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Study of intersubband transitions in GaN-ZnGeN₂ coupled quantum wells

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In this work, we design and analyze a closely lattice-matched wide bandgap GaN-ZnGeN₂ coupled quantum well (QW) structure targeting for near-infrared (IR) (λ < 3 μm) intersubband transition for quantum cascade laser applications. The coupled quantum well structure comprised two GaN wells separated by a thin ZnGeN₂ barrier layer. The QW active region is surrounded by thick ZnGeN₂ layers as barriers. The computations of the electron-phonon and electron-photon scattering rates are carried out by employing the Fermi’s golden rule for transitions. The calculation takes into consideration the conservation of energy and momentum in scattering processes. The coupled QW structure is optimized through tuning the confined subband energy levels in the conduction band to achieve (1) electron-LO phonon resonant scattering when the energy separation between the first and second conduction subband levels matches the phonon energy of GaN (92 meV); and (2) dominant electron-photon transition in near-IR between the third and second conduction subband levels.

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I. INTRODUCTION

Quantum cascade lasers (QCLs) exploiting intersubband transitions between the confined subband energy states of quantum well (QW) heterostructures have gained tremendous developments in the past two decades, due to their attractive properties of compactness, high power, and room-temperature continue-wave (CW) operation capabilities. The intersubband transitions allow the emission or absorption wavelengths extending to the long wavelength regions (e.g., infrared (IR) to terahertz (THz) regions). InP- and Ga(In)As-based QCLs have been demonstrated with superior performance in the wavelength ranging from mid-IR to far-IR for various applications, such as gas sensing, medical imaging, security screening, etc. However, QCL operating at shorter wavelength regions (λ < 3 μm) remains a challenge mainly due to the material limitations from the requirements of a larger conduction band offset and material transparency. III-Nitride semiconductors (GaN, AlN, and their alloys) have been considered as promising candidates for near-IR intersubband devices due to their large band gaps, large conduction band offsets (>1 eV between AlN and GaN), and large electron-longitudinal optical phonon energy (92 meV for GaN). In contrast to the InAs (LO phonon energy of 29 meV) based QCL, the large optical phonon energy in III-nitrides allows the laser devices to be operated at higher temperature with high output power. Recently, III-nitride intersubband structures and devices have been reported by using GaN/AlGaN and lattice-matched GaN/AlInN superlattices. The main challenge associated with the GaN/AlGaN superlattice growth is from the lattice mismatch between GaN and AlGaN with high-Al content which is necessary for near-IR operation. For the lattice-matched GaN/Al₀.₈₃In₀.₁₇N superlattice structures, significant progress has been made recently. However, it is still challenging to achieve high quality AlInN growth which is associated with alloy non-uniformity, In-clustering, and interface roughness.

In this work, we introduce a novel heterostructure based on a closely lattice-matched GaN-ZnGeN₂ coupled QW. ZnGeN₂ belongs to the group II-IV-nitrides, which are derived from the III-nitrides by replacing every two group III atoms by an ordered pair that consisted of one group II and one group IV atoms (e.g., ZnGeN₂, ZnSnN₂, and ZnSiN₂). Among the Zn-IV-nitrides, ZnGeN₂ represents the most studied material from both theoretical and experimental studies. ZnGeN₂ has been demonstrated with an energy band gap of 3.4 eV, very similar to that of the GaN (3.5 eV). The lattice constant of orthorhombic ZnGeN₂ (a) is 6.44 Å, which has <1% of lattice-mismatch with wurtzite GaN (a = 2a_wurtzite = 6.378 Å). Recently, the first principle density functional theory (DFT) calculations predicted a large band offset between GaN and ZnGeN₂ (∆Eₐ = 1.4 eV; ∆Eₓ = 1.5 eV). Calculations also revealed that ZnGeN₂ has a much smaller spontaneous polarization as compared with that of the III-nitrides. From the reported experimental synthesis of ZnGeN₂, the key growth parameter such as growth temperature is similar as that of the GaN. The above-mentioned unique properties of ZnGeN₂ promise the GaN-ZnGeN₂ based heterostructures for intersubband QCL applications in near-IR wavelength regime.

