Rare-Earth Monopnictide Alloys for Tunable, Epitaxial, Designer Plasmonics

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Supporting Information

ABSTRACT: We demonstrate that plasmonic response can be tuned spectrally via the alloy composition of an epitaxial semimetallic film. Specifically, attenuated total reflectance studies show that the surface plasmon resonance of rare-earth monopnictide La$_x$Lu$_{1-x}$As alloy films can be tuned across the mid-IR, while lattice-matching to technologically important substrates. The electrical properties are a strong function of the composition, which, in turn, manifests as tunability of the optical properties. The ability to produce tunable (semi)-metals that can be epitaxially integrated with III–V emitters and absorbers is expected to enable a new generation of novel nanophotonic device architectures and functionality.

KEYWORDS: rare-earth monopnictide, semimetal, tunable metal, epitaxial metal, mid-infrared optoelectronics, plasmonics, molecular beam epitaxy

A variety of opportunities motivate the development of epitaxial (semi)metals, including the ability to design fully integrated structures where metallic films and nanostructures can be seamlessly integrated into the heart of devices. Applications include high-performance tunnel-junctions for solar cells, epitaxial transparent Ohmic contacts, photonics THz sources, and thermoelectrics, to name only a few. Additionally, the integration of metallic nanostructures and films into optoelectronic devices has shown potential for improving device performance and functionality through subwavelength confinement of plasmonic modes and enhancement of light/matter interactions, for applications including sensing, energy harvesting, communications, and so on.

Tailoring the plasmonic response is essential for optimum device performance, motivating the pursuit of spectral tunability via alloying, such as Ag–Au alloys, binary and ternary compounds, nitrides, germanides, and so on. However, single crystal materials are highly desirable for (1) their greatly enhanced plasmonic response and (2) the potential for epitaxial integration into devices, rather than being restricted to their periphery. As an epitaxial alternative, heavily doped semiconductors, such as InAs and silicon, are being explored for their plasmonic properties. While these materials can be grown epitaxially, they are thus far limited to wavelengths >5 μm. Extensive work has also been conducted on the growth and characterization of the ternary II–VI materials, ZnCdTe and HgCdTe, in their semimetallic regimes, and the dependence of structural, optical, and electrical properties on composition. However, these material systems are difficult to integrate with conventional III–V substrates because of a large lattice mismatch and incompatible growth parameters. The transition metal nitrides and conductive oxides are also attractive candidates for tunable, epitaxially compatible plasmonic materials; however, their epitaxial integration with III–V materials has yet to be explored. Additionally, despite the excellent plasmonic properties of Ag and tunability of Ag–
Au alloys, monolithic integration of these materials with active III–V semiconductors remains an open question.

The inability of current approaches to offer the flexibility of epitaxial integration into III–V-based optoelectronic devices, response in the mid-infrared (3–5 μm), and wavelength tunability motivates this study. We demonstrate a significant step forward in this vein with the realization of a tunable epitaxial metallic material system, creating a path toward designer (semi)metallic films that can be seamlessly integrated with traditional III–V semiconductor photonic materials. These tunable metals enable lattice-matching across a variety of relevant substrates, as well as tunability of both the optical transparency windows and plasmonic response, all while maintaining moderate resistivity and carrier mobility.

Many of the rare-earth monopnictides (RE-V) are rocksalt semimetals and can be epitaxially integrated with III–V semiconductors as nanoparticles and thin films. Additionally, it has been shown that ErAs films can be overgrown with high-quality III–V materials via a nanoparticle-seeded growth technique, providing a path toward the integration of epitaxial metals into the core of devices. The RE-V system is a viable pathway toward epitaxially integrated metals, having widely varying structural, electrical, and optical properties. Furthermore, RE-V alloys can be used for the development of tunable, epitaxial metallic films and nanostructures, with the potential to integrate customized metals into III–V heterostructures devices.

Most investigations thus far have studied binary RE-V materials, with some reported use of ternary alloys to lattice-match ScErAs/GaAs, ScYbAs/GaAs, and ScErSb/InAs. However, the full range of optical, electrical, and structural properties accessible through RE-V ternary alloy growth has not been studied. Specifically, the properties of LaAs and LuAs have been shown to vary greatly in their optical spectra, lattice parameters, and bulk room-temperature resistivity. These divergent properties make these two materials particularly interesting for alloy growth and characterization because they may offer a large range of tunable parameters. Here we demonstrate, with the growth of high-quality Lu1−xAs films, the ability to produce tunable epitaxial metals, with (1) a range of peak transmission spectra from near- to mid-IR wavelengths, (2) moderate resistivity, and (3) potential lattice-matching to many technologically relevant III–V substrates. This investigation demonstrates the full range of the potential of the RE-V ternary alloys and of their electrical, structural, and optical properties.

