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Energy band engineering of flexible gallium arsenide through substrate cracking with pre-tensioned films

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Flexible electronics based on the otherwise rigid conventional crystalline semiconductors is emerging as a new class of technology. However, the existing layer-transfer approaches for implementing such technologies is mostly focused on maintaining the performance of the original device. Here we show that layer transfer through substrate cracking with a pre-tensioned nickel film readily enables the manipulation of the electronic band structure in flexible gallium arsenide (GaAs) devices. We empirically and theoretically quantify the effect of 'engineered' residual strain on the electronic band structure in these flexible GaAs devices. Photoluminescence and quantum efficiency measurements indicate the widening of the GaAs energy bandgap due to the residual compressive strain. The experimental results are in good agreement with our theoretical calculations. This study introduces a new way for strain engineering in flexible compound semiconductors with important implications for electronic and optoelectronic applications.

1 Introduction In the past few decades, there have been significant technological advances for realizing high-performance rigid devices made of crystalline semiconductors such as silicon and compound semiconductors. Recently, high-performance flexible electronics derived from these otherwise rigid semiconductors is emerging as a new class of technology [1, 2]. In principle, the maximum bending radius of a semiconductor, that is the radius before it breaks, significantly improves by reducing the material thickness. Therefore, thin semiconductor materials and devices lend themselves to flexible electronics. However, most electronic and optoelectronic devices despite having thin structures are commonly formed on rigid semiconductor substrates for practical considerations such as ease of handling. Therefore to make those devices flexible, a critical need lies in the development of innovative layer transfer processes for separating the thin device structure from the rigid support substrate.

So far, the main strategy for enabling high-performance flexible devices has focused on maintaining the superb properties of the initially rigid semiconductor materials and devices during the layer transfer and film handling processes. Despite the seemingly diverse nature of those approaches, they can be classified in three general categories: (i) brute force methods that use combinations of chemical and mechanical thinning methods [3], (ii) epitaxial layer lift-off and its variants that are based on the selective removal of a sacrificial layer sandwiched between the device layer and the substrate [4], and (iii) delamination through substrate cracking, also known as spalling [5]. These approaches have generally proven to be effective in maintaining the properties of high-performance materials and devices during the layer transfer process. However, new device engineering concepts are yet to emerge for enhancing the performance of the flexible devices beyond their rigid counterparts, which leverage the thin geometrical forms of flexible materials.

The high performance of electronic and optoelectronic devices often arises not only from the excellent material properties of the crystalline semiconductors but also from the advanced device engineering concepts such as strain engineering [6]. In particular, strain engineering has continuously played a key role in enhancing the performance of the state-of-the-art semiconductor devices through en-

ergy band engineering, i.e. manipulation of the electronic band structure. So far, there have been two main approaches to strain engineering in conventionally rigid device technologies. One prominent approach involves the epitaxial growth of a semiconductor film on a substrate with dissimilar lattice constant, referred to as heteroepitaxy. In this approach, the ensuing elastic strain in the semiconductor is proportional to the difference of the lattice constants. However, there is a trade-off between the strain level and the maximum thickness of the epitaxial layer, at which the elastic strain begins to relax through the formation of structural defects. A second prominent approach for strain engineering involves the use of strain-inducing capping layers with built-in tensile or compressive stress that are *locally* deposited over a device [7]. This approach is commonly used in manufacturing of advanced integrated circuits for enhancing the performance of the silicon transistors. Despite the far-reaching utility of strain engineering and its widespread adoption in conventionally rigid device technologies, little has been done to perform strain engineering in flexible devices.

In this study, we introduce a new way for performing strain engineering in flexible electronics by exploiting the thin geometrical forms of flexible devices. In particular, we use the substrate cracking process aimed at producing thin semiconductor devices to tailor the strain level in freestanding thin semiconductor materials. A p–n junction indium gallium arsenide device with 0.7% indium content (InGaAs) is used as the model system to illustrate this concept. Photoluminescence (PL) and quantum efficiency (QE) measurements were performed to independently examine the change in the energy bandgap of the flexible InGaAs due to the built-in engineered strain introduced during the layer transfer process. Furthermore, the electrical characteristics of the flexible and rigid devices were found to be nearly matching. Tight binding modeling and theoretical calculations were also performed to study the effect of strain on the energy band structure of InGaAs. Our results demonstrate the ability to engineer the energy band gap of flexible InGaAs through substrate cracking layer transfer technique. More importantly, since the spalling fracture can occur in a wide range of brittle materials, the proposed strain engineering method can be readily extended to other flexible material systems such as layered transition metal dichalcogenides and gallium nitride [8].

