Coherent Phonons At A Semiconductor Surface

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Abstract. Coherent surface phonon at a GaAs(100)-c(8×2)-Ga reconstructed surface has been investigated by time resolved second harmonic generation (TRSHG). The phonon mode is impulsively excited by an ultrashort laser pulse and subsequent coherent nuclear motion is monitored through the intensity modulation of the second harmonics of a probe pulse. Oscillatory traces are clearly observed in TRSHG signals and their Fourier transformation show two components, bulk LO-phonon at 8.8 THz and the surface phonon at 6.0-8.6 THz. The frequency of the surface phonon shows red shift as the pumping power increases. The shifts are indicative of a marked electron phonon interaction or anharmonicity of the surface phonon modes.

INTRODUCTION

Laser pulses with the duration sufficiently shorter than the period of a vibrational mode allow us to excite the mode with a high degree of spatial and temporal coherence and to follow the nuclear motion directly in the time domain. In contrast to a number of works on coherent bulk phonon excitation reported [1], studies on the excitation of coherent phonons or vibrations at surfaces are scarce. Recently, Chang et al. have shown that time resolved second harmonic generation (TRSHG) is a powerful method to probe surface coherent phonons [2-4]. In this work, we focus on TRSHG on a GaAs(100)-c(8×2)-Ga surface, and describe new features in TRSHG traces of this surface that has not been reported in the previous works [2-4].

EXPERIMENT

The experiment was performed with a UHV chamber evacuated to a base pressure better than 3.0 x 10^{-10} Torr by cascaded turbo-molecular pumps. It is equipped with a retractable LEED and a retractable cylindrical mirror analyzer for Auger electron spectroscopy (AES). A GaAs(100) sample (n-type, Si doped, 1-5 x 10^{18} cm^{-3}) was held by a Ta foil welded to Ta wires. It could be heated up to 1000 K by resistive heating of the Ta wires, and could be cooled down to 110 K by liquid nitrogen. Sample was cleaned by cycles of Ar⁺ sputtering (1μA, 500 V) and annealing. The surface condition was checked by LEED and AES. A GaAs(100)-c(8×2)-Ga
reconstructed surface was obtained by annealing the sputtered surface to higher than 900 K.

We used a chirped-mirror-compensated femtosecond Ti:sapphire laser (Femtosource, Femto-pro, 800 nm, 12 fs, 75 MHz, 800 mW) as a light source. The output laser beam was passed through a prism pair for compensating further chirping by optical components mounted between the laser and the sample. A part (30%) of the output beam was used as a probe beam, and the rest was passed through a variable neutral density filter and used as a pump beam. The time delay $t$ between the pump and the probe pulses was controlled by a computer-controlled mechanical mirror stage. The pump and the probe beams were introduced in the chamber through a window of a 1mm-thick quartz plane plate. Then both of the beams were focused onto the sample surface by a quartz lens of the 100-mm focal length held in the chamber.

The incidence angles of the two beams onto the sample surface were $\sim 70^\circ$. The electric vectors of the beams were in the incidence plane ($p$-polarization) parallel with the [0-11] direction. The $p$-polarized component of the second harmonics (SH) of the probe beam generated on the sample surface was passed through a band pass filter to reject the fundamental light and detected by a photomultiplier thermoelectric-cooled down to $-30^\circ$ C. The output signal of the photomultiplier was amplified by a current pre-amplifier and fed into a lock-in amplifier synchronized with an optical chopper that was inserted in the optical path of the pump beam. The sample temperature was kept at 180 K during the measurements.

RESULTS

FIGURE 1(a) shows a typical TRSHG trace obtained on the GaAs(100)-c(8×2)-Ga surface. A clear oscillatory component is superimposed on the background component with a rapid rise and a slow decay. The derivative of the curve in FIGURE 1(a) is plotted in FIGURE 1(b) after subtracting low frequency ($<3$THz) components. While a large amplitude oscillation component appears immediately after the excitation pulse almost decays within $t < 1$ ps, a small oscillation component is persistent in $t > 1$ ps.

