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Raman spectroscopy and atomic force microscopy study of interfacial polytypism in GaP/Ge(111) heterostructures

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ABSTRACT

Effects of lattice and polar/nonpolar mismatch between the GaP layer and Ge(111) substrate are investigated by spatially resolved Raman spectroscopy. The red shifted transverse optical (TO) and longitudinal optical (LO) phonons due to residual strain, along with asymmetry to TO phonon ~358 cm^{-1} are observed in GaP/Ge(111). The peak intensity variation of mode ~358 cm^{-1} with respect to TO phonon across the crystallographic morphed surface of GaP micro structures is associated with the topographical variations using atomic force microscopy mapping and Raman spectroscopy performed on both in plane and cross-sectional surface. Co-existence of GaP allotropes, i.e. wurtzite phase near heterojunction interface and dominant zinc-blende phase near surface is established using the spatially resolved polarized Raman spectroscopy from the cross sectional surface of heterostructures. This consistently explains effect of surface morphology on Raman spectroscopy from GaP(111). The study shows the way to identify crystalline phases in other advanced semiconductor heterostructures without any specific sample preparation.
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1. Introduction

High quality epitaxial structures of compound semiconductors on Si and Ge is the key for the development of high efficiency multijunction solar cells, wide range of detectors, low threshold quantum dot lasers and spin-photonic devices [1–11]. However, it is reported that growth of high quality III–V semiconductor on a non-polar substrate, inevitably poses various challenges such as polar/non-polar interface, lattice mismatch, diffusion of Ge or Si along the interface, etc. [12–15]. These complexities give rise to formation of different kind of defects, e.g. misfit dislocations, stacking faults, twin boundaries and anti-phase domains (APDs) in the native crystal structure [13,16–19]. In spite of these many issues several groups have reported successful integration of such devices [1–7,20–23]. However, in order to improve the performance of the devices, it is essential to improve the crystalline quality of the nucleating layer that is grown prior to the growth of complete structure. Therefore, in the recent time several attempts are made to understand the growth mechanism of GaP nucleating layer grown on Si by in situ and ex situ measurements [4,12,16,24,25]. It is observed that surface energy, reconstruction and kinetics play pivotal role for controlling the crystalline properties of the grown layer. However, the surface reconstructions strongly depend on the orientation and surface energy of the substrates. It is therefore essential to understand the role of surface energy for the given growth kinetics on the morphology and crystalline properties of GaP nucleating layer. In view of these issues, we have grown GaP nucleating and thick layer using MOVPE on Ge(111) substrates which has low surface energy compared to Si(111) and Si(001) [26]. There exist a possibility that APD and dislocations free GaP/Ge(111) based heterostructures can find applications in photonic and MOSFET based devices. Subsequently, heterojunction boundaries and the top of the crystallographic morphed surface are examined by spatially resolved Raman spectroscopy (SRRS) in conjunction with atomic force microscopy (AFM). It is because local distributions of strain and crystal imperfection can distort the lattice which is expected to influence their vibrational spectra. Raman spectroscopy is extremely sensitive probe to study strain, crystalline imperfection of different allotropes (if any), etc. [27–30]. Raman and AFM is the powerful combination, when used on the same site for micro/nanostructured materials. This can allow us to correlate the information obtained from Raman spectroscopy with the morphology, opening new doors in understanding the nanos-

Abbreviations: SRPRS, spatially resolved polarized Raman spectroscopy; CSS, cross-sectional surface; RSRs, Raman selection rules; BSG, backscattering geometry.

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tructured materials. Further, spatially resolved polarized Raman spectroscopy (SRPRS) can detect the submicron scale variations in the crystalline phases of nanostructures. To the best of our knowledge, this is the first of its kind work of Raman and AFM mapping performed on the same site of GaP/Ge heterostructure, which establishes one to one correlation between partial breaking of Raman selection rules (RSRs) and morphology. Further, SRPRS measurements at the interface and surface region reveals the presence of wurtzite (WZ) phase of GaP near GaP–Ge interface and dominance of zinc-blende (ZB) phase of GaP near the surface.

