

# Structure and interface bonding of $\text{GeO}_2 / \text{Ge} / \text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ heterostructures

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Alessandro Molle, Sabina Spiga, Andrea Andreozzi, Marco Fanciulli, Guy Brammertz, and Marc Meuris



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# Structure and interface bonding of $\text{GeO}_2/\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ heterostructures

Alessandro Molle,<sup>1,a)</sup> Sabina Spiga,<sup>1</sup> Andrea Andreozzi,<sup>1</sup> Marco Fanciulli,<sup>1,2</sup>  
Guy Brammertz,<sup>3</sup> and Marc Meuris<sup>3</sup>

<sup>1</sup>CNR-INFM Laboratorio Nazionale MDM, Via C. Olivetti 2, 20041 Agrate Brianza (MI), Italy

<sup>2</sup>Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, I-20041 Milano, Italy

<sup>3</sup>IMEC, 75 Kapeldreef, B-3001 Leuven, Belgium

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The structural and chemical details of  $\text{GeO}_2/\text{Ge}$  layers grown on  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  substrates by molecular beam deposition were studied *in situ* by diffraction and spectroscopic techniques. The formation of semiconductor-oxygen bonds at the  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface, which may play a decisive role in dictating the quality of the Ge passivation, was assessed after using two different surface preparations, namely Ar sputtering and atomic hydrogen cleaning. © 2008 American Institute of Physics. [DOI: 10.1063/1.2992560]

The future perspective for ultrascaled metal-oxide-semiconductor (MOS) device technology is reliably committed to the integration of high- $\kappa$  gate dielectrics in high-mobility III-V compound substrates.<sup>1</sup> However, owing to the lack of a device-quality native oxide, the search of a passivation method is an imperative task for the implementation of III-V compounds in microelectronics. Several approaches were attempted to face this issue such as chemical pretreatments,<sup>2,3</sup> epitaxial growth of  $\text{Gd}_2\text{O}_3/\text{Ga}_2\text{O}_3$  stack,<sup>4,5</sup> interface “self-cleaning” in direct atomic layer deposition,<sup>6</sup> as well as intentional fabrication of interface passivation layers (IPL).<sup>7,8</sup> In the latter framework, owing to the small lattice mismatch between Ge and several III-V compound surfaces, molecular beam epitaxy of Ge films is expected to be a promising solution to reduce the density of interface traps. Outcomes about the insertion of Ge IPLs in III-V-based devices have recently been reported in Ref. 9. The quality of the Ge IPL is expected to depend on the chemistry of the  $\text{Ge}/\text{III-V}$  interface, where the formation of As–O or Ga–O bonds are responsible for the Fermi level pinning and, hence, for the electrical degradation of the final metal-insulator-semiconductor structure.<sup>10</sup> From this viewpoint, it is important to elucidate the details of the interface bonding configuration with the aim of selecting the more adequate Ge growth mode for an efficient semiconductor passivation.

In this work, 30 nm thick  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  *n*-doped ( $5 \times 10^{17} \text{ cm}^{-3}$ ) epilayers grown on *n*-type GaAs(001) substrates by metal organic chemical vapor deposition at 550 °C were introduced in a multichamber ultrahigh vacuum system (base pressure  $1 \times 10^{-11}$  mbar) to perform molecular beam deposition and *in situ* characterization of Ge films. According to the latest advances in the Ge-based MOS research,<sup>11</sup> the Ge films have been subsequently capped with ultrathin  $\text{GeO}_2$  overlayers in order to passivate the Ge surface. The bonding configuration at the  $\text{GeO}_2\text{--Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface has been assessed *in situ* for various growth conditions. After a preliminary outgas at 300–450 °C, the substrates were prepared with two different *in vacuo* treatments, 10 min long  $\text{Ar}^+$  (700 eV) sputtering at 500 °C and 60 min long atomic hydrogen (AH) irradiation at 400 °C. Reports on the

