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以氣態源分子束磊晶法成長砷化鎵於奈米矽溝渠之光

學特性

Optical Properties of GaAs in Si nano-trench grown by

Gas Source Molecular Beam Epitaxay

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中文摘要

我們利用掃描式電子顯微鏡(SEM)、陰極螢光(CL)及拉曼(Raman)光譜量測以 氣態源分子束磊晶法成長在平面矽基板及有圖樣的矽基板上的砷化鎵。

從 SEM 的觀測,我們可以看到 300 奈米厚的砷化鎵成長於平面矽基板時,呈 現連續山狀的樣貌,並且有<100>方向的小縫隙分佈其間,砷化鎵的覆蓋率超過 95 %。而成長於有圖樣的矽機板的砷化鎵,幾乎全部都長入矽奈米溝渠中,藉由氫 等離子體的幫助,成功地達成選擇性成長,在溝渠寬度小於 200 奈米之後,才有 眼形的小塊堆積在溝渠邊緣的二氧化矽上。

砷化鎵成長於平面矽基板及成長於奈米矽溝渠內的室溫(RT)和低溫(LT)的 CL 光譜也被量測。無論是成長於平面矽基板還是成長於奈米矽溝渠內,室溫陰極螢 光的波峰相較於同質磊晶的砷化鎵皆呈現相同程度約三倍的變寬,以及 30 meV 左 右的藍移。我們認為波峰變寬主要歸因於各個被拉張或擠壓的結晶為了達到費米 能階一致而造成的能帶變形,以致於原有的能階數減少,在電子束產生大量載子 的同時,也同時填滿能階到更高/低能階,造成放光時波峰的變寬。而大程度的藍 移則歸咎於成長時的自動摻雜,或所謂的 Burstein-Moss shift。成長於矽奈米溝 渠內的砷化鎵 LTCL 光譜在溝渠寬度介於 90 奈米至 140 奈米間的波形呈現雙峰態。 較低能量的波段被歸因於深層載子與碳受體的復合,而較高能量的波段則被歸因 於施體與受體的復合。在溝渠寬度大於 140 奈米之後,其放光波形接近成長於平 面矽機板的砷化鎵,藉由高斯(Gaussian)分佈擬合波峰,可以得到三至四個波峰。 而溝渠邊緣的二氧化矽由於缺陷結構放光,共有三個波段。常溫時為 1.9 eV 的放 光,歸因於非橋接氧電洞中心; 2.2 eV 的放光,歸因於類空洞與空隙氣分子間電 子電洞的復合; 2.7 eV 的放光,歸因於矽孤對電子與電洞的復合。在 LTCL 的觀察 中, 2.2 eV 及 2.7 eV 這兩種放光會縮減,起因於降溫時對這兩種缺陷結構的消滅。

常温的拉曼光譜也觀察到不尋常的現象:在所有的試片中我們均量測到強烈

的原本禁帶的橫向聲子模態。我們認為此一現象是源於晶體中大量的微雙晶缺陷,此種缺陷會把原本(001)面轉成{122}面。另一現象是在溝渠寬度小於 100 nm 以後,我們使用 Lorentz 分佈擬合的實驗值在橫向聲子與縱向聲子模態之間有多一「表面聲子」模態,起因於較大的表面積/體積比。



Abstract

We have utilized scanning electron microscopy (SEM), cathodoluminescence (CL) spectroscopy and Raman spectroscopy to investigate heteroepitaxial GaAs on planar Si and patterned Si wafer samples grown by gas source molecular beam epitaxy (GSMBE) system.

With the observation of SEM image of the sample top view, the hydrogen-plasma -assisted-grown-300-nm-thick-GaAs on Si planar substrate formed a successional mountain-like "perforated film". This structure composed by GaAs covers more than 95% area of the planar Si substrate. The filling ratio of GaAs in the trenches is estimated to be nearly 100%. GaAs in the trenches break to become nanowires with lengths varying from hundreds nanometer to several micron. When the trench widths decrease less than 200 nm, the epi-GaAs overflow the trench onto the SiO₂ sidewall and form eye-shaped islands whose dimension is about 500 nm.

Room temperature CL (RTCL) and low temperature CL (LTCL) are also performed at trenches whose widths vary from 50 nm to 500 nm. The RTCL GaAs peaks of all trenches are about 3 times broadened and the same blue shifted about 30 meV regardless of the trench width. Meanwhile, the energies of SiO_2 peaks remain unchanged. This phenomenon indicates that the blue shift and the broadening are due to the same mechanism. We attribute the blue shift to the Burstein-Moss shift. The broadening is attributed to the Fermi-level-consistency of grains induced band banding. The LTCL GaAs peaks reveal a two-peak feature when trench width between 90 nm and 140 nm. The low energy band is attributed to deep level carrier to carbon acceptor and the high energy band is attributed to donor to acceptor recombination, respectively. When trench width is larger than 140 nm, the peak form is like GaAs on planar (001) Si. With the assistance of Gaussian fitting, there are three or four bands. The origins of three SiO₂ RTCL peaks are also surveyed. The 1.9 eV peak is attributed to the NBOHC; the 2.2 eV peak is attributed to the (V₀;(O₂)_i) structure and the 2.7 eV peak is attributed to E' center. From the observation of LTCL, we find out that the elimination of 2.7 eV and 2.2 eV peaks, which represents the elimination of these defects

The RT Raman spectra of GaAs on planar Si (001) substrates are measured in z(XX)z' and z(xx)z' configurations. Regardless of the growth condition, all samples reveal a strong originally forbidden transverse optical (TO) phonon mode. The RT Raman spectra of GaAs in variant trench widths are measured in z(YY)z' configuration. Each of the epi-GaAs in Si nanotrenches also reveals a strong TO phonon mode and the longitudinal optical (LO) phonon mode broadens. Furthermore, there is an additional peak between the TO and the LO peak while trench width is under 100 nm, which is attributed to the surface optical (SO) phonon mode. The SO mode is measured because

of the large surface-to-volume ratio.



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Chapter 1

Introduction

From the 1980s, the properties of microns thick GaAs grown on Si and the applications have been studied tremendously [1-6]. The superlattice method was used to avoid the threading dislocation due to the 4% lattice mismatch [1-2]. The off cut little angle along [100] of the Si (001) substrate provides the double step layer, which can efficient avoid the anti phase boundary [3-4]. Low temperature photoluminescence (LTPL) of GaAs on Si was measured and cross-section transmission electron microscopy (TEM) was taken to observe the interface quality [5-6].

In the view of applications, since the invention of semiconductor transistor at 1947, the booming of the Silicon based semiconductor industry has been commencing a revolution of human livelihood. Forty six years ago, Moore [7] proposed a theory which predicted a double of the number of transistors on chips every twelve months and later refined the period to two years. Since then, the Moore's law has kept going during the past four decades by overcoming mountains of problems such as the limitation of photolithography, high-k gate dielectric materials and strained-Si channel. However, there exists a natural confinement: the size of a single transistor must lager than the Si atom and the law will come to an end in the near future. In a tiny transistor, the dominate feature is the driving current, which determine the speed of every single transistor. While the current $I_D = \frac{\mu_n C_{ox}}{2} \frac{W}{L} (V_{GS} V_{th})^2$, we spotlight on the mobility enhancement in order to increase the gate current. High mobility materials such as GaAs, InAs and Ge gained a lot of attentions and defect-free heteroepitaxial growth of these materials becomes the research topic. Table 1.1 [1.8-9] shows the basic parameters of these materials.



