Low interface state density oxide-GaAs structures fabricated by \textit{in situ} molecular beam epitaxy

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Several oxide-GaAs heterostructures were fabricated using \textit{in situ} multiple-chamber molecular beam epitaxy. The oxides include SiO\(_2\), MgO, and Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\)), all evaporated by an electron beam method. The SiO\(_2\) and Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\)) films are amorphous while the MgO films are crystalline and part of the films are epitaxially grown on GaAs(100). Among these heterostructures, the Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\))–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 \textit{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, SiO\(_2\), and Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\)). The oxide-GaAs heterostructures with intrinsic interface properties were produced and investigated. Only the Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\))–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 10\(^9\) eV\(^{-1}\) cm\(^{-2}\) range.\(^9\) The formation of inversion and accumulation layers in both \textit{n}- and \textit{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 10\(^{10}\) eV\(^{-1}\) cm\(^{-2}\). Furthermore, the Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\))–GaAs interfaces exhibit virtually flat bands in thermal equilibrium. In contrast to the results obtained on the Ga\(_2\)O\(_3\)(Gd\(_2\)O\(_3\))–GaAs interfaces, \textit{in situ} fabricated MgO–GaAs and SiO\(_2\)–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\(\times\)4) surface was transferred under a vacuum of 6\(\times\)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 \textit{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 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

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![Fig. 1. Pressure (solid line) and surface exposure (dashed line) measured between completion of GaAs epitaxial growth (\(t_1\)) and start of oxide deposition (\(t_2\)). 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.](image-url)
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 $9 \times 10^{10}$ 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-$\mu$m-thick GaAs $n$-type ($1.6 \times 10^{16}$ cm$^{-3}$) or $p$-type ($4.4 \times 10^{16}$ cm$^{-3}$) layers grown on Si- or Zn-doped (100) GaAs substrates, respectively. Three different oxide films of MgO, SiO$_2$, and Ga$_2$O$_3$ were deposited by e-beam evaporation from single-crystal source materials of MgO, SiO$_2$, and Gd$_3$Ga$_5$O$_{12}$ 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 Ga$_2$O$_3$, not Ga$_2$O$_3$ (Gd$_2$O$_3$) films. The reason that Ga$_2$O$_3$ (Gd$_2$O$_3$) films, with Gd$_2$O$_3$ as a minor phase, were produced is explained as follows: the Gd$_3$Ga$_5$O$_{12}$ target was chosen because no single crystal Ga$_2$O$_3$ was available for e-beam evaporation. The Gd$_3$Ga$_5$O$_{12}$ source material represents a chemical combination of the relatively covalent oxide Ga$_2$O$_3$, which volatilizes near 2000 K, and the pretransition oxide Gd$_2$O$_3$, which has a boiling point of 4000 K. The compound Gd$_3$Ga$_5$O$_{12}$ deprecipitates during heating by the e beam, slowly releasing Ga$_2$O$_3$. Therefore, if the deposition is kept low, one would expect the majority of the films to be Ga$_2$O$_3$, with Gd$_2$O$_3$ 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, SiO$_2$, and Ga$_2$O$_3$ (Gd$_2$O$_3$) on GaAs are shown in Figs. 2(a)–2(c), respectively. For MgO and SiO$_2$ 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 SiO$_2$ films with low trap
density cannot be easily obtained by simple e-beam evaporation. There may be a 5% uncertainty in the dermination of the Si-to-O ratio using RBS. It is very likely that the real composition is SiO$_x$ (1 < x < 2). For Ga$_2$O$_3$(Gd$_2$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 Ga$_2$O$_3$(Gd$_2$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 GaAs$^{13}$ 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 MgO and GaAs. MgO has a NaCl crystal structure with a conductor structure, alterations in sample reflectivity were be determined for identical light intensity entering the semiconductor structure, alterations in sample reflectivity were taken into account. For Ga$_2$O$_3$(Gd$_2$O$_3$)~/n-GaAs (solid circles) and Al$_{0.45}$Ga$_{0.55}$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 $20\leq P\leq 5000$ W/cm$^2$. Interface recombination velocities of $7000–45000$ cm/s and 800 cm/s have been inferred for Ga$_2$O$_3$(Gd$_2$O$_3$)/n-GaAs and the reference Al$_{0.45}$Ga$_{0.55}$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 $f > 10$ kHz; and (iii) inversion occurs in p- and n-type samples, respectively. The origin of frequency dispersion in accumulation below $f = 10$ 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 technique$^{16}$ is in the mid 10$^{10}$ eV$^{-1}$ cm$^{-2}$ range.$^{13}$ Furthermore, the Ga$_2$O$_3$(Gd$_2$O$_3$)~/GaAs interfaces exhibit virtually flat bands in thermal equilibrium (not shown).

In sharp contrast to the results obtained on the Ga$_2$O$_3$(Gd$_2$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$_2$O$_3$–GaAs and have observed that the Al$_2$O$_3$–GaAs interfaces are also
intrinsically pinned at midgap, as demonstrated by PL measurements.\textsuperscript{12}

It should be noted that Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3}) \textit{in situ} deposited on Ga-stabilized (4\texttimes{}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\texttimes{}4) surface presented in this article.

Thermodynamic and photochemical stability has been studied by exposure to temperature and laser excitation, respectively. Degradation of PL intensity has not been observed after temperature exposure of 800 °C, indicating completely preserved interface properties.\textsuperscript{15}

**IV. CONCLUSIONS**

This article has shown that a low interface state density and a low surface recombination velocity were achieved in the Ga\textsubscript{2}O\textsubscript{3}(Gd\textsubscript{2}O\textsubscript{3})–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 \textit{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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\textsuperscript{3}A review can be found in W. F. Crydon and E. H. C. Parker, Dielectric Films on Gallium Arsenide (Gordon and Breach, New York, 1981).

\textsuperscript{4}A review can be found in Physics and Chemistry of III–V Compound Semiconductor Interfaces, edited by C. W. Wilmsen (Plenum, New York, 1985).