QCLs have been demonstrated with emission in the mid-infrared range of 3–24 μm, as well as in the range of >60 μm for THz generation. For the proposed lattice-matching GaN-ZnGeN₂ material system with large band-offset and large phonon energy, it allows the extension of the emission wavelength into near-infrared wavelength range of 1.5–3 μm, as well as far-infrared range of 30–60 μm. In addition, nitride based semiconductors have higher thermal conductivities as compared with III–V semiconductors, which...
allows QCLs with cw operation and high output power. For example, the thermal conductivity of GaN \( \sim 130 \, \text{W/K m} \) is much higher than that of the InAs (\( \sim 27 \, \text{W/K m} \)) or InP (\( \sim 65 \, \text{W/K m} \)).

This paper presents the analysis of the c-plane GaN-ZnGeN\(_2\) coupled QW structures with the focus on the studies of the dependence of the coupled QW structure parameters on the intersubband transitions. Our studies revealed that both the QW thicknesses and barrier layer thickness play an important role in determining the band structure of the coupled QW, in turn on the confined conduction subband levels and their corresponding wavefunctions. Electron-photon scattering and electron-LO phonon scattering between the conduction subband levels were comprehensively calculated and analyzed.

II. THEORETICAL FORMULATION OF SCATTERING RATES IN GaN-ZnGeN\(_2\) COUPLED QWs

In this work, we focus on the studies of the intersubband transition processes within the conduction band of the GaN-ZnGeN\(_2\) coupled QW structures. The carrier induced effects were taken into account by solving the Schrödinger and Poisson equations self-consistently. In addition, the strain effect and spontaneous and piezoelectric polarizations were considered during the band structure calculation.\(^{28-31}\) The built-in electric field in the QW structure induced from the spontaneous and piezoelectric polarizations leads to the band bending of the QW which significantly modifies the confined conduction subband energy levels and their corresponding wavefunctions. The material parameters of GaN for the band structure calculation were obtained from Refs. 28, 32, and 33. The material parameters of ZnGeN\(_2\) were obtained from Refs. 22 and 34.

The intersubband transition rate (\( W_{gf} \)) for the emission of a photon from an initial state ‘\( i \)’ to a final state ‘\( j \)’ is given by the Fermi’s golden rule and is derived by using the time-dependent perturbation (\( \hat{H} \)) theory

\[
W_{gf} = \frac{2\pi}{\hbar} \sum_{f} |\langle f | \hat{H} | i \rangle|^2 \delta(E_f - E_i + \hbar \omega),
\]

where the carrier (electron) in the initial state \( |i\rangle \) of energy \( E_i \) scatters into any one of the final state \( |f\rangle \) of energy \( E_f \) and \( \hbar \) is the reduced Planck’s constant, i.e., \( \hbar = h/2\pi \) (\( h \) is the Planck constant). \( \omega \) is the angular frequency and \( \hbar \omega \) represents the phonon energy.

For QCL designs with a three level system \((E_1, E_2, E_3)\), one key requirement is to achieve a slow transition between the upper two levels \((E_3 \rightarrow E_2)\) which emit photons, and to achieve a fast process through the phonon emission \((E_2 \rightarrow E_1)\). The reverse of the scattering rates represents the lifetime of the transitions.

By taking into account the conservation of energy and momentum, the averaged electron-photon scattering rate \( \left( \frac{1}{\tau_{photon}} \right) \) can be expressed as the following:\(^{35}\)

\[
\frac{1}{\tau_{photon}} = \frac{e\omega^2}{2\hbar^2c^2W_z} |\mu_{gf}|^2,
\]

where \( e, \omega, \) and \( c \) represent the vacuum permittivity, elementary charge, and speed of light in vacuum, respectively. \( W_z \) is the well thickness. \( \mu_{gf} \) is the intersubband dipole moment between the initial state ‘\( i \)’ and the final state ‘\( j \)’ given by

\[
\mu_{gf} = \langle \phi_f | e \cdot z | \phi_i \rangle = \int \phi_f^* e \cdot z \phi_i \, dz,
\]

where \( \phi_i \) and \( \phi_f \) are the initial and final state wavefunctions.

