1550 nm Compatible Ultrafast Photoconductive Material Based on a GaAs/ErAs/GaAs Heterostructure

Kedong Zhang, Yiwen Li, Yifeng Ren, Xing Fan, Chen Li, Jianfei Li, Yafei Meng, Yu Deng, Fengqiu Wang,* Hong Lu,* and Yan-Feng Chen

The sub-bandgap absorption and ultrafast relaxation in a GaAs/ErAs/GaAs heterostructure are reported. The infrared absorption and 1550 nm-excited ultrafast photo-response are studied by Fourier transform infrared spectrometry and time-domain pump–probe technique. The two absorption peaks located at 2.0 (0.62 eV) and 2.7 µm (0.45 eV) are originated from the ErAs/GaAs interfacial Schottky states and the ErAs itself, respectively. The photogenerated carrier lifetime, excited using 1550 nm light, is measured to be as low as 190 fs for the GaAs/ErAs/GaAs heterostructure, making it a promising material for 1550-nm-technology-compatible, high critical-breakdown-field THz devices. The relaxation mechanism is proposed and the functionality of ErAs is revealed.

1. Introduction

Terahertz technology is widely used in many fields such as security screening, biological and environmental sensing, medical diagnosis, broadband communication, and so on.1–6 Photomixers and pulse-driven dipolar antennas fabricated from the ultrafast photoconductive materials, such as low-temperature grown GaAs (LT-GaAs), have been regarded as promising sources for coherent terahertz radiation with large tunability.7–10 LT-GaAs has been the dominating ultrafast material since 1990s as it features all the required properties including high resistivity, high carrier mobility, and short carrier lifetime.11–14 The excess arsenic resulting from the low growth temperature forms AsGa antisites which create deep defect levels within the GaAs bandgap. The presence of these defect states provides an effective non-radiative relaxation pathway for the excited carriers and results in significantly shortened lifetimes. However, the defects are hard to be controlled, so the crystalline quality can be sacrificed and the reliability is therefore affected. Other than LT-GaAs, GaAs heavily doped with Er (ErAs:GaAs) was found to be an alternative candidate to be implemented into ultrafast photoconductive devices driven by 800 nm lasers.9,15,16 The Er atoms can be readily and heavily incorporated into a high-quality GaAs matrix to form ErAs precipitates and these semi-metallic precipitates provide the relaxation channel for the photo-excited carriers.9,17,18 The promises of ErAs:GaAs for photomixer have been studied extensively. Compared to LT-GaAs, ErAs:GaAs can obtain a higher crystalline quality, a higher operating temperature, and yet better transport characteristics. But foremost, the potentially highly tunable feature makes it a promising ultrafast photoconductive material, alternative to the widely used LT-GaAs. In addition, thanks to the compatibility between ErAs and GaAs, an ErAs/GaAs superlattice structure can be suitably designed to control the lifetime in a deterministic manner.9,19

Usually, the GaAs-based material system needs to be excited by cross-bandgap energies, that is, 800 nm, which are more expensive and less flexible than their 1550 nm counterparts. To simplify the pumping scheme, people turn the focus onto LT-In0.53Ga0.47As and ErAs:In0.53Ga0.47As that can be grown on InP16,20–22 because the cross-bandgap transition in In0.53Ga0.47As can be excited by 1550 nm. However, such change would bring problems such as lower critical breakdown fields and higher dark currents, due to the reduced bandgap. A promising solution is to explore the sub-bandgap absorption in ErAs:GaAs to achieve both a 1550 nm-excited ultrafast photo-response and high critical breakdown field. And E. R. Brown et al. have demonstrated the 1550 nm continuous-wave photomixer using ErAs:GaAs.23–25 However, to achieve a high quality, the total amount of ErAs is somewhat limited. Therefore, it is limited to increase the absorption coefficient of the ErAs:GaAs as the 1550 nm-excited absorption is mainly determined by the amount of ErAs.26 The material quality would
be deteriorated if the amount of ErAs were pushed to a higher level in both the superlattice and codeposition cases.\textsuperscript{19,27} Also, the physical mechanism of the infrared absorption and ultrafast relaxation has not been clarified yet. In particular, the functionality of ErAs itself has been neglected, mainly due to the difficulties to achieve high quality ErAs bulk films and prevent it from oxidation. How to employ this material more effectively to achieve better performance in sub-bandgap photo-response deserves more exploration.

