Annealing-induced Modifications of Carrier Dynamics and Plasmon-phonon Coupling in Low-temperature-grown GaAs

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The annealing temperature dependence of the carrier dynamics was studied for a GaAs layer grown at 290 °C by using molecular beam epitaxy. The modified carrier lifetime is interpreted to be a result of the increased defect-to-defect distance caused by the aggregation process of As-related point defects. The disappearance of the plasmon-phonon coupling and the carrier-induced phonon dephasing, which are observed in coherent phonon experiments for the layer annealed at 400 °C, is consistent with the instantaneous trapping of photoexcited carriers as, observed in pump-probe measurements.

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I. INTRODUCTION

Gallium arsenide grown at low temperature (LT-GaAs) is known to be very useful for such applications as photoconductive switches, ultrafast photodetectors, and terahertz emitters and detectors [1,2]. All these applications of the LT-GaAs material utilize the ultrafast decay time of the photoexcited carriers, which is a factor determining the operational bandwidth of the fabricated device. For instance, Zheng et al. demonstrated an electrical transient as short as 360 fs for an optically excited free-standing LT-GaAs photodetector [3].

As-grown LT-GaAs is highly nonstoichiometric with excess As atoms forming such point defects as As interstitials (Asi), As antisite defects (AsGa), As-microclusters, and gallium vacancies (VGa) [4]. The short carrier lifetime in LT-GaAs is the consequence of the fast trapping of free carriers by point defects, among which the strongest attractor for an electron is the positively ionized As antisite, which is similar to the EL2 defects in semi-insulating GaAs [5,6]. The As antisite is known to be the most popular defect state in LT-GaAs and generally exists as a neutral charge state AsGa0 or as a ionized charged state AsGa+. For an as-grown LT-GaAs sample grown at 210 °C, the concentration of AsGa0 was found to be ~1.6 × 10^18 cm^-3 from the magnetic circular dichroism of absorption measurements while that for the AsGa+ was determined to be ~6.5 × 10^18 cm^-3 from the near-infrared absorption measurements [7].

While the point defects exist individually in as-grown LT-GaAs, the As atoms in the defect states can be activated to move freely forming energetically more stable As precipitates. In general, the size of the As precipitates becomes larger and the density is reduced as the annealing temperature becomes higher [8]. Thus, the annealing process modifies the structural, electrical, and optical properties of the material, allowing another degree of freedom, along with the growth temperature, in the search for the optimal specifications for the material. Recently, after comparing different preparation conditions, we showed that a terahertz radiation efficiency is optimal for photoconductive switches based on an LT-GaAs layer that had undergone annealing at 600 °C or 700 °C after having been grown at 290 °C by using molecular beam epitaxy (MBE) [9].

In polar materials like GaAs or GaN, the interactions between carrier and polar optical phonon modes are relatively strong. Electrons excited with large excess energies above the conduction band edge were found to relax to the bottom states, losing their energy to optical phonon modes, and longitudinal optical (LO) phonon can also decay through the interactions with electrons [10–12]. Up to now, the influence of lattice vibrations on the ultrafast dynamics of electronic states was widely studied by analyzing the temperature dependence [13, 14]. On the other hand, there have been just a few reports on the modifications of lattice vibrations by the
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existence of the free carriers.

In this paper, we report on the systematic modification of the free carrier decay time and on the dramatic change of the plasmon-phonon couplings, as functions of the post-growth annealing for an LT-GaAs material. The ultrafast carrier dynamics and the coherent LO phonon oscillations for a series of annealed LT-GaAs layers were studied by performing time-resolved reflectance and electro-optic sampling measurements.

II. EXPERIMENTS

The 1.2 µm thick LT-GaAs layers used for this study were grown on (001) GaAs substrates by using molecular beam epitaxy at a growth temperature of 290 °C. After growth, LT-GaAs samples were annealed in a rapid thermal annealing (RTA) furnace at annealing temperatures ranging from 400 °C to 800 °C for a fixed annealing time of 90 s. To verify the compositional and spatial modification of the defect states upon annealing processes, we took cross-sectional TEM images for different annealing conditions.

The evolution of the carrier dynamics upon annealing, which includes the ultrafast free carrier trapping into defect states, was measured by performing a typical pump-probe experiments using a mode-locked Ti:sapphire laser. In the pump-probe measurements, the pump polarization was set to be perpendicular to the probe polarization to minimize the coherent artifact signal near time delay zero. Coherent LO phonon oscillations could be generated and detected via the time-resolved electro-optic sampling measurements, where coherent lattice vibrations excited by the pump beam accompanied the rotation of the probe polarization [15,16]. The lattice dynamics and the plasmon-phonon coupling could be studied by analyzing the coherent phonon signals for samples annealed at different temperatures. For both the pump-probe and the electro-optic sampling measurements, the center wavelength and the pulse duration were ∼790 nm and ∼30 fs, respectively.

