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Optical properties of Ge nanowires grown on Si(100) and (111) substrates: Nanowire-substrate heterointerfaces

B. V. Kamenev¹, V. Sharma¹, L. Tsybeskov^{*, 1}, and T. I. Kamins²

¹ Department of Electrical and Computer Engineering, New Jersey Institute of Technology, Newark, New Jersey 07102, USA

² Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California 94304, USA

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We report photoluminescence (PL) and Raman scattering (RS) measurements of (111) oriented Ge nanowires (NWs) grown by chemical vapor deposition on (100) and (111) silicon substrates. Our PL measurements strongly suggest that the observed emission originates at low-defect density Ge NW – Si substrate interfaces. Both, PL and RS data indicate that Si–Ge intermixing and strain are more pronounced for the Ge NW – (111) Si interface, while NWs grown on (100) Si substrates are relaxed.

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1 Introduction

Semiconductor nanometer-scale, one-dimensional structures or nanowires (NWs) have attracted much attention due to their interesting physical properties and possible applications in nanoscale electronic and optoelectronic devices [1-7]. Semiconductor NWs by definition are anisotropic nanocrystals with large aspect ratios; their diameters are typically smaller than 100 nm, and their length can be many micrometers. Important issues in the fabrication of these one-dimensional (1D) materials are their crystallographic order and the influence of a substrate. It has been reported that Si and Ge NWs exhibit preferential (111) crystallographic orientation along the growth direction [8–11], similarly to elongated Si nanocrystals fabricated by solid-phase crystallization [12]. Therefore, it is reasonable to expect that the substrate crystallographic orientation plays an important role in the formation of NW-substrate heterointerfaces. Optical measurements including Raman scattering (RS) and photoluminescence (PL) can provide detailed information about these heterointerfaces; properties of such quasi-one-dimensional heterojunctions can be critically important for applications in electronic devices. In this work we present results of RS and PL studies confirming that Ge NWs grown on (100) and (111) single crystal Si substrates have significant differences in the formation of such junctions. We show that Si-Ge intermixing, which so far was mostly ignored because of relatively low (<400 °C) Ge NW growth temperatures, is important in the initial stages of Ge NW growth.

2 Samples and experimental setup

Samples for this work were grown by the vapor-liquid-solid (VLS) technique using chemical vapor deposition of Ge with pre-formed, 20-nm-diameter Au-nanoparticles as the catalyst, as described before [11]. The nanoparticles were deposited from aqueous solution onto cleaned Si substrates with both (100)

^{*} Corresponding author: e-mail: tsybesko@adm.njit.edu





2754

and (111)-4° crystal orientations. After inserting the substrates into the lamp-heated CVD reactor, they were annealed in H₂ for 10 min at approximately 650 °C to remove surface contamination from the nanoparticles and to alloy them with the Si substrates. The temperature was reduced to 320 °C, and GeH₄ was introduced into the H₂ ambient in the process chamber. Deposition times of 9, 18, and 36 minutes were used to form nanowires of different lengths – measured to be 360, 710, and 1400 nm by scanning electron microscopy after nanowire growth. For a given deposition time, the nanowires were simultaneously grown on both substrate orientations to minimize the effect of process variations and allow better comparison of behavior on the two substrate orientations. The samples were cooled in H₂ and then N₂ to <200 °C to minimize oxidation, but the Ge NW surfaces were not otherwise passivated.

For PL excitation we used an Ar⁺ laser with an excitation intensity of $0.1-10 \text{ W/cm}^2$ and an excitation wavelength of 514 nm. The PL signal was dispersed using a single-grating Acton Research 0.5-meter focal-length monochromator, and detected by a liquid-nitrogen cooled InGaAs diode array in the spectral range $0.9-1.6 \mu m$. The measurements were performed in the temperature range 4-300 K. RS spectra were collected at room temperature in a backscattering geometry using different lines of an Ar⁺ laser as an excitation source. The scattered light was analyzed using a JY-1000 one-meter focal-length double monochromator equipped with a thermo-electrically cooled photomultiplier and a photon counting system.

