

Low interface state density oxide-GaAs structures fabricated by *in situ* molecular beam epitaxy

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Several oxide-GaAs heterostructures were fabricated using *in situ* multiple-chamber molecular beam epitaxy. The oxides include SiO₂, MgO, and Ga₂O₃(Gd₂O₃), all evaporated by an electron beam method. The SiO₂ and Ga₂O₃(Gd₂O₃) films are amorphous while the MgO films are crystalline and part of the films are epitaxially grown on GaAs(100). Among these heterostructures, the Ga₂O₃(Gd₂O₃)-GaAs shows a photoluminescence intensity comparable to that of Al_{0.45}Ga_{0.55}As-GaAs, and forms accumulation and inversion layers as measured from capacitance voltage measurement in quasistatic and high frequency modes. © 1996 American Vacuum Society.

I. INTRODUCTION

One of the key challenges in compound semiconductor device technology is to deposit dielectric films on the compound semiconductors^{1,2} that provide a low interface state density and a low surface recombination velocity, and are thermodynamically stable. Efforts of fabricating such heterostructures were taken as early as in 1965.¹ The most intensively studied and widely used compound semiconductor is GaAs. Thermal, anodic, photochemical, and plasma oxidation of the GaAs surface produced highly resistive films, but could not provide the oxide-GaAs interfaces with a low interface state density.^{1,3} Approaches of using various dry, wet, and photochemical surface treatments prior to the deposition of dielectric films produced limited success,^{1,4-6} since major sources of interface states such as nonstoichiometry, structural defects, and surface contamination still exist.

In this article, a fabrication process has been developed by depositing oxide films *in situ* on freshly grown GaAs(100) surfaces in a multichamber molecular beam epitaxy (MBE) system.^{7,8} Three different oxides were e-beam evaporated: MgO, SiO₂, and Ga₂O₃(Gd₂O₃). The oxide-GaAs heterostructures with intrinsic interface properties were produced and investigated. Only the Ga₂O₃(Gd₂O₃)-GaAs structures show a photoluminescence (PL) intensity close to that of a reference structure Al_{0.45}Ga_{0.55}As-GaAs that has a measured midgap interface state density in the mid 10⁹ eV⁻¹ cm⁻² range.⁹ The formation of inversion and accumulation layers in both *n*- and *p*-type GaAs has been clearly demonstrated by quasistatic and high frequency *C-V* measurements. The apparent midgap interface state density inferred from a combined quasistatic and high frequency technique is in the range of 10¹⁰ eV⁻¹ cm⁻². Furthermore, the Ga₂O₃(Gd₂O₃)-GaAs interfaces exhibit virtually flat bands in thermal equilibrium. In contrast to the results obtained on the Ga₂O₃(Gd₂O₃)-GaAs interfaces, *in situ* fabricated MgO-GaAs and SiO₂-GaAs interfaces are intrinsically pinned at midgap, as demonstrated by capacitance voltage (*C-V*) and PL measurements.

II. EXPERIMENT

GaAs was grown in a solid source GaAs-based III-V MBE chamber. The freshly grown film with an As-stabilized (2×4) surface was transferred under a vacuum of 6×10⁻¹¹ Torr to another chamber for oxide deposition. Prior to oxide deposition, the authors have achieved using this technique an atomically ordered surface [observed by *in situ* reflection high energy electron diffraction (RHEED)] and a low GaAs surface chemical contamination. A typical GaAs surface exposure in the III-V chamber, the transfer modules, and the oxide evaporation chamber before the deposition are shown in Fig. 1. Note that before the oxide evaporation, the GaAs surface was exposed to a vacuum with pressure lower than 10⁻¹⁰ Torr during the transfer and heating of the substrates to 350–620 °C. For the last 2 min, the e beam was turned on to