GaAs preparation suggest that both treatments are effective in giving highly ordered and defect-free surfaces. Indeed the former was found to reproduce a well-defined Ga-rich ( $4 \times 6$ ) reconstructed GaAs(001).<sup>12</sup> On the other hand, AH exposure was efficiently exploited in III-V compound surfaces to remove native oxides then releasing a As-rich ( $2 \times 4$ ) reconstruction<sup>13,14</sup> as well as Ga-rich reconstructed GaAs(001) surfaces as a function of the AH dose.<sup>15</sup> Recently the AH cleaning has been also implemented in the oxide growth on Si-passivated GaAs.<sup>16</sup>

Ar ions were generated by a standard ion gun working in a differential pumping assembly. The AH beam was provided by a radio frequency plasma source at a power of 350 W starting from a forming gas (4%  $\text{H}_2$ , 96 % Ar) supply as high as  $1 \times 10^{-4}$  mbar. The deposition of Ge film with thickness of 1.5 and 3 nm was performed by an effusion cell with a rate of 1 Å/min (base pressure of  $9 \times 10^{-10}$  mbar during growth), and it was monitored by reflection high energy electron diffraction (RHEED). A 1.7 nm thick  $\text{GeO}_2$  layer was subsequently formed by 7 min long atomic oxygen exposure at 300 °C to 3 nm thick Ge films. Details of the  $\text{GeO}_2$  formation are reported elsewhere.<sup>17</sup> *In situ* chemical analysis of Ge-passivated  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  was carried out by x-ray photoelectron spectroscopy (XPS)—provided by a standard Mg  $K\alpha$  source (1253.6 eV)—and low energy ion scattering (LEIS). LEIS was performed with He ions accelerated with an energy of 1000 eV at a scattering angle of 128°.

The XPS check on the as-prepared substrates rules out residual presence of native oxides and adventitious contaminations. The Ar sputtering provokes an In poor surface due to the preferential In removal in the ion-surface collision. Analogously, a recent study on the AH exposure of  $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$  at 390 °C evidences also the In depletion at the surface region as a function of the process time.<sup>14</sup> A ( $2 \times 4$ ) surface reconstruction was identified after both surface preparations from the relevant streak periodicity in the RHEED patterns along the  $[110]$  and  $[1\bar{1}0]$  directions shown in Figs. 1(a) and 1(b). Despite the similar surface structure, the choice of the surface preparation deeply affects the structure of the overgrown Ge film. Indeed, the RHEED patterns of the 1.5 nm thick Ge films grown at room temperature (RT) on the Ar-sputtered surface in Fig. 1(e) loses the reconstruction fashion of the underlying substrates, but maintains

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: alessandro.molle@mdm.infm.it.

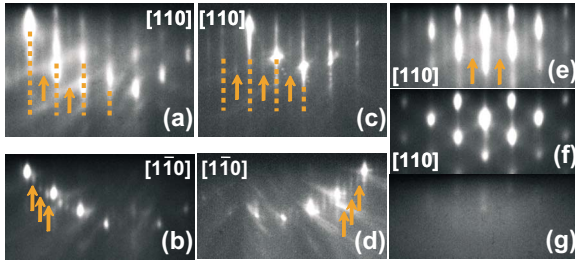


FIG. 1. (Color online) RHEED patterns recorded: after 10 min Ar sputtering at 500 °C [(a) and (b)], after AH cleaning [(c) and (d)], after Ge deposition at RT (e), and 400 °C (f), on an Ar sputtered surface and at RT (g) on an AH cleaned surface. The beam direction is reported in the panels. The dotted lines and the arrows point to the primary streaks and the reconstruction streaks, respectively.

the primary diffraction streaks thus indicating the epitaxial character of the Ge growth even at relatively low  $T_g$ . At  $T_g = 400$  °C a spotty RHEED pattern is observed [Fig. 1(f)], which reflects the formation of three-dimensional (3D) islands, i.e., surface roughening.<sup>18</sup> Given the very low mismatch between the surface lattice constants of Ge and  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  (5.658 versus 5.705 Å) and hence the negligible effect of a strain field during growth, the formation of Ge clusters in the growth at 400 °C can be regarded as kinetic in nature, i.e., driven by the temperature dependent surface diffusion of Ge adatoms as discussed in Ref. 19. The shape of the Ge islands is then dictated by the minimization of the surface free energy. However, further microscopic investigations are needed to elucidate this feature.