3 Experimental results

Figure 1 shows scanning-electron micrographs of ~40 nm diameter Ge NWs grown on (100) (Fig. 1a)) and (111) (Fig. 1b)) single-crystal Si substrates. In both cases the Ge NW (111) crystallographic growth orientation determines the NW spatial growth direction: Ge NWs on a (100) Si substrate form an angle of ~+/-55° to the Si substrate normal [requires a cautious use of the laser excitation for Raman and PL measurements and an independent check of the sample temperature during photoexcitation. We measured both Stokes and anti-Stokes Raman peaks (not shown) and found that 50–60 mW intensity laser beam does not increase the NW temperature significantly, most likely due to the good thermal conductivity of Ge NWs attached to a c-Si substrate.

Figure 2a) shows the Raman spectrum of Ge NW's grown on a (100) Si substrate. Two Raman peaks are clearly observed. The peak at ~520 cm⁻¹ is related to Si–Si vibrations; it originates from the c-Si substrate and will not be discussed further. The second Raman peak at ~300 cm⁻¹ is related to Ge–Ge vibrations, and its intensity strongly depends on the excitation wavelength with a clear maximum at an excitation wavelength of ~500 nm (Fig. 2b)). For wavelength excitation >500 nm, the Raman spectrum at 300 cm⁻¹ is fully symmetric with a full width at half maximum (FWHM) of ~6 cm⁻¹ (Fig. 3). The narrow Raman peak and its intensity dependence on the excitation wavelength in Ge NWs are similar to



Fig. 1 Scanning electron micrographs of ~40 nm diameter Ge NWs grown on (a) (100) and (b) (111)-4° single-crystal Si substrates.

Original Paper



Fig. 2 (a) Raman spectra from the Ge NW sample grown on a (111) Si substrate with a NW length of 360 nm. The observed Si–Si and Ge–Ge vibrations are shown. The arrow indicates the known position of the Raman peak of Si–Ge vibrations, which are not observed in these measurements. (b) Intensity of Raman signal at $\sim 300 \text{ cm}^{-1}$ as a function of the excitation wavelength. Note the logarithmic scale of the Raman signal intensity.

the Raman data in single crystal Ge structures [14, 15]; they confirm the high crystallinity of the Ge NW core. Using the 458 nm Ar^+ line as an excitation source (and presumably probing more of the NW outer surface due to a shorter penetration depth), we observe that the 300 cm⁻¹ Raman peak becomes asymmetric and almost twice as broad for Ge NWs on (111) Si compared to NWs grown on (100) Si substrates (Fig. 3). The observed asymmetry of the Raman signal near 300 cm⁻¹ with a tail extending down to 250 cm⁻¹ might be associated with presence of the strain, or/and partially disordered Ge at the surface of NWs grown on (111) Si substrates.



Fig. 3 Raman spectra of Ge NWs grown on (a) Si(111) and (b) Si(100) substrates measured under excitation with different wavelengths.

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Fig. 4 Low-temperature PL spectra of c-Si and Ge NWs grown on (100)- and (111)-oriented Si substrates. The NP PL line and PL bands associated with characteristic phonons are shown.

Figure 4 compares low-temperature PL spectra in single-crystal Si and in Ge NWs grown on (100) and (111) substrates. The main PL peak in Ge NWs (presumably the TO-phonon PL band) is slightly red-shifted compared to the PL spectrum of c-Si – by ~20 meV in the Ge NW sample grown on Si(100), and by ~45 meV for Ge NWs grown on a Si(111) substrate. The positions of no-phonon (NP) PL lines (indicated by arrows), as well as TA_{Si} and $TO_{Si} + O(\Gamma)_{Si}$ phonons, are also shown (for Si phonon energies see Ref. [16]). Note that the ~20 meV FWHM of the PL spectrum from the Ge NW sample grown on the (111) Si substrate is almost twice as broad as that for the sample of Ge NWs grown on the (100) substrate. In addition, the PL spectrum of Ge NWs grown on the (111) substrate shows an additional PL feature at 1.074 eV located between the TA_{Si} and TO_{Si} phonon replicas. It is possible that the PL band centered at 1.074 eV is associated with one of the Si–Ge (Ge) phonons [17].