The Fermi–Dirac distribution of electrons in initial state ‘\( i \)’ is employed to obtain the average electron-LO phonon scattering rate as the following:\(^{36}\)

\[
\text{mean} \left( \frac{1}{\tau_{phonon}} \right) = \frac{\int_{E_{g}}^{\infty} f^{FD}(E) dE}{\int f^{FD}(E) dE},
\]

where the Fermi–Dirac distribution of electrons is \( f^{FD}(E) = \frac{\exp[\frac{E-E_F}{k_B T}] + 1}{\exp[\frac{E-E_F}{k_B T}] + 1} \), and the Fermi level \( E_F \) is calculated with the sheet carrier density of \( 1.5 \times 10^{13} \, \text{cm}^{-2} \). The electron-LO phonon scattering rate \( \left( \frac{1}{\tau_{phonon}} \right) \) depends on the scattering rate for an electron with a particular initial energy \( E_i \), which is expressed as the following:\(^{36}\)

\[
\frac{1}{\tau_{phonon}} = \frac{r''}{2} \Theta \left( \frac{k_i^2 - 2m^*\Delta}{\hbar^2} \right) \times \int_{-\infty}^{\infty} \frac{\pi|G_g(K_z)|^2}{\sqrt{K_i^2 + 2K_z^2 \left( 2k_i^2 (E_i) - \frac{2m^*\Delta}{\hbar^2} \right) + \left( \frac{2m^*\Delta}{\hbar^2} \right)^2}},
\]

where the constant prefactor \( r'' = \frac{2m^*e^2\lambda_f^p}{2\pi^2\hbar^6} \), and \( P'' = \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) (N_0 + 1) \), in which \( m^*, N_0, \varepsilon_\infty \), and \( \varepsilon_0 \) represent the effective mass, phonon density within the crystal, and the high- and low-frequency permittivities of the material, respectively. Note that \( \Delta = E_f - E_i + \hbar \omega \). The parameter \( \Theta(k_i - \frac{2m^*\Delta}{\hbar^2}) \) is the Heaviside unit step function that ensures only finite lifetimes \( \tau_i \). And \( k_i \) is in-plane phonon wave vector in the initial state ‘\( i \)’. \( G_g(K_z) \) is known as the intersubband form factor.
that depends on the initial- and final-state wavefunctions $\varphi_i$ and $\varphi_f$, and the phonon wave vector $K_z$ along the growth (z-) axis, which is given by

$$G_y(K_z) = \int \varphi_f^*(z)e^{-iK_z\cdot\varphi_i(z)dz}, \quad (7)$$

where $R(K_z)$ is defined as resonant function, as given by

$$R(K_z) = \frac{1}{\sqrt{K_z^4 + 2K_z^2\left(2K_z^2(E_i) - \frac{2m^*\Delta}{h^2}\right) + \left(\frac{2m^*\Delta}{h^2}\right)^2}}. \quad (8)$$

According to the experimental ZnGeN$_2$ Raman spectrum results in Ref. 37, the dominant vibrational mode appears near $\sim 612 \text{ cm}^{-1}$, i.e., 76 meV. Therefore, the phonon energy of GaN ($\sim 92 \text{ meV}$) is similar to that of the ZnGeN$_2$. The heterostructure interface between GaN and ZnGeN$_2$ may affect the phonon vibration mode and phonon energy in the GaN quantum wells. However, in this study, we focus on the design of CQWs with emission in the near infrared wavelength range ($<3 \mu\text{m}$, i.e., $>400 \text{ meV}$). The energy separation between $E_3-E_2$ is much larger than that of the energy separation between $E_2-E_1$. Even with some deviation of the phonon energy in GaN quantum well as compared with that of the bulk GaN, the design approach and results are still valid. In addition, considering the close lattice-matching between GaN and ZnGeN$_2$ and thus minimized strain at the heterointerface, we assume that the phonon vibration modes in the GaN quantum wells are similar as those in the bulk GaN. Therefore, the optical phonon energy of GaN (92 meV) is used in this calculation.