Power spectra are obtained by Fourier transformation of the derivative curve in FIGURE 1(b). Here we plot the power in two different time domains: one in the range from 70 fs to 5.8 ps in FIGURE 2(a) and the other from 1.0 ps to 5.8 ps in FIGURE 2(b). Two peaks at 8.9 THz and 8.4 THz are prominent and a sharp dip at 8.7 THz appears in FIGURE 2(a). On the other hand, the power spectrum of a longer delay times after the rapid damping of the initial large oscillation (FIGURE 2(b)) shows only one peak at 8.8 THz. The frequency of a bulk LO-phonon was reported to be 8.8 THz by time-resolved linear reflectivity measurements of GaAs [5]. Chang et al. have also observed the bulk LO-phonon peak at 8.8 THz in the TRSHG measurements, in addition to the four surface phonon modes in the region of 6.2–8.2 THz [4].

We simulated the observed oscillatory traces, $D(t)$, with a linear combination of two underdamped modes, as in eq (1).

$$D(t) = A_1 \sin(\omega_1 t + \phi_1) \exp(-t/\tau_1) + A_2 \sin(\omega_2 t + \phi_2) \exp(-t/\tau_2)$$  \hspace{1cm} (1)
A typical TRSHG trace taken from a GaAs (100)-c(8×2) surface. The pump power was 140 mW, and the SH signal with p-polarization was detected. The incidence plane was parallel to [0-11] direction. (b) Dotted curve: A derivative curve of the trace (a). Solid curve: a simulation curve with two components \( \alpha \) and \( \beta \) in eq. (2). See text for the parameters employed in the simulation.

A simulated curve (solid curve) is superimposed on the measured data in FIGURE 1(b). The employed parameters are as follows: \( \omega_1 = 8.67 \text{ THz} \), \( \tau_1 = 3 \text{ ps} \), \( \phi_1 = -12^\circ \), \( \omega_2 = 8.52 \text{ THz} \), \( \tau_2 = 0.22 \text{ ps} \), \( \phi_2 = -128^\circ \), and \( A_1:A_2 = 1:23 \). The power spectrum of the simulated curve is also plotted in FIGURE 2(a). It is obvious that the essential features of the oscillatory curve measured by TRSHG are well represented by a linear combination of the two underdamped oscillators. Hereafter we denote the first one as the \( \alpha \) component that has a decay time of about 3 ps and a center frequency at 8.7 THz, and the second one as the \( \beta \) component that has a decay time of 220 fs and a center frequency at about 8.5 THz.

Note that the initial phase of the \( \alpha \) components \( \phi_1 \) is shifted relatively from that of the \( \beta \) component \( \phi_2 \) by about 120°. The relative phase shift is crucial to obtain the satisfactory simulation of the waveform. The asymmetric spectral shape and the slight frequency shift of the peak at 8.9 THz and a dip at 8.7 THz in FIGURE 2(a) are due to the interference between the \( \alpha \) and the \( \beta \) components. The \( \beta \) component has a center frequency lower than that of the \( \alpha \) component, and possesses much shorter decay times (200-400 fs). The \( \beta \) component is reduced by surface sputtering and recovers its intensity by annealing.

FIGURE 3 shows the excitation power dependence of the power spectra. At the lowest pump power of 70 mW, two peaks appear at 8.6 THz and 8.9 THz, and as the pump power is increased, the lower frequency peak increases in its relative intensity and are shifted to red. All the waveforms under the three different pump power conditions could be reproduced qualitatively by a linear combination of two underdamped oscillators, eq. (1). The power spectra of these simulated curves are also shown in FIGURE 3. The parameters used for the simulations are listed in TABLE I.
FIGURE 2. The power spectra obtained from the Fourier transformations of the TRSHG traces in FIGURE 1(b). (a) The transformation is performed for the data in the range from 70 fs to 5.8 ps of the measured (thick curve) and the simulated (thin curve) traces. (b) The power spectrum obtained from the experimental data in FIGURE 1(b) in the range from 1.0 ps to 5.8 ps.