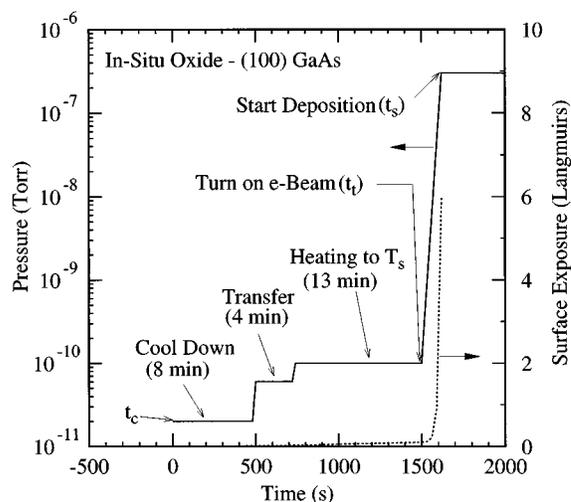


FIG. 1. Pressure (solid line) and surface exposure (dashed line) measured between completion of GaAs epitaxial growth (t_c) and start of oxide deposition (t_s). Cooling down usually takes about 8 min in the III-V chamber. Transferring samples from the III-V chamber to the oxide chamber takes 4 min. Heating the sample to a desired substrate temperature in the oxide chamber generally takes 10–15 min before oxide deposition. One Langmuir is defined as 10⁻⁶ Torr for 1 s.

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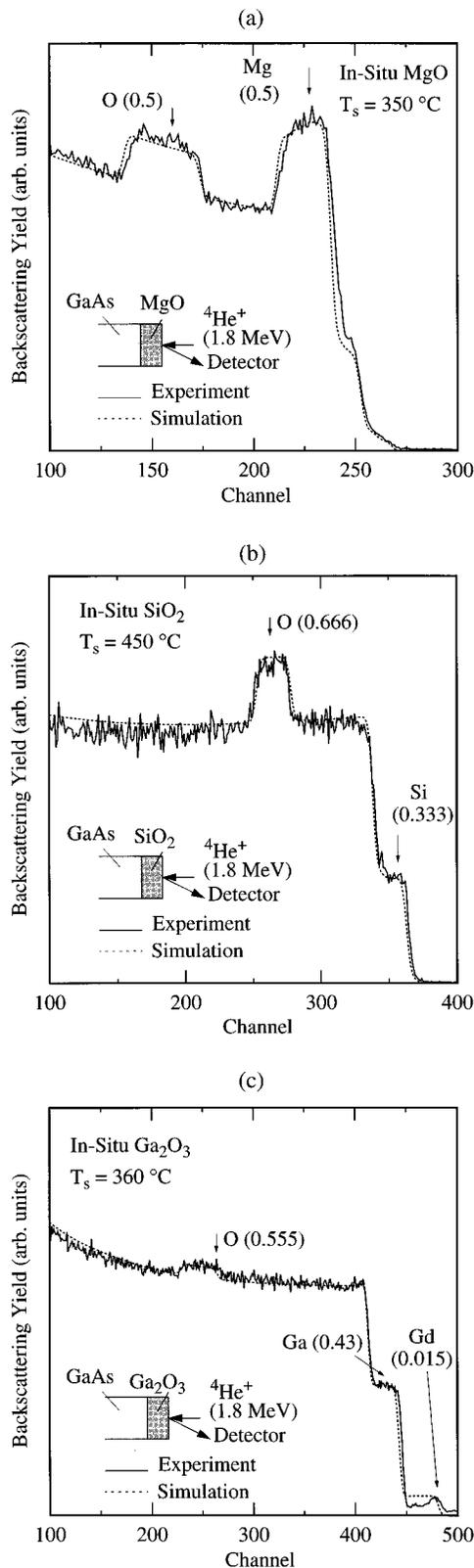


FIG. 2. RBS for (a) MgO, (b) SiO₂, and (c) Ga₂O₃(Gd₂O₃) on GaAs.

heat the oxide targets. Only then did the GaAs surface begin to experience the pressure from 10^{-10} – 10^{-7} Torr. The pressure rise was caused by oxygen decomposed from the e-beam evaporation of oxide targets. The low GaAs surface

exposure to impurity gases (in particular, oxygen) may be necessary to achieve the low interface state density, since the surface was pinned at the midgap for a GaAs(110) cleaved surface exposed to 10^{-6} Torr of oxygen for 10^3 – 10^4 seconds.¹⁰