On the other hand, when the AH cleaning is added, no diffraction features can be observed in the RHEED [Fig. 1(g)]. The growth of an amorphous Ge film was also observed in case of Ge deposition on AH-cleaned GaAs surfaces (data not shown). The observation of an amorphous Ge film is specific of the AH exposure, and it might be related to the hypothetical occurrence of a H-terminated  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  surface.

LEIS analysis shown in Fig. 2 highlights another remarkable feature of the Ge/ $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interfaces. The LEIS spectra were recorded in the kinetic energy (KE) range 780–920 eV for 1.5 nm thick Ge films grown at RT after Ar sputtering (a), at 400 °C after Ar sputtering (b), and at RT after AH cleaning (c). All the spectra exhibit two main components, peaks A and B, which were fitted by multiple

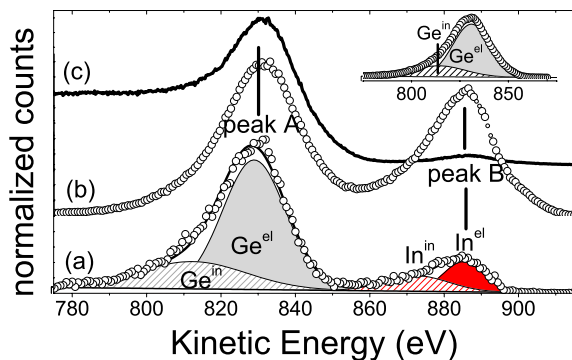


FIG. 2. (Color online) LEIS spectra of 1.5 nm thick Ge films grown at RT on Ar-sputtered  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  (a), at 400 °C (b) on Ar-sputtered  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$ , and at RT on AH-cleaned  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  (c). Inset: spectrum of a 5 nm thick Ge/oxide reference sample. The spectra have been normalized to their maxima.

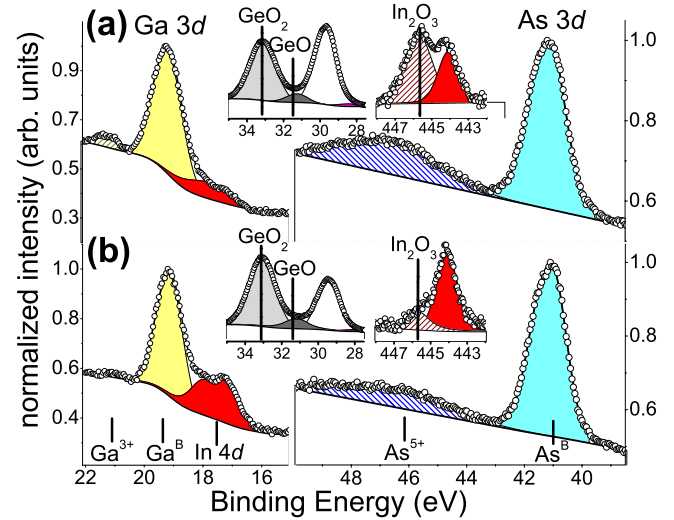


FIG. 3. (Color online) XPS Ga 3d and As 3d lines (take-off angle of 90°) of the 1.7 nm  $\text{GeO}_2$ /1.3 nm Ge/ $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  configurations using Ar sputtering (a) and AH cleaning (b) as surface preparations. Insets: Ge 3d lines (left side), In 4d lines (right side) after Ge oxidation for both surface preparations. The spectra have been normalized to their maxima.