	Si	Ge	GaAs	InAs
Crystal structure	Diamond	Diamond	Zincblende	Zincblende
Bandgap (eV)	1.12	0.66	1.42	0.354
Lattice constant (Å)	5.43102	5.64613	5.6533	6.0584
Electron mobility $\mu_n(cm^2/V\text{-}s)$	1450	39 <mark>00</mark>	8000	33000
Hole mobility $\mu_p(cm^2/V\text{-}s)$	450	1900	400	460
Effective electron mass (m/m ₀)	m _i =0.98	m/=1.64	m=0.063	m=0.023
	m _t =0.19	$m_t = 0.082$		
*Effective hole mass (m/m ₀)	m _{hh} =0.49	m _{hh} =0.33	m _{hh} =0.51	m _{hh} =0.41
	m _{lh} =0.16	m _{1/1} =0.043	m _{lh} =0.082	m _{1/1} =0.026
*Thermal Expansion Coefficient	2.6×10 ⁻⁶	5.9×10 ⁻⁶	5.73×10 ⁻⁶	4.52×10 ⁻⁶
(°C ⁻¹)				

 Table 1.1 Physical properties of Si 、 Ge and III-V semiconductors at 300K [8-9]

Note: *l*=longitudinal, *t*=transverse, *lh*=light-hole, *hh*=heavy-hole.

Note: The parameters with * mark are derived from the website of Ioffe institute [9]

Chapter 2

Patterned Si Substrate, Experimental Apparatus and Scanning Electron Microscopy (SEM) Observations

2.1 Patterned Si Substrate

The patterned Si substrates used in this thesis were provided by Taiwan Semiconductor Manufacturing Company (TSMC). Our goal is to selectively grow high-quality GaAs and other relative III-V compound semiconductors, for example, InAs, into the [1-10] direction trenches. The side walls are SiO₂ of the trenches of the shallow trench isolation (STI), which was fabricated on a (001) p-type Si substrate using 193-nm immersion lithography and reactive ion etching (RIE) techniques. Figure 2.1 (a) and (b) show the SEM top view and the schematic cross-section graph of a GaAs-grown trench, respectively. Table 2.1 lists the widths of all trenches, with length of all trenches all the same about three millimeters and the same depth of 250nm.

2.2 Gas Source Molecular Beam Epitaxy

The specimens investigated in this thesis were grown by VG-V80H gas source molecular beam epitaxy (GSMBE) system. The gallium cell and the arsenic cell disposition were shown in Fig. 2.2(a). The gallium beam was supplied by EPI SUMO cell and the arsenic dimmer beam for epitaxial growth was cracked from precursor arsine at 1000 °C in a gas effusion cell. In addition to III - V sources, hydrogen plasma species were generated by flowing H₂ gas into EPI uni-bulb RF plasma cell operating at 13.56 MHz.

Before the epitaxial growth, both planar and nano-patterned Si substrates were dipped in dilute HF solution (HF:H₂O = 1:100) for 10 seconds to remove the native oxide. After nitrogen blow drying, the chips were bonded onto molybdenum disk with indium and inserted immediately into preparing chamber. The planar Si (001) substrate was used to monitor the in-situ growth condition by Reflection high-energy electron diffraction (RHEED) pattern. With the IRCON pyrometer monitoring the temperature, the substrates were firstly heated up to 800 °C for 3 minutes to remove the residual native oxide and the surface contaminations. After high temperature thermal cleaning, the substrates temperature was cooled down to low temperature for subsequent epitaxial growth.

During the epitaxial growth, the hydrogen plasma was always on until the end of the growth to enhance the epitaxial selectivity [10]. In order to avoid shadowing effect, the molecular beams was set parallel to the long side of the trenches as shown in figure 2.2(b). The growth temperature was set at 580 °C, and the deposition rate was 0.33 micron per hour, which was carefully calibrated on the Gallium beam flux using an ion gauge. There were five periods of deposition, each growth 60 nanometer thick film and than annealed at 640 °C for 10 minutes. After every period, the sample was rotated 180 degrees to enhance the epitaxial uniformity.

2.3 Scanning Electron Microscopy and Cathodoluminescence

SEM is a powerful tool to observe the surface appearance by using accelerated electrons whose energy are thousands to tens of thousands electron volts as a light source in optical microscopy. When the electrons hit into the sample, they diffuse and scatter to a water-drop form distribution, providing Auger electron in the top 1nm range, secondary electron in the top 5 to 50nm range, backscattered electrons, as shown in figure 2.3 (a). With the detecting of secondary electrons, we can obtain the sample appearance of a resolution up to 1nm.

Furthermore, the additional parts such as Auger electron spectrometer (AES), electron energy loss spectrometer (EELS), and energy dispersive spectrometer (EDS) can measure the chemical composition of samples; photoluminescence (PL), and cathodoluminescence (CL) parts can measure the luminescence properties of samples to receive detail information of the sample.

In CL measurements, a high energy electron beam whose energy was thousands electron volts is utilized as an exciting source. Compared to the conventional PL technique, CL measurement can provide higher spatial resolution, and with the in situ SEM images, one can obtain the luminescence spectra at a precise position of the sample, in our cases, i.e., the middle of the trench. Furthermore, the luminescence images, or the chromatic CL mapping of samples, can be performed to analysis the anti-phase boundaries and the non-radiation centers.

In this study, SEM images and CL spectrum were performed with JEOL JSM-7001 field emission gun SEM (FEGSEM). The SEM images were taken at a gun voltage of 8keV with a 12nA gun current and the CL spectra were taken at a gun voltage of 18keV with a 16nA gun current, respectively. There are two modes to measure the CL spectrum: scanning mode and spot mode. When using the scanning mode, the magnification of SEM is fixed, and the luminescence signal contains the whole SEM image range. On the other hand, when using the spot mode, the luminescence signals are exactly produced from the spot we appointed about a range of several microns, regardless of the magnification. The CL signals coming out from the samples are reflected by a parabolic mirror into Horiba Jobin Yvon iHR550 spectrometer with 1200gr/mm grating through a 2000µm slit. After the signal collection and dispersion, the final spectrum is obtained by a 1024x 256 pixel Si CCD detector with liquid nitrogen cooling. A schematic graph of the apparatus is shown in figure 2.3 (b).

The spectra have a resolution about 0.03nm. In all cases, the raw data includes a white noise about one thousand counts over entire spectrum. Besides, the data points slightly zigzag everywhere. Figure 2.5 (a) is the room temperature (RT) CL spectra of

VPEC heteroepitaxial high purity GaAs with variant exposure time. We can see the peak intensities are proportional to the exposure time, which represents that the high energetic electrons bombardment does not influence the luminescence mechanism.

2.4 Micro Raman Spectroscopy

When a monochromatic light beam incident to a material, it would be scattered elastically or inelastically. The elastically scattering is known as Rayleigh scattering and inelastically scattering is known as Raman scattering. The Raman scattering was first introduced by C. V. Raman and K. S. Krishnan at 1928 in liquid [11]. There are two kinds of Raman scattering, providing a phonon referred as a Stokes scattering and absorbing a phonon referred as an anti-Stokes scattering, respectively, as shown in figure 2.15(a). The phenomenon can be expressed mathematically as:

$$\hbar\omega_{\rm s} = \hbar\omega_{\rm i} \pm \hbar\Omega \tag{2.1}$$

$$\vec{k}_s = \vec{k}_i + \vec{q} \tag{2.2}$$

where \hbar the reduced Plank constant, ω_i the angular frequency of incident light, ω_s the angular frequency of scattered light, Ω the angular frequency of phonon, \bar{k}_s the momentum of scattered photon, \bar{k}_i the momentum of incident photon and \bar{q} the momentum of phonon. Since the angular wavenumber of phonon ($2\pi/a$, where a is the lattice constant) is much larger than photon ($2\pi/\lambda$, where λ is the wavelength of the photon), the first order Raman scattering only accepts first Brillouin zone optical phonon.

In this thesis, the properties of GaAs in single trench are of most interest. As a result, we used HORIBA Jobin-Yvon T64000 system, a backscattering configuration micro Raman system. The excitation light source is a 6 W Verdi V10 Diode-Pumped Solid-State (DPSS) 532 nanometer Laser, which goes through two beam splitter and an attenuator in order to make the beam power stable at 120 mW. Meanwhile, the laser beam is focused to a 1 µm spot on the specimens by the 100X microscopic objective lens. The backscattered light from the specimens transmit through a beam splitter and enter into a triple monochromator, including a double premonochromator as a filter stage and a single monochromator as a dispersive stage [12].