The PL intensities are found to be comparable for Ge NWs grown on (111) and on (100) Si substrates. The PL intensity does not depend on the NW length for either substrate orientation. The PL signal is temperature independent for T < 16 K; it decreases exponentially with increasing temperature, exhibiting a PL thermal-quench activation energy of $E_{PL} \sim 13$ meV (not shown). This activation energy is close to the exciton binding energy in Si-rich SiGe alloys [17]. The polarization dependence of the PL intensity has been measured and found to be insignificant.

4 Discussion

Our data clearly suggest that the observed PL originates at the Ge NW – Si substrate heterointerfaces, and not within the Ge NW volume or the Si substrate. First, the PL main peak is strongly blue shifted compared to the crystalline Ge bandgap and red shifted compared to crystalline Si bandgap. The shift does not result from any realistic value of axial strain (as also indicated by the Raman measurements), and the NWs average diameter of ~40 nm is too large for any significant influence of quantum-confinement effects. We note that similar PL spectra are also found in SiGe nanostructures with Ge content <10% [18]. Second, the PL intensity shows no correlation with the Ge NW length; it is similar for all three NW lengths and both substrate orientations used in this study. Why does the Ge NW volume not show a significant PL signal near the crystalline Ge bandgap? The main reason, most likely, is the known poor properties of germanium–germanium oxide interfaces with high concentrations of non-radiative recombination centers combined with the high NW surface-to-volume ratio. Also, possible incorporation of Au into the Ge NW during VLS growth with Au nanoparticles as catalysts may induce deep energy levels in crystalline Ge. However, our measurements in the IR region (1.5 μ m < λ < 2.5 μ m) do not reveal any measurable PL signal characteristic of deep levels of Au in Ge.

Original Paper

Our Raman measurements do not detect any significant SiGe vibrations at ~400 cm⁻¹ (Fig. 2a)), pointing out that the NW-substrate interface transition region is very thin. At the same time, our PL measurements under the chosen excitation (Fig. 4) do not show any PL from the Si substrate, which at T < 10 K may have quantum efficiency approaching 1%. Therefore, we conclude that the internal quantum efficiency of Ge NW-Si substrate heterointerface is high.

Another significant result is the observed difference in PL spectra between Ge NWs grown on (111) and (100) Si substrates: the PL spectrum from Ge NWs grown on (111) Si substrates is red-shifted and broader compared to the PL spectrum from NWs grown on (100) substrates. This observation indicates that SiGe intermixing near the NW base is more efficient in samples grown on (111) Si substrates even though the growth temperature ($T_G = 320$ °C) is the same for both types of samples. Similarly to PL measurements, our Raman data collected under 458 nm excitation also show that the spectrum of Ge NW on (111) Si is broader compared to Ge NWs on (100) Si (Fig. 3).

The explanation of these results is based on details in the Ge NW VLS growth. At the initial stage of the VLS growth, Ge islands are formed in the region of the Si–Au nanoscale alloy droplets, creating NW bases [7–9]. The 4.2% lattice mismatch between Si and Ge induces strain and SiGe intermixing. However, the growth temperature is rather low, and only limited SiGe intermixing is observed. Since Ge NWs grow along (111) crystallographic directions, their growth on a (111) Si substrate results in the NW direction perpendicular to the substrate surface. The Ge NW core is relaxed due to a limited interaction with the substrate (i.e., small diameter NW base). However, residual strain is detected at the Ge NW outer surface, possibly due to redistribution of the strain field and accumulation of stressed Ge bonds at NW surfaces and possibly due to the native oxide formed on the NW surfaces.

