

Growth and characterization of short-period silicon isotope superlattices

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Abstract

We report molecular beam epitaxy (MBE) growth of silicon isotope superlattices (SLs) composed of alternating layers of isotopically enriched ^{28}Si and ^{30}Si . In this work, we have prepared short-period $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope SLs, where n is the number of atomic monolayer, with $n = 1, 2, 3, 4,$ and 7 . Zone-folded optical phonon frequencies due to artificial mass periodicity in the growth direction have been observed by Raman spectroscopy. We have used planar bond-charge model to calculate the frequencies. We found that the frequencies of the observed Raman shift agree well with those of optical phonon modes calculated for each SL structure. A detailed analysis revealed that the degree of intermixing between adjacent layers for our condition is approximately two monolayers.

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1. Introduction

Semiconductor isotope superlattices that are composed of alternating layers of different isotopes have attracted much attention recently. They have been realized using Si [1], Ge [2–4], GaAs, GaP and GaSb [5]. For example, naturally available silicon ($^{\text{nat}}\text{Si}$) is composed of three stable isotopes in fixed proportion (^{28}Si : 92.2 at.%, ^{29}Si : 4.7 at.%, ^{30}Si : 3.1 at.%). We have reported the world's first tentative growth and characterization of silicon isotope SLs ($^{28}\text{Si}_n/^{30}\text{Si}_n$ where n is the number of atomic monolayer, each one 0.136 nm thick) with $n = 8, 12,$ and 24 recently and concluded based on Raman characterization of the isotope effect of phonons that there was very few intermixing of Si atoms between the ^{28}Si and ^{30}Si adjacent layers during our MBE growth at 650°C [1].

In this work, we have grown a series of much shorter period $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope SLs and characterized them systematically by Raman spectroscopy, with which structural perfection of isotope SLs can be probed nondestructively. With the isotope SLs, we expect to observe characteristic phonon frequencies

which appear due to confinement longitudinal optical (LO) phonons in specific isotope layers [1–5]. Comparison of such peaks with calculation assuming appropriate number of monolayer (ML) n and degree of interface intermixing l will allow for determination of n and l in each superlattice. It also allows us to test the validity of the standard phonon calculation model. It should be noted that the resolution of other techniques such as secondary ion mass spectrometry (SIMS) is not sufficient to characterize the short-period isotope SLs. We report excellent agreement between experimental Raman peak positions and the calculated ones by planar bond-charge model [6] taking into account intermixing at interfaces between the ^{28}Si and ^{30}Si adjacent layers.

2. Calculation of LO phonons in isotope SLs

We calculated phonon frequencies in the $\langle 100 \rangle$ growth direction of the $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope SLs by planar bond-charge model [6], which has been widely used to calculate phonon dispersion in isotope SLs [1–5]. We assumed that the force constants between ^{28}Si – ^{28}Si , ^{28}Si – ^{30}Si and ^{30}Si – ^{30}Si are the same because the isotope effect on the spring constant is negligibly small in the present case. The force constant parameters are the same as the ones given for bulk Si in Ref. [6]. LO phonon frequencies at Γ -point ($k \sim 0$) in the phonon dispersion can be detected by Raman spectroscopy.

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It is possible to induce intermixing between ^{28}Si and ^{30}Si adjacent layers during the growth. Therefore, it is necessary to consider imperfect interfaces between the adjacent layers in calculation. We introduced here a parameter l as a degree of intermixing in SLs defined by [3]

$$M(z) = \frac{m_1 + m_2}{2} + \sum_{k=0}^{2p} \frac{M_{k+1} - M_k}{2} \text{erf}\left(\frac{z - d_k}{2l}\right) \quad (1)$$

where z is the position in the growth direction, $m_1=28.0$ and $m_2=30.0$ are masses of isotopes, M_k is the average mass of the k th layer assuming ideal profile, p is the number of periods, and d_k is the position of the interface. In the calculation of the phonon dispersion in the SL structures, average mass distribution along the growth direction is important to solve the dynamical matrix. The depth profile shown in Eq. (1) is similar to a convolution of ideal depth profile with a Gaussian shape. We can characterize the degree of intermixing in SLs by the planar bond-charge model assuming mass distribution with Eq. (1).