The filter stage has two gratings. First one disperses the incident light and second one is coupled to the first one to collect the parallel light in order to diminish the dispersion before light incident into the dispersive stage. There is a slit between the first and the second grating. The size of slit and the dispersion power, DISP, of grating decides the bandwidth and removes the stray light. The dispersive stage providing a high level of stray light rejection and allow one to require low frequency Raman modes. The dispersive stage with 1800gr/mm grating could disperse the inelastic Raman scattering light and then the spectrum is collected by a 1024x 256 pixel Si CCD detector with liquid nitride cooling. There are curtains around the system during experiment to eliminate white noises.

Figure 2.5 (b) shows the incident laser beam polarization and the settled directions and figure 2.5 (c) is the spectra of VPEC GaAs with different surface direction.

2.5 SEM images of GaAs in trenches with variant widths

The SEM images of GaAs in trenches with variant widths are shown in figure 2.6 to 2.14, with the orientation the same as figure 2.1. Through the investigation of SEM images, we observed the filling rate is near hundred percent. In addition, there are rhombic/eye-shaped GaAs islands above the STIs, with lengths about 1µm and widths about 300nm, as a result of relatively low growth temperature compared to a previous work presented by A. Okamoto et al. [13]. Inside the trenches, there are [110] direction breakings between the GaAs bars and separate the entire GaAs bar in trenches into several-microns-length bars. The breaking facets are all Si (1-10) facets. The heights of the bars are not the same according to the contrast difference of the images.

number	Trench width (nm)
5	40
6	45
7	50
8	55
9	60
10	70
11	80
12	90
13	100
14	120
15	140
16	160
17	180
18	200
19	300
20	500

 Table 2.1 Different trench widths



Figure 2.1 (a) SEM image of 55nm trench, the lightest parts are the STI SiO_2 . Between the STI are the trenches. There are 16 trenches at the upper side. The lowers are 1 micron, 500nm, and two 250nm trenches. (b) The schematic graph of the cross section of the trenches. The side walls are amorphous silica and the bottom of trench are silicon.



Figure 2.2 (a) The source assembly of Ga and As port in VG-V80H GSMBE. (b)

The molecular beams were paralleled to the long side of the trenches.



Figure 2.3 (a) The schematic graph of electron distribution, where X_d is the diffusion path and R the maximum range (b) The schematic graph of FEGSEM with CL system, where C1 and C2 are the electromagnetic lenses.



Figure 2.4 (a) Schematic graph of photon scattering (b) Schematic graph of the configuration of HORIBA Jobin-Yvon T64000 system



Figure 2.5 (a) VPEC GaAs room temperature CL with variant exposure time. We can see the peak intensity is proportional the exposure time, which means the high energy 16kV and 18nA electron gun does not influence the luminescence mechanism of GaAs. (b) The laser polarization of T64000 is X direction. The incident direction is set to be z direction. (c) Different polarization of (001) VPEC GaAs Raman spectra.



Figure 2.6 The SEM images of GaAs in 40nm Si trenches: (a-d) middle of the trench long side with different magnification (e-h) right of the trench of the trench long side



Figure 2.7 The SEM images of GaAs in 55nm Si trenches: (a-d) middle of the trench long side with different magnification (e-h) right of the trench of the trench long side



Figure 2.8 The SEM images of GaAs in 70nm-wide Si trenches: (a-c) middle of the trench long side with different magnification (d-f) right of the trench of the trench long side with different magnification



Figure 2.9 The SEM images of GaAs in 80nm-wide Si trenches: (a-c) middle of the trench long side with different magnification (d-f) right of the trench of the trench long side with different magnification



Figure 2.10 The SEM images of GaAs in 100nm-wide Si trenches: (a-c) middle of the trench long side with different magnification (d-f) right of the trench of the trench long side with different magnification


Figure 2.11 The SEM images of GaAs in 120nm-wide Si trenches: (a-c) middle of the trench long side with different magnification (d-f) right of the trench of the trench long side with different magnification



Figure 2.12 The SEM images of GaAs in 140nm-wide Si trenches: (a-b) middle of the trench long side with different magnification (d-f) right of the trench of the trench long side with different magnification



Figure 2.13 The SEM images of GaAs in 160nm-wide Si trenches: (a-b) middle of the trench long side with different magnification (c-e) right of the trench of the trench long side with different magnification



Figure 2.14 The SEM images of GaAs in 180nm-wide Si trenches: (a-b) middle of the trench long side with different magnification (c-d) right of the trench of the trench long side with different magnification



Figure 2.15 The SEM images of GaAs in 200nm-wide Si trenches: (a-b) middle of the trench long side with different magnification (c-d) right of the trench of the trench long side with different magnification



Figure 2.16 The SEM images of GaAs in (a-b) 300nm-wide trenches: middle of the trench long side with different magnification (c) 500nm-wide trenches (d) 1 μ m-wide trenches (e) 1.25 μ m-wide trenches (f) 1.5 μ m-width trenches

Chapter 3

Cathodoluminescence of GaAs in Si Nanotrenches

3.1 Excitation Volume of Electron

As shown in figure 2.3 (a), when the electrons incident into a solid, the electron diffuse to a water-drop shape distribution. The max penetration distance according to K. Kanaya et al. [14] found to agree well with experimental results in a wider range of atomic numbers [15] is

$$R_{K} = (0.0276A / \rho Z^{0.889}) E_{b}^{1.67} (\mu m)$$
(3.1)

, where A is the atomic weight in g/mol, ρ is the density in g/cm³, Z is the atomic number and E_b is the electron energy in keV.

In our cases, setting E_b to 16 keV as we used in CL spectrum measurements, for GaAs, A to 144.65, ρ to 5.316, Z to 64, R_K^{GaAs} is 1.909 μ m, respectively. Furthermore, for Si, we can substitute A to 28.0855, ρ to 2.329, Z to 14, R_K^{Si} is 3.257 μ m, respectively, and for SiO₂, we can substitute A to 60.08, ρ to 2.648, Z to 30, $R_K^{SiO_2}$ is 3.122 μ m, respectively. All the data of densities, atomic weights and atomic numbers used above are based on Wikipedia. According to these theoretical estimations, the accelerated electrons would diffuse about 3 microns deep at the set point with a water-drop form. Finally, since GaAs is only about 300 nm thick on or in the planar Si

or patterned Si substrates, the effective diffusion diameter at the bottom of GaAs is estimated to be $2.6 \ \mu m$.

3.2 CL spectrum analysis of SiO₂ as the shallow trench isolation

3.2.1 Typical CL spectrum of SiO₂ as STI

Figure 3.1(a) shows typical CL spectra of STI measured by scan mode. We can see that there three bands, which are located at 1.9eV (645 nm), 2.2eV (560 nm) and 2.7eV (460 nm), respectively. It is worth to mention that the intensity of these three peaks is proportional to exposure time, as shown in Fig.3.1 (a), indicating that the 18 keV-energetic electrons bombardment does not influence the luminescence mechanism.

Figure 3.1(b) and (c) show the CL spectra measured by spot mode at 11K from the side and the bottom of the trench, respectively. We can see both of the spectra are almost the same. Since the trench width is 1 μ m, implying the electron dispersion range much lager than 1 μ m, as we discussed in the end of section 3.1,

3.2.2 Luminescence theory of SiO₂

The defects in glass, vitreous-SiO₂ quartz and fused silica were characteristic by electron spin resonator (ESR) or electron magnetic resonator (EPR), photoluminescence (PL), optical absorption and SEM/CL technology. Scientists could recognize the energy level of defects by the hyperfine structure with isotopes characterized by ESR method. On the other hand, optical absorption, CL and PL still can do a lot favor for evaluating

the quality of various SiO₂.

3.2.2.1 The red band (R-band) luminescence of 1.9 eV (645 nm)

The oxide hole center network defect structure of this band, widely observed on silica optical fibers and gate oxides, was firstly deduced by M. Stapelbroek et al [16]. The origin of this luminescence is generally attributed to the electron-hole recombination at the non-bridging oxide hole center (NBOHC). This intrinsic defect structure in SiO₂ network is represented by \equiv Si-O·, where " \equiv " represents three oxygen atoms connected to a silicon atoms and "·" represents a single electron. The structure was characterized by the ²⁹Si hyperfine structure using ESR method [17]. Due to the variation of this red band, different precursors have been proposed, like energetic electron induced defect [18], trapped Si³⁺[19], or interstitial ozone [20]. We believe that the 1.9eV band is attributed to NBOHC, which had been reported tremendously.