In this work, we design a GaAs/ErAs/GaAs heterostructure where ErAs is a complete film and sandwiched between two GaAs layers. A series of samples with different ErAs thicknesses were grown on GaAs (100) substrates by molecular beam epitaxy (MBE). The high crystalline properties of the epitaxially grown films were characterized by X-ray diffraction (XRD) and high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM). Fourier transform infrared (FTIR) spectroscopy and a time-domain pump–probe technique were used to study the infrared absorption and ultrafast photoresponse, respectively. Finally, we established an energy band model and proposed the energy transition mechanism for the GaAs/ErAs/GaAs heterostructure.

2. Experimental Section

All the heterostructure samples for the photo-excited carrier lifetime study were grown with a III–V solid-state source MBE (Veeco GENxplor) with different ErAs thicknesses on semi-insulating GaAs (100) substrates. Reflection high energy electron diffraction was used for in-situ monitoring of the sample surface. Elementary erbium (Er) material with a purity of 99.995\% was used in a high-temperature effusion cell. All the GaAs substrates were thermally heated under an As\textsubscript{2} flux of 9 \times 10^{-6} torr to remove the native oxides before a 100 nm GaAs buffer layer was grown at 580 °C. Then the substrates were cooled to 500 °C for the growth of the ErAs films. Finally, a 5 nm GaAs was grown on the top at 500 °C, to form a sandwich structure where the ErAs is confined, and to protect the ErAs from oxidation. The ErAs growth rate is 200 nm h\textsuperscript{-1}. The layered sample structure is shown as the insert of Figure 1a. The thickness of ErAs in each sample was confirmed by high resolution XRD (Bruker D8 Advanced). Cu K\textsubscript{α}1 line is used in the high-resolution XRD and the wavelength is 0.15406 nm. The optical absorption in the range of 1.0 to 4.5 \(\mu\)m is measured by FTIR (Nicolet iS50). The source for the pump–probe

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\caption{Structural characterization of the GaAs/ErAs/GaAs heterostructures grown on GaAs substrates. a) XRD spectrum of two theta-omega scan on an epitaxially grown GaAs/ErAs/GaAs heterostructure. The layered sample structure is shown as the insert. b) XRR spectra of three GaAs/ErAs/GaAs heterostructures with different ErAs thicknesses. And the actual ErAs thickness can be fitted using the fringes. c) Cross-sectional HAADF STEM image of an ErAs/GaAs sample, showing the sharp interface. The inset is the SAED pattern. d) The interfacial roughness, within 4 ML, can be seen in a STEM image with higher magnification.}
\end{figure}
technique is a Ti:Sapphire amplifier pumped OPA (Coherent Inc.) that outputs 1550 nm with a pulse width of $\approx 150$ fs.

3. Results and Discussion

Both the ErAs and GaAs diffraction peaks of a GaAs/ErAs/GaAs heterostructure can be observed in the XRD spectrum, as shown in Figure 1a. The two theta-omega scan was done on (200) plane to obtain the strongest diffraction signal of ErAs. The ErAs (200) diffraction peak is located at 31.1°, while the GaAs (200) diffraction peak is located at 31.6°. Thickness fringes are clearly shown around the ErAs (200) peak, indicating the high quality of the ErAs film and the ErAs/GaAs interfaces. To accurately characterize the thickness of the ErAs films, an X-ray reflectivity (XRR) measurement was also carried out. The thickness can be fitted using the periodic peaks between 1° and 2° in Figure 1b, and is inversely proportional to the peak period. The ErAs thicknesses turn out to be 46, 67, and 88 nm, respectively. Reciprocal space mapping has shown that all the ErAs films are relaxed as they exceed the critical thickness.

The ErAs/GaAs interface was studied by cross-sectional HAADF STEM on the GaAs (01-1) plane, as shown in Figure 1c,d, to further confirm the crystalline quality of the ErAs film. The sharp interface can be seen in Figure 1c. The inset is the selected area electron diffraction (SAED) showing the coherence between ErAs and GaAs with a slight mismatch in lattice constant. Although ErAs has a rock salt structure while GaAs is a zinc blende, they share the same As matrix,[28] so the As sub-lattice is continuous across the ErAs/GaAs interface. In addition, the higher quadruple symmetry of ErAs ensures its epitaxy on GaAs. The atomic resolution image is shown in Figure 1d to further confirm the interfacial quality. Although there is still some interfacial roughness which is within four monolayers (ML), the lattice is continuous through the interface without obvious defects.