Gaussian functions.<sup>20</sup> The assignment of peak A is not trivial since LEIS cannot resolve elements with consequential atomic masses such as Ga, Ge, and As. To elucidate the nature of peak A, the LEIS spectrum of a 5 nm thick Ge film grown on an oxide substrate has been taken into account as a reference (see the inset). This spectrum can be decomposed in an elastic component  $\text{Ge}^{\text{el}}$  centered at  $\text{KE}=830$  eV (width  $w=20$  eV) and a secondary broad component  $\text{Ge}^{\text{in}}$  at  $\text{KE}=812$  eV ( $w=34$  eV) due to inelastic events, e.g., second ionization. This decomposition is fully consistent with the shape profile of peak A. Therefore peak A is assigned to surface Ge only with no trace of Ga and As. On the other hand, peak B ( $\text{KE}=885$  eV) can be unambiguously attributed to surface In (decomposed in elastic  $\text{In}^{\text{el}}$  and inelastic  $\text{In}^{\text{in}}$  peaks). The observation of an In fraction in the surface composition of the Ge film grown at RT [Fig. 2(a)] may reflect two different scenarios, In segregation during Ge growth or noncontinuous Ge wetting. Conversely, at  $T_g = 400$  °C, a 3D growth mode takes place and hence the corresponding In signal can be attributed to both contributions [Fig. 2(b)]. In case of AH cleaning, the remarkably lower In LEIS signal reveals a negligible In surface fraction on the Ge surface [Fig. 2(c)]. In addition, the increased background profile in the lower KE regime is here probably related to the amorphous structure of the film [see Fig. 1(g)].

The heterostructures 1.7 nm  $\text{GeO}_2$ /1.3 nm Ge/ $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  were fabricated by growing Ge films at RT in order to inhibit a pronounced 3D growth and a high surface In content. As the thickness of the  $\text{GeO}_2$ /Ge IPL is still below the mean free paths for bulk photoelectrons,<sup>21</sup> the bonding configuration at the Ge/ $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface can be investigated by probing the relevant core level photoemission lines, In 4d, Ga 3d, Ge 3d, As 3d recorded at a take-off angle of 90°, i.e., normally to the sample surface. These lines are reported in Fig. 3 upon Shirley background insertion and deconvolution in physically different components by using doublets of Lorentzians–Gaussians in the best fit<sup>22</sup> for both surface preparations, AH cleaning (a) and Ar sputtering (b). The Ga 3d and In 4d line partially overlap. The Ga 3d and

TABLE I. The ratio  $\zeta_{\text{Ga-O}}$  and  $\zeta_{\text{As-O}}$  (between the oxide and the bulk semiconductor XPS components) in  $\text{GeO}_2/\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  heterostructures (Ge grown at RT) are reported for two different surface preparations in order to give an indication of the amount of interfacial Ga–O and As–O bonds which correspond to the  $\text{Ga}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$  species, respectively. The amount of surface In is estimated from the ratio between the elastic components of In and Ge in the LEIS spectra taken for 1.5 nm thick  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  structures.

Surface Preparation	$\zeta_{\text{Ga-O}}$	$\zeta_{\text{As-O}}$	$\text{In}^{\text{el}}/\text{Ge}^{\text{el}}$
Ar sputtering (500 °C)	0.12	0.44	0.14
AH cleaning (400 °C)	0.02	0.30	0.04