III. RESULTS AND DISCUSSION

As-related point defects generated during low-temperature growth are well known to move and aggregate together to form As precipitates when annealing processes are treated at high enough temperatures. Fig. 1(a) shows the cross-sectional TEM images for LT-GaAs regions for samples annealed at different temperatures of 400 °C, 600 °C, and 800 °C. For an annealing temperature of 400 °C, As-related point defects with very small sizes are dispersed uniformly and are difficult to identify in the TEM image. However, one can clearly identify As-clusters and its size to be several nanometers for LT-GaAs annealed at 600 °C and 800 °C. With comparing the TEM images for different annealing temperatures, the As-cluster density decreases but the size becomes larger with increasing annealing temperature.

The substitutions of As for Ga, which are dominant defect states in LT-GaAs, were shown to induce a lattice expansion, as the As-As bond is slightly longer than the As-Ga bond [7,17]. A loosening of the inter-atomic bonding strength is expected in LT-GaAs due either to the expanded lattice distance caused by AsGa defects or to the lattice imperfections caused by VGa or Asi defect states. During annealing at high temperatures, point defects can move and aggregate together, making the remaining portion closer to pure GaAs. Thus, annealing can change the lattice constant and the phonon energies for LT-GaAs. As shown in Fig. 1(b), the LO phonon frequency, which was extracted from the coherent phonon oscillation signals as a function of the annealing temperature.

Fig. 1. (a) Cross-sectional TEM images for LT-GaAs regions for samples annealed at different temperatures of 400 °C, 600 °C, and 800 °C, respectively. (b) LO phonon frequency extracted from coherent phonon oscillation signals as a function of the annealing temperature.

The annealing temperature dependence of the carrier lifetime was studied by measuring time-resolved reflectance changes as a function of the time delay between
the pump pulse for carrier generation by photo-excitation and the probe pulse for monitoring the carrier dynamics. As is shown in Fig. 2, the initial reflective change is positive for most samples, but for samples annealed at 400 °C or at 550 °C, it is interesting that the reflectance change becomes negative too instantaneously not to be measured even with 30 fs temporal resolution of our system. Considering the used wavelength of 790 nm, which lies above the band gap of GaAs, the reflectance change in the positive direction corresponds to the reduced absorption change according to the Kramers-Kronig relations. The reflectance change (ΔR/R) towards a positive direction reflects the decreased absorption coefficient through the band-filling effect by photoexcited carrier generations. The band-filling effect, where occupation of the conduction and the valence bands by pump-generated photo-carriers decreases the absorption probability of the following probe photons, is agreed to be one of the most dominant contributions to the pump-probe signal. For LT-GaAs layers annealed at temperatures higher than 600 °C, we could extract the free carrier lifetime by fitting with a single exponential decay curve the reflectance change induced by carrier-induced band filling effects. The increase in the carrier lifetime with elevated annealing temperature, as is shown in the inset of Fig. 2, is consistent with previous results that explain the ultrafast carrier decay in LT-GaAs by fast carrier trapping into defect states. As the annealing temperature increases, the density of As-related defect complexes decreases with longer inter-complex distance, as was confirmed from the TEM images in Fig. 1, and free carriers excited by pump photons can have longer drifting time before they encounter and get captured by defect states.

On the contrary to samples annealed at high temperatures, the LT-GaAs layers annealed at 400 °C or 550 °C show almost instantaneous drop of the ΔR with photoexcited carrier generations. Referring to previous pump-probe results performed on low-temperature grown III-V semiconductors, we interpret the modified ΔR to a negative sign for our samples as follows [5,18]: as photoexcited carriers are trapped into the AsGa antisite defects, which lie in the forbidden gap between the conduction and the valence band, as is depicted in Fig. 3, these trapped electrons can serve as additional probe photon absorption centers by being re-excited into the conduction bands from the trapped states. This kind of induced absorption will be proportional to the number of photoexcited carriers trapped by AsGa antisite defects. Thus, the overall pump-probe signals in LT-GaAs results from two main contributions; one is the band filling effect by free carriers in the conduction or the valence bands, and the other is the induced absorption by carriers trapped by defect states.

