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Surfactant-assisted growth and properties of rare-earth arsenide InGaAs nanocomposites for terahertz generation

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We explore the effects of surfactant-mediated epitaxy on the structural, electrical, and optical properties of fast metal-semiconductor superlattice photoconductors. Specifically, application of a bismuth flux during growth was found to significantly improve the properties of superlattices of LuAs nanoparticles embedded in In0.53Ga0.47As0.47. These improvements are attributed to the enhanced structural quality of the overgrown InGaAs over the LuAs nanoparticles. The use of bismuth enabled a 30% increase in the number of monolayers of LuAs that could be deposited before the InGaAs overgrowth degraded. Dark resistivity increased by up to ~15 x while carrier mobility remained over 2300 cm2/V-s and carrier lifetimes were reduced by >2 x at comparable levels of LuAs deposition. These findings demonstrate that surfactant-mediated epitaxy is a promising approach to enhance the properties of ultrafast photocconductors for terahertz generation. Published by AIP Publishing.

The development of efficient, compact, tunable, room-temperature-operable, continuous-wave (CW) terahertz (THz) sources has been an ongoing area of research for several decades due to the potential applications in areas such as remote sensing, communications, and defense.1–3 Efforts to increase output powers of compact solid state devices beyond the microwatt range have been approached from the low frequency side of optical devices4–7 and high frequency side of RF devices.8,9 However, despite considerable progress, these sources remain limited by low output powers and uncertainty in frequency tunability. Photomixing is a promising method for generating tunable, CW, THz radiation from a single compact device.10 By utilizing the interference of two CW single-frequency lasers incident on a material, the material’s photoconductivity is modulated at the difference frequency. The induced photogenerated current is subsequently coupled to a planar antenna where THz radiation is emitted.11,12

Suitable photoconductive materials for photomixing must exhibit high dark resistivities, high carrier mobilities, and short carrier lifetimes.13 Early and current photomixer work focused primarily on low-temperature-grown (LTG) GaAs14 or superlattices of epitaxially-embedded self-assembled nanoparticles of ErAs15–17 and LuAs18–20 in GaAs. Development of fast photoconductive materials with smaller bandgaps, such as In0.53Ga0.47As0.47, would benefit greatly from the mature telecommunication component infrastructure available at 1550 nm.21 Unfortunately, previous investigations of devices with small bandgap materials, such as InP-based nipi22,23 and uni-traveling carrier24,25 diodes, plasmonic enhancements,26,27 and mixers with promising materials such as LTG-InGaAs28 and LTG-InGaAs/AlGaAs multilayer heterostructures,29 have also yielded output powers that remain in the microwatt range at THz frequencies. InGaAs nanocomposite materials based on ErAs nanoparticle superlattices30,31 and codeposited32,33 structures, as well as TbAs codeposited structures,33 have also been investigated, but currently possess prohibitively low dark resistivities. Further investigations into other rare-earth arsenide (RE-As) species such as LuAs, GdAs, and LaAs containing superlattices in InGaAs34 suggest that the quality of the matrix overgrowth has a significant but underexplored effect on the nanocomposite properties. The research exploring matrix overgrowth enhancement techniques on RE-As nanocomposites is sparse.

Surfactant-mediated growth is a promising growth enhancement technique. First introduced by using arsenic to improve Si/Ge interfaces,55,56 surfactants have been an integral part in the development of high-quality epitaxial materials.37,38 The addition of a surfactant alters the surface kinetics of adatoms and even promotes layer-by-layer growth in some cases.39–41 Antimony has been used extensively as a surfactant for growing germanium films on Si (100)36,42,43 and InP (100).44 It has also been used as a method to grow highly-strained InGaAs45 and increase the incorporation of nitrogen in GaInNAS46 and GaInNASb47,48 quantum well layers for high-performance lasers on GaAs. However, antimony tends to incorporate in these materials under standard growth temperatures and conditions. Bismuth, on the other hand, is a much larger atom with a slightly lower electronegativity and incorporates at substrate temperatures much lower than the standard growth conditions.52,53 Bismuth, much like antimony, has also been demonstrated as a surfactant to improve Ge/Si interfaces.54,55 improve the structural and optical quality of highly strained InGa1-xAs/GaAs56 and InGa1-xAsSb1-y heterostructures, increase the incorporation of nitrogen in dilute GaNAS and GaNAlNAS layers on GaAs,52,58 and improve the quality of lattice-matched layers of InGaAs on InP.59 Despite the range of improved materials through surfactant-mediated growth, there has been no report exploring its application to the growth of RE-As nanocomposites. Here, we report the structural quality, electrical properties, and carrier lifetimes of superlattices containing...
LuAs nanoparticles embedded in an InGaAs matrix where bismuth surfactant was applied during the InGaAs overgrowth and assess the enhanced nanocomposite for photocative sources.