III. DESIGN AND ANALYSIS OF GaN-ZnGeN$_2$ COUPLED QWs

In the conventional single QW system, quantum mechanics determined that the energy separations between the lower subband energy levels are always larger than those between the upper subband energy levels. Thus, in order to achieve a larger energy separation between the upper subband energy levels, and a narrower energy separation between the lower subband energy levels, the concept of coupled QW is introduced as shown in Fig. 1. In Fig. 1, the coupled QW heterostructure is composed of two GaN wells ($L_{W1}$ and $L_{W2}$) which are separated by a thin ZnGeN$_2$ barrier layer ($L_b$), and surrounded with ZnGeN$_2$ layers as outer barriers. The coupled QW structure allows the tuning of the confined conduction subband energy levels (e.g., $E_1$, $E_2$, $E_3$) separately. The goal is to achieve a dominant photon transition between $E_1$ and $E_2$ in the near-IR wavelength range, and meanwhile a resonant electron-phonon scattering process between $E_2$ and $E_1$ to deplete electrons at subband energy level $E_2$.

The computations of the electron-LO phonon and electron-phonon scattering rates are carried out by employing Fermi’s golden rule for transitions as described in Section II. Here, we calculated the electron-phonon scattering rates and electron-LO phonon scattering rates between the three confined subband energy levels ($E_3\rightarrow E_2$, $E_3\rightarrow E_1$, and $E_2\rightarrow E_1$), through comprehensive tuning of the thicknesses of the ZnGeN$_2$ barrier ($L_b$) and GaN wells ($L_{W1}$ and $L_{W2}$) in the GaN-ZnGeN$_2$ coupled QWs.

Figure 2 plots the averaged electron-LO phonon scattering rates [Fig. 2(a)] and the averaged electron-photon scattering rates [Fig. 2(b)] of transitions $E_3\rightarrow E_2$, $E_3\rightarrow E_1$, and $E_2\rightarrow E_1$ for the ZnGeN$_2$-GaN-ZnGeN$_2$-GaN-ZnGeN$_2$ coupled QWs. The calculations were performed for the structures of ZnGeN$_2$(10 nm)-GaN(1.5 nm)-ZnGeN$_2$(L$_b$)-GaN(2.5 nm)-ZnGeN$_2$(10 nm) with fixed GaN well thicknesses and varying ZnGeN$_2$ barrier thickness $L_b$ at 300 K. As shown in Fig. 2, the tuning of the ZnGeN$_2$ barrier layer thickness $L_b$ leads to an effective tuning of the energy separations between the confined subband energy levels ($E_1$, $E_2$, and $E_3$).

In Fig. 2(a), the resonant electron-LO phonon scattering rate occurs when the energy separation between $E_2$ and $E_1$ is $\Delta_{21} = 92.3 \text{ meV}$ at $L_b = 0.5 \text{ nm}$, which is similar to the phonon energy of GaN (92 meV). At the resonant condition, the electron-LO phonon scattering rate of $W_{\text{phonon}}(E_2\rightarrow E_1)$ is dominant with 4 orders higher magnitude than those of $W_{\text{phonon}}(E_2\rightarrow E_1)$ and $W_{\text{phonon}}(E_3\rightarrow E_2)$. This indicates the feasibility to achieve the population inversion in the GaN-ZnGeN$_2$ coupled QW for QCL applications. With the tuning of the ZnGeN$_2$ barrier thickness ($L_b$), the confined subband energy levels are modified together with their corresponding wavefunctions. Fig. 2(b) plots the transition wavelengths between different subband energy levels ($E_3\rightarrow E_2$, $E_3\rightarrow E_1$, and $E_2\rightarrow E_1$) and their corresponding electron-photon scattering rates $W_{\text{photon}}$. Among the three different transitions, the transition between $E_1$ and $E_2$ ($\lambda_{23}$) is dominant, with the transition wavelength varying between 2.6 $\mu\text{m}$ to 2.8 $\mu\text{m}$.

In addition to the ZnGeN$_2$ barrier layer thickness, the GaN QW thicknesses ($L_{W1}$ and $L_{W2}$) also show a strong impact on the confined subband energy levels and their corresponding wavefunctions. As shown in Fig. 3, the calculated electron-LO phonon scattering rate and electron-photon scattering rate were plotted as a function of the first GaN well thickness $L_{W1}$ ($L_{W1} = 1.3 \text{ nm} - 1.8 \text{ nm}$), with the fixed ZnGeN$_2$ barrier layer $L_b$ of 0.5 nm and the second GaN well thickness $L_{W2}$ of 2.5 nm. Fig. 3(a) shows a similar trend.
as Fig. 2(a): when the energy separation $\Delta_{21}$ between $E_1$ and $E_2$ is close to 92 meV ($L_{W1} = 1.5$ nm), it corresponds to the resonant condition with the peak electron-LO phonon scattering rate. The electron-LO phonon scattering rates between $E_3 \rightarrow E_2$ and $E_3 \rightarrow E_1$ are several orders lower as compared with that of the transition between $E_2 \rightarrow E_1$. The electron-photon scattering rate calculations as shown in Fig. 3(b) show that the electron-photon scattering between $E_3 \rightarrow E_2$ is dominant with the varied transition wavelength ranging between 2.66 $\mu$m and 2.97 $\mu$m.