FIGURE 3. The pump power dependence of the Fourier power spectra of TRSHG traces. Thick curves represent the results taken from the surface with 3 hours annealing after the Ar$^+$ sputtering. The pump power for each curve is (a) 70 mW, (b) 140 mW, and (c) 210 mW, respectively. Thin curves represent the results simulated by the two components analysis with eq. (1). The used parameters for the components $\alpha$ and $\beta$ are tabulated in TABLE I.
**TABLE 1. Parameters Used For The Simulation In FIGURE 3.**

<table>
<thead>
<tr>
<th>Pump power (mW)</th>
<th>Center Frequency (THz)</th>
<th>Decay Time (ps)</th>
<th>Center Frequency (THz)</th>
<th>Decay Time (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>8.80</td>
<td>2.8</td>
<td>8.65</td>
<td>0.40</td>
</tr>
<tr>
<td>140</td>
<td>8.67</td>
<td>3.0</td>
<td>8.52</td>
<td>0.22</td>
</tr>
<tr>
<td>210</td>
<td>8.66</td>
<td>2.3</td>
<td>8.34</td>
<td>0.24</td>
</tr>
</tbody>
</table>

In the simulated curves, the \( \alpha \) component is always with a decay time of 2-3 ps and with a center frequency of 8.7-8.8 THz. Differences of the initial phases of the \( \alpha \) and \( \beta \) components are 69°, 116°, and 103° for pump power of 70, 140, and 210 mW, respectively, and these phase differences give a dip at 8.7 THz in each spectrum.

**DISCUSSION**

**Origins Of The Oscillatory Components**

The observed features of the oscillatory signals apparent in the TRSHG traces are summarized as follows. The oscillatory parts are decomposed into two underdamped modes: the components \( \alpha \) and \( \beta \). The \( \alpha \) component has a frequency of 8.7-8.8 THz and a decay time of 2-3 ps, and appears irrespective of the surface sputtering and annealing, and the pump power. Thus, this component is assigned to the bulk LO-phonon mode. On the other hand, the \( \beta \) component is very sensitive to long-range regularity of the surface. In addition, the \( \beta \) component changes its frequency and the width (decay time) as a function of the pump power.

There are some candidates for the origin of the \( \beta \) component: surface phonon, and the bulk plasmon–bulk phonon coupled mode [2-4,6-8]. Since the intensity of the \( \beta \) component is strongly reduced by surface sputtering, the bulk mode cannot be the origin of the signal. Thus, this is due to surface phonon modes localized in a few atomic layers near the surface.

Here we discuss the initial phases of the observed modes. We observed the surface phonon components exhibit different initial phases from that of the bulk LO-phonon component. The initial phase of a coherent phonon oscillation depends on its excitation mechanism [9]. Mechanisms for coherent optical phonon excitation are categorized as either a Raman or a non-Raman process. In the Raman process, the initial phase of coherent nuclear motion depends on the detuning of laser photon energy from the resonant energy for an electronic transition. It is claimed that the driving force is purely displacive for \(|\omega_R-\omega_0| \ll \delta_k\), but impulsive for \(|\omega_R-\omega_0| \gg \delta_k\), where \(\omega_R\) is the resonance frequency of the electronic transition, \(\omega_0\) is the excitation laser frequency, and \(\delta_k\) is the width of the resonance [9]. Thus, in the former case, coherent nuclear motion is described as \(\cos(\omega t)\), while in the latter case, it is described as \(\sin(\omega t)\).

On the other hand, some non-Raman processes have been proposed to explain coherent phonon excitation in opaque solids [1,10]. One of the most prominent models
is denoted as Displacive Excitation of Coherent Phonons (DECP), which is based on interband excitation from bonding to antibonding states. Since the lattice equilibrium position changes abruptly by the excitation, the coherent amplitude is modulated as \( \cos(\omega t) \). As for the space charge layer in semiconductors, another non-Raman mechanism for coherent bulk LO-phonon generation is well accepted, which is based on the ultrafast screening of a depletion field by photocarriers [11]. The initial phase of the nuclear motion induced by this mechanism is similar to that of DECP.

