SiO\textsubscript{2} growth could indicate a change in the degree of surface diffusion. At 675°C, adsorbed species may have time to diffuse on the surface and incorporate in a favorable location. However, when the deposition rate is increased with the change in temperature to 715°C, the time allowed for surface transport and relaxation decreases. Both the deposition rate and surface diffusion are exponentially dependent on temperature and different values of the activation energy would change the relative importance of the two phenomena at different temperatures changing the r.m.s. roughness of the growing layer as a function of temperature. The activation energy for TEOS-reactant species diffusion on silica surfaces was not measured in these experiments nor was it available in the literature.

An increase in roughness with boron content may also be caused by the catalytic effect of TMB and O\textsubscript{2}. The separate effects of growth rate and boron content were determined by growing 30 mole % B\textsubscript{2}O\textsubscript{3} BSG at 655°C which leads to a reduced growth rate compared to the standard 675°C growth temperature. Since the temperature does not alter the boron content of the film, this growth tests the effect of growth rate independent of the chemical composition. BSGs deposited at a reduced temperature exhibited decreased roughness suggesting that the growth rate, not the composition, affects the surface morphology. The trend is complicated by the phenomenon of BSG reflow for very long growth times, however. Reflow is a smoothing of the surface morphology that BSG films undergo due to a reduced viscosity caused by thermal annealing. While the trend of increased roughness with BSG composition was readily observed for 100 nm thick layers, longer growth times did not necessarily result in increased layer roughness for high boron content layers due to the planarization by glass reflow.
Chemical Investigations of GaAs to Borosilicate Glass Wafer Bonding

GaAs, wafer bonded to oxide layers, is being investigated for the integration of GaAs and Si and for the development of structures such as glass-bonded compliant substrates. For these applications, the native or thermally grown GaAs oxides are not useful. As a result, oxide-bonding medium are formed by a variety of other deposition techniques. GaAs bonded to LPCVD BSG/GaAs is investigated after a variety of growth pretreatments. The nature of the effect of these pretreatments on the bonding interface was investigated.

LPCVD BSG layers are readily bondable after O₂ plasma exposure and DI H₂O rinse pre-bonding treatments. The plasma treatment was performed in reactive ion etching (RIE) mode for 5 minutes at 0.6 W/cm². The RIE atmosphere was pure O₂ at 30 mTorr. Samples were rinsed with DI H₂O under megasonic agitation and spun dry. Room temperature bonded wafers were diced into 2.5 x 1.5 cm² samples. Individual pieces were annealed for 1 hour in N₂ without additional applied pressure. The interfacial bonding chemistry was investigated using multiple internal transmission (MIT) FTIR. Samples were ground and polished into trapezoids with 45° beveled edges. The IR light transmits through the bonded interface ∼21 times based on the sample length and the angle of the beveled edge. Both p- and s-polarized spectra were obtained for each sample by placing a polarizing optic between the light source and the sample to be measured. Three separate spectral regions were presented. The oxide region containing spectral features associated with O-based bonds, excluding OH bonds, covers 770 cm⁻¹ to 1500 cm⁻¹. The hydride region associated with H-based vibrations covers 2000 cm⁻¹ to 2500 cm⁻¹. The H₂O/OH region covers 2700 cm⁻¹ to 4000 cm⁻¹.

The adjacent figure shows MIT-FTIR spectra for GaAs-to-GaAs (—) and GaAs-to-SiO₂/GaAs (—–) as-bonded samples: (upper) and (lower) present spectra for the oxide and hydride and water regions, respectively. The spectra are presented as a ratio of the p:s polarization spectra for the samples referenced to a p:s ratio of the background signal. The spectra have been offset for clarity.

FTIR-MIT spectra for GaAs-to-GaAs (—) and GaAs-to-SiO₂/GaAs (—–) as-bonded samples: (upper) and (lower) present spectra for the oxide and hydride and water regions, respectively. The spectra are presented as a ratio of the p:s polarization spectra for the samples referenced to a p:s ratio of the background signal. The spectra have been offset for clarity.
but the presence of Ga-O and As(III)-O bonds at the interface independent of the specific stoichiometry. The GaAs ‘oxide’ composition is not well known, but certainly consists of mixed species, i.e. AsO₃ and GaOₓ. The peaks at 790 cm⁻¹ and 900 cm⁻¹ are labeled Ga-O related and As(III)-O related oxides, respectively.