Samples were grown by solid-source molecular beam epitaxy (MBE) in an EPI Mod. Gen. II system on semi-insulating (100) GaAs. Films were grown at 460 °C, measured with a pyrometer with a wavelength response centered at 900 nm, with an As:RE flux ratio of 21:3:1, corresponding to a beam equivalent pressure ratio of 46:1. The reflection high-energy electron diffraction (RHEED) patterns observed in situ during growth suggest high-quality material, with roughening observed only from films that exceeded the critical thickness for lattice relaxation. We have previously reported the complications for growth of LaAs directly on III–V substrates, and developed a method for the growth of high quality lanthanum-containing RE-V films, utilizing thin LuAs barrier layers at the RE-V/III–V heterointerfaces. The growth of lanthanum-containing Lu1−xAs films therefore employed thin, 5 monolayer (ML) thick, LuAs barrier layers to ensure the growth of high quality single-crystalline rocksalt epitaxial La1−xLu1−xAs films. We observed that for films of low lanthanum content, <15%, these LuAs barriers were unnecessary, as the resulting in situ RHEED patterns and ex situ X-ray diffraction (XRD) ω-2θ scans of the low-content films (not shown) did not exhibit poor film morphology.

La1−xLu1−xAs samples were grown with La content varying from x = 5–67% and XRD ω-2θ measurements about the (002) reflection of the samples were conducted to verify La content and assess film quality. The La1−xLu1−xAs alloys of varying compositions obeyed Vegard’s Law, as shown in Figure 1, with a linear dependence of lattice constant on lanthanum content. This linearity enables the growth of alloys that span a large range of lattice parameters, from nearly lattice-matched to GaAs at 5.68 Å to lattice-matched to the 6.1 Å materials. A reciprocal space map (not shown) of a 67 nm film of Lu0.48As with 48% La content indicated a nearly fully relaxed film, with <1% residual strain. The residual strain may be due to a difference in thermal expansion coefficients between the III–V zincblende and the RE-V rocksalt layers.

Electrical resistivity measurements were conducted using the van der Paw (vdP) configuration. The effect of parallel resistances in the LaAs with LuAs barrier layers was accounted for using a 10 ML thick LuAs sample. The room-temperature resistivity of the Lu0.48As films exhibited a linear trend, shown in Figure 2, with resistivity increasing with the La content. The disparity between the resistivity of the Lu0.48As films and of pure LaAs may arise due to the severe mismatch and resulting relaxation into a dislocated film of the LaAs/GaAs system. Band structure calculations are needed to better understand the dependence of Lu1−xAs film resistivity on La content, and may clarify how the lanthanum affects the band structure and, in turn, the carrier concentration. Temperature-dependent resistivity measurements (Figure 2, inset) were conducted using etched mesa VdP structures. Details of sample processing appear elsewhere. Lu0.48As films of ~48% La content and 30, 100, and 500 nm thickness exhibit a reduction in resistivity of ~2× over a temperature range of 77–300 K. The behavior of these RE-As alloy films follows that of previous works in ErAs, LuAs, and LaAs, decreasing in resistivity with decreasing temperature. Further investigations into the temperature-dependence of various RE-V binary and ternary alloy films at

![Figure 1. Lattice constant of La1−xLu1−xAs films](image-url)
4 K are underway, and may give more insight into the carrier scattering behavior of the La$_x$Lu$_{1-x}$As alloys. Transmittance and reflectance measurements of the La$_x$Lu$_{1-x}$As alloys showed a similar linear dependence of their optical properties on alloy content. The peak transmission of the 0.5 μm La$_{0.48}$Lu$_{0.52}$As film was intermediate those of the constituent materials, as seen in Figure 3. The transmission peak occurred at ~2.3 μm with a transmittance of >30%. Similarly, the reflectance spectra (Figure 3, inset) showed a sharp Drude edge at ~4.5 μm, midway between the previously reported Drude edges for LuAs and LaAs, which appeared at ~3.1 and ~8 μm, respectively. The reflectance spectra of several 100 nm La$_x$Lu$_{1-x}$As samples with varying lanthanum content (Figure 4) more clearly illustrate the tunability of the Drude edge with increasing lanthanum content. This shifting of the apparent Drude edge with La content demonstrates a shifting of the plasma frequency with alloy composition. We would expect, then, that the surface plasmon frequency, which is proportional to the plasma frequency, to undergo a similar shift. Indeed, Figure 5 plots the attenuated total reflectance (ATR) of a 0.5 μm film of La$_{0.48}$Lu$_{0.52}$As grown on GaAs, compared to the transmittance and reflectance spectra of the same film. ATR spectroscopy allows coupling to surface plasmons and has previously been used to study surface plasmon polaritons (SPP) in polar dielectrics. The ATR spectra were collected using a Thermo Nicolet 6700 FTIR coupled to a Continuum IR microscope. The IR beam, generated by the FTIR, was focused onto a ZnSe (n = 2.4) prism at a 45° angle. We controlled the sample-prism distance with submicron resolution using a nanopositioning stage. The ATR spectra were then averaged over 128 collections with 4 cm$^{-1}$ spectral resolution. Figure 5 indicates that many of the higher energy attenuations in the ATR spectrum may be attributed to peaks in the transmission spectra. We observe an ATR dip corresponding to surface plasmon coupling (denoted with arrows in Figure 6) that consistently appears at frequencies slightly below the plasma frequency across the range of tunable alloy films of La$_x$Lu$_{1-x}$As. For each composition, this dip spectrally shifted as the gap between the film and the ZnSe crystal was varied with a piezo actuator (which in turn, altered the local dielectric environment), while the other features remained spectrally unchanged, leading to its unambiguous identification as the surface plasmon resonance. Additionally, by comparing the ATR spectra of LuAs, LaAs, and La$_{0.48}$Lu$_{0.52}$As in Figure 6, we observed that there appears to be a suppression of the short-wavelength peak observed in LuAs at ~2.5 μm, attributed to...
interband absorption, through composition adjustment of the alloy. Note that the ATR-excited SPP mode using this measurement geometry is not a pure air-metal SPP. Rather it is a perturbed mode due to the spatial overlap of the prism with the SPP. This mode perturbation, however, does not influence the electron-concentration dependence of the ATR dip. These measurements further confirm the features observable through specular reflectance and transmittance, indicating clear tunability of the La$_{x}$Lu$_{1-x}$As alloy optical and plasmonic properties.