From the above interpretations on the origin of the pump-probe signals, the abrupt negative drop of ΔR/R for samples annealed at low temperatures demonstrates almost instantaneous capture of band carriers into defect states, as inferred from the fact that the process is not discernable, even by pump-probe measurements with 30 fs time resolution. For the sample annealed at the lowest temperature of 400 °C, we know from the gradual decrease of the negative ΔR/R signal that the trapped carriers also disappear very fast with an exponential de-
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Fig. 4. Coherent LO phonon oscillations obtained in the time-resolved electro-optic sampling measurements at pump intensities of 80 mW and 10 mW for the LT-GaAs annealed at (a) 400 °C and (b) 800 °C.

...cay time of 350 fs through the recombination processes.

When the free carriers density is high enough that plasmon frequency is comparable to the LO phonon energy, plasmon-LO phonon coupling occurs, with the mode energy being shifted towards the TO phonon energy. Band carriers can also play a role of decaying LO phonon oscillations in GaAs through the relative strong electron-phonon coupling. The ultrafast carrier dynamics for LT-GaAs will have influences on lattice vibrations for the coupling with charge oscillations and its decay rate. By performing a time-resolved electro-optic sampling technique to measure coherent LO phonon oscillations for samples annealed at different temperatures, we studied the effect of ultrafast carrier dynamics on the lattice vibrations in LT-GaAs.

Figure 4(a) shows the coherent LO phonon oscillations for LT-GaAs annealed at 800 °C at pump intensities of 80 mW and 10 mW, which correspond to electron and hole excitation densities of around 4.6 × 10^{17} cm^{-3} and 5.7 × 10^{16} cm^{-3}, respectively in our case. The plasmon frequency of GaAs becomes equal to the LO phonon energy at a carrier density of 6.4 × 10^{17} cm^{-3}, and strong plasmon-LO phonon coupling can occur for a pump intensity of 80 mW. The beating signals observed at early time delays of less than 1 ps for 80 mW pumping are due to the onset of a new plasmon-phonon coupled mode besides the bare LO phonon mode. On the contrary, plasmon-phonon coupling does not occur for a 10 mW pump intensity because the plasmon frequency is much lower than the LO phonon energy.

Generally, the coherent phonon amplitude is proportional to the pump intensity. However, the phonon oscillation amplitude for an 80 mW pump intensity is comparable to that for a 10 mW pump intensity. We interpret this saturation-like behavior of the coherent LO phonon generation as originating from the initial ultrafast coherent phonon dephasing through the interactions with band electrons.

Because the plasmon-phonon coupling or the ultrafast phonon dephasing via the carrier-phonon interaction are due to free carriers in the conduction or the valence bands, these phenomena will show an annealing temperature dependence. It is interesting that the sample annealed at 400 °C does not have the plasmon-phonon-coupled mode, not even at a pump intensity of 80 mW, and that the phonon amplitude is almost linear in the pump intensity, as is shown in Fig. 4(b). This clear contradiction is coming from the instantaneous trapping of the photoexcited carriers at an annealing temperature of 400 °C while the carrier lifetime for an annealing temperature of 800 °C is long enough for the photoexcited carriers to contribute to the plasmon-phonon coupling and the phonon dephasing processes.

Shown in Fig. 5(a) are the Fourier-transformed spectra of the temporal domain phonon oscillations for the LT-GaAs annealed at 800 °C at pump intensities of 80 mW and 10 mW, respectively. At a pump intensity of 80 mW, the plasmon-LO phonon-coupled mode appears near the TO phonon frequency together with the LO phonon peak at 8.77 THz while only the LO phonon peak is observed at a pump intensity of 10 mW. For the LT-GaAs annealed at 400 °C, the Fourier-transformed spectra show only the LO phonon peak, irrespective of the pump intensity up to 80 mW. The ratio of the plasmon-phonon-coupled mode intensity relative to the LO phonon intensity, as shown in Fig. 5(b), demonstrates a clear distinction between the plasmon-phonon...
The carrier lifetime in LT-GaAs was modified by controlling the annealing temperature, which induces an aggregation of As-related point defects to form As-clusters. For LT-GaAs annealed at 400 °C or at 550 °C, the instantaneous change of photoreflectance in the pump-probe signal in the opposite direction to that for the samples annealed at higher temperatures is interpreted as being due to an absorption induced by carriers trapped into defect states, manifesting free carrier lifetime less than 30 fs for the LT-GaAs annealed at temperatures lower than 550 °C. The annihilation of both plasmon-phonon coupling and LO phonon dephasing via the electron-phonon interactions for the LT-GaAs annealed at 400 °C is consistent with the pump-probe results, which predict almost simultaneous trapping of photoexcited carriers for the sample.

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