Following the discussion given in ref. 11, the ultrafast screening of the depletion field at the GaAs(100)-c(8×2) surface is expected to be a dominant mechanism for driving the coherent bulk LO-phonon. On the other hand, the phase difference between the \( \alpha \) and the \( \beta \) components clearly indicates that the excitation mechanism of the surface component is different from that of the bulk phonon. In fact, Chang et al. have claimed that the surface phonon components are generated via the Raman process [2], since the relative contributions of the surface phonon modes depend on the pump polarization and the crystal azimuth angle in the light incidence plane.

### Excitation Power Dependence

In the above discussion, the \( \beta \) component is ascribed to the surface phonons confined in a few atomic layers. Here, we focus on the frequency shift of the \( \beta \) component as a function of the pump power. There are two possible origins for the frequency shift: (1) the softening of the bonds at the surface owing to excitation of the surface states, and (2) the anharmonicity of the bonds at the surface.

If electrons (holes) are generated in antibonding (bonding) surface states by photoexcitation, the surface phonon modes are softened. A similar red shift of coherent bulk phonon frequency of Tellurium as a function of pumping power has been reported [12]. The excitation of about 2% of valence electrons of bulk Tellurium causes the weakening of the crystal lattice and results in the low frequency shift from 3.6 THz to 3.0 THz. In the present case, although the bulk carrier density is too low to modify the bulk phonon frequency, the 2D confined surface mode might be perturbed by the excess carrier density in the unoccupied surface states.

Next we consider a possible role of the anharmonicity of surface bonds. As has been discussed earlier, the excitation mechanism of the coherent surface phonon on the GaAs surface is considered to be the impulsive Raman scattering. In the classical damped oscillator picture, the amplitude of the induced oscillation would be proportional to the fluence of the excitation laser. The coherent phonon amplitude becomes larger with increase of the excitation power, and finally the red shift of the phonon frequency is expected by the anharmonicity of the potential at the surface. Therefore, another possibility for the red shift is due to the anharmonicity of surface bonds.

Generally, the anharmonicity of surface phonon modes is considered to be greater than that of bulk phonon modes. Baddorf et al. have revealed that the anharmonicity for the motion normal to the surface on a Cu(110) surface, is 4-5 time greater than that in bulk copper [13].
Chang et al. have suggested that the coherent phonon amplitudes observed at the surface and in the bulk are the same order of magnitudes on the GaAs [4]. Since the excitation conditions in this study are close to those in ref. 4, the situation would be similar. Since the $\alpha$ component (bulk LO-phonon) does not show significant power dependence of its frequency, the employed pump power is not so intense as to realize the anharmonic effect in the bulk. As in FIGURE 3, the $\beta$ component frequency shifts from 8.6 THz to 8.3 THz with the pump power changing from 70 mW to 210 mW. This shift is larger than that of the bulk mode observed between at 10 K and 300 K, in which occupation at the phonon mode of 300 cm$^{-1}$ increases from ~0 to 0.3 [14]. It is intriguing that such a large shift is induced with the moderate pump power conditions. This could be a manifestation of larger anharmonicity at the surface than that in the bulk.

CONCLUSION

We performed TRSHG measurements on a GaAs(100)-c(8×2) surface, and identified the surface phonon mode in the time domain. The surface phonon signals show dramatic dependence on the surface annealing, which indicates that the observed mode is sensitive to the long-range regularity of the surface. Clear interference dips were observed in the power spectra, which are indicative of the initial phase difference between the bulk and the surface phonon modes. The surface phonon frequency showed a red shift as the pump power increases. This might be ascribed to the change of the interatomic force constant by the photocarriers in the antibonding unoccupied surface state, or to the anharmonicity of the potential energy curve for the surface lattice motion.

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REFERENCES