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Sol–gel deposition of $Pb(Zr,Ti)O_3$ on GaAs/InGaAs quantum well heterostructure via $SrTiO_3$ templates: Stability of the semiconductor during oxide growth

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ABSTRACT

$Pb(Zr,Ti)O_3$ (PZT) layers were grown by sol–gel deposition on a InGaAs/GaAs quantum well heterostructure. Prior to PZT deposition, a thin $SrTiO_3$ template is fabricated by molecular beam epitaxy. X-ray diffraction and transmission electron microscopy are used to analyse the structural quality of the epitaxial stack. Photoluminescence experiments allow for assessing the effect of PZT growth on the quantum well emission. Despite significant oxygen diffusion through the III–V heterostructure, conditions are found to maintain room temperature photoluminescence of the quantum wells.

1. Introduction

Further progress of the microelectronic industry needs diversification of the functionalities combined on the same chip. For this purpose, integration of different materials having different physical properties on the same wafer is required [1]. Amongst the material of interest, III–V semiconductors offer unique optoelectronic and transport properties and functional oxides present a wide range of physical properties (ferroelectricity, ferromagnetism, piezoelectricity, etc.) [2] that could be used in various applications in the micro-optoelectronic field. Combining these materials on the same chip, and ultimately combining them at the heterostructure level by heteroepitaxy could open the way to the fabrication of devices having new and/or enhanced functionalities. For instance, piezoelectric oxides can add agility to III–V based emitters by providing an efficient way to tune their emission wavelength.

The possibility of using molecular beam epitaxy (MBE) to grow high quality single-crystalline $SrTiO_3$ (STO) templates on Si [3,4] and on GaAs [5] has been demonstrated around 2000. This has opened a path towards the monolithic integration of single crystalline functional oxides on these semiconductors, bulk STO being a widely used substrate for a variety of functional oxides. Such templates have been used to integrate single-crystalline (001)-oriented ferroelectric $BaTiO_3$ (BTO) [6–9] and lead magnesium niobate-lead titanate [10] on silicon, and more recently high-quality ferroelectric BTO layers on GaAs [11,12]. Amongst the oxides that can be integrated on STO templates, $Pb(Zr,Ti)O_3$ (PZT) is of particular interest because of its high remanent polarization (P_r), its low coercive field (E_c) and its outstanding piezoelectric properties [13]. Ferroelectric PZT layer deposition has already been achieved on STO/Si template [14–17]. Sol–gel process [18] has been applied for the deposition of PZT on Pt/Si, TiN/Si and GaN. The films described in those study show polycrystalline textured PZT suitable for RF devices [19], MEMS [20] and optoelectronic applications [21]. Integration of ferroelectric PZT thin film on STO/GaAs has been demonstrated using pulsed laser deposition [22].

The integration of PZT layers on GaAs substrates is of high interest for optoelectronic applications involving for instance modulation of the optical properties of GaAs based heterostructures using the strain induced by a piezoelectric layer, and has not been demonstrated yet. Here, we report the growth of PZT on InGaAs/GaAs-based quantum well heterostructures using sol–gel method. A STO layer is grown by MBE on top of the GaAs heterostructure and acts as template layer for further PZT growth. X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescence (PL) are used to probe the structural and optical properties of the samples. In particular, a specific

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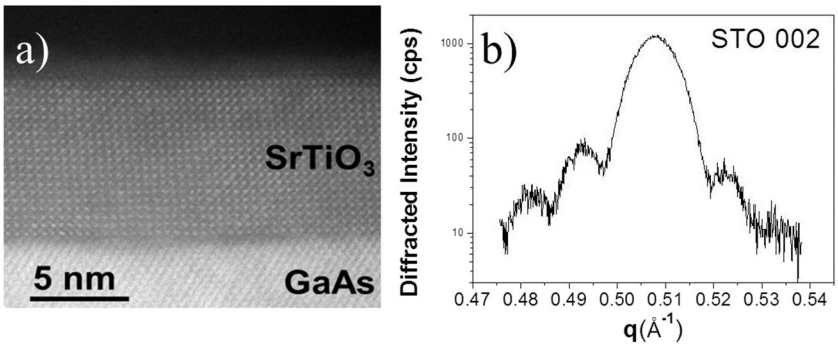

Fig. 1. (a) STEM cross-sectional view of the STO/GaAs heterostructure recorded in HAADF mode. (b) X-ray diffraction radial scan recorded around the STO(002) reflection.

multi-quantum well heterostructure was designed including 4 quantum wells emitting at different wavelengths and placed at different depths, in order to assess the effect of possible defect diffusion from the oxide/GaAs interface on the optical properties of the structure.