Samples were grown by solid-source molecular beam epitaxy (MBE) in an EPI Mod. Gen. II system on (001)-oriented, Fe-doped, semi-insulating InP substrates. InGaAs layers were grown at 490°C and 2.4 Å/s with an As$_2$/group-III beams equivalent pressure (BEP) ratio of 15 and $1 \times 10^{-5}$ Torr BEP of As$_2$, which was held constant throughout the growth of the structures. A bismuth BEP of $1 \times 10^{-7}$ Torr, corresponding to an ~20% surface coverage, was applied on select samples during growth of the InGaAs layers only and was not expected to incorporate at this substrate temperature. Nanoparticles of LuAs with a growth rate of 0.07 monolayers per second (ML/s) were epitaxially incorporated in a superlattice structure with the depositions of LuAs nanoparticles repeated at each period.

The growth rate and depositions are reported in terms of equivalent number of LuAs ML, as determined from reflection high-energy electron-diffraction (RHEED) intensity oscillations and high-resolution X-ray diffraction (HR-XRD) measurements of full LuAs films. The superlattice structure consisted of a 150-nm InGaAs buffer layer followed by 30 periods of LuAs deposition with 40 nm of InGaAs overgrowth, similar to the structures previously investigated. All materials grown used equal LuAs depositions per period except for those used for transmission electron microscopy (TEM) studies, which varied in the amount of LuAs deposited per period. Specifically, TEM structures began with the depositions of 0.2 ML in the first period and increased by 0.2 ML per period up to 3.0 ML.

Previous studies of LuAs nanocomposites indicate that LuAs, like other rocksalt RE-As monopnictides, nucleates as nanoparticles before the formation of films when grown on zincblende III-V materials. The amount of RE-As deposited and the growth rate of the RE-As can alter both the density and size of the nanoparticles, changing the exposed area of the underlying III-V matrix needed to seed the overgrowth. For all superlattices containing effective LuAs depositions of 1.2 ML per period or less, the observed RHEED pattern during growth blurred slightly within the first 10 nm of InGaAs overgrowth and subsequently recovered a streaky ($2 \times 4$) pattern. The superlattice with an effective LuAs deposition of 1.6 ML per period initially needed ~28 nm of overgrowth to recover the streaky RHEED pattern, and the recovery degraded as the number of periods increased. In contrast, when using bismuth as a surfactant, the LuAs-containing superlattices recovered the streaky RHEED pattern after only ~14 nm of overgrowth for depositions of 1.6 ML, ~20 nm for 2.0 ML, and ~26 nm for 2.4 ML. The increase in InGaAs overgrowth required to recover the streaky RHEED pattern is attributed to the increased surface roughness during the initial stages of III-V overgrowth. This makes increasing depositions of RE-As more challenging since defects and roughening that begin at the RE-V/III-V interfaces have a cumulative effect on subsequent periods grown in the superlattice.

For an effective deposition of 1.6 ML per period without bismuth, asymmetric $\omega$-20 HR-XRD scans around the (004) InP substrate diffraction peak showed degraded superlattice peak fringes, indicative of poor quality period interfaces.