In order to find out if there is sub-bandgap absorption in the GaAs/ErAs/GaAs heterostructure, the transmittance of all the samples were measured by FTIR from 1.0 to 4.5 µm. The corresponding absorbance was calculated by $-\log(T/T_0)$ and is plotted in Figure 2a, where $T$ is the measured sample transmittance and $T_0$ is the transmittance measured on a GaAs substrate. A continuous absorption is observed between 1.6 and 4.5 µm and the absorption increases as the wavelength increases. Two absorption peaks E1 and E2 are found at 2.7 (0.45 eV) and 2.0 µm (0.62 eV), respectively, on the increased absorption background. And the peak intensity increases with the ErAs thickness. We believe that the continuous absorption is due to free carrier absorption by the semi-metallic ErAs layer. It is worth mentioning that the broadband absorption can be beneficial in applications using saturable absorption. To establish the physical origins of the two absorption features, we plot the peak intensity of E1 and E2 as a function of the ErAs thickness, as shown in Figure 2b. The absorption coefficient was approximated by $-\Delta \ln(T/T_0)/\Delta t$, where $t$ is the ErAs film thickness. We can obtain an absorption coefficient to be $5.26 \times 10^4$ cm$^{-1}$ for E1, which is four times higher than that reported in ErAs:GaAs,[29] and $2.04 \times 10^4$ cm$^{-1}$ for E2. For E1, the linear fitting passes the coordinate zero point, suggesting the E1 absorption is intrinsic and mainly from the ErAs itself, while the E2 absorption seems to correspond to the interaction between ErAs and GaAs. A band structure of the GaAs/ErAs/GaAs heterostructure is proposed to show the band alignments and transitions due to the experimental observations, as shown in Figure 2c.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Infrared absorption of the GaAs/ErAs/GaAs heterostructures using FTIR. a) The absorbance (calculated by $-\log(T/T_0)$) as a function of wavelength. b) $-\ln(T/T_0)$ as a function of the ErAs film thickness $t$ for peak E1 and E2, and the linear fitting to obtain the absorption coefficient $-\Delta \ln(T/T_0)/\Delta t$. c) Schematics of the band structure of the GaAs/ErAs/GaAs heterostructure, showing the two transitions due to ErAs. The interfacial states region is indicated by the light blue area.
For the ErAs films with thicknesses of tens of nanometers, the quantum confinement effect is negligible, so the absorption mainly shows the bulk nature of ErAs. The intensity of the absorption peak increases with the ErAs thickness while there is no shift in the peak position. It is well accepted that the conduction band minimum in ErAs is composed of the Er 5d states, while the valence band maximum is made up of the As 4p states. The semi-metallic nature of ErAs is defined as the conduction band minimum located at X point which has an overlap with the valence band maximum at Γ point. And the Γ–X overlap in bulk ErAs was reported to be 0.7 ± 0.1 eV with E₀ being close to the midgap between the band extrema.[29]

However, the band alignment of the ErAs/GaAs interface is primarily determined by the Schottky states. These interfacial Schottky states between the GaAs and ErAs had been studied theoretically,[30,31] and confirmed using scanning tunneling spectroscopy by Palmstrøm et al.[32] In our case, the bulk ErAs nature is considered as the ErAs film is thick enough so only the bottom ErAs/GaAs interface is demonstrated. As the interfacial Schottky states play an important role so we highlight the band bending at the interface as shown in Figure 2c. The Fermi level is pinned by the interfacial Schottky states. The band bending of the ErAs band is due to the pinning.