3.2.2.2 The 2.2 eV (560 nm) band

This band is not that common as 1.9eV peak and 2.7eV peak in a-SiO₂. The literatures provide some perspectives: e-beam induced defect luminescence [21], singlet transition of the oxygen vacancy and the oxygen vacancy–interstitial pairs self trapped exciton $(V_O;(O_2)_i)$ [22] and intensity increase with electron irradiation [21]. To summarize, we believe that this band is originated with the oxygen vacancy and the oxygen vacancy and the oxygen vacancy interstitial pairs self trapped exciton $(V_O;(O_2)_i)$ [22] and intensity increase with electron irradiation [21]. To summarize, we believe that this band is originated with the oxygen vacancy and the oxygen vacancy–interstitial pairs self trapped exciton $(V_O;(O_2)_i)$. We confirm the

postulation by the elimination of luminescence at low temperature, which represents this kind of defect prone to break when the temperature decreases.

3.2.2.3. The 2.7eV (460nm) band

The luminescence mechanism of this band is mostly attributed to the so-called E' -centers or related to trivalent pure Si [23]. The E' center represents a Si attach to three oxide atoms and a single electron represented by \equiv Si · in the SiO₂ composition network [16]. Nevertheless, electron bombardment and temperature influence the luminescence peak intensity [23]. A. V. Amossov et al. claim that increasing of temperature may increase the luminescence peak intensity [20]. Another group mentioned that the peak intensity increase when Si surplus [24]. A. N. Trukhin et al. point out this band is usual for oxygen deficient center (ODC) luminescence in a-SiO₂. In SiO₂ - Si, oxygen deficiency is increased, so for that sample the mentioned luminescence is characteristic of SiO_(2- δ), where δ =2e-4 [25]. According to M. Watanabe, the recombination of oxide vacancy and interstitial oxygen as $(V_0; O_i)$ pair give rise to the luminescence [26]. Finally, A. Zatsepin et al. believe this luminescence is due to trivalent silicon, intensity increasing when silicon is surplus and H^+ implant will reduce the emission [27]. Finally, we attributed this band to the E' center.

3.2.2.4 The reduction of 2.2eV and 2.7eV bands at low temperature (11K)

After the temperature decrease, we have seen the reduction of 2.2eV and 2.7eV

band at low temperature, as shown in Fig.3.1 (c) and (d). Since the 2.2 band still exist, 2.7eV band almost vanished. At the same moment, the 1.9eV peak slightly red shift to 1.858eV. The peak form an asymmetry peak, the low energy side shows a polynomial-like decay while the high energy side decays almost linearly. We consider that at 11K, the intrinsic NBOHC structures remain robust, while $(V_0;(O_2)_i)$ s partially break by the recombination of oxygen and vacancy, accompanying with creating NHBOC structures, explaining the 2.2eV band decaying at 11K. The 2.7eV band disappearing may be attributed to the rebond of E' electron and NHBOC, forming original SiO₂ structure, then no luminescence would occur.

3.3 Growth Condition of GaAs on planar and patterned Si (001) wafer

Samples were grown by almost the same procedure: C2584 was grown at 580°C with a growth rate of 0.33 μ m/hr. After every 60 nm thick film was grown, sample was rotated by 180° and raised to 650°C for 10 minutes. During the annealing, the sample was illuminated by hydrogen plasma from a plasma cell. The plasma power was 230W. For convenience, the growth conditions of C2584, C2585, C2586, C2587 and C2588 are listed in table 3.1.

To discuss the surface configuration, figure 3.2 (c), (d) and (e) are the SEM top view image of C2585, C2586, and C2588 on planar Si, respectively. We can see that epi-layer of C2585 has much more "holes" on the surface, yet the GaAs grains are

continuum everywhere. The C2588 surface also has holes on it, but they are slimmer, and we can see many facets, like wrinkled paper with slots. C2586 is mostly like film, with triangle vines toward [110] direction.

3.4 RTCL spectra of GaAs on bulk/patterned Si

Luminescence phenomena in GaAs are caused by radiative recombination of holes and electrons. The direct band gap nature of GaAs gives rise to a high efficiency conduction band to valance band transition during the recombination. The typical RTCL of GaAs which is fabricated by VPEC with molecular organic vapor phase epitaxial (MOVPE) growth is shown in figure 3.2(a), with 1.42eV peak position and 37meV full width half maximum (FWHM). Its high energy side decays slowly owing to the high energy tail states, and low energy side decay more sharply, representing that the density of state (DOS) of radiative impurities inner the energy band are relatively less.

3.4.1 The RTCL peaks discussion of GaAs grown on planar Si (001) samples

1. C2585

Figure 3.3 (a) is the RTCL spectrum of C2588 GaAs on planar Si. Due to the zigzag of the data of the spectrum, we utilize Fourier low pass filter with frequency 500 and two peak Gaussian fitting, the original spectrum resolved two Gaussian-like peaks, one peak at 1.440eV with 127meV FWHM and another peak at 1.285eV with 88 meV. 2. C2586

Figure 3.3 (b) is the RTCL spectrum of C2586 GaAs on planar Si. Using the same method as C2585, the peak is at 1.438eV with 167meV FWHM.

3. C2588

Figure 3.3 (c) is the RTCL spectrum of C2588 GaAs on planar Si. Utilizing Fourier low pass filter with frequency 150 and first order derivative, the peak of C2588 is 9meV blue shift from the VPEC GaAs peak. We use Gaussian fitting and received one peak at 1.433eV with 107meV FWHM and another 1.287eV peak with 89meV FWHM. Note that the deviation of the 1.43eV peak, which is not totally normal distribution yet has a trend like heteroepitaxial GaAs. A 1.44eV band was reported at 4 K and was attributed to deep acceptor level luminescence [28]. In our cases, the RT three times broadening near 1.44eV band may be attributed to other mechanisms. The 1.28eV peak was reported by M. F. Millea using electroluminescence (EL) at 80 K, recognizing as a donor-acceptor pair model [29]. We also attributed this peak to the deep donors to the deep acceptors inner band transition. With the SEM image observation, we consider that the 1.429eV peak broaden is due to the structure of GaAs. Inside the excitation volume, every grain is postulated to be compressed or tensile because of the slots on the Si surface, then due to the Fermi level consistency, the band gap of every grain overlapping mutually and many localized states giving rise to the finally broaden peak. Finally, we consider that the Burstein-Moss shift cause the blue shift effect.

3.4.2 RTCL spectra of GaAs in patterned Si

The RTCL spectra of GaAs in different trench width are shown in figure 3.4-3.7. The GaAs signals are not that clear when trench width is less than 100nm. In figure 3.4(a), (b), (c) and (d), the luminescence of GaAs in 50nm trench to GaAs in 70nm trench have almost the same shape. Even though the GaAs-like bands are so weak, after subtract the SiO₂ RTCL signal, we can see a 1.4eV neighboring band, which is attributed to the GaAs band to band transition. The GaAs peak is much more broadening then the VPEC GaAs and red shifted. The red shift is due to the STI stretching inducing tensile strain. The broadening is due to the defects inducing deep levels.

When trench width becomes larger, the GaAs peak intensity gradually become larger than the SiO_2 luminescence and the FWHM of the peak is much larger than the one of intrinsic GaAs. The broaden phenomenon has also been seen on the C2588 bulk.

In figure 3.4 (d), 3.5 (b) and 3.6(c), we can see higher luminescence intensity of spot mode rather than scan mode. Since the higher efficiency, we finally use spot mode to measure the whole trench.