3. Experimental details

We have grown five short-period $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope SLs with $n=1, 2, 3, 4,$ and 7 by solid-source MBE system equipped with an electron beam evaporator for growing $^{\text{nat}}\text{Si}$ buffer layers and Knudsen cells for growing isotopically enriched ^{28}Si and ^{30}Si layers. The isotopic enrichments of the ^{28}Si and ^{30}Si are 99.92% and 99.3%, respectively [7]. The $^{\text{nat}}\text{Si}$ buffer layer of 100–200 nm was grown on $^{\text{nat}}\text{Si}$ (001) substrates at 650 °C prior to the growth of isotope SL. The growth rate of silicon isotopes is ~ 0.1 nm/min. Total thicknesses of SLs are ~ 100 nm as shown in Fig. 1. Raman spectra of the isotope SLs were recorded in the backscattering geometry at $T \sim 8$ K using Ar^+ 514.5-nm line.

4. Results and discussion

The measured Raman spectra of $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope SLs with $n=1, 2, 3, 4, 7,$ and 8 are shown in Fig. 2. We can observe some small peaks of the confined LO phonons due to the artificial mass periodicity in $^{28}\text{Si}_n/^{30}\text{Si}_n$ SLs appear clearly on

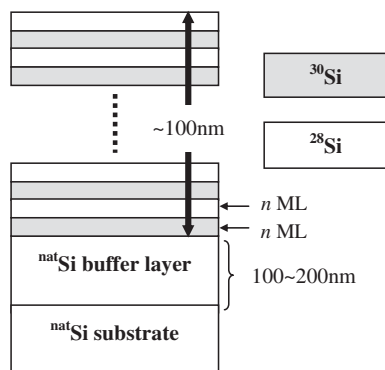


Fig. 1. Schematic illustration of $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope superlattices structure grown in the $\langle 100 \rangle$ direction.

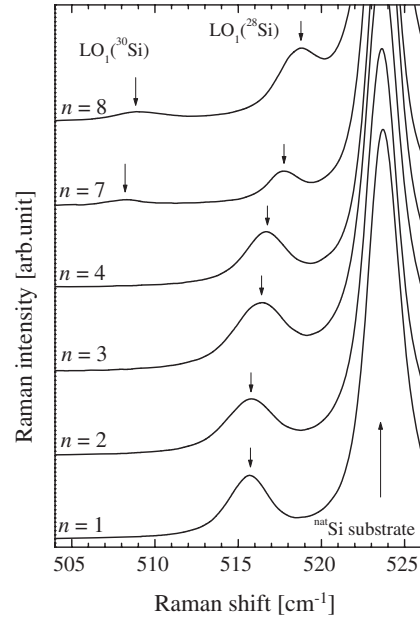


Fig. 2. Raman spectra of $^{28}\text{Si}_n/^{30}\text{Si}_n$ SLs with $n=1, 2, 3, 4, 7,$ and 8 recorded in the backscattering geometry at $T \sim 8$ K using Ar^+ 514.5-nm line.

the left side of the large $^{\text{nat}}\text{Si}$ substrate LO peak 523.5 cm^{-1} . Two LO phonon peaks, $\text{LO}_1(^{28}\text{Si})$ and $\text{LO}_1(^{30}\text{Si})$, in the $n=7$ and 8 samples are observed. The $\text{LO}_1(^{28}\text{Si})$ peak position shifts to lower frequency as n decreases. $\text{LO}_1(^{30}\text{Si})$ peak disappears for n smaller than 4 samples. Due to the mass periodicity of ^{28}Si and ^{30}Si in the growth direction, the highest energy vibrational modes are confined in ^{28}Si layers because ^{28}Si is lighter than ^{30}Si . Their frequencies are very sensitive to the periodicity and intermixing. We can theoretically calculate the frequencies of ^{28}Si localized phonons as a function of the periodicity and degree of intermixing using planar bond-charge model. The comparison between calculation and experiment is shown in Fig. 3. This figure shows the wavenumbers (Raman

