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Interface analysis of Ge ultra thin layers intercalated between GaAs substrates and oxide stacks

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ABSTRACT

Capping III–V compound surfaces with Ge ultra-thin layer might be a viable pathway to passivate the electrically active interface traps which usually jeopardize the integration of III–V materials in metal-oxide-semiconductor devices. As the physical nature of such traps is intrinsically related to the chemical details of the interface composition, the structural and compositional features of the Ge/GaAs interface were thoroughly investigated in two different configurations, the atomic layer deposition of La-doped ZrO_2 films on Ge-capped GaAs and the ultra-high vacuum based molecular beam deposition of GeO_2/Ge double stack on *in situ* prepared GaAs. In the former case, the intercalation of a Ge interface layer is shown to suppress the concentration of interface Ga–O, As–O and elemental As bonding which were significantly detected in case of the direct oxide deposition on GaAs. In the latter case, the incidence of two different *in situ* surface preparations, the Ar sputtering and the atomic H cleaning, on the interface composition is elucidated and the beneficial role played by the atomic H exposure in reducing the semiconductor–oxygen bonds at the interface level is demonstrated.

1. Introduction

As far as superior transport properties of channel semiconductors are required to face the aggressive shrinking of the gate length in advanced metal-oxide-semiconductor (MOS) devices, III–V compounds are regarded as a viable option to replace the Si-based technology. Indeed, the in-channel effective electron mass of III–V semiconductors, lower than that of Si, leads to a higher electron velocity [1]. Among the III–V compounds, GaAs has so far retained the greater consideration. Nonetheless, it has recently been argued that ternary $In_xGa_{1-x}As$ compound might provide a more forgiving material in terms of density of interface defects [2] and higher mobility in MOS device for high In concentration [3]. An open concern on the integration of GaAs channel in MOS devices relies on the still non-established passivation of semiconductor/gate insulator interface, i.e. how to saturate the electrically active interface defects which cause pinning of the semiconductor Fermi level irrespectively to the externally applied voltage [4]. The physical nature of the defects nearby the GaAs surface region or at the GaAs/oxide interface is currently matter of investigation. A first general distinction can be made by sorting defects with energy level in the midgap region from those with energy level placed in the vicinity of the semiconductor band-edges. The former was originally rationalized by Spacer et al. [5] in the advanced unified model for defects of the GaAs class of semiconductors as bulk bonding disruption and re-organization, e.g. formation of anti-bonding defects (As_{Ga} antisites). However this picture was revisited by Kummel et al. [6], who conversely attributed the midgap defects at the oxide/GaAs interface to oxygen chemisorption to Ga atoms based on local scanning tunneling microscopy/spectroscopy. On the other hand there is a general consensus in associating band-edge defects with interface bonding states (e.g. semiconductor–oxygen bonding and homopolar As or Ga bonding) induced during the oxide deposition processing [7,8]. The midgap defects are somehow hard to remove because they are related to GaAs bonding re-organization extrinsically induced by subsequent oxide deposition. Only the molecular beam epitaxy of Gd–Ga–O was proved to be successful in passivating As-rich GaAs surfaces by positioning interfacial Ga_2O molecules between adjacent As dimers [9]. On the other hand, several solutions have been proposed to improve the interface bonding configuration with *ad hoc* surface treatments or interface engineering processes. A promising approach to III–V passivation is combining a chemical or *in vacuo* surface treatments for the native oxide removal along with the deliberate deposition of ultra thin interface passivation layer (IPL) of group V semiconductors [10,11], or nitrides [12]. In particular, the interest for Ge-based IPL has recently increased [13,14] in concomitance with the promising advances in the Ge passivation through various oxidation approaches [15–17]. Indeed, the good crystallographic matching of Ge with III–V

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compound surface lattice may alleviate bonding disruption in the GaAs surface arrangement and the intercalation of a Ge IPL in between the III–V compound substrate and the gate oxide stack may prevent the formation of interfacial semiconductor–oxygen bonds. In the present work, the structural and compositional details of ultra-thin Ge IPL on GaAs substrates were investigated in two different process configurations, the atomic layer deposition (ALD) of ultra thin La-doped ZrO_2 (L–ZO) films on Ge-capped GaAs (Section 3) and the ultra high vacuum (UHV) based molecular beam deposition (MBD) of GeO_2/Ge passivation double stacks on GaAs (Section 4).

2. Experimental details

Commercial Si-doped (1×10^{17} cm^{-3}) GaAs(001) substrates were used either for ALD and MBD-grown samples. In case of the ALD samples the substrates were chemically pre-treated via dipping in $NH_4(OH)$ solution (4%) for 3 min. The deposition of a 2 nm (nominally) thick Ge layer was performed in a high-vacuum chamber by an e-beam evaporator at room temperature (RT). La-doped ZrO_2 (L–ZO) films were subsequently grown in an ALD reactor at 300 °C directly onto as-prepared GaAs and after Ge IPL insertion. L–ZO was deposited using O_3 as oxidizing precursor in combination with La $[(^iPrCp)_3La]$ and Zr $[(MeCp)_2ZrMe(OMe)]$ metal precursors as described in Ref. [18]. The use of O_3 as oxidizing agent addresses the further passivation of the Ge overlayer surface according to the low density of interface states previously achieved after O_3 exposure to Ge [16] or O_3-based ALD growth of HfO_2 [17]. On the other hand, La incorporation in ZrO_2 can effectively improve the dielectric features of the oxide stack by changing the polarizability of the oxide molecules and by stabilizing a crystallographic phase endowed with a higher dielectric constant [19]. Interface diagnostic was performed by x-ray photoelectron spectroscopy (XPS) of 3 nm-thick L–ZO films and by spectroscopic ellipsometry (SE) on 10 nm-thick L–ZO films.