2 Methods Epitaxial growth of the p–n junction InGaAs devices was performed on 100 mm diameter (100)Ge substrates with 6° miscut angle toward [111] using the Veeco's K475 commercial MOCVD reactor at ~640 °C. The ohmic metal contact consists of Pd/Ge/Au layers (10 nm/40 nm/100 nm) that were formed through electron beam evaporation and a lift-off process, followed by annealing at 175 °C for 60 min in N_2 ambient. The active area of the p–n junction devices was defined through a lithographic process (0.25 cm^2) followed by a wet chemical etch using $HNO_3:HCl:H_2O$ (1:1:5). The elastic plane stress of the Ni film was estimated from the curvature of bulk monitor wafers using the Stoney's formula [22]

$$\sigma = \frac{E}{6R(1-\nu)}\frac{h_s^2}{h_f}, \tag{1}$$

where E, ν, h_s, h_f, and R are Young's modulus, Poisson's coefficient, substrate thickness, film thickness, and radius of curvature, respectively.

3 Experiments Films under tension in bilayer or multilayer structures may result in the formation of delamination cracks at the edges of a sample. Those cracks can then dive into the substrate and propagate parallel to the interface, if the fracture toughness of the substrate is sufficiently low. This type of substrate cracking (spalling fracture) was originally considered a mode of failure because it generally occurs spontaneously. Therefore, the early research in this field was mainly focused on developing a theoretical framework to predict and subsequently avoid the occurrence of the spalling fracture in thin film semiconductor structures [9, 10]. However, there have been recent developments in exploiting this mode of substrate cracking for making high-performance flexible electronics [2]. Recent studies suggest that the spontaneous delamination can be transformed into a controlled layer transfer process simply by using a stressor film that has intrinsic tensile stress and by applying a flexible handle layer above the stressor film [5, 11]. Once the fracture is initiated at

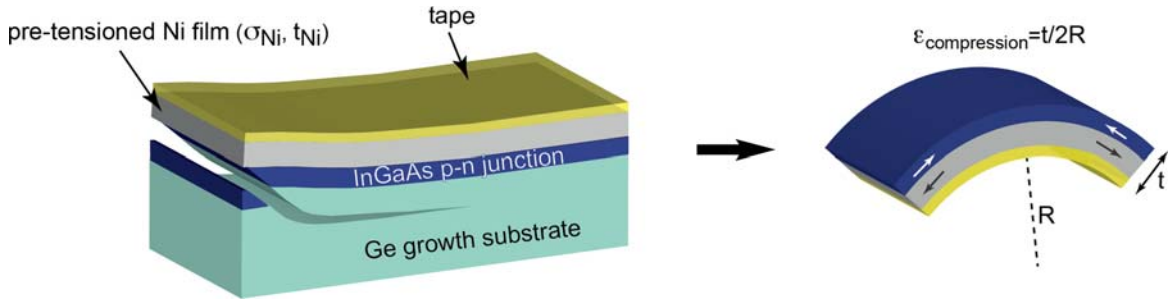

Figure 1 Conceptual illustrations of the layer transfer process and the resulting strain engineering method through substrate cracking. After separation of the surface layers, the nickel film tends to relax, inducing a residual compressive strain in the freestanding semiconductor layer. As a result, the value of the residual compressive strain is proportional to the intrinsic stress of the Ni film.