The spectrum of trench 11, figure 3.5 (a), with 80nm width, has a triangle form GaAs peak, with intensity much lower than the $1.9eV SiO_2$ peak. After subtraction the SiO₂ signal, utilizing Fourier low pass filter with frequency 1000, forming a peak at

1.452eV with 292meV FWHM. From figure 3.5 (b), trench 12, with 90nm width, also reveals a band belongs to GaAs, utilizing the same method as trench 11, forming a peak at 1.4626eV with 224meV FWHM. After the trench is larger than 100nm, the GaAs peak intensity starts to exceed the SiO₂ luminescence intensity of 1.9eV peak, with much wider FWHM and blue shifts than the heteroepitaxial one. Trench 13, with 100nm trench width, minus oxide signals and using Gaussian fitting, we receive three bands: 1.4358eV with 150meV width, 1.2932eV with 88meV width and 1.6297eV with 243meV width. Trench 14, 120nm width, minus oxide signals and using Gaussian fitting, we receive four bands: 1.4404eV with 99meV width, 1.2987eV with 120meV width, 1.4904eV with 170meV width and 1.7362eV with 160meV width. Trench 15, 140nm width, minus oxide signals and using Gaussian fitting, we receive two bands: 1.4590eV with 174meV width and 1.1562eV with 111meV. Trench 16, with 160nm width, minus oxide signals and using Gaussian fitting, we receive three bands: 1.4505eV with 137meV width, 1,2763eV with 72meV and 2.1645 with 148meV. Trench 17, with 180nm width, minus oxide signals and using Gaussian fitting, we receive two bands: 1.4533eV with 136meV width and 1.2732 with 80meV. Trench 18, with 200nm width, minus oxide signals and using Gaussian fitting, we receive two bands: 1.4464eV with 136meV and 1.2742eV with 84meV. Trench 19, with 300nm width, minus oxide signals and using Gaussian fitting, we receive two bands: 1.4516eV with 111meV and 1.2856eV with 72meV width. Trench 20, with 500nm width, is similar to the bulk GaAs luminescence in spectrum line shape, performing the high energy tail and sharp low energy side and still has the 1.27eV band, using Gaussian fitting, we receive two bands: 1.445eV with 103meV FWHM and 1.284eV with 83meV.

In the end of these RT measurements, we provide the figure 3.7 (c) to make sure the reliability of these works. Meanwhile, figure 3.7 (d) shows the main two peaks of trenches widths larger than 100 nm. We can see the positions of the two peaks of all the trenches larger than 100 nm are near the same. This fact indicates that the luminescence mechanism has nothing to do with the trench width, in other words, the strain induced by side walls. Besides the strain model, high density of twinning and stacking faults inducing inner band states may be the reason of the overwhelmingly broadening peak. The blue shift may because of the cross-doping effect or the Burstein-Moss shift.

3.4.3 LTCL spectra discussion of C2588 bulk

At low temperature about 11K, we had done a series of CL experiments. Figure 3.2(b) reveals the 12K CL spectrum of VPEC GaAs, which shows the exciton bound to neutral acceptor-like point defect at 1.510eV and exciton (doublet) bound to neutral carbon at 1.512eV.

Surprisingly, the spot mode on the same spot produced different results of the C2588 GaAs on planar Si, different from the STI RTCL. This phenomenon indicated

that the 16kV with 18nA energetic electron at 11K would break some bonding in the grains and induced other bands of GaAs. The figure 3.8 (b) to (d) was set on the same dot and (e), (f) set on another. Figure 3.8 (b) contains three parts of Gaussian fitting: 1.5084eV with 29meV width, 1.4734eV with 142meV width, 1.3001eV with 157meV width, 2.707eV with 556meV width. Figure 3.8 (c) contains three parts of Gaussian fitting: 1.4193eV with 150meV width, 1.2647eV with 111meV width, 1.5067eV with 21meV width. Figure 3.8 (d) contains four parts of Gaussian fitting: 1.5681eV with 70meV width, 1.4439eV with 102meV width, 1.3621eV with 47meV width, 1.2893eV with 124meV. Figure 3.8 (e) contains two parts of Gaussian fitting: 1.4696eV with 106meV width, 1.3213eV with 162meV width. Figure 3.8 (f) contains four parts of Gaussian fitting: 1.2609eV with 112meV width, 1.4348eV with 51meV width, 1.3977eV with 107meV width, 1.5398eV with 147meV. Figure 3.11 (a) shows the fitted peaks and their FWHM.

The LTCL of the C2588 sample gives problems to discussion. First, the 1.508eV band is attributed to bound exciton to neutral acceptor like point defect. Second, the Gaussian fitted peaks separately distribute from 1.2 simplest two spectra both have near 1.45eV peak and a 1.32eV peak. The 1.45eV peak may be the donor to Si acceptor. The adjacent 1.26eV and 1.32eV peaks may be the GaAs inner band defect level..

3.4.4 LTCL spectra discussion of patterned C2588

We can see from figure 3.9 (a) and (b) that the spectra only reveal the silicon dioxide luminescence parts, since the trench widths are too small. From trench width larger than 80nm, there bands gradually reveals around 1.4eV and 1.55eV while the vitreous glass luminescence still plays a rule in the excitation volume.

Observing figure 3.9 (c), the 80nm-width trench luminescence additional luminescent 1.35eV and 1.5eV peaks. By the trench width enlarging, the intensity of these two peaks enlarging in the mean time. After the trench width larger than 160nm, the Gaussian fitting results new peak near 1.25eV. These three or four peaks compared to the VPEC GaAs 1.42eV are obscure. Figure 3.11 (b) shows the Gaussian fitted peaks positions versus trench width. In our opinion, we attribute this luminescence to the shape-induced band splitting.

Sample	Growth	AsH ₃	Growth	Step	Total	Annealing
No.	temperature	(torr)	rate	thickness	thickness	temperature(°C)
	(°C)		(µm/hr)	(nm)	(nm)	/ time(s) at interval
C2584	580	990	0.33	60	300	650/10
C2585	580	990	0.33	100	300	650/10
C2586	580	990	0.33	300	300	650/10
C2587	580	990	0.33	300	300	650/10
C2588	580	990	0.33	60	300	620/10

Table 3.1 The growth condition of C2584, C2585, C2586, C2587 and C2588 $\,$





Figure 3.1 (a) The CL spectra of SiO₂ STI side wall at RT using scan mode with variant exposure time: 3 seconds, 10 seconds and 30 seconds. The peak energy intensities of spectra are proportional to exposure time. (b) A CL spectrum of SiO₂ STI sidewall at 11K using spot mode (c) a CL spectrum of SiO₂ as STI at 11K using spot mode, the cursor set at the bottom of the trench



Figure 3.2 (a) RTCL of GaAs on GaAs substrate obtained by SEM/CL method with exposure time to be 1 second (b) The 11K case (c) C2585 SEM top view of GaAs grown on planar substrate (d) C2586 SEM top view of GaAs grown on planar substrate (e) C2588 SEM top view of GaAs grown on planar substrate



Figure 3.3 (a) RTCL of C2585 GaAs on planar Si with exposure time 10 seconds and 2 cycle (b) RTCL of C2586 GaAs on planar Si with exposure time 10 seconds and 2 cycle (c) RTCL of C2588 GaAs on planar Si with exposure time 10 seconds and 2 cycle



Figure 3.4 (a) 50 nm trench CL spectrum using scan mode at X20k (b) 55 nm trench CL spectrum using scan mode at X20k (c) 60 nm trench CL spectrum using scan mode at X20k (d) 70nm trench CL spectra, there are spot modes results and scan modes results. The GaAs peak of scan mode at X40k slightly red shifts and broadens compared to scan mode at X20k.



Figure 3.5 (a) 80 nm trench RTCL spectrum using spot mode (b) 90 nm trench RTCL spectrum using spot mode (c) 100 nm trench RTCL spectrum using spot mode (d) 120nm trench RTCL spectrum using spot modes



Figure 3.6 (a) 140nm trench RTCL peaks using variant measure modes and variant exposure time (b) 160nm trench RTCL peaks using spot mode (c) 180nm trench RTCL peaks using spot mode



Figure 3.7 (a) 300nm trench RTCL peaks (b) 500nm trench RTCL peaks (c) no beam emission spectrum (d) peaks positions by Gaussian fitting versus trench widths, after the trench larger than 100nm, mainly 2 peaks: around 1.29eV and around 1.45eV are fitted.



Figure 3.8 (a) RTCL spectrum of C2588 GaAs on planar Si with Gaussian fitting, (b)-(d) are LTCL spectra on the same spot, (e) (f) are on another spot; the green curves are Gaussian fittings. Note that (a) and (e) are almost the same.