2. Experimental details

The GaP nucleating and thick layers are grown in a horizontal MOVPE reactor (AIX-200) with a rotating substrate holder at 20 mbar pressure, on Ge(111) substrate. Phosphine (PH_3) and trimethyl gallium (TMGa) precursors are used for the growth of MOVPE layers. Prior to growth, Ge substrates are cleaned following the modified Radio Corporation of America (RCA) cleaning and annealing procedure [25]. The cleaned Ge(111) substrate is loaded in the MOVPE reactor for the growth of GaP nucleating and thick layers. GaP nucleating layer sample (S1) of thickness ~60 nm with high V/III ratio ~1725 is grown at 425 °C. Further, for the thick layer sample (S2), GaP is grown using the two step growth process where first S1 is grown at 425 °C that is followed by the growth of GaP layer of thickness ~760 nm at 770 °C with V/III ratio of ~100, which is similar to the growth of GaP/Si epilayers [25]. The optimum growth conditions for samples S1 and S2 have been reported previously [25,31]. Raman spectroscopy and mapping are performed using Acton SP-2500i (single) spectrograph with air cooled CCD detector, which is a part of scanning probe microscopy integrated Raman system (WiTec, Germany). Raman spectroscopy is performed at room temperature in backscattering geometry (BSG). The excitation wavelengths used are 488 nm (Ar ion laser) and 442 nm (He-Cd laser). The spectral resolution of the Raman spectrograph at the wavelengths of measurement is ~1.5–2.0 cm^{-1}. The spatial resolution of the system using 100× objective at 442 nm and 488 nm are ~0.5 μm and ~0.6 μm, respectively.

3. Results and discussion

3.1. Phonons of GaP/Ge(111) heterostructures and determination of biaxial strain

Fig. 1(a) shows the schematic of Raman scattering from (111) surface of GaP/Ge(111) heterostructures, i.e. samples S1 and S2. Representative Raman spectra for both the samples S1 and S2 are shown in Fig. 1(b). It shows mainly two dominant peaks ~362 cm^{-1} and ~399 cm^{-1} corresponding to TO and LO phonons of GaP, respectively. The additional mode observed ~389 cm^{-1} in between TO and LO phonon is attributed to surface optical (SO) phonon [32]. The SO phonon is more significant in sample S1 as shown in Fig. 1(b). Additionally, an asymmetric broadening is also observed on lower frequency side of TO phonon which is attributed to the anharmonic interaction of TO phonon with two phonon density of states for bulk GaP [33,34]. The optical phonon corresponding to Ge substrate layer in GaP/Ge(111) heterostructures is observed ~300 cm^{-1}. Asymmetric broadening observed on lower frequency side of GaP TO phonon, for samples S1 and S2, is deconvoluted (Fig. 1(c)) into one Lorentzian A_1 ~349 ± 0.4 cm^{-1}, and two Gaussians A_2 ~358 ± 0.1 cm^{-1} and A_3 ~361.5 ± 0.02 cm^{-1}. Similarly, Raman spectra of S1 and S2 in the range 376–405 cm^{-1} (Fig. 1(d)) are also deconvoluted into one Lorentzian B_1 ~389.5 ± 0.5 cm^{-1}, and two Gaussians B_2 ~396.4 ± 0.1 cm^{-1} and B_3 ~398.5 ± 0.1 cm^{-1}. Generally, one would expect all phonon modes to be fitted using Lorentzian line shape and this was performed initially. However, it did not give proper fit and line shape suggesting that the high frequency modes, i.e. TO and LO phonons may have Guassian profile. Indeed, best fit has been obtained using Guassian profiles for A_2, A_3, B_2 and B_3 modes. The use of Gaussian profile for these modes will become clear in subsequent sections. The phonon mode A_1 on lower frequency side of TO has the same origin as the bulk GaP and the modes A_3 and B_3 are attributed to the TO and LO phonons arising from GaP layer. The full width half maxima (FWHM) of the LO phonon (B_3) for layer is ~4.0 cm^{-1} and is indicative of good crystalline quality of GaP.