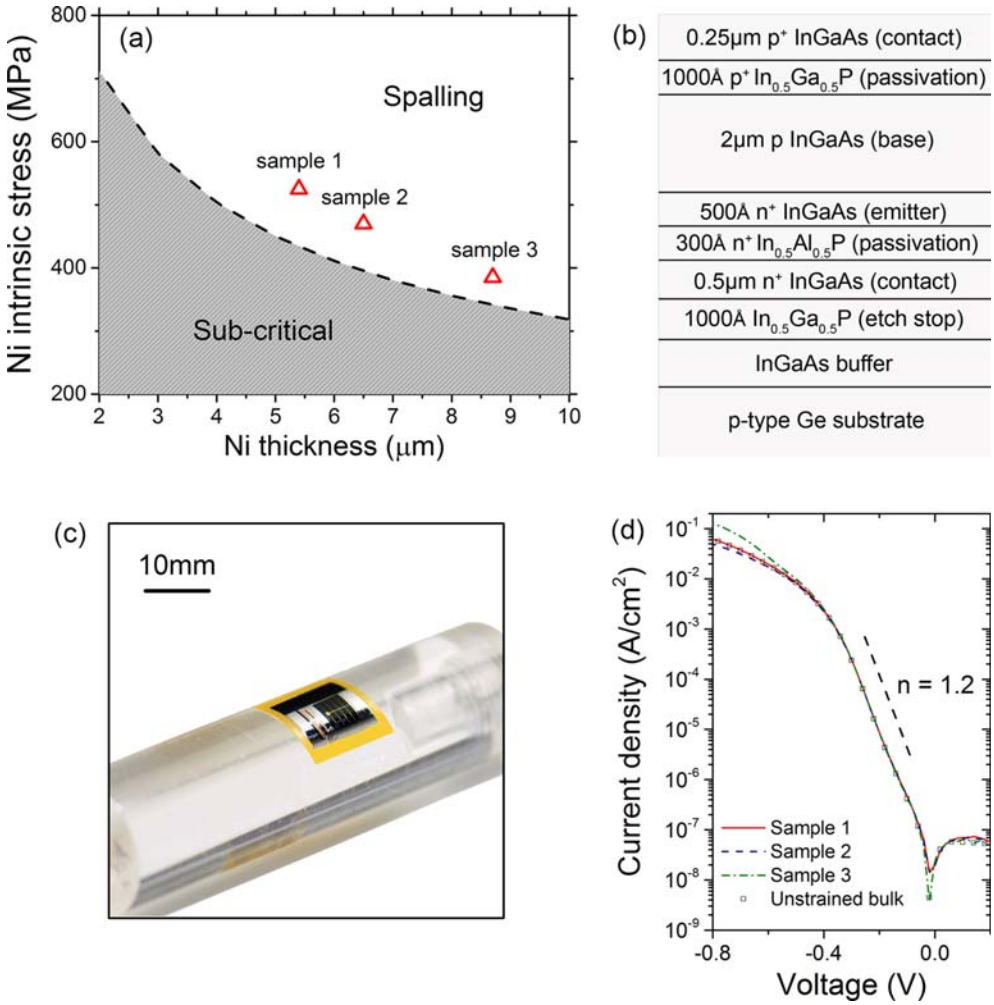

Figure 2 (a) Plot of the critical spalling condition for a simplified fracture problem in a Ni/Ge bilayer system indicates that the spalling fracture can occur for many combinations of the Ni stress and thickness. To investigate the strain engineering through substrate cracking, we prepared three flexible samples with different Ni stress levels. (b) Schematic illustration of the p–n junction InGaAs structure grown on a Ge substrate. (c) Representative optical image of a flexible InGaAs sample prepared using the substrate cracking method. The sample is mounted a glass cylinder to illustrate its mechanical flexibility. (d) Dark current–voltage measurement results for the flexible and rigid devices, showing nearly similar electrical characteristics.

one edge of the sample, the stressor film drives the subinterface fracture front inside the semiconductor. The flexible handle layer allows the fracture front to be guided mechanically. In addition, it facilitates film handling after the release of the surface layers by providing mechanical support. Here, we leverage these attributes of the layer transfer through substrate cracking to create a facile approach for adjusting the strain level and thus tailoring the electronic band structure of flexible InGaAs devices. Figure 1 schematically illustrates the proposed strain engineering concept in flexible devices. In this work, we used nickel (Ni) as the tensile stressor layer due to its excellent fracture toughness. Furthermore, polyimide tape was used as the flexible handle layer owing to its desirable chemical and thermal properties. Upon the release of the surface layers, the Ni stressor layer will relax and consequently force the thin semiconductor film to conform to the Ni layer. As a result of this transformation, a residual compressive strain is induced in the thin flexible semiconductor structure, where the strain level depends on the amplitude of the Ni stress.