Note that during the sample transfer, a short pressure burst of $<10^{-9}$ Torr may occur due to the transfer mechanism. The authors have measured the possible contamination of the GaAs surface caused by the transfer of the samples between the chambers by preparing fresh GaAs films, transferring them through the modules, moving them back to the III–V chamber, and overgrowing another layer of GaAs. Secondary ion mass spectrometry (SIMS) analysis of this interface reveals no oxygen or silicon, and only a very slight carbon contamination of 9×10^{10} cm⁻² in areal density. This contamination may not be typical, since in other samples of similar exposure in the transfer module, SIMS analysis could not detect the carbon signal. A separate study is needed to investigate the effect on the surface states by the carbon contamination at such a small level.

The sample fabrication was comprised of 1.5- μ m-thick GaAs *n*-type (1.6×10^{16} cm⁻³) or *p*-type (4.4×10^{16} cm⁻³) layers grown on Si- or Zn-doped (100) GaAs substrates, respectively. Three different oxide films of MgO, SiO₂, and Ga₂O₃(Gd₂O₃) were deposited by e-beam evaporation from single-crystal source materials of MgO, SiO₂, and Gd₃Ga₅O₁₂¹¹ at substrate temperatures ranging from room temperature to 620 °C. Reference samples of Al_{0.45}Ga_{0.55}As–GaAs were also prepared. Single crystal source materials, instead of the compact powder, were chosen for achieving high purity oxide films.

Note that the authors intended to deposit Ga₂O₃, not Ga₂O₃(Gd₂O₃) films. The reason that Ga₂O₃(Gd₂O₃) films, with Gd₂O₃ as a minor phase, were produced is explained as follows: the Gd₃Ga₅O₁₂ target was chosen because no single crystal Ga₂O₃ was available for e-beam evaporation. The Gd₃Ga₅O₁₂ source material represents a chemical combination of the relatively covalent oxide Ga₂O₃, which volatilizes near 2000 K, and the pretransition oxide Gd₂O₃, which has a boiling point of 4000 K. The compound Gd₃Ga₅O₁₂ decrepitates during heating by the e beam, slowly releasing Ga₂O₃. Therefore, if the deposition is kept low, one would expect the majority of the films to be Ga₂O₃, with Gd₂O₃ as a minor phase.

Structural properties and compositional profiles of the oxide films were studied by RHEED, transmission electron microscopy (TEM), and Rutherford backscattering spectrometry (RBS). Electronic interface properties were investigated by quasistatic and high frequency *C*–*V* measurements and by steady-state PL measurements.

III. RESULTS AND DISCUSSION

RBS results for MgO, SiO₂, and Ga₂O₃(Gd₂O₃) on GaAs are shown in Figs. 2(a)–2(c), respectively. For MgO and SiO₂ films, the compositional profiles for Mg and Si are uniform, and the ratios with oxygen are approximately 1:1 and 1:2, respectively. It is known that SiO₂ films with low trap

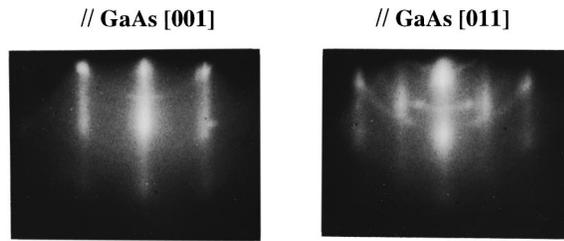


FIG. 3. Reflection high energy electron diffraction (RHEED) for MgO on GaAs (100). Note that besides the epitaxial streaks, there are faint ring RHEED patterns indicative of randomly oriented polycrystals.

density cannot be easily obtained by simple e-beam evaporation. There may be a 5% uncertainty in the determination of the Si-to-O ratio using RBS. It is very likely that the real composition is SiO_x ($1 < x < 2$). For $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ films, however, the distribution of Gd is not uniform, as shown in Fig. 2(c). At the oxide-GaAs interface, Gd is deficient, while there is more Gd on the oxide film surface. Gd distribution in the films depends on the substrate temperature.¹² The non-uniform Gd distribution may also affect some of the $C-V$ measurements, as will be discussed.