2. $SrTiO_3$ thin film on GaAs(001)

2.1. MBE growth of STO thin film

MBE was used for the fabrication of the III–V epitaxial heterostructure on GaAs substrate which is composed, from the bottom to the top, of a 500 nm thick GaAs buffer, a 10 nm thick $Al_{0.3}Ga_{0.7}As$ layer, four InGaAs quantum wells of different thickness (respectively 16 nm, 12 nm, 8 nm and 4 nm) separated by 20 nm thick GaAs spacers, another 10 nm thick $Al_{0.3}Ga_{0.7}As$ barrier and a 10 nm thick GaAs cap layer (Fig. 2(b)). The structure was capped by an amorphous As layer deposited at room temperature, aimed at preventing its oxidation during the transfer under atmospheric pressure from the III–V MBE reactor to the oxide MBE reactor. After transfer of the sample to the oxide-dedicated MBE chamber, the STO template layer was grown. For this purpose, the protective amorphous As layer was desorbed by annealing the sample under ultra-high vacuum (UHV) at 400 °C, leading to the formation of a clean, As-rich, (2×4) reconstructed GaAs surface. A submonolayer of Ti was deposited at this temperature leading to the formation of a (4×2) reconstructed GaAs:Ti surface (see Ref. [23] for more details). The temperature was then ramped down to 250 °C, the surface was exposed to an oxygen partial pressure of 7 μPa for 1 min, and 7 ML of STO were deposited under the same oxygen partial pressure, leading to the formation of a partially amorphous oxide layer. Finally, the sample was annealed under UHV at 500 °C for 20 min, leading to complete recrystallization of the oxide layer. STO was then thickened at 500 °C under an oxygen partial pressure of 70 μPa.

2.2. Characterization of STO epitaxial layer

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) cross-sectional view of the sample displayed in Fig. 1(a) shows a STO crystal of excellent structural quality having an abrupt heterointerface (free of any interfacial compound) with GaAs. In particular, no sign of GaAs oxidization (formation of an amorphous oxide at the interface) is detected on this image, showing that STO growth conditions preserve the integrity of the GaAs substrate. X-ray diffraction (XRD) was performed on a Rigaku Smartlab diffractometer equipped with a rotating anode. A radial scan across the STO(002) reflection is shown in Fig. 1(b). The presence of Pendellösung fringes attests for the good crystallinity of the thin film and further confirms, at the macroscopic scale, the absence of significant interface roughness caused by GaAs oxidation or chemical reactions between STO and GaAs.

3. Sol–gel deposition of $Pb(Zr,Ti)O_3$ on STO/GaAs template

Spin-coating was employed to spread PZT 52/48 precursor solution from Mitsubishi Materials Corp. on the STO/GaAs heterostructure. The sample was then calcined at 350 °C in air for 5 min to dry the sol film, leading to a smooth surface without hillocks. After these operations, a 33 nm-thick amorphous PZT was obtained. The process was then repeated in order to reach a PZT thickness of ~100 nm. Then, the sample was introduced in a rapid thermal annealing furnace to be annealed at 525 °C in a pure oxygen flux (1000 sccm) for 120 s in order to crystallize the amorphous film.

Fig. 2 displays a wide range radial XRD scan as well as angular scans (recorded by rotating the sample around its surface normal at constant Bragg angle) of the PZT (110), STO (110) and GaAs (220) asymmetric reflections. Only PZT (00l) reflections are detected in Fig. 2(a) (the peak at $q = 0.44$ Å^{-1} corresponds to the diffraction of Pt metal contacts deposited on the sample for further electrical measurements, not shown here), and the angular scan has fourfold symmetry, showing that PZT is successfully crystallized, single crystalline and in epitaxial relationship with the GaAs substrate. XRD measurements performed over a restrained range around the PZT (002) and STO (002) reflections are shown in Fig. 3(a). Photoluminescence (PL) measurements were carried out at both 77 K and room temperature and are displayed in Fig. 3(c) and (d). A 632 nm He–Ne laser was used to excite PL. Before PZT deposition, at 77 K, four peaks are clearly resolved in the PL spectrum. They correspond to the emission of the four quantum wells of different thicknesses and placed at different depths in the structure. After PZT growth, the PL signal is strongly modified: the signal arising from the two quantum wells placed at the smallest distance of the interface almost vanishes. The signal corresponding to the two deepest InGaAs quantum wells of the heterostructure can still be detected, but the two peaks can no longer be resolved. This suggests that the two first quantum wells have been damaged during PZT deposition while In-Ga intermixing leads to significant widening of the PL emission of the two other quantum wells. Fig. 3(d) compares the PL signal of both samples at room temperature. At this temperature, the peaks corresponding to the different quantum wells cannot be resolved due to inhomogeneous broadening. In the same experimental conditions, the PL intensity is reduced by a factor of 2 for the PZT/STO/GaAs sample as compared to the STO/GaAs sample, thus confirming that PZT growth partially degrades the structural quality of the quantum wells placed near the oxide/GaAs interface. However, one can note that despite this degradation, a clear intense PL peak can still be detected at room temperature for the sample containing the crystalline PZT layer.

4. TEM characterization of PZT/STO/GaAs heterostructure and discussion

To understand the reason for PL signal degradation during PZT deposition, we performed a TEM analysis of the sample. A TEM cross-sectional view of the sample is displayed in Fig. 4, together with a composition

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