In principle, the occurrence of the spalling fracture in a brittle material depends on a combination of the stress level and the thickness of the stressor film. The pioneering theoretical studies by Suo and Hutchinson suggest that the spalling fracture occurs at a depth inside the substrate when the opening mode (mode I) stress intensity factor (K_I) exceeds the fracture toughness of the substrate (K_{Ic}) and simultaneously the in-plane shear mode (mode II) stress intensity factor (K_{II}) becomes zero [10]. Figure 2a illustrates the critical relationship between the film stress and its thickness in a bilayer system comprising geranium (Ge) substrate (assuming fracture toughness of $K_{Ic,Ge} = 0.59$ MPa $m^{1/2}$) [12] and Ni film with tensile stress

(see Supporting Information). In this plot, the region under the curve represents the sub-critical combinations of the Ni thickness and the amplitude of the tensile stress, for which the spalling fracture does not occur. On the other hand, the area above the curve indicates that the spalling fracture can occur for a wide range Ni stress levels. This, therefore, presents an opportunity to readily engineer the residual compressive strain in the flexible device during the layer transfer process by selecting the desired tensile stress of the Ni film and subsequently finding the required Ni thickness in the region above the critical spalling curve where the spalling takes place.

4 Results and discussion To investigate the viability of strain engineering by means of substrate cracking, we prepared three samples (named samples 1, 2, and 3, 1 cm × 1 cm) with different Ni stress values (open data points in Fig. 2a). The Ni films with different stress levels were deposited using dc sputtering on three identical samples [13]. The samples include a 2 μm thick p–n junction InGaAs structure that was grown epitaxially on (100)Ge substrates, shown in Fig. 2b. Due to a small mismatch in the lattice constant of GaAs and Ge, a small amount of indium (0.7%) was incorporated in the structure to avoid the formation of structural defects due to strain relaxation. After the deposition of the Ni film, a 60 μm polyimide tape was applied on the top surface of the Ni. In these experiments, the spalling fracture for all samples occurred within the Ge substrate because of the prescribed thickness of the Ni film. After separating the surface layers, the excess Ge film was selectively removed with respect to the InGaAs structure through a wet chemical process using hydrogen peroxide. The front ohmic metal contacts were then formed using a low temperature process to complete the device fabrication (see Section Methods) [14]. In this structure, Ni additionally serves at the back ohmic contact. Figure 2c shows the representative photograph of a fully processed flexible InGaAs device. For comparison, we also prepared InGaAs devices on thick Ge substrates, which are unstrained. Next, we measured the dark current–voltage characteristics of the flexible and bulk devices, shown in Fig. 2d. The data illustrates that the ideality factor (n) and the saturation current of the devices remained unchanged as a result of the spalling process. The slight discrepancy in the ON current of the devices might be attributed to the difference in the quality of the low temperature ohmic contacts.

In our experiments, the plane elastic stress of the Ni film (σ_{Ni}) was estimated using the Stoney's equation (see Section 2). Furthermore, the residual strain of the flexible samples in the x and y directions (i.e. ε_x and ε_y) was estimated from the corresponding radii of curvature in each direction (i.e. R_x and R_y) using $\varepsilon = t/2R$, where t is the total thickness of the flexible sample. The radii of curvature for the flexible samples 1, 2, and 3 were measured from the side-view optical image shown in Fig. 3a. In our calculations, R_y was assumed to be infinite because the flexible InGaAs samples exhibit a cylindrical shape, thereby indicating the presence of uniaxial strain in flexible InGaAs devices (i.e. $\varepsilon_y = 0$). Figure 3b illustrates the plot of the Ni plane stress estimated from the Stoney's equation as a function of the corresponding strain estimated from the radii of curvature for the three flexible InGaAs samples. We determined the Young's modulus of Ni (E_{Ni}) to be about 224 GPa from the slope of the stress–strain curve shown in Fig. 2b and using the stress–strain relationship:

$$\sigma_x = \frac{E_{Ni}}{1-\nu_{Ni}^2} \times \left[\varepsilon_x + \nu \cdot \varepsilon_y\right]. \quad (2)$$

The Poisson coefficient of Ni (ν_{Ni}) is taken as 0.31. It is notable that the extracted value for E_{Ni} is in good agreement with the previously reported Young's modulus of Ni, indicating that Ni is almost fully relaxed upon the release of the surface layers and the strain is almost fully transferred to the thin semiconductor layer. This finding therefore corroborates the viability of strain engineering through the substrate cracking layer transfer process.