Ellipsometry measurements of LuAs, LaAs, and La$_{0.48}$Lu$_{0.52}$As were performed to extract the real and imaginary components of the permittivity. Plotting $\varepsilon'$ and $\varepsilon''$, the real and imaginary components of the permittivity, respectively, in Figure 7 demonstrates the potential to tune the low-loss wavelength ranges of the RE-V alloys. Identifying the full extent of tunable features for the RE-Vs will allow for better understanding and development of novel device structures.

In conclusion, tunable epitaxial metals with a broad range of optical, electrical, and structural properties are accessible with ternary alloy RE-V monopnictides. We have demonstrated the growth of high-quality La$_{1-x}$Lu$_{x}$As films with plasmonic properties tunable across the mid-IR, as well as the potential to lattice-match to a number of technologically important III–V substrates. This demonstrates the full range of the potential of the RE-V ternary alloys, and of their electrical, structural, and optical properties. Future work will focus on utilizing the nanoparticle-seeded growth technique for exploring the incorporation of RE-V ternary alloys into III–V heterostructures. A more in-depth theoretical study of the plasmon resonance is currently underway.

ASSOCIATED CONTENT
$\checkmark$ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.8b00288.

Composition dependent plasma frequency, Drude damping, and SPP figure of merit (PDF).

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Notes
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REFERENCES


2. Hanson, M. P.; Gossard, A. C.; Brown, E. R. ErAs as a transparent contact at 1.55μm.

3. Bjarnason, J. E.; Chan, T. L. J.; Lee, A. W. M.; Brown, E. R.; Driscoll, D. C.; Hanson, M.; Gossard, A. C.; Muller, R. E. ErAs:GaAs photomixer with two-decade tunability and 12μW peak output power. 


5. Luttmann, M.; Bertin, F.; Chabli, A. Ellipsometric studies of Cd1−xMgxTe epitaxial layers: A variable-angle spectroscopic ellipsometry study. 


7. Ebina, A.; Kazuyuki, S.; Takahashi, T. Crystal growth of Zn1−xMnxTe solid solutions and their optical properties at the photon energies of the lowest band-gap region. 

8. Choi, S. G.; Kim, Y. D.; Yoo, S. D.; Aspnes, D. E.; Miotkowski, I.; Ramdas, A. K. Ellipsometric studies of Cd1−xMgxTe (0≤x≤0.5) alloys.


10. Scott, M. W. Energy Gap in Hg1−xCd1−xTe by Optical Absorption. 


17. Ebina, A.; Kazuyuki, S.; Takahashi, T. Crystal growth of Zn1−xMnxTe solid solutions and their optical properties at the photon energies of the lowest band-gap region. 

18. Choi, S. G.; Kim, Y. D.; Yoo, S. D.; Aspnes, D. E.; Miotkowski, I.; Ramdas, A. K. Ellipsometric studies of Cd1−xMgxTe (0≤x≤0.5) alloys.


20. Scott, M. W. Energy Gap in Hg1−xCd1−xTe by Optical Absorption. 


26. Allen, S. J., Jr; DeRosa, F.; Palmstrøm, C. J.; Zrenner, A. Band structure, quantum confinement, and exchange splitting in Sc1−xMgxTe epitaxial layers buried in GaAs. 


32. Crook, A. M.; Nair, H. P.; Ferrer, D. A.; Bank, S. R. Suppression of planar defects in the molecular beam epitaxy of GaAs/ErAs/GaAs heterostructures. 


34. Palmstrøm, C. J.; Mounier, S.; Finstad, T. G.; Miceli, P. F. Lattice-matched Sc1−xErAs/GaAs heterostructures: A demonstration