SiO_2 and $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ films are amorphous for substrate temperatures from room temperature to 500 °C, as observed from TEM and RHEED studies. Part of the MgO films, however, is epitaxially grown on GaAs¹³ with substrate temperatures around 275–350 °C. MgO films grown at lower substrate temperatures tend to be randomly oriented polycrystalline. Figure 3 shows a RHEED pattern of 28.5-nm-thick MgO grown on GaAs. The orientation relationship between MgO and GaAs is MgO (100) on GaAs (100) with the in-plane epitaxial relationship being MgO [001]||GaAs [100]. Notice that there is a large lattice mismatch (25.4%) between MgO and GaAs. MgO has a NaCl crystal structure with a lattice constant of 4.213 Å. The ring pattern in the RHEED indicates that certain part of the film is polycrystalline, although the intensity of the ring pattern is not as strong as that of the epitaxial streaks (Fig. 3). This is consistent with the TEM observation.¹²

Among *in situ* fabricated oxide-GaAs structures, the $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ -GaAs structures show a GaAs PL intensity as high as that of the corresponding $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ -GaAs reference structure. Figure 4 shows the steady-state PL ratios inferred from the measured PL peaks of $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)/n$ -GaAs and $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}/n$ -GaAs structures normalized to the measured PL peak of a corresponding bare GaAs surface. The excitation power density (P) and wavelength (λ_0) are 580 W/cm^2 and 514.5 nm, respectively. Since PL ratios must be determined for identical light intensity entering the semiconductor structure, alterations in sample reflectivity were taken into account. For $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)/n$ -GaAs (solid circles) and $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}/n$ -GaAs structures, typical PL ratios of 440–550 and 570 were obtained for substrate temperatures of 360–620 and 660 °C, respectively. In order to determine the interface recombination velocity, PL ratios have been measured as a function of power density (P) for $20 \leq P \leq 5000 \text{ W}/\text{cm}^2$. Interface recombination velocities of

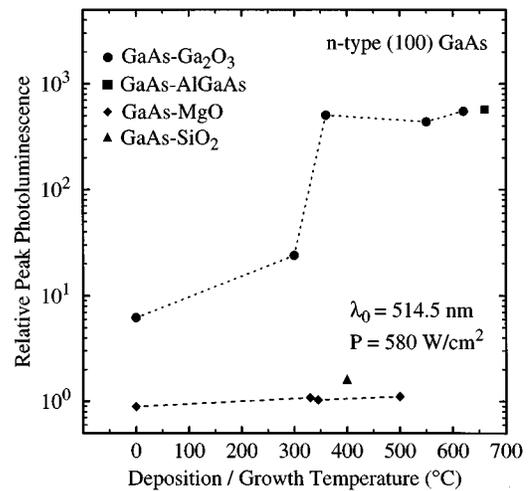


FIG. 4. Measured PL ratios of oxide-GaAs as a function of substrate temperature. Also included is the PL ratio from the $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ -GaAs reference sample.

7000–45000 cm/s and 800 cm/s have been inferred for $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)/n$ -GaAs and the reference $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}/n$ -GaAs structures, respectively, using a self-consistent model based on Poisson's ratio and continuity equations.^{14,15}

The formation of inversion and accumulation layers in both n - and p -type GaAs has been clearly demonstrated by quasistatic (C_{qs}) and high frequency (C_{hf}) $C-V$ measurements. Figure 5 shows typical high frequency (100 kHz) and quasistatic characteristics measured on 2 in. (a) n -type and (b) p -type wafers. The oxide thickness t_i is 46.2 and 59.4 nm, and the substrate temperatures during deposition T_s are 620 and 590 °C, respectively. Although C_{qs} and C_{hf} are not identical for (a) positive bias and (b) negative bias, accumulation is observed since (i) C_{qs} and C_{hf} scale correctly with t_i ; (ii) C_{hf} is independent of frequency f and GaAs doping concentration for $f > 10 \text{ kHz}$; and (iii) inversion occurs in p - and n -type samples, respectively. The origin of frequency dispersion in accumulation below $f = 10 \text{ kHz}$ (not shown) may be due to the inhomogeneous oxide properties as measured by the RBS compositional profile [see Fig. 2(c)]. Alterations in oxide composition, in particular an enhanced incorporation of Gd with increasing film thickness, were also demonstrated by x-ray photoelectron spectroscopy.¹² The midgap interface state density inferred from a standard quasistatic and high frequency technique¹⁶ is in the mid $10^{10} \text{ eV}^{-1} \text{ cm}^{-2}$ range.¹⁵ Furthermore, the $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ -GaAs interfaces exhibit virtually flat bands in thermal equilibrium (not shown).