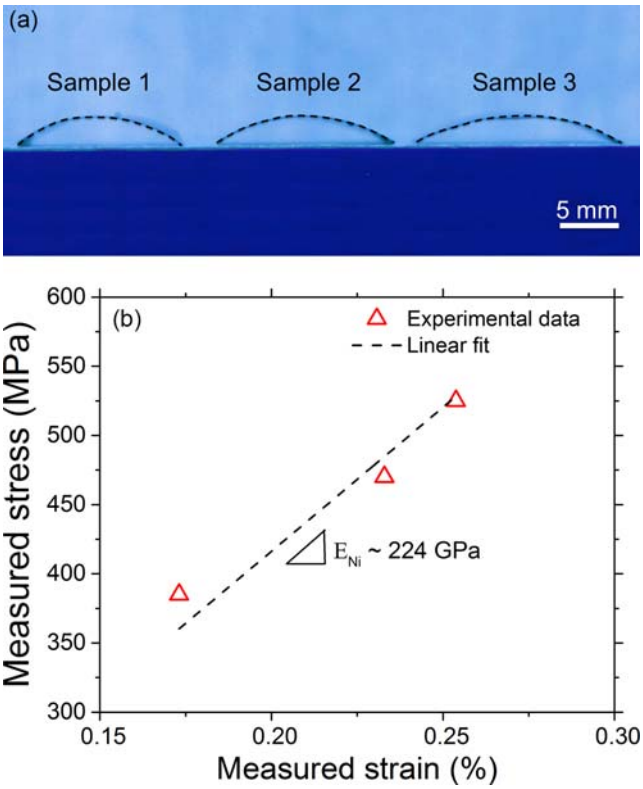

Figure 3 (a) Cross-sectional optical image of the flexible InGaAs samples 1, 2, and 3. The residual compressive strain for these samples was estimated from the radii of curvature using Eq. (1). (b) The plot of the Ni stress vs. residual strain. The elastic plane stress of Ni was estimated from the Stoney's formula and the residual compressive strain was approximated from the radii of curvature of the flexible samples shown in (a). The extracted value of E_{Ni} from the slope of the fitted line to the experimental data is in agreement with the Young's modulus of Ni.