Similarly, the second GaN well thickness $L_{W2}$ is another important parameter to tune the confined subband energy levels and their corresponding wavefunctions, with the fixed ZnGeN$_2$ barrier layer thickness $L_b$ of GaN-ZnGeN$_2$ coupled QW structure at 300 K. The ZnGeN$_2$ barrier thickness $L_b$ varies between 0.3 nm and 0.8 nm with fixed $L_{W1} = 1.5$ nm and $L_{W2} = 2.5$ nm. The energy separation $(\Delta E_{21} = E_2 - E_1)$ is indicated at each given $L_b$ in (a). The transition wavelength for $E_3 \rightarrow E_2 (\lambda_{32})$ is indicated at each given $L_b$ in (b).

The above studies of the GaN-ZnGeN$_2$ coupled QW structures indicate the following properties: (1) The coupled QW structures allow to achieve electron-LO phonon scattering resonance between $E_2 \rightarrow E_1$, with intensities several orders higher than those between $E_3 \rightarrow E_1$ and $E_3 \rightarrow E_2$. (2) The electron-photon transitions between $E_3 \rightarrow E_2$ are generally dominant as compared with those of $E_3 \rightarrow E_1$ and $E_2 \rightarrow E_1$ with appropriate QW structure parameters studied here. The transition wavelength $\lambda_{32}$ and its intensity are highly dependent on the ZnGeN$_2$ barrier thickness $L_b$, and the GaN well thicknesses $L_{W1}$ and $L_{W2}$. Therefore, it is promising to achieve an intersubband transition wavelength $< 2 \mu$m by using the closely-lattice-matched GaN-ZnGeN$_2$ coupled QW structures.
conduction subband energy levels and their corresponding wavefunctions. From our studies, the intersubband transition down to 1.9 µm can be achieved by tuning the coupled QW structures. With a large band offset and being closely lattice-matched, the GaN-ZnGeN$_2$ heterostructure is promising to pave a new way to achieve high performance intersubband transitions in the near-IR. This also provides a new solution to the challenges that the current GaN-AlN or GaN-AlInN heterostructures for intersubband transitions are facing.

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FIG. 4. (a) Averaged electron-LO phonon scattering rates; and (b) average electron-photon scattering rates of $E_2 \rightarrow E_1$, $E_3 \rightarrow E_2$, and $E_3 \rightarrow E_1$ transitions as a function of the GaN well ($L_{w2}$) for GaN-ZnGeN$_2$ coupled QW structure at 300 K. The GaN well thickness $L_{w2}$ varies between 1.5 nm and 2.8 nm with fixed $L_{w1} = 0.5$ nm and $L_{w1} = 1.5$ nm. The energy separation ($\Delta E_{12} = E_2 - E_1$) is indicated at each given $L_{w2}$ in (a). The transition wavelength $E_1 \rightarrow E_2$ is indicated at each given $L_{w2}$ in (b).

This paper theoretically studies the intersubband transition processes in the GaN-ZnGeN$_2$ coupled QWs with ideal sharp interfaces. From an experimental point of view, possible interfacial roughness induced scattering may play an important role in addition to the LO-phonon scattering, which may cause leakage current and reduce gain. 38,39 Atomic interdiffusion at the heterojunction interface may occur during the growth process, which can cause band structure modifications and shift of subband energy levels and their wavefunction. Future experimental growth studies and structure designs should consider these aspects.

IV. SUMMARY

In summary, we designed and studied a closely-lattice-matched heterostructure based on wide bandgap GaN-Zn GeN$_2$ coupled QW structure for near-IR QCL applications. The thicknesses of both the ZnGeN$_2$ barrier layer and the GaN QWs provide a wide range of tuning of the confined conduction subband energy levels and their corresponding
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