Liquid-phase epitaxy is significantly different on Si(100) and on Si(111) [19], and VLS growth on substrates with different crystallographic orientations should also be different. We think that Ge clusters on (100) Si form (111) facets first [19], and then continuous VLS growth results in (111) Ge NWs inclined to the (100) Si surface (Fig. 1a). Perhaps because of the larger contact area between the inclined (111) Ge nanowire and (100) Si substrate (i.e., Ge NW bases) compared to vertical nanowires, the lattice mismatch is not as easily accommodated, and structural defects (e.g., NW dislocations) are formed. These defects relax the Ge NW structure, reduce Si–Ge strain-induced intermixing at NW bases, and result in narrower PL and Raman spectra in Ge NW – (100) Si compared to Ge NW – (111) Si samples.

5 Conclusion

In conclusion, the Raman and PL spectra presented here highlight differences at the Ge NW–substrate interface for Ge NWs grown on (111) and (100) crystalline Si substrates. These results are especially important for novel devices utilizing such NW-substrate quasi one-dimensional heterojunctions.

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References

- [1] T. Ruecks, K. Kim, E. Joselevich, G. Y. Tseng, C. Cheung, and C. M. Lieber, Science 289, 94 (2000).
- [2] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science 292, 1897 (2001).
- [3] A. M. Morales and C. M. Lieber, Science 279, 208 (1998).
- [4] J. Yu, S. Chung, and J. R. Heath, J. Phys. Chem. B 104, 11864 (2000).
- [5] J. D. Holmes, K. P. Johnston, R. C. Doty, and B. A. Korgel, Science 287, 1471 (2000).
- [6] W. S. Shi, H. Y. Peng, Y. F. Zheng, N. Wang, N. G. Shang, Z. W. Pan, C. S. Lee, and S. T. Lee, Adv. Mater. 12, 1343 (2000).
- [7] T. I. Kamins, R. Stanley Williams, D. P. Basile, T. Hesjedal, and J. S. Harris, J. Appl. Phys. 89, 1008 (2001).



2758

- [8] Y. Wu, H. Yan, and P. Yang, Chem. Eur. J. 8, 1260 (2002).
- [9] Y. Wu, H. Yan, and P. Yang, Top. Catalysis 19, 197 (2002).
- [10] J. Qi, J. M. White, A. M. Belcher, and Y. Masumoto, Chem. Phys. Lett. 372, 763 (2003).
- [11] T. I. Kamins, X. Li, R. Stanley Williams, and X. Liu, Nano Lett. 4, 503 (2004).
- [12] G. F. Grom, D. J. Lockwood, J. P. McCaffrey, H. J. Labbe, P. M. Fauchet, B. White, Jr., J. Diener, D. Kovalev, F. Koch, and L. Tsybeskov, Nature 407, 358 (2000).
- [13] D. Li, Y. Wu, R. Fan, and P. Yang, Appl. Phys. Lett. 83, 3186 (2003).
- [14] P. Y. Yu and M. Cardona, Fundamentals of Semiconductors: Physics and Materials Properties (Springer-Verlag, New York, 2001), p. 617.
- [15] Z. Sui, H. H. Burke, and I. P. Herman, Phys. Rev. B 48, 2162 (1993).
- [16] G. Davies, Phys. Rep. 176, 83 (1989).
- [17] J. Weber and M. I. Alonso, Phys. Rev. B 40, 5683 (1989).
- [18] B. V. Kamenev, L. Tsybeskov, J.-M. Baribeau, and D. J. Lockwood, Appl. Phys. Lett. 84, 1293 (2004).
- [19] T. Füller, M. Konuma, J. Zipprich, and F. Banhart, Appl. Phys. A 69, 597 (1999).

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