As 3d line present a multishaped profile arising from the interplay of the contributions from the Ga–As bulk bonds (marked as  $\text{Ga}^{\text{B}}$  and  $\text{As}^{\text{B}}$ ) with valence state components at higher binding energy,  $\text{Ga}^{3+}$  (chemical shift  $\Delta=1.6$  eV from  $\text{Ga}^{\text{B}}$ ),  $\text{As}^{3+}$ , and  $\text{As}^{5+}$  ( $\Delta=3.6$  eV and 5.0 eV from  $\text{As}^{\text{B}}$ ) for As 3d. The valence state components denote the presence of  $\text{Ga}_2\text{O}_3$  and  $\text{As}_2\text{O}_5$ , respectively,<sup>3,14,23</sup> which are located at the  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface as deduced from the angle resolved XPS analysis (not shown). From the As 3d line deconvolution, no  $\text{As}_2\text{O}_3$  species can be recognized. It should be added that no significant evidence of Ge–O and In–O bonds can be detected from the Ge 3d and In 3d lines after Ge deposition (not shown). The Ge oxidation is demonstrated by the largely dominant  $\text{GeO}_2$  contribution to the Ge 3d line (right inset) as previously reported.<sup>17</sup> From the In 3d lines (left inset), one can see that  $\text{In}_2\text{O}_3$  forms upon Ge oxidation and its content is significantly lower in case of AH cleaning. This fact is consistent with the more limited In surface concentration in the AH-cleaned sample as evidenced by the LEIS analysis.

To quantitatively assess the relative amount of interfacial Ga–O and As–O bonds, from the best-fit parameters it is useful to calculate the ratios  $\zeta$  between the areas of the valence state component(s) ( $\text{Ga}^{3+}$  for Ga 3d,  $\text{As}^{3+}$  and  $\text{As}^{5+}$  for As 3d) and the bulk component,  $\zeta_{\text{Ga-O}}=\text{Ga}^{3+}/\text{Ga}^{\text{B}}$  and  $\zeta_{\text{As-O}}=(\text{As}^{3+}+\text{As}^{5+})/\text{As}^{\text{B}}$ . The results are summarized in Table. I for both surface preparations. From the spectra comparison, we conclude that the relative amount of oxide bonds at the  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface strikingly changes with surface preparation. Indeed, the  $\zeta_{\text{Ga-O}}$  and  $\zeta_{\text{As-O}}$  values are significantly reduced after Ge oxidation from 0.12 and 0.44 in the Ar-sputtered sample down to 0.02 and 0.30 in the AH cleaned one. The fraction of interfacial Ga–O bonds is negligible in the latter configuration. In both cases, the nature of the As–O bonding is exclusively identified by the  $\text{As}^{5+}$  valence state corresponding to the  $\text{As}_2\text{O}_5$  species only. The different chemical quality of the  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface achieved with the two surface preparations might be also here tentatively attributed to the occurrence of a H-termination in the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  (and GaAs) surface after the AH treatment similarly to the H-passivated Si. However, further theoretical investigations are needed to elucidate the interaction between AH and III-V compound surfaces.

To conclude, the structural and chemical details of molecular beam deposited  $\text{GeO}_2/\text{Ge}$  overlayers on  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  were investigated for two different surface preparations: Ar sputtering and AH cleaning. Ge grows epitaxial in the former case and amorphous in the latter one. The  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  is unavoidably affected by the formation of Ga–O and As–O bonding. Nevertheless, the XPS analysis shows that the AH cleaning is beneficial in reducing either the oxide species at the  $\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  interface with respect to the Ar sputtering. Although the process conditions for the AH cleaning should be still optimized to reduce the In loss,<sup>14</sup> the AH cleaning of  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  appears as a promising route to improve the interface quality of Ge-passivated  $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  for the integration in MOS devices.

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- <sup>21</sup>From the Tanuma–Powell–Penn formula ([www.nist.gov/srd/nist71.htm](http://www.nist.gov/srd/nist71.htm)), the inelastic mean free paths for Ga 3d and As 3d photoelectrons are 2.7 and 2.4 nm, thus allowing the interface diagnostic of the  $\text{GeO}_2/\text{Ge}/\text{In}_{0.15}\text{Ga}_{0.85}\text{As}$  samples.
- <sup>22</sup>From NIST Database (<http://srdata.nist.gov/xps/>) the doublet separation were set as 0.86 eV for In 4d, 0.44 eV for Ga 3d, 0.58 eV for Ge 3d, 0.67 eV for As 3d.
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