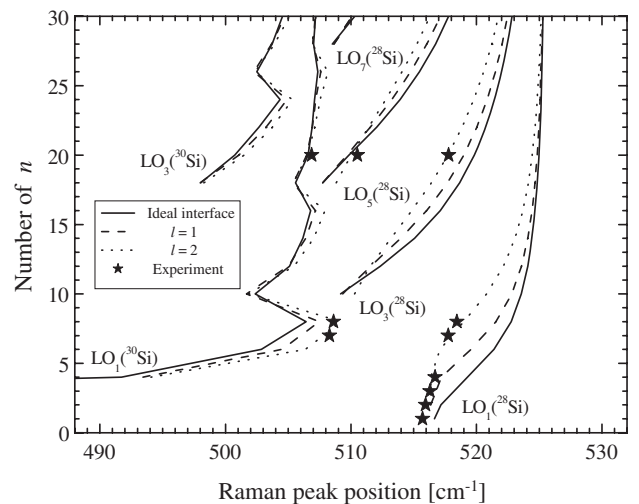


Fig. 3. Theoretical Raman peak shifts as a function of n calculated by planar bond-charge model assuming no intermixing (solid curves), $l=1$ intermixing (broken curves), and $l=2$ intermixing (dotted curves). Calculated curves were shifted by 7 cm^{-1} to lower wavenumber as was done in Ref. [1]. Experimental results (stars) agree with the theory assuming $l=2$.

shift) of SLs modes predicted by the calculation assuming no intermixing ($l \sim 0$) of Si atoms between the adjacent ^{28}Si and ^{30}Si layers (solid curves), about one layer of intermixing $l=1$ (broken curves), and two layers of intermixing $l=2$ (dotted curves). The calculated peak positions are shifted approximately 7 cm^{-1} to lower frequencies to fit the experiment as was done in Ref. [1]. We find in Fig. 3 excellent agreement between experimental Raman peak positions (stars) all the way down to $n=1$ SLs and the calculated ones by planar bond-charge model with $l=2$, taking into account intermixing at the interface between the ^{28}Si and ^{30}Si adjacent layers.

The source of intermixing can be (i) imperfect shutter open–close timing control and/or (ii) anomalously fast diffusion of Si across the interface. The shutter should terminate the growth when the layer is filled completely by one type of isotope. However, such precise shutter control is not possible so that one layer of intermixing is unavoidable. Atomic-scale roughening of the surface also contributes to the intermixing, though our AFM images show very flat growth of less than 1 ML disorder. At the growth temperature of $650 \text{ }^\circ\text{C}$, the expected self-diffusion coefficient of Si (D_{Si}) is $6.3 \times 10^{-24} \text{ cm}^2/\text{s}$ [8]. With our typical growth rate, the total growth time is approximately 20 h. With these numbers, we obtain the diffusion length $2\sqrt{D_{\text{Si}}t} \sim 0.01 \text{ nm}$, where t is growth time. Therefore, a much faster diffusion mechanism is needed to explain the intermixing of 2 MLs. At this point, we see no evidence for such an unusual diffusion. Finally, we should note that Raman measurement using Ar^+ 514.5-nm probes the sample area of a few micrometers and the depth $0.77 \text{ }\mu\text{m}$ [9]. Therefore, any fluctuation of the layer thickness will contribute to the Raman peak positions and widths obtained as an average. Further studies are necessary to understand these details.

5. Summary

We have successfully grown short-period $^{28}\text{Si}_n/^{30}\text{Si}_n$ isotope SLs with $n=1, 2, 3, 4,$ and 7 by MBE. We have performed

Raman spectroscopy analysis to observe the confined LO phonon frequencies in the SLs due to artificial mass periodicity in the growth direction as a function of layer thickness, n . Consequently, the Raman peak positions of each SL agree well with the theoretical calculation. We have investigated the degree of intermixing in SLs by planar bond-charge model assuming average mass distribution with the error function. We obtained excellent agreement with theory, with $l=2$ intermixing parameter.

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