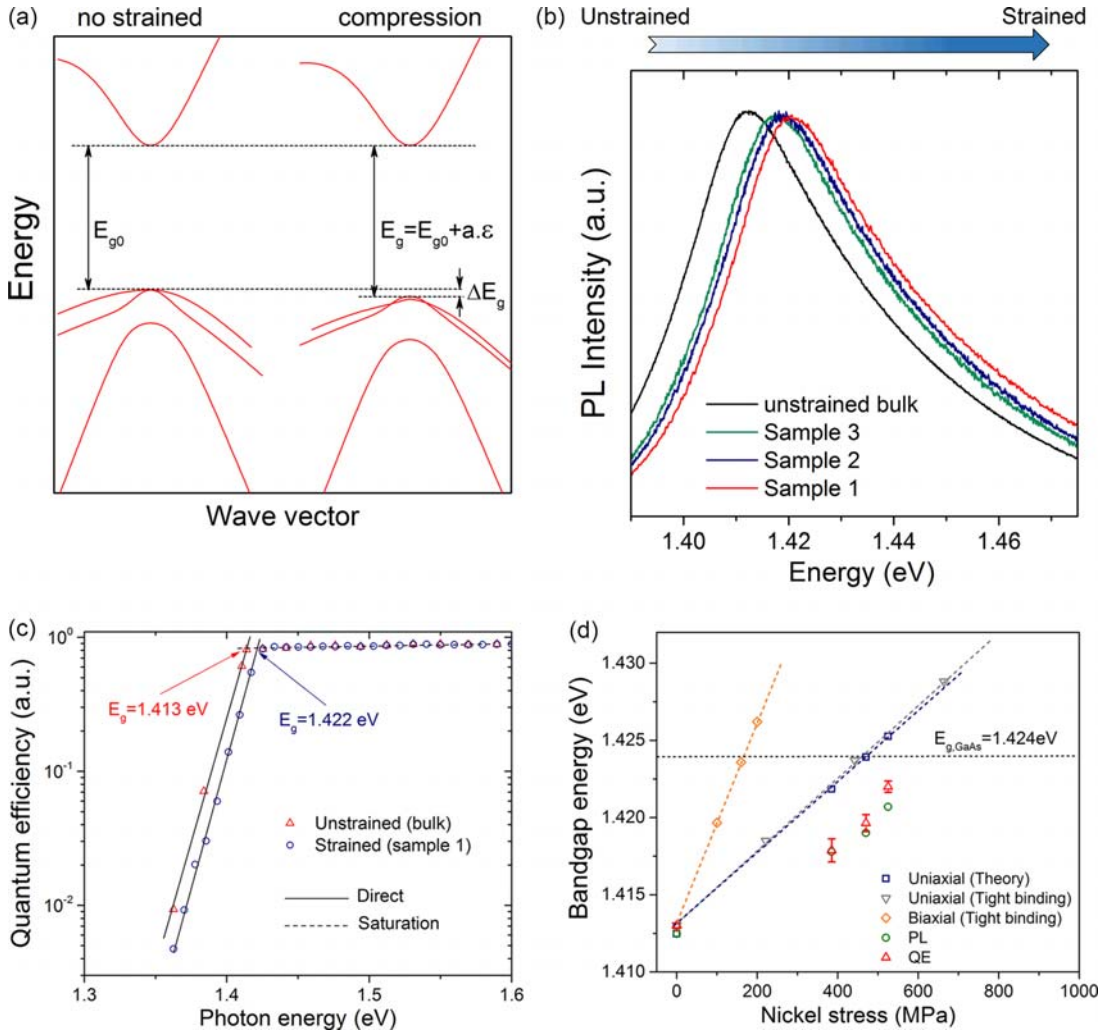

Figure 4 (a) Schematic illustration of InGaAs energy band structures with no strain and under compression. The energy bandgap begins to widen as the strain level increases. Energy bandgap of the InGaAs devices was measured using (b) PL and (c) QE at room temperature. (d) Comparison of the experimental bandgap measurements from PL and QE with tight binding simulations and theoretical calculations. The experimental results are in good agreement with those from the tight binding model and the theoretical calculations for InGaAs films under uniaxial compressive strain.

The application of strain to semiconductors is known to reduce the symmetry of the material and result in noticeable change in their energy band structure [15]. In particular, the energy bandgap of compound semiconductors under compression becomes larger than that of the unstrained layer [16]. Figure 4a conceptually illustrates the effect of compressive strain on the InGaAs energy bands. To reveal the effect of the engineered compressive strain on the electronic band structure of the flexible InGaAs devices, we examined the change in the energy bandgap of the samples 1, 2, and 3. We initially performed PL measurements at room temperature to determine the energy band gap of the strained (flexible) and unstrained (rigid) InGaAs devices. Photoluminescence measurements provide a straightforward method for probing the energy bandgap of most materials. In the case of GaAs, care must be taken for probing the energy bandgap using PL method because of the doping and thickness dependence of the PL line spectrum of n-type GaAs layers [17]. As a result, the PL line spectrum of n-type GaAs might differ from that of the intrinsic material. This characteristic is attributed to the significant difference between the effective mass of the electron and hole carriers in GaAs. Unlike n-type GaAs layers, the PL line spectrum of p-type layers does not exhibit doping and thickness dependence and is similar to that of the intrinsic layers. For this reason, the n-type emitter layer was made very thin (~50 nm) in our p–n junction devices (see Fig. 2b). Figure 4b illustrates the PL line spectra of the flexible InGaAs samples 1, 2, and 3 together with that of the unstrained InGaAs sample. The PL line spectra of the flexible InGaAs devices clearly exhibit blue shift with respect to the unstrained sample. The data additionally indicates the increase in the PL peak energies of the flexible devices by increasing the amplitude of the Ni stress.