Further, it is also observed that both TO and LO phonons for GaP/Ge heterostructure are red shifted with respect to that of bulk GaP(111) by ~2.5 cm^{-1} and ~3.5 cm^{-1} respectively. The origin of redshift of TO and LO phonons and presence of additional modes on lower frequency side of TO and LO phonons are analyzed. GaP layer grown on Ge(111) substrate is expected to undergo a biaxial tensile strain due to lattice mismatch between substrate and epilayer. However, thickness of the grown GaP layer is greater than its critical thickness and therefore it is expected to be relaxed via the generation of dislocations. In addition, due to dissimilar nature of the layer and substrate, i.e. polar/non-polar, sufficient twins, twin boundaries and anti-phase domains are also expected [13,16–19]. It has been observed from the area scan of HRXRD experiments that in spite of relaxation, layers contain residual strain with anisotropic distribution for in plane and out of plane directions [31]. Thus the observed shift in the TO and LO frequency and the additional modes may be due to the presence of residual strain. Thus, considering the residual biaxial strain in (111) plane as the cause of the observed shift in TO and LO phonons, the frequencies of triply degenerate **k** ≈ 0 optical phonons of strained (deformed) crystal are given by the solution of secular equation [35]:

$$\begin{vmatrix} (p+2q)\varepsilon_{xx} - \lambda & 2r\varepsilon_{xy} & 2r\varepsilon_{xy} \\ 2r\varepsilon_{xy} & (p+2q)\varepsilon_{xx} - \lambda & 2r\varepsilon_{xy} \\ 2r\varepsilon_{xy} & 2r\varepsilon_{xy} & (p+2q)\varepsilon_{xx} - \lambda \end{vmatrix} = 0 \quad (1)$$

where the eigenvalues $\lambda = \omega^2 - \omega_0^2$ with ω and ω_0 representing the strained and unstrained frequencies of the phonon modes. Also, ε_{xx} and ε_{xy} are the hydrostatic and shear components of the strain respectively. Secular Eq. (1) has been obtained under quasi-harmonic approximation by retaining the terms linear in strain. The aforementioned results can be generalized to ZB crystals (e.g. GaP) taking into account the LO–TO splitting due to long range coulomb interaction (ionicity of the bond) and the strain effects on LO–TO splitting can be explained by considering the two different sets of phonon deformation potentials p, q and r for TO and LO phonons. The GaP film has (111) orientation and the secular Eq. (1) and the strain tensor are defined in crystallographic basis, i.e., $x \equiv (100)$, $y \equiv (010)$ and $z \equiv (001)$. The three eigen values obtained from Eq. (1) are:

$$\lambda_1 = \lambda_2 = \omega_d^2 - \omega_0^2 = (p+2q)\varepsilon_{xx} - 2r\varepsilon_{xy}, \quad (2a)$$

$$\lambda_3 = \omega_s^2 - \omega_0^2 = (p+2q)\varepsilon_{xx} + 4r\varepsilon_{xy}. \quad (2b)$$

where ω_d (doubly degenerate) and ω_s (singlet) are eigen frequencies of TO and LO phonons with polarization in and out of (111) plane respectively. The relevant parameters [36] of bulk GaP used for estimation of strain are listed in Table 1. Using these parameters and observed values of TO and LO phonon frequencies, we have calculated the in plane strain parameter $\varepsilon_{\text{parallel}}$ due to biaxial strain present in the GaP film from Eqs. (2a) and (2b). The results of the calculation are summarized in Table 2. These values are different than values reported from HRXRD analysis (0.0030 for thick layer)

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