To find out the location of the interfacial Schottky states, we grew a Schottky junction of ErAs/GaAs to measure the Schottky barrier height (SBH) between ErAs and GaAs. The GaAs substrate used for the Schottky junction growth is heavily doped by Si to 1 × 10¹⁸ cm⁻³, and a 500 nm GaAs buffer slightly doped with Si (5 × 10¹⁶ cm⁻³) was grown at 580 °C, followed by a 100 nm ErAs grown at 500 °C to form a Schottky junction. The results show that the SBH is about 0.65 eV. The measured E2 (0.62 eV) value is close to the SBH, so we attribute the E2 transition to the interfacial states. The difference may be due to a number of factors and one is that the GaAs substrate used for the Schottky junction growth is heavily doped, while the other samples were grown on semi-insulating substrates. Although the STEM images show that the epitaxially grown ErAs/GaAs is of high quality and free of interfacial defects, the pinned states may originate from the difference in lattice structures between GaAs and ErAs and the GaAs lattice termination. According to the band alignment, two possible transitions which might correspond to the E1 (0.45 eV) absorption are proposed since the relevant transition mechanism has not been clarified yet for the extra absorption apart from the free carrier absorption.[19,34] One possible transition is between the ErAs VB and the GaAs CB at Γ point, the other is excited from the ErAs CB at X point to a higher CB level or possible exciton states.[35] The intensity of E1 is much stronger than E2 and proportional to the ErAs thickness, suggesting that E1 originates from the ErAs itself whose density of state is much higher than the interfacial Schottky states, where E2 comes from. In addition, there is an absorption tail below 1.5 μm, which might come from the structural and impurity defects. Another possibility is due to the transition between GaAs VB and ErAs VB (≈0.97 eV, 1278 nm).[35]

The time-domain pump–probe transmittance measurement was carried out to study the dynamics of carrier relaxation in the GaAs/ErAs/GaAs heterostructures. The schematic of the measurement is shown as the insert in Figure 3a. The light source is a Ti:Sapphire amplifier pumped OPA (Coherent Inc.) that outputs 1550 nm with a pulse width of ~150 fs. The wavelength is 1550 nm for both the pump and probe beams to investigate the sub-bandgap excitation, as GaAs is highly transparent to this wavelength. It can be seen that all the samples are characterized by a single sharp positive photo-bleaching (PB) peak followed by an exponential decay as shown in Figure 3a. A rapidly increasing ΔT/T around time zero represents a salient PB signal, which can be attributed to Pauli blocking induced phase space filling.[36–38] The following dynamics is due to the ultrafast capture process. The signal rapidly decreases by more than 80% of the peak value, which can be fitted by a single exponential Y(t) = Aexp(−t/τ) in the figure, where τ is the carrier lifetime. The time constants for the ErAs films of 46, 67, and 88 nm are 360, 190, and 290 fs, respectively, which bode well for terahertz performance.

Figure 3b shows the band transitions of the ultrafast capture process in the GaAs/ErAs/GaAs heterostructures. When the sample is excited by the 1550 nm light (0.8 eV), carriers are excited from the interfacial Schottky states to the GaAs CB and from the possible states in ErAs, then the carriers can be captured through an ultrafast relaxation to the ErAs VB. As

Figure 3. Ultrafast photo-response measurement using 1550 nm pump–probe technique. a) Differential transmittance of the GaAs/ErAs/GaAs heterostructures. The insert is a schematic of the pump–probe measurement. b) The band structure showing the corresponding band transitions in the process.
the degenerate pump–probe setup has excess energies to fill up the GaAs CB, relaxation within the band (thermalization) is possible. We propose two possible relaxation passes, one is to be trapped by ErAs VB directly before they have time to reach the bottom of the GaAs CB, the other is to relax to the bottom of the GaAs CB due to thermalization and then be trapped by ErAs VB. As the dominating relaxation process can be fitted by a single exponential factor, it is likely to be dominated by the former pass rather than the combinational pass. This mechanism has been proposed in a similar system LT-GaAs. More systematical studies using tunable excitation wavelengths can further distinguish the relaxation mechanisms. The appearance of a plateau-like slow relaxation may correspond to the trap emptying time or recombination time. The composite of a fast femtosecond relaxation coupled with a relatively slow relaxation component is long known to benefit other ultrafast applications as well, such as a saturable absorber. There is no obvious dependence of the carrier lifetime on the ErAs thickness. We think that the lifetime is largely equivalent in the tested GaAs/ErAs/GaAs heterojunction system, and the difference may lie in the quality of the ErAs and ErAs/GaAs interface.

4. Conclusion

In summary, we have introduced a new structural design utilizing semi-metallic ErAs for ultrafast photo-conductive applications. A series of high quality GaAs/ErAs/GaAs heterostructures have been grown by MBE on GaAs (100) substrates. Sub-bandgap absorption has been observed in these GaAs/ErAs/GaAs heterostructures with two absorption peaks located at 2.0 and 2.7 μm, which are attributed to the transitions from the interfacial Schottky states and the ErAs itself, respectively. Ultrafast carrier relaxation (<400 fs) is revealed by the degenerate pump–probe spectroscopy operated at 1550 nm, showing the significance in applications such as cost-effective, telecom-compatible Terahertz devices.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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