PHYSICAL REVIEW B, VOLUME 63, 161304(R)

Coherent confined LO phonons in $^{70}Ge/^{74}Ge$ isotope superlattices generated by ultrafast laser pulses

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(Received 28 July 2000; revised manuscript received 16 January 2001; published 5 April 2001)

Generation of high-order coherent confined LO phonon modes by 20-fs ultrashort laser pulse irradiation was observed in a new class of nonpolar semiconductors; $^{70}Ge/^{74}Ge$ isotope superlattices. The phonon oscillations were Fourier transformed and compared with a theoretical calculation based on a planar force-constant model and a bond polarizability approach. The comparison between the calculated and Fourier transformed spectra shows clearly that the amplitudes of coherent phonons are determined solely by the degree of the atomic displacement and that only the Raman active odd-number-order modes are observable. The spectra taken with variety of polarization of pump beam show clearly that the generation mechanism of coherent phonons in nonpolar semiconductor like Ge is stimulated Raman scattering.

DOI: 10.1103/PhysRevB.63.161304 PACS number(s): 63.22.+m, 78.47.+p, 78.66.−w

The dynamics of coherent phonons generated by ultrashort laser pulses has attracted much attention because propagation and localization of phonons can be observed directly in the time domain. Active discussions continue on the details of generation and detection mechanisms of coherent phonons with laser pump and probe beams, respectively.[1–3] The pioneering work on polar semiconductors such as GaAs and GaAs/AlAs superlattices (SL's) by Kurz and his colleagues suggests that carriers, photogenerated by the pump-pulse, play an important role,[1] and that the generation is mediated by the combination of the Raman process,[4] and other non-Raman processes such as the one occurring only in polar semiconductors via rapid surface field screening.[5] The investigation involving SL's such as GaAs/AlAs is especially interesting since the number of accessible coherent phonons increases with respect to that in bulk due to superlattice effects, i.e., zone folding of the phonon dispersion. Moreover, SL's are better suited than bulk crystals for the investigation of the dynamics since the coherent phonons can either propagate or remain confined in specific layers. A two-color pump-probe experiment performed by the present group on GaAs/AlAs SL's has shown that the wave-vector conservation holds only for the probe beam but not for the pump beam, i.e., the Raman process is clearly important for the probing of coherent phonons as well.[6]

The investigation of the dynamics of coherent longitudinal optical (LO) phonons confined to constituent layers of a SL is an interesting subject from the viewpoint of comparison between the propagation of folded longitudinal acoustic (FLA), longitudinal acoustic (LA), and localized LO phonons. With regard to the coherent confined LO phonons, a GaAs-like mode has been observed in GaAs/AlAs SL's (Ref. 7) and coherent LO phonons screened by interwell plasmon oscillations have been observed in GaAs/AlGaAs SL's.[8] But higher-order coherent LO phonon modes have not been observed in any superlattice. If the generation and/or detection mechanisms of localized coherent LO phonons are indeed governed by the Raman process, the higher-order confined LO modes are allowed by Raman process and should be observed. However, there is an experimental difficulty in verifying this prediction when examining GaAs/AlAs SL's with a conventional excitation source such as a Ti:sapphire laser at ~800 nm. GaAs/AlAs SL's with thin well layers are almost transparent at low temperatures to this near-IR light, thus the substantial photocarrier generation needed for coherent phonon generation does not occur.

In this work we have employed $^{70}Ge/^{74}Ge$ isotope superlattices (Ge I-SL's) for investigating the generation and detection mechanism of higher-order coherent confined LO phonons. Ge I-SL's are best suited for such studies for the following reasons. The electronic properties of Ge I-SL's are practically the same as those of a bulk crystal with the natural isotope abundance, because the constituent layers have the direct transition energies at the gamma point (~0.9 eV at

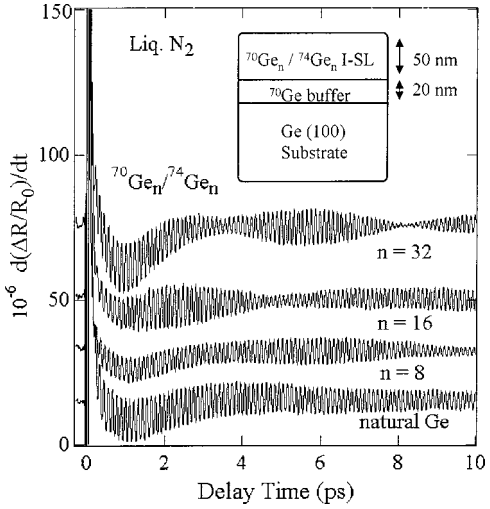

FIG. 1. Oscillatory component of the time-domain signals in $^{70}Ge_n/^{74}Ge_n$ isotope superlattices with various layer thicknesses and in natural Ge. Inset shows the structure of $^{70}Ge_n/^{74}Ge_n$ isotope superlattices ($n=8$, 16, and 32: the number of monolayers).