To further elucidate the effect of the compressive strain on the energy bandgap of the flexible InGaAs devices, we performed QE measurements (see Supplementary information). A previous study suggests that the bandgap of a semiconductor can be determined from the QE plot by taking advantage of the exponential behavior of the absorption coefficient α near the band edge (Urbach's rule) [18]. More specifically, the QE tends to be proportional to the absorption coefficient for devices with adequately large diffusion length. An additional requirement includes making devices with sufficiently thick absorber layer in order to allow strong absorption at the band edge. Under these conditions, the QE exhibits exponential behavior at the band edge and saturates to a value near unity for photon energies larger than that of the bandgap. The work by Helmers et al. demonstrates that the bandgap of a semiconductor can be determined from the intersection of the saturation and the exponential regions in the semilogarithmic QE-energy plot [18]. Figure 4c illustrates the representative QE-energy plot for two InGaAs devices located on the unstrained bulk sample and the flexible sample 1. The data clearly indicates the increase in the bandgap of the flexible InGaAs device due to the built-in compressive strain induced by the Ni film.

Next, we calculated the energy band structure of InGaAs for a range of uniaxial and biaxial compressive strain values using tight-binding model utilizing the Nanohub Band Structure Lab program [19]. Tight-binding method is an atomic-level formalism that utilizes the nearest-neighbors coupling for calculating the energy band structure of materials while capturing important physical effects such as strain, band coupling, and spin. Figure 4d illustrates the summary of the experimental and theoretical results. The plot illustrates that the extracted energy bandgap values from the $sp^3d^5s^*$ tight-binding model for InGaAs film under uniaxial compression is in agreement with the experimental PL and QE results. Furthermore, we applied a theoretical framework for estimating the change in the energy bandgap of the InGaAs under uniaxial compression. This theoretical formulation was originally developed for studying the effect of hydrostatic uniaxial stress on the energy band structure of various semiconductors including GaAs, germanium, and so on [15, 20]. The shift in the energy of the light-hole band (ΔE_{lh}), which is tantamount to the shift in the energy bandgap of the semiconductor under compression (ΔE_g), was estimated by $\Delta E_g = \Delta E_{lh} = 6.48\varepsilon$ (eV) (see Supporting Information). For these calculations, we employed the elastic stiffness constants and the deformation potentials that were previously reported for GaAs [21]. The theoretical calculation (solid line in Fig. 4d) is also in good agreement with the experimental results, further confirming the utility of the layer transfer by means of substrate cracking for tailoring the energy band structure of flexible semiconductors, in this case InGaAs. Note that the bigger change in the energy gap is achievable by increasing the Ni stress level used for performing the substrate cracking process. Furthermore, strain engineering often allows the realization of electronic band structures that would not be otherwise possible to achieve without changing the composition of the material. More specifically, Fig. 4d reveals the possibility of achieving an energy bandgap for InGaAs that is larger than that of GaAs without having to incorporate phosphorous (P) or aluminum (Al) atoms. This is an important accomplishment, in particular for applications where the charge carrier transport is central because the incorporation of P or Al atoms in the lattice unavoidably results in the steep degradation of the transport properties of electron and hole charge carries.

5 Conclusions In summary, we demonstrated the ability to tailor the energy bandgap of flexible InGaAs devices through judicious engineering of the layer transfer process. The experimental PL and QE measurements of the energy bandgap for the strained and unstrained devices are consistent with the theoretical calculations. Our results indicate that the layer transfer through substrate cracking offers a facile way for performing strain engineering in high-performance flexible devices. Although, the size of the samples in this study was chosen to be 1 cm × 1 cm, the spalling process can be easily performed on big samples [2, 5, 11]. Furthermore, this strain engineering method can be readily extended to other flexible semiconductor devices due to the versatility of the spalling fracture.

Supporting Information Additional supporting information may be found in the online version of this article at the publisher's website.

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