The GaAs-to-SiO₂/GaAs as-bonded IR spectrum is similar to the GaAs-to-GaAs bonded spectrum within the oxide region. However, the peaks in this region have different intensities. In this case, the 790 cm⁻¹ peak intensity is slightly greater than the 900 cm⁻¹ peak intensity. The SiO₂ rocking mode at 800 cm⁻¹ adds to the 790 cm⁻¹ Ga-O spectral-related feature in structures containing both SiO₂ and GaOₓ. The peak at 2340 cm⁻¹ is characteristic of H-related vibrations. This peak position also coincides with a characteristic CO₂ vibration energy. However, CO₂ is not the source of this feature since a single peak, not the doublet characteristic of CO₂, is observed. This feature is assigned to H-based modes within the GaAs oxide since it is noted on samples with and without BSG present. It is difficult to state definitively at this point whether it is a H-Ga or H-As related vibration. This figure also has two ‘inverse’ peaks at 2850 and 2915 cm⁻¹. These peaks are inverted because they are more intense in the s-polarized scans than in the p-polarized scans. A p:s ratio is used to present the MIT-FTIR spectra so they appear inverted. These peaks are attributed to C-H bonds from contamination on the bonded sample outer surface. Surface contamination-related peaks will be stronger in the s-polarized scan than the p-polarized scan since the p-polarized spectra are more sensitive to the bonded interface than to the outer surface. The peaks at 2850 and 2915 cm⁻¹ were present for all samples studied at all annealing conditions, further supporting the outer-surface hydrocarbon contamination peak assignment.

The MIT-FTIR spectra for GaAs-to-SiO₂/GaAs and GaAs-to-30 mole% BSG/GaAs bonded samples, annealed for 1 hour in N₂ at several annealing temperatures, showed initially intense H₂O/OH peaks that decreased in intensity with anneal temperature for both glass compositions. The integrated intensity is lower for the 30 mole % B₂O₃ BSG-based samples than for SiO₂-based samples indicating that H₂O/OH groups are more easily removed from the bonding interface for 30 mole % B₂O₃ BSG samples. The final DI H₂O rinse selectively removes B₂O₃ from the near surface region of the 30 mole % B₂O₃ BSG leaving a SiO₂-rich, and possibly more porous, surface. The possible surface porosity may provide more space for the accommodation of evolved species, modifying the H₂O/OH species evolution rate between the two glass-bonded samples analyzed.

The MIT-FTIR spectra lead to a model of the bonding chemistry occurring at the GaAs-to-oxide/GaAs wafer bonded interface is schematically presented below. Initially, Ga-O and As(III)-O related oxides are bonded to the BSG via an intermediate H₂O/OH layer. Moderate temperature anneals cause the As(III)-O related oxides to react with GaAs, forming more Ga-O related oxides and As species. Concurrently, the H₂O/OH groups present at the room temperature bond begin to react, evolving H that becomes absorbed into the oxide. H continues to evolve during higher temperature anneals, forming H₂ bubbles or voids at the bonded interface as occasionally noted in the IR transmission images. As(V)-O related oxides begin to form above 500°C. Anneal temperatures greater than 600°C are difficult to perform with GaAs. At these temperatures, GaAs begins to thermally decompose, evolving As₂ or As₄ gaseous species.
These measurements indicate at the bonding chemistry evolves with temperature and pressure during the processing. The final thermally stable state of the glass-to-GaAs interface is probably common to many of the materials systems involving compound semiconductors. These measurements provide some of the first measurements of the detailed interfacial chemistry in these systems that focus on the atomic-level interfacial chemistry in a non-Si system.

Schematic representation of the bonding chemistry based on the MIT-FTIR measurements. Initially the samples are bonded at room temperature with H₂O/OH groups (A). After a moderate temperature anneal (300°C-400°C) the H₂O/OH group reacts as do As(III)-O oxides (B). For high temperature anneals (500°C-600°C), the H₂O/OH groups continue to react and As(V)-O is formed (C). In (C) voids due to IR inactive H₂ are occasionally noted. The up and down arrows indicate the trend with anneal temperature for the IR peak intensity associated with these groups.
Listing of Publications Associated with this Grant:


Presentations with Peer-reviewed, Published Abstracts


Personnel Supported:

Graduate Students Receiving Support

All listed have been partial support. Their research activities are indicated.

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<td>Kimberly Rickert</td>
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<td>Darren Hansen</td>
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Inventions Reported

No inventions reported during the grant period.