In parallel, the GaAs(001) substrates were inserted in a multi-chamber UHV system (base pressure 1×10^{-11} mbar) to perform MBD growth and *in situ* characterization of GeO_2/Ge double stack layer as a function of the surface treatment. After a preliminary outgas at 450 °C, the substrates were prepared by means of two different *in vacuo* treatments, 30 min long Ar ion (1 keV) sputtering at 600 °C and 30 min long exposure to an atomic H beam at 400 °C. Ar ions were generated by a standard ion gun working in a differential pumping assembly. The atomic H beam was provided by a radio frequency plasma source at a power of 350 W starting from a forming gas (4% H_2, 96 % Ar) supply as high as 1×10^{-4} mbar. A 3 nm-thick Ge film was then deposited by an effusion cell with a rate of 1 Å/min (base pressure of 9×10^{-10} mbar during growth, growth rate calibrated by an *in situ* quartz balance thickness monitor). Ge growth was monitored by reflection high energy (30 keV) electron diffraction (RHEED). A 1.7 nm-thick GeO_2 layer was subsequently formed by 7 min long atomic O exposure at 300 °C to the 3 nm-thick Ge film to subsequently address the Ge surface passivation. Details of the GeO_2 formation are reported elsewhere [20,21]. The multistacked GeO_2/Ge/GaAs heterostructure can be thus used as interface engineered substrate for the subsequent deposition of high permittivity oxides aiming at the fabrication of GaAs-based MOS [14]. Each step of the surface preparation and double stack deposition on the latter samples was monitored in situ by RHEED and XPS.

XPS was provided by a standard Mg Kα source (1253.6 eV) with a pass energy of 20 V as a function of the take-off angle (angle-resolved analysis). Deconvolution of the relevant XPS 3d core-level photoemission lines was performed by using Shirley baseline removal and Lorentzian-Gaussian doublets as fitting components. Doublets accounts for the spin-orbit splitting in *d* core-level photoemission lines. According to Ref [21,22] the following doublet separations (DS) were used, $DS_{Ga3d}=0.44$ eV, $DS_{As3d}=0.67$ eV, $DS_{Ge3d}=0.60$ eV. SE evaluates changes in the polarization state of a reflected light beam in terms of the ellipsometric angles Ψ and Δ thus enabling one to determine the thickness of the GaAs heterostructures through data interpolation based on a multiple layers model by means of the WVASE32 software. SE data are collected by means of a rotating compensator spectroscopic ellipsometer (J. A. Woollam M2000F) in the spectral range of 1.0–5.0 eV and by using a light beam with an incidence angle of 75° [23].

3. Atomic layer deposition of La-doped ZrO_2

A general overview of the XPS compositional analysis accounting for the Ga 3*d*, In 4*d*, In $3d_{5/2}$, As 3*d* core-level photoemission lines is reported in Fig. 1(a) and (b) for 3 nm thick L–ZO films on GaAs without and with Ge IPL, respectively. The binding energy (BE) of the spectra was referred to the pre-calibrated position of adventitious carbon in the C 1*s* line (BE = 284.8 eV). Direct ALD of L–ZO onto GaAs is studied in Fig. 1(a). Here, the Ga 3*d* line exhibits an interplay of three components, from GaAs bulk (Ga^B at BE = 18.7 eV), from Ga_2O_3 interfacial bonding (Ga^{3+} at BE = 19.9 eV) and from the O 2 *s* line coming due to the overlying oxide (BE = 22.2 eV). The As 3*d* line deconvolution involves three

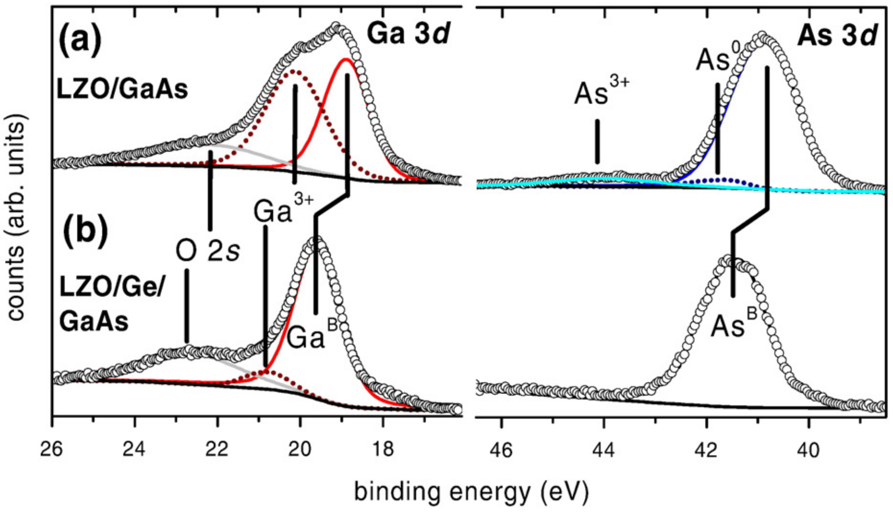

Fig. 1. Ga 3*d* and As 3*d* XPS lines recorded for L–ZO/GaAs (a) and L–ZO/Ge/GaAs (b). LZO thickness is 3 nm, Ge IPL thickness is 2 nm. Ga^B and As^B denote the bulk contributions, the displacement between the bulk peaks in case (a) and (b) is marked. Ga^{3+} and As^{3+} components reflect the presence of interfacial Ga_2O_3 and As_2O_3, respectively. As^0 indicates interfacial elemental As bonding.