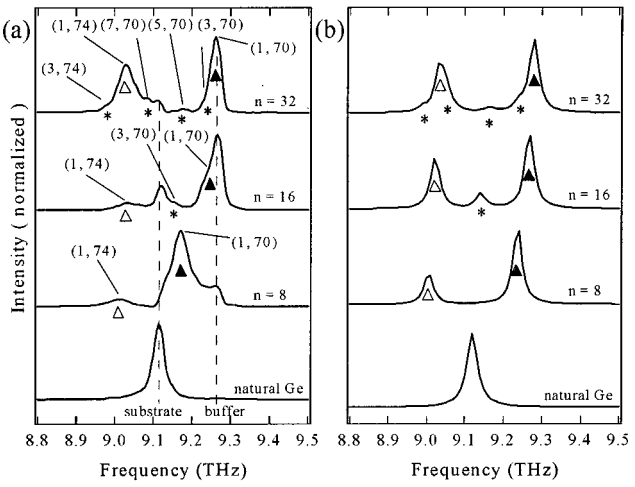

FIG. 2. (a) Fourier transformed spectra of the time-domain signals shown in Fig. 1, and (b) calculated spectra. (m,70) or (m,74) means mth order confined mode in ^{70}Ge or ^{74}Ge layers, respectively. Vertical dashed lines in (a) denote LO phonon frequencies in the bulk ^{70}Ge buffer layers and in the natural Ge substrate. Asterisks, and filled and open triangles denote confined LO phonon modes.

1.5 K: Γ_8-Γ_7),[9] well below the excitation energy ($\sim$1.5 eV). This condition allows for the uniform photogeneration of carriers throughout the Ge I-SL's having different isotopic layers. The vibrational properties, on the other hand, are modulated due to the periodicity of the different isotopic layers. In contrast to the widely investigated GaAs/AlAs SL's, the Ge I-SL's are nonpolar semiconductors that allow investigations of phonons in purely covalent, diamond-crystal structures. This article reports the observation of higher-order coherent confined LO phonons in semiconductor SL's. A pump-probe technique using ultrashort laser pulses was used. We achieved a resolution better than 1 cm^{-1}, sufficiently high to resolve such phonon modes. It is shown that the observed modes are limited to those of Raman active, odd-number order. Variation of the frequency and intensity of the confined LO modes with the constituent layer thickness and with the polarization of the excitation and detection beams has been studied in detail. Fourier-transformed spectra of the coherent confined LO phonon oscillations have been compared with a theoretical calculation based on a planar force-constant model and a bond polarizability approach. All of our findings are consistent with previous proposals for nonpolar semiconductors like Ge,[10,11] i.e., the deformation mechanism contributes to the generation and detection of coherent phonons as in the observation of optical phonons by Raman scattering.

The $(^{70}Ge)_n/(^{74}Ge)_n$ I-SL's were grown by molecular-beam epitaxy (MBE) at 600 °C. Here, n (= 8, 16, 32) is the number of monolayers in the constituent layer where one monolayer of Ge has the thickness of 0.141 nm. As shown in the inset of Fig. 1, the Ge I-SL's were grown on high purity Ge (100) wafers of natural isotopic composition (abbreviated hereafter as natural Ge) with ^{70}Ge buffer layers of 20 nm thickness in-between. The total thickness of each Ge I-SL's was fixed to 50 nm, i.e., the total number of periods of each SL changed with n. The expected phonon confinement was confirmed for all the samples using Raman spectroscopy.[12] A reflection-type pump-probe measurement was performed at liquid N_2 temperature by using a mode-locked Ti:sapphire laser delivering 20-fs pulses at $\sim$820 nm (1.51 eV). The power of the pump and probe beams was adjusted to 200 and 10 mW, respectively. The delay time of the probe beam was adjusted by a variable optical delay line. The optical path of the pump beam was modulated by a shaker. The time derivative of the reflectivity change, $\partial(\Delta R/R_0)/\partial t$, was recorded in order to highlight the oscillatory component.