Figure 3.9 C2588 variant trench width LTCL (a) 40 nm, (b) 55 nm, (c) 80 nm, (d) 90

nm (e) 100 nm, (f) 120 nm



Figure 3.10 C2588 variant trench width LTCL (a) 140 nm (b) 160 nm (c) 180 nm (d)

200 nm (e) 300 nm (f) 500 nm



Figure 3.11 (a) LTCL Gaussian fitted C2588 GaAs on planar Si (001) substrate FWHM versus peaks (b) LTCL Gaussian fitted C2588 GaAs on patterned Si (001) substrate peak position versus trench width

Chapter 4

Raman Spectroscopy of GaAs in Si Nanotrenches

4.1 T64000 calibration

To ensure the T64000 work well, we utilized high quality TSMC Si and VPEC GaAs to be the standard sample to calibrate the module. Figure 4.1 (a) is the calibration standard, calibrating the Si (001) TO mode to 520 cm⁻¹ with 4.67cm⁻¹ FWHM in the z(XX)z' configuration [30] to make sure the module works properly. Figure 4.2 (b) shows the VPEC GaAs z(XX)z' result: allowed LO mode at 297 cm⁻¹ with 6.65cm⁻¹ width, and a little forbidden TO peak at 273cm⁻¹.

4.2 C2584-C2587 on Si bulk

From figure 4.1 (c) and (d), the C2584 Raman spectrum shows entire no GaAs signal, yet reveals silicon Raman spectra compared to figure 4.1 (e) proposed by Paul A. et al. [31]. The spectrum performs with the $\Gamma_1+\Gamma_{12}+\Gamma_{25}$ symmetry. This concludes that this sample has no GaAs epitaxied. Figure 4.2 (a) is the Raman spectrum with the z(XX)z' configuration of C2585 GaAs on planar Si in log scale and figure 4.2 (c) is the GaAs peaks in linear scale with cutting a baseline of 170. With Lorenzian fitting, the normally forbidden TO phonon (271.5 cm⁻¹ peak and 5.5 cm⁻¹ FWHM) is much more

intense than the normally allowed LO phonon (294.5 cm-1 peak and 11.9 cm⁻¹ FWHM) ,broadening tremendously. Figure 4.2 (b) shows the C2586 Raman spectrum of the z(yX)z' configuration in log scale and figure 4.2 (d) is the GaAs peaks in linear scale with cutting a baseline of 200. With extrapolation, the normally forbidden TO phonon (271.4 cm⁻¹ peak and 6.8 cm⁻¹ FWHM) and LO phonon (294.1 cm-1 peak and FWHM estimated to be 13 cm^{-1}). Figure 4.3 and 4.4 is the same orientation as figure 4.2, showing the C2586 and C2587 GaAs on planar Si, respectively. The C2586 z(XX)z' configuration Raman spectrum with cutting a baseline of 300 and Lorenzian fitting give rise to a TO phonon (271.2 cm⁻¹ peak and 6.5 cm⁻¹ FWHM) and a broad relatively small LO phonon (294.8 cm⁻¹ peak and 11.9 cm⁻¹ FWHM). At the same time, the GaAs TO peak is also larger than the Si TO peak, representing that GaAs film of C2586 has low slots density. The C2586 z(yX)z' configuration Raman spectrum with cutting a baseline of 200 and Lorenzian fitting give rise to a TO phonon (271.5 cm⁻¹ peak and 5.7 cm⁻¹ FWHM) and an LO phonon (294.9 cm⁻¹ peak and 6.6 cm⁻¹ FWHM). The C2587 z(XX)z' configuration Raman spectrum with cutting a baseline of 200 and Lorenzian fitting give rise to a TO phonon (271.4 cm⁻¹ peak and 4.8 cm⁻¹ FWHM) and a broad relatively small LO phonon (294.7 cm⁻¹ peak and 10.4 cm⁻¹ FWHM). The C2587 z(yX)z' configuration Raman spectrum with cutting a baseline of 200 and Lorenzian fitting give rise to a TO phonon (271.4 cm⁻¹ peak and 5.2 cm⁻¹ FWHM) and an LO

phonon (294.8 cm^{-1} peak and 10.1 cm^{-1} FWHM).

In summary, all the spectra reveal a strong GaAs (100) forbidden TO phonon peak at 271 cm⁻¹ and a 3.3 cm⁻¹-broadened reduced LO mode at 295cm⁻¹. Look back to figure 3.2 (c) to (e). Since the facets vertical to the Si (001) substrate are supposed to be GaAs {110} facets, the laser beam may be direct incident on {111} facets and other non-(001) facets. From this observation, we can conclude that the TO mode is attributed to the diverse facets, and the little broadening LO mode is because of the relatively less GaAs (001) facet.

4.3 C2588 GaAs on patterned Si substrate

Figure 4.5-4.7 shows the Raman spectra with z(XX)z' configuration of all the trenches of C2588 with Lorenzian fitting. All the spectra reveal the strong TO phonon mode as the GaAs on planar Si substrate. Figure 4.5 (a) is the 40 nm trench, with Lorenzian fitting, we receive four peaks (236.2 cm⁻¹ with 5.23 cm⁻¹ FWHM, 272.9 cm⁻¹ with 3.5 cm⁻¹ FWHM, 288.5 cm⁻¹ with 10.2 cm⁻¹ FWHM and 295.8 cm⁻¹ with 3.6 cm⁻¹ FWHM). Figure 4.5 (b) is the 45 nm trench, with Lorenzian fitting, we receive four peaks (263.5 cm⁻¹ with 4.8 cm⁻¹ FWHM, 273.2 cm⁻¹ with 3.4 cm⁻¹ FWHM, 289.6 cm⁻¹ with 9.3 cm⁻¹ FWHM and 296.2 cm⁻¹ with 3.4 cm⁻¹ FWHM). Figure 4.5 (c) is the 50 nm trench, with Lorenzian fitting, we receive four peaks (262.3 cm⁻¹ with 1.7 cm⁻¹ FWHM, 271.7 cm⁻¹ with 5.4 cm⁻¹ FWHM, 287.0 cm⁻¹ with 10.3 cm⁻¹ FWHM and 294.0