In sharp contrast to the results obtained on the $\text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3)$ -GaAs interfaces, the MgO-GaAs and SiO_2 -GaAs interfaces are intrinsically pinned at midgap, as demonstrated by $C-V$ (not shown) and PL (Fig. 4) measurements. The PL intensity of the MgO-GaAs and SiO_2 -GaAs is almost the same as that of the bare GaAs surface.

The authors have recently *in situ* deposited Al_2O_3 -GaAs and have observed that the Al_2O_3 -GaAs interfaces are also

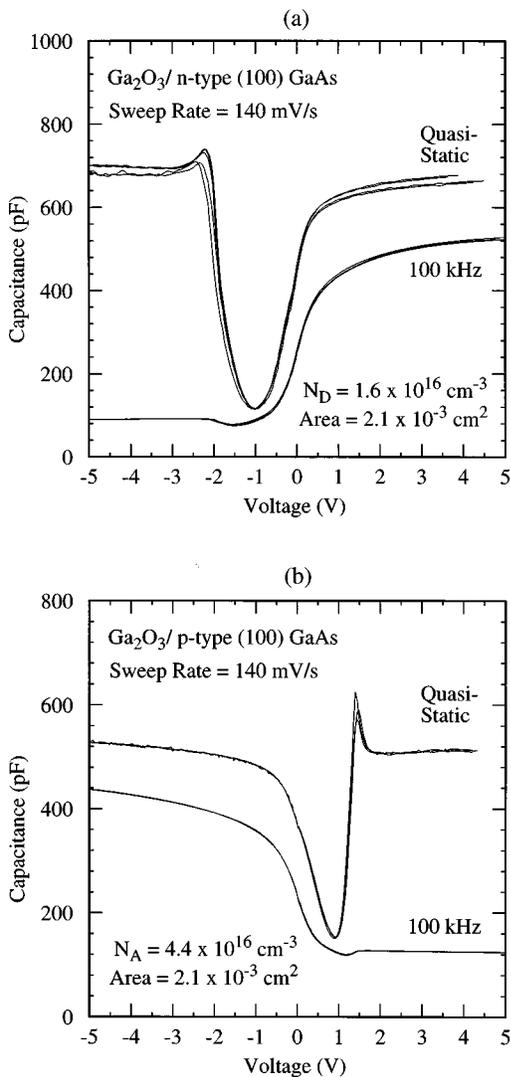


FIG. 5. Quasistatic and high frequency capacitance as a function of voltage measured on (a) *n*-type and (b) *p*-type samples.

intrinsically pinned at midgap, as demonstrated by PL measurements.¹²

It should be noted that Ga₂O₃(Gd₂O₃) *in situ* deposited on Ga-stabilized (4×6) GaAs (100) surfaces in another of our recent experiments was found to produce a high intensity of PL as well, compared to those on the As-stabilized (2×4) surface presented in this article.

Thermodynamic and photochemical stability has been studied by exposure to temperature and laser excitation, re-

spectively. Degradation of PL intensity has not been observed after temperature exposure of 800 °C, indicating completely preserved interface properties.¹⁵

IV. CONCLUSIONS

This article has shown that a low interface state density and a low surface recombination velocity were achieved in the Ga₂O₃(Gd₂O₃)–GaAs heterostructure. It is not clear, however, that a low interface density was not observed in the other oxide-GaAs heterostructures, even though they were all fabricated using *in situ* multichamber MBE. Additional studies on the chemical bonding and the atomic arrangement between the oxide and GaAs are needed to understand the interfaces and to further reduce the interface state density.

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