Traces in Fig. 1 show the time-derivative signals of reflectivity changes in Ge-I-SL's at liquid N_2 temperature. The result for natural Ge is also shown for comparison at the bottom. The beatings, which are observed for all the samples except for the natural Ge, indicate that there are multiple phonon modes in each I-SL sample. The period of beating becomes shorter as n increases. A Fourier transformation of the time-domain signals is shown in Fig. 2(a). The pump pulse has a penetration depth of about 200 nm,[13] therefore, it excites not only the SL layers but also the buffer ^{70}Ge layers and the natural Ge substrates. Phonon peaks for bulk ^{70}Ge at 9.26 THz and for natural Ge at 9.12 THz appear clearly for all SL's due to this penetration effect. The assignment of the peaks marked by asterisks, filled triangles, and open triangles will be determined based on the comparison with a theory which we discuss in the following paragraph.

The theoretical spectrum was calculated in the framework of a planar force-constant model and a bond polarizability approach:[14,15] First, we calculated the vibrational frequencies and atomic displacement patterns of the phonon modes at the center of the Brillouin zone ($k=0$) with the planar force-constant model. Then, we calculated the spectra from the atomic displacement patterns using the bond polarizability model. The force constants[15] were obtained from the phonon dispersion curves for natural Ge as determined by neutron

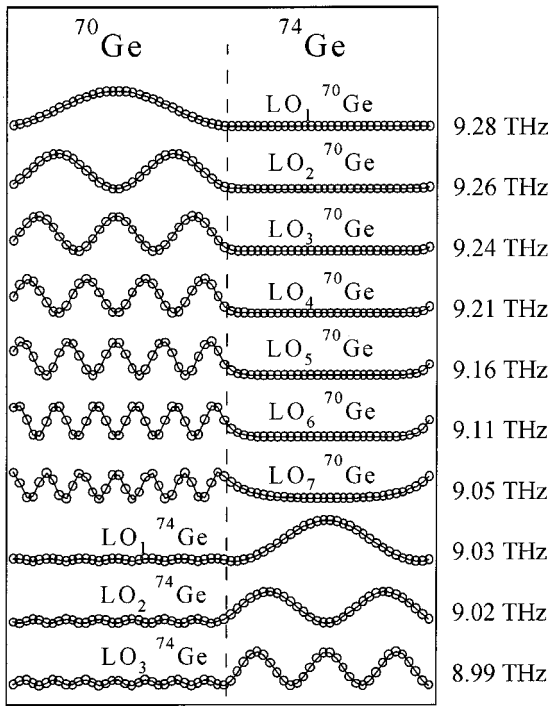

FIG. 3. Calculated squared displacement patterns of LO phonons in $^{70}Ge_{32}/^{74}Ge_{32}$ I-SL. LO_m ^{70}Ge or LO_m ^{74}Ge means mth order confined mode in ^{70}Ge or ^{74}Ge layers, respectively. The phonon frequencies at $k=0$ are indicated.

scattering.[16] Diagonalization of the dynamical matrix allowed us to obtain the vibrational frequencies and their corresponding eigenvectors (atomic displacement patterns). The spectral intensity for $(^{70}Ge)_n/(^{74}Ge)_n$ SL's in the framework of the bond polarizability approach is given by[17]

$$I_{\mathrm{LO}} \propto \{\alpha[u_1-u_2+u_3-\cdots+(-1)^{n-1}u_n+(-1)^n\nu_1 +(-1)^{n+1}\nu_2+\cdots+(-1)^{2n-1}\nu_n]\}^2, \quad (1)$$

where u_i (ν_i) is the atomic displacement of the ith monolayer of ^{70}Ge (^{74}Ge). α is the bond polarizability which is a constant for nonpolar semiconductors like Ge. Thus, unlike the case of polar semiconductors, the spectral intensity is simplified significantly and determined solely by the magnitude of atomic displacement. Figure 3 shows the calculated squared displacement patterns for LO phonon modes of various frequencies. Note here that the longitudinal displacement is shown as a transverse vibration for clarity and that, since the displacements are squared, optical vibrations are depicted as in-phase acoustic vibrations. Figure 3 shows clearly that all the optical phonon modes are confined in either the ^{70}Ge or the ^{74}Ge layers.

The resulting calculated spectra shown in Fig. 2(b) reproduce very well the observed characteristics shown in Fig. 2(a). An assignment (3, 70) in Fig. 2 corresponds to the third-order confined mode in the ^{70}Ge layers. As n is increased, the intensity of the first-order confined mode in the ^{74}Ge layers [(1, 74), open triangle] is enhanced relative to the one confined in the ^{70}Ge layers [(1, 70), filled triangle]. The mode (1, 70) shifts to the higher frequency as n increases. Higher-order modes confined in ^{70}Ge layers [(5,70), (3,70), asterisk] are also observed clearly for the $n=16$ and 32 samples at frequencies between the first-order modes (1, 70) and (1, 74). Such overall agreement between the calculated and experimental spectra supports the suggestion that the amplitude of coherent phonons in Ge I-SL's is determined solely by the displacement of Ge atoms in the constituent layers as expressed by Eq. (1).