 cm^{-1} with 5.9 cm^{-1} FWHM). Figure 4.5 (d) is the 55 nm trench, with Lorenzian fitting, we receive three peaks (272.4 cm^{-1} with 3.4 cm⁻¹ FWHM, 290.7 cm⁻¹ with 9.4 cm⁻¹ FWHM and 295.7 cm^{-1} with 3.7 cm^{-1} FWHM). Figure 4.6 (a) is the 60 nm trench, with Lorenzian fitting, we receive two peaks (273.2 cm⁻¹ with 5.6 cm⁻¹ FWHM and 295.2 cm⁻¹ with 11.8 cm⁻¹ FWHM). Figure 4.6 (b) is the 70 nm trench, with Lorenzian fitting, we receive three peaks (273.1 cm^{-1} with 11.0 cm⁻¹ FWHM, 283.3 cm⁻¹ with 7.2 cm⁻¹ and 290.2 cm⁻¹ with 13.8 cm⁻¹ FWHM). Figure 4.6 (c) is the 80 nm trench, with Lorenzian fitting, we receive three peaks (271.9 cm⁻¹ with 6.2 cm⁻¹ FWHM, 289.7 cm⁻¹ with 14.2 cm⁻¹ FWHM and 295.2 cm⁻¹ with 3.2 cm⁻¹ FWHM). Figure 4.6 (d) is the 90 nm trench, with Lorenzian fitting, we receive four peaks (264.4 cm⁻¹ with 6.1 cm⁻¹ FWHM, 272.8 cm⁻¹ with 3.9 cm⁻¹ FWHM, 289.7 cm⁻¹ with 8.7 cm⁻¹ FWHM and 296.0 cm⁻¹ with 8.7 cm⁻¹ FWHM). Figure 4.7 (a) is the 100 nm trench, with Lorenzian fitting, we receive two peaks (272.1 cm^{-1} with 4.4 cm⁻¹ FWHM and 293.7 cm⁻¹ with 13.2 cm⁻¹ FWHM) Figure 4.7 (b) is the 120 nm trench, with Lorenzian fitting, we receive two peaks (271.7 cm^{-1} with 4.8 cm⁻¹ FWHM and 294.2 cm⁻¹ with 10.7 cm⁻¹ FWHM). Figure 4.7 (c) is the 140 nm trench, with Lorenzian fitting, we receive two peaks (271.3 cm^{-1} with 10.2 cm^{-1} FWHM and 291.1 cm^{-1} with 9.4 cm^{-1} FWHM). Figure 4.7 (d) is the 160 nm trench, with Lorenzian fitting, we receive two peaks (272.2 cm⁻¹ with 4.9 cm⁻¹ FWHM and 293.1 cm⁻¹ with 17 cm⁻¹ FWHM). Figure 4.8 (a) is the 180 nm trench, with Lorenzian fitting, we receive two peaks (272.7 cm^{-1} with 3.8 cm⁻¹ FWHM and 294.2 cm⁻¹ with 12.7 cm⁻¹). Figure 4.8 (b) is the 200 nm trench, with Lorenzian fitting, we receive two peaks (272.3 cm^{-1} with 5.6 cm⁻¹ FWHM and 293.5 cm⁻¹ with 8.4 cm⁻¹ FWHM). Figure 4.8 (c) is the 300 nm trench, with Lorenzian fitting, we receive two peaks (272.3 cm^{-1} with 5.6 cm⁻¹ FWHM and 293.5 cm⁻¹ with 8.4 cm⁻¹). Figure 4.8 (d) is the 500 nm trench, with Lorenzian fitting, we receive two peaks (272.3 cm^{-1} with 5.6 cm⁻¹ FWHM and 293.5 cm⁻¹ with 8.4 cm⁻¹ with 4.5 cm⁻¹ FWHM and 294.6 cm⁻¹ with 13.0 cm⁻¹ FWHM).

Figure 4.8 (a) shows the positions of the main three peaks versus trench widths. We can see that the trend is not obvious, while every peak position oscillates. Figure 4.8 (b) shows the FWHM of TO and LO phonon with variant trenches. Besides four extraordinary large values, others reveal no trend but in a certain range. These four large FWHM is due to the relatively small intensity and the asymmetric peak structure.

4.4 Theory of Raman scattering

According to G. Irmer [32], for long-wavelength polar phonons in the cubic crystal classes the Raman scattering efficiency is given by

$$S = \left| \sum_{ijk} \overline{e}_i^s \overline{R}_{ijk} \overline{p}_k \overline{e}_i^j \right|^2, \tag{4.1}$$

where the polarization unit vectors of the incident light \overline{e}^i , scattered light \overline{e}^s , and phonons \overline{p} are expressed in the principal crystallographic axes system as denoted by strokes. The Raman tensor \overline{R} of the phonons with symmetry $\Gamma_{25}(F_2)$ in crystals of the point group T_d has the form $\left(\overline{R}_{ij}\right)_k$

$$= a \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \ a \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \ a \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(4.2)

with one independent element a which is a measure of the changes of susceptibility with the phonon displacement.

Consider the zinc-blende (001) facet. In the backscattering configuration, the TO phonon has the polarization $\bar{p} = (p_x, p_y, 0)$, with incident light polarization at <110> direction and scattered light polarization at <110> direction, the Raman scattering efficiency is calculated to be zero. With the same condition, the LO phonon has the polarization $\bar{p} = (0,0, p_z)$ and the Raman scattering efficiency is calculated to be $2ap_z$, meaning allowed in this configuration.

To explain our experimental results of the large TO mode, since our work has done with the z(XX)z' configuration, the only parameter changed should be the Raman tensor. The values of the Raman tensor are based on the symmetry of the lattice. In our case, we consider that the micro-twins in the micro-crystals would change the symmetry of (001) facet, which cause the large TO signal.

In the nano-trenches, there is an additional mode between TO and LO mode. This mode is attributed to the "surface phonon" (SO) mode due to a large surface-to-volume ratio. With the calculation of R. Ruppin et al. [33], SO phonon has three main
characteristics:

- (a) The SO mode is locate between the bulk TO and LO peaks.
- (b) The SO mode shifts to lower frequency as the dielectric constant of the surrounding medium increases.
- (c) The intensity of the SO mode increases as the particle size decreases.

The SO mode is fitted when the trench width is less than 100 nm. No obvious trend can be seen in figure 4.5 and 4.6.





z(XX)z' 30 seconds 2cycle (c) RT C2584 (100) bulk z(XX)z' 30 seconds 2 cycle (d) RT C2584 (100) bulk z(XX)z' 30 seconds 2 cycle (e) P. A. Temple et al. [31]'s result



Figure 4.2 (a) C2585(100) bulk z(XX)z' 30 seconds 2 cycle in log scale (b) C2585 (100)

bulk z(yX)z' 30 seconds 2 cycle in log scale (c) C2585(100) bulk z(XX)z' 30 seconds 2 cycle GaAs signal in linear scale (d) C2585 (100) bulk z(yX)z' 30 seconds 2 cycle GaAs signal in linear scale



Figure 4.3 (a) C2586 Si (100) bulk z(XX)z' 30 seconds 2 cycle in log scale (b) C2586

Si (110) bulk z(yX)z' 30 seconds 2 cycle in log scale (c) C2586 Si (100) bulk z(XX)z' 30 seconds 2 cycle GaAs signal in linear scale (d) C2586 Si (110) bulk z(yX)z' 30 seconds 2 cycle GaAs signal in linear scale



Figure 4.4 (a) C2587 Si (100) bulk z(XX)z' 30 seconds 2 cycle in log scale (b) C2587

Si (110) bulk z(yX)z' 30 seconds 2 cycle in log scale (c) C2587 Si (100) bulk z(XX)z' 30 seconds 2 cycle GaAs signal in linear scale (d) C2587 Si (110) bulk z(yX)z' 30 seconds 2 cycle GaAs signal in linear scale



Figure 4.5 (a) C2588 GaAs in 40nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (b) C2588 GaAs in 45nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (c) C2588 GaAs in 50nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (d) C2588 GaAs in 55nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting



Figure 4.6 (a) C2588 GaAs in 60nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (b) C2588 GaAs in 70nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (c) C2588 GaAs in 80nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (d) C2588 GaAs in 90nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting



Figure 4.7 (a) C2588 GaAs in 100nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (b) C2588 GaAs in 120nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (c) C2588 GaAs in 140nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (d) C2588 GaAs in 160nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting



Figure 4.8 (a) C2588 GaAs in 180nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (b) C2588 GaAs in 200nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (c) C2588 GaAs in 300nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting (d) C2588 GaAs in 500nm trench 30 seconds 2 cycle Raman spectrum in linear scale with Lorentzian fitting



Figure 4.9 (a) The trends of TO phonon, SO phonon and LO phonon in variant trenches,

respectively. (b) The trends of FWHM of TO and LO phonon, respectively.

Chapter 5

Conclusion

We have successfully deduced the theoretical formation origin of the anomalous spectra of 300 nm GaAs on planar and patterned Si (001) substrate. From the observation of SEM images of GaAs on Si (001) bulk spectra, we believe that the RTCL peak broadening is due to the band gap overlap of the strained grain. From the observation of C2588 GaAs on patterned Si (001) substrate, we conclude that the ultrabroaden 1.45 eV peak is attributed to the GaAs band to band luminescence and the 1.29 eV shoulder is attributed to the Si deep level luminescence. The LTCL GaAs peaks reveal a two-peak feature when trench width between 90 nm and 140 nm. The low energy band is attributed to deep level carrier to carbon acceptor and the high energy band is attributed to donor to acceptor recombination, respectively.

The origins of three SiO₂ RTCL peaks are also surveyed. The 1.9 eV peak is attributed to the NBOHC; the 2.2 eV peak is attributed to the $(V_0;(O_2)_i)$ structure and the 2.7 eV peak is attributed to E' center. From the observation of LTCL, we find out that the elimination of 2.7 eV and 2.2 eV peaks, which represents the elimination of these defects. In the analysis of GaAs on planar Si, the basic two peaks at 1.32 eV and 1.47 eV are attributed to the deep level transition and the GaAs band to band transition,

respectively. The other bands are attributed to the Fermi-level consistency inducing band gap changing of strained grains.