Significant improvement of the superlattice fringe peaks was observed when bismuth was used. Root-mean-squared (RMS) surface roughness measurements, as determined by atomic force microscopy (AFM) scans, are shown in Fig. 1. RMS roughnesses were over 10 nm for the superlattice grown without bismuth at an effective deposition of 1.6 ML per period. The application of bismuth as a surfactant improved the RMS roughness dramatically and resulted in an ~30% increase in the per-period LuAs deposition in the superlattices that was achievable without significant degradation in structural quality, consistent with the observations from RHEED and HR-XRD. Cross-sectional TEM studies with increasing depositions of LuAs nanostructures per period, shown in Fig. 2(a), indicate severe surface roughening after an effective LuAs deposition of 1.6 ML as shown previously and consistent with other superlattice studies of ErAs on InGaAs with a similar ErAs growth rate. By contrast, cross-sectional TEM studies that utilized bismuth as a surfactant during the InGaAs overgrowth, shown in Fig. 2(b), shows a substantial improvement in the quality of the period interfaces. Slight surface modulations appeared for effective LuAs depositions exceeding 2.4 ML, with progressively degraded period interfaces at still higher depositions. The improved morphology of the InGaAs can be attributed to the surfactant effect of the bismuth atoms on the growth surface of the material, which decrease the adatom surface diffusion length suppressing phase segregation and islanding in heteroepitaxy and promoting a layer-by-layer growth mode.

Room-temperature Hall measurements of these superlattices indicated electrons as the majority carriers, consistent with previous studies of other RE-As:InGaAs nanocomposites. The Hall measurements showed an initial decrease in the dark resistivity at low LuAs depositions, compared to measured resistivity values of 0.07 Ω-cm for control samples of epitaxial InGaAs, and then a gradual increase with increasing depositions of LuAs, as shown in Fig. 3. This trend

![Figure 1](image-url)
is consistent with the previous studies of RE-As:InGaAs superlattices, where RE-As nanostructures appear to dope the material at low depositions and act as recombination centers at higher depositions, reducing the mobility and conductivity.30,34 The superlattices that employed bismuth as a surfactant during the InGaAs overgrowth showed an increase in dark resistivity to a maximum of 0.44 Ω-cm, a 15× improvement over the otherwise identical superlattices that did not use bismuth. The improved structural quality of the InGaAs matrix and subsequent improvement in overgrowth quality likely reduce the scattering and diffusion-limited transit times of the charge carriers64,69 before recombination at the LuAs nanostructures. The carrier mobility, shown in Fig. 4, exhibited a decreasing trend with increasing deposition of LuAs. The superlattices grown with bismuth maintained mobilities over 2300 cm²/V-s, even at high LuAs depositions of 2.4 ML per period. These improvements in the electrical properties can be attributed to the improved material quality of the InGaAs overgrowth after every period.

Temperature-dependent Hall measurements showed strong dependence of the measured charge carrier concentration to the amount of LuAs deposited per superlattice period. As previously demonstrated,30,34 the data can be fitted to an exponential equation that relates the change in the carrier concentration as a function of the temperature to extract the effective activation energy of the charges. This activation energy is not a measure of the true Fermi level alignment at the RE-As and InGaAs interface, but rather a reasonable proxy for the average position of the Fermi level at the nanoparticle/matrix interface throughout the superlattice.34 Higher activation energies signify the Fermi level aligning closer to the middle of the InGaAs bandgap, decreasing the free carrier concentration and increasing the dark resistivity. The extracted activation energies, shown in Fig. 5, increased with increasing depositions of LuAs, reaching a maximum of 72 meV for a deposition of 1.2 ML grown without bismuth before falling to 68 meV for a deposition of 1.6 ML. The superlattices grown with bismuth exhibited significant

FIG. 3. Room-temperature dark resistivity measurements of superlattices as a function of equivalent LuAs deposition per period. Superlattices grown with bismuth exhibited significantly higher resistivities than the bismuth-free superlattices. The dashed line represents the resistivity of epitaxial InGaAs.

FIG. 4. Room-temperature electron mobility as a function of LuAs deposition. Superlattices grown with bismuth exhibited mobilities that remained above 2300 cm²/V-s, even for LuAs depositions as high as 2.4 ML per period, which exceeds the deposition levels that could be successfully overgrown without bismuth.