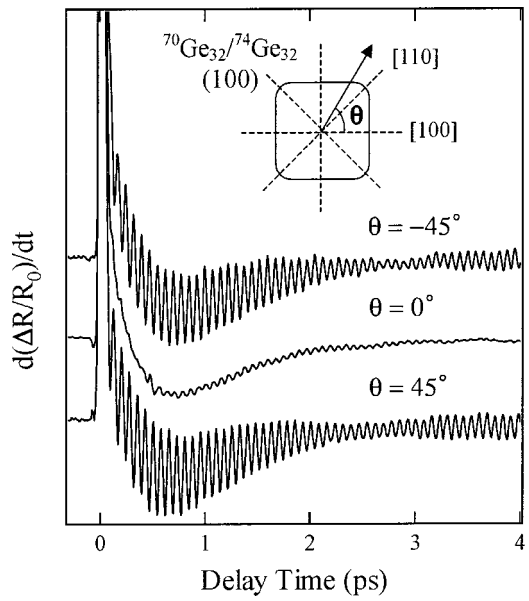

FIG. 4. Polarization dependence of pump beam of the oscillation in $^{70}Ge_{32}/^{74}Ge_{32}$ I-SL. Inset shows the parameter θ is the angle between pump polarization and [100] crystal axis. The polarization of the probe beam is fixed at [110].

It is important to point out that the order of all the confined modes observed in Fig. 2 is odd, i.e., only the Raman-active modes are detected. In fact, the spectra resemble very much the Raman spectra obtained for exactly the same[12] and similar series of Ge I-SL's.[17,18] In order to demonstrate that Raman processes are responsible both for the generation and for the detection of coherent phonons in Ge, we have performed pump-probe measurements for various combinations of polarizations of the excitation and detection beams. Figure 4 shows the polarization dependence of the pump beam in $^{70}Ge_{32}/^{74}Ge_{32}$ I-SL. The angle of the polarization of the pump (and probe) beam with respect to the [100] crystal axis is θ (and ϕ), respectively. The polarization of the probe beam is fixed at [110], $\phi=45°$. For $\theta=45°,-45°$, i.e., when the pump field is parallel to [110] and $[1\bar{1}0]$, respectively, the oscillations are observed clearly. For $\theta=0°$ and 90°, i.e., for polarization along [100] and [010], the oscillations disappear. A phase change of π occurs on the oscillations by rotating the pump beam from $\theta=45°$ to $-45°$. The polarization dependence of the pump beam shows a $\sin^2(2\theta)$ dependence on the intensity of the phonon. Furthermore, we measured the polarization dependence of probe beam. At the fixed pump beam $\theta=45°$, the polarization dependence of the probe beam shows a $\sin^2(2\phi)$ dependence on the intensity of the phonon. A phase change of π occurs on the oscillations by rotating the probe beam from $\phi=45°$ to $-45°$. These re-

sults agree very well with the selection rule of Raman process[3] and support previous measurements on bulk Ge performed by Pfeifer *et al.*[11] It has been proposed that the coherent phonon generation in Ge is mediated by the anisotropy of the hole distribution related to the anisotropy of the interband dipole matrix.[10] In this case the selection rules for the polarization of both the pump and probe beams obey that of Raman process.

In order to distinguish between propagating and localized phonons, we have looked for spectral peaks arising from propagating FLA phonons in Ge I-SL's. However, neither the pump-probe nor Raman scattering measurements showed any signatures of such FLA phonons. Although the atomic displacement of the FLA phonons is larger than that of confined LO phonons, the mass difference between the two Ge isotopes might be too small for an effective modulation of the photoelastic constants resulting in the Raman intensities of FLA phonons which would be too weak for detection.[19]

In summary, we have observed coherent higher-order confined LO phonon oscillations in ^{70}Ge/^{74}Ge isotope superlattices with a pump-probe technique using ultrashort laser pulses. Our experiments have demonstrated that the coherent LO phonons confined in the constituent layers are of odd integers. The Fourier-transformed spectra of the time-domain signal agree well with a calculation based on a planar force-constant model and the bond polarizability approach. The agreement between the observed and calculated spectra demonstrates that the relative amplitudes of the coherent confined LO mode are determined solely by the atomic displacement of Ge atoms in the constituent layers. The observed phonons were limited to Raman-active modes, demonstrating that the generation and detection mechanisms of the coherent confined LO phonons in Ge I-SL's are governed by the Raman process.

K.M. acknowledges support from a Grant-in-Aid for the Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. E.E.H. acknowledges support from US NSF Grant No. DMR 97 32707.

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