The RT Raman spectra are studied. Large originally forbidden TO mode was observed in the z(XX)z' configuration of GaAs on planar Si (001) substrates. The large TO mode is attributed to the large density of the micro-twins, which transform the (001) facet to the {122} facets. The same as the planar Si (001) substrates, the patterned Si (001) sample shows large LO phonon mode. Additionally, the surface optical (SO) phonon mode is observed in the trenches thinner than 100 nm. The SO mode is due to the large surface-to-volume ratio.



Reference

- [1] T. Soga, S. Hattori, S. Sakai, M. Takeyasu and M. Umeno, "Charaterization of epitaxially grown GaAs on Si substrates with III-V compounds intermediate layers by metalorganic chemical vapor deposition", *J. Appl. Phys.*, vol. 57, p. 4758, 1984.
- [2] T. Ishida, T. Nonaka, C. Yamagishi, Y. Kawarada, Y. Sano, M. Akiyama and K. Kaminishi, "GaAs MESFET Ring Oscillator on Si Substrate" *IEEE TRANSACTIONS ON ELECTRON DEVICES*, Vol. ED-32, No. 6, 1985.
- [3] H. Zabel, N. Lucas, R. Feldenhans'l, J. Als-Nielsen and H. Morkoc, "Structure of Heteroepitaxal GaAs on Si", *Superlattices and Microstructures*, vol. 3, no. 5, 1987.
- [4] R. Fischer, H. Morkoc, D. A. Neumann, H. Zabel, C. Choi, N. Otsuka, M. Longerbone and L. P. Erickson, "Material properties of high-quality GaAs epitaxial layers grown on Si substrates", J. Appl. Phys., vol. 60, p. 1640, 1986.
- [5] P. Sheldon, B. G. Yacobi, K. M. Jones and D. J. Dunlavy, "Growth and characterization of GaAs/Ge epilayers grown on Si substrates by molecular beam epitaxy", J. Appl. Phys., vol. 58, p. 4186, 1985.
- [6] R. Hull, S. J. Rosner, S. M. Koch and J. S. Harris, Jr., "Atomic structure of the GaAs/Si interface", *Appl. Phys. Lett.*, vol. 49, p. 1714, 1986.
- [7] Gordon E. Moore, "Cramming more components onto integrated circuits,"

Electronics, Vol. 8, 1965

- [8] S. M. Sze and K. K. Ng, "Physicals of Semiconductor Devices", 3rd edition, Jonn Wiley & Sons, Inc, pp. 789-791, 2007.
- [9] "Electronic archive: New Semiconductor Materials. Characteristics and Properties." Ioffe Physico-Technical Institute, June 30, 2009. ">http://www.ioffe.ru/SVA/NSM/>.
- [10] N. Kuroda, S. Sugou, T. Sasaki and M. Kitamura, "Selective Growth of InGaAs/InP Layers by Gas Source Molecular Beam Epitaxy with Atomic Hydrogen Irradiation", *Jpn. J. Appl. Phys.*, vol. 32, pp. L1627-L1630, 1993.
- [11] http://www.uky.edu/~holler/raman.html
- [12] http://www.cc.ncu.edu.tw/~w3neutro/nanolab/main35-2.html
- [13] A. Okamoto and K. Ohata, "Selective epitaxial growth of gallium arsenide by molecular beam epitaxy", *Appl. Phys. Lett.*, vol. 51, p. 1512, 1987.
- [14] K. Kanaya and S. Okayama, "Penetration and energy-loss theory of electrons in solid targets" J. Phys. D: Appl. Phys., Vol. 5, p. 43, 1972.
- [15] B. G. Yacobi and D. B. Holt, Cathodoluminescence Microscopyof Inorganic Solids Plenum Press New York and London, p.58.
- [16] M. Stapelbroek. D. L. Griscom, E. J. Friebele and G. H. Sigel, Jr., "Oxygen-Associated Trapped-hole Centers in High-purity Fused Silicas", J.

Non-Cryst. Solids., vol. 32 pp. 313-326, 1979.

- [17] D. L. Griscom and E. J. Friebele, "Fundamental defect centers in glass: ²⁹Si hyperfine structure of the nonbridging oxygen hole center and the peroxy radical in a-SiO₂", *Phys. Rev. B*, vol. 24, p. 4896, 1981.
- [18] T. Suzuki, T. Sakai, L. Zhang, and Y. Nishiyama, "Evidence for cathodoluminescence from SiO_x in porous Si", *Appl. Phys. Lett.*, vol. 66, p. 215, 1995.
- [19] M. A. S. Kalceff and M. R. Phillips, "Cathodoluminescence microcharacterization of the defect structure of quartz", *Phys. Rev. B*, vol. 52, p. 3122, 1995.
- [20] A. V. Amossov and A.O. Rybaltovsky, "Oxygen-deficient centers in silica glasses: a review of their properties and structure", J. Non-Cryst. Solids., vol. 179 pp. 75-83, 1994.
- [21] H. Koyama, "Cathodoluminescence study of SiO₂", J. Appl. Phys., vol. 51, p. 2228, 1979.
- [22] M. Yoshikawa, K. Matsuda, Y. Yamaguchi, T. Matsunobe, Y. Nagasawa, H. Fujino and T. Yamane, "Characterization of silicon dioxide film by high spatial resolution cathodoluminescence spectroscopy", J. Appl. Phys., vol. 92, p. 7153, 2002.
- [23] X Liu, J. C. H. Phang, D. S. H. Chan and W. K. Chim, "The properties of 2.7 eV

cathodoluminescence from SiO₂ film on Si substrate", *J. Phys. D: Appl. Phys.*, vol. 32 p. 1563, 1999.

- [24] H. J. Fitting, T. Barfels, A.N. Trukhin, B. Schmidt, A. Gulans, A. von Czarnowski,
 "Cathodoluminescence of Ge⁺, Si⁺, and O⁺ implanted SiO2 layers and the role of mobile oxygen in defect transformations", *J. Non-Cryst. Solids.*, vol. 303 pp. 218-231, 2002.
- [25] A.N. Trukhin, A. Sharakovski, J. Grube and D.L. Griscom, "Sub-band-gap-excited luminescence of localized states in SiO₂ Si and SiO₂ Al glasses", *J. Non-Cryst. Solids.*, vol. 356 pp. 982-986, 2010.
- [26] M. Watanabe, S. Juokazis, H. B. Sun, S. Matsuo and H. Misawa, "Luminescence and defect formation by visible and near-infrared irradiation of vitreous silica", *Phys. Rev. B*, vol. 60, p. 9959, 1998.
- [27] A. Zatsepin, V. S. Kortov and H. J. Fitting, "Short-lived excited states of oxygen-deficient centers in amorphous SiO₂", J. Non-Cryst. Solids., vol. 351 pp. 869-876, 2005.
- [28] P. W. Yu and D. C. Reynolds, "Photoluminescence identification of ~77-meV deep acceptor in GaAs", J. Appl. Phys., vol. 53, p. 1263, 1981.
- [29] M. F. Millea and L. W. Aukerman, "The 1.0- and 1.28-e V Emission from GaAs Diodes", J. Appl. Phys., vol. 37, p. 1788, 1966.

- [30] J. H. Paker, Jr., D. W. Feldman and M. Ashkin, "Raman Scattering by Silicon and Germanium", *Phys. Rev.*, vol. 155, p. 712, 1966.
- [31] P. A. Temple and C. E. Hathaway, "Multiphonon Raman Spectrumof Silicon", *Phys. Rev. B*, vol. 7, p. 3685, 1971.
- [32] G. Irmer, "Local crystal orientation in Ill-V semiconductors: Polarization selective Raman microprobe measurements", *J. Appl. Phys.*, vol. 76, p. 7768, 1994.
- [33] R. Ruppin and R. Englman, "Optical phonons of small crystals", Rep. Prog. Phys.,

vol. 33, pp. 149-196, 1970.