FIG. 5. Activation energy, $E_a$, of LuAs-containing InGaAs superlattices with increasing equivalent LuAs deposition per period. The superlattice with a 1.6 ML effective deposition of LuAs per period that used bismuth exhibited the largest improvement in activation energy, reaching 177 meV. The inset shows a (1-D Poisson) band diagram for this superlattice using the 177 meV activation energy as the Schottky barrier height and the carrier concentration from room temperature Hall as the doping level for the InGaAs.
improvement in the activation energy reaching a maximum of 177 meV, a $\sim 2.6 \times$ improvement for a deposition of 1.6 ML. The improvement is attributed to the surfactant effect of the bismuth on the structural quality of the InGaAs matrix. The nanoparticle/matrix interface, normally dominated by the (001) plane is increasingly exposed to other crystallographic planes as the InGaAs overgrowth surface roughens with increasing depositions of RE-As or through accumulated structural defects from increasing superlattice periods. Other crystallographic planes expose different Fermi level alignments and Schottky barrier heights $^{77,70,71}$ to the nanoparticle/matrix interface and can affect the measured average position of the Fermi level. The observed degradation for the superlattices with 2.0 and 2.4 ML depositions is attributed to the bismuth no longer being sufficient to compensate for the increasing deterioration in the structural quality of the InGaAs, hence exposing the nanoparticle/matrix interface to crystal planes with different Fermi level alignments that lower the measured activation energy.

Time-resolved differential pump-probe transmission at 1550 nm was performed to measure the carrier lifetime of the different superlattice structures. The normalized differential intensity of the transmitted probe signal was fitted to an exponential relation to extract the carrier lifetime of the charges following the method in previous investigations $^{34,72}$. The measured carrier lifetimes decreased with increasing deposition of LuAs, as shown in Fig. 6, to a minimum of 3.4 ps for an effective deposition of 1.6 ML per period grown without bismuth. The superlattices that used bismuth exhibited a nearly $2 \times$ decrease in the carrier lifetime down to 1.8 ps for the 1.6 ML depositions of LuAs and increasing to $\sim 2.1$ ps for depositions of 2.0 and 2.4 ML per period. This suggests that the improved quality of the InGaAs overgrowth also improved the carrier lifetime possibly by decreasing the diffusion time of the carriers to the LuAs nanoparticles where electron-hole recombination is favored. As the InGaAs overgrowth deteriorated for the 2.0 and 2.4 ML LuAs deposition samples, the additional crystal defects likely increased the scattering, resulting in longer carrier lifetimes.

In summary, we have comparatively investigated the material quality, electrical properties, and the carrier lifetimes of superlattices of LuAs embedded in an InGaAs matrix under growth conditions both with and without the use of bismuth as a surfactant during the InGaAs growth. The material quality, through HR-XRD and surface roughness characterization, shows substantial improvement through the use of bismuth, allowing for an $\sim 30\%$ increase in the amount of RE-As deposited before the onset of morphological degradation. The electrical properties showed a $15 \times$ improvement in the dark resistivity, reaching a maximum of 0.44 $\Omega$-cm, while maintaining mobilities over 2300 cm$^2$/V-s for effective LuAs depositions up to 2.4 ML per superlattice period. The activation energies were uniformly higher for the structures grown with bismuth, reaching a maximum of 177 meV. The degradation in activation energy at the highest depositions can be attributed to the degradation in the material quality potentially affecting the integrity of the nanoparticle/matrix interface. Carrier lifetimes showed a substantial decrease for the structures that used bismuth, achieving a lifetime of 1.8 ps for a 1.6 ML per-period deposition of LuAs, despite the rather large, 40 nm, InGaAs thickness between LuAs layers. By using bismuth as a surfactant during the InGaAs growth, we have demonstrated a significant improvement in the material quality and the properties of RE-As nanocomposites that are key for candidate photomixer materials. Further study is required to explore the effect of the magnitude of the bismuth flux during growth on nanocomposite properties. Growth enhancements that further improve the structural quality of the InGaAs overgrowth in RE-As nanocomposites could result in very promising photocoductive materials for THz generation.

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![FIG. 6. Carrier lifetimes, as measured by differential pump-probe transmission, of superlattices with increasing deposition of LuAs per period.](image)
