Tailoring the electronic properties of $Ga_xIn_{1-x}P$ beyond simply varying alloy composition

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(Received 2 February 2009; accepted 13 February 2009; published online 5 March 2009)

Spontaneous ordering in $Ga_xIn_{1-x}P$ provides the possibility of tuning electronic structure and improving transport properties. A quasiperiodic twinning structure of two ordered variants offers additional flexibilities in designing the material properties. The superstructure is shown to have distinctively different electronic and electrical properties from the single-variant ordered structure, as revealed in polarized elecroreflectance and cross-sectional scanning Kelvin probe force microscopy measurements. The entire potentially accessible range of the "direct" bandgap is defined for this alloy system, and thus the optimal bandgap for any intended application can be achieved through the interplay of the effects of alloying, ordering, and domain structure engineering. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3094918]

The $Ga_xIn_{1-x}P$ alloy system is becoming ever more important in modern technology applications, such as telecommunications, photovoltaics, and solid-state lighting.[1–5] In the past, the composition of the alloy was typically chosen to lattice match to GaAs, i.e., with $x_0=0.516$. However, for a multijunction solar cell as well as other applications, the electronic structure of the disordered alloy of x_0 is not necessarily optimal for the intended application.[1–3] Recently, a triple-junction (TJ) solar cell involving metamorphic junctions between $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$ was shown to yield a higher efficiency (>40%) than the lattice-matched structure and has the potential for significantly improved efficiencies approaching 45%.[3] The optimal bandgaps of GaInP layers are suggested to be from 1.75 to 1.86 eV for TJ cells,[3] higher bandgaps are required for cells with more junctions or alternative approaches (e.g., light splitting). It is well known that $Ga_xIn_{1-x}P$ grown by organometallic vapor phase epitaxy (OMVPE) is often found to exhibit spontaneous ordering, and the ordering provides a way to tune the electronic structure at a fixed x or lattice parameter by varying the order parameter.[6] Additionally, an ordered structure can offer the same bandgap of a disordered alloy, but reduce alloy fluctuations.[7] The attainable tunability using the interplay of alloying and ordering for the fundamental bandgap as well as the conduction and valence band edges has recently been calculated for $0<x<1$.[5,8] In this letter, we show that an additional approach can be used to adjust the electronic structure of the $Ga_xIn_{1-x}P$ alloy, that is, the domain structure of the CuPt ordering, which can be controlled by varying the orientation of the substrate miscut. Furthermore, the electrical properties of $Ga_xIn_{1-x}P$ are also found to depend sensitively on the miscut orientation.

It has been well established that GaInP epilayers grown on a GaAs substrate miscut toward an $[111]_B$ direction (by 6° in particular) can have a large uniform domain (on the order of a micron) in a single $CuPt_B$ ordered variant,[9] whereas the use of an [001] or $[111]_A$ miscut substrate can result in a quasiperiodic layered structure of two alternating $CuPt_B$ ordered variants[10] that may exhibit interesting quantum effects.[11] In this work, we perform comparative studies of the single and double variant ordered GaInP epilayers, using a contactless electroreflectance (ER) technique[12] for determining the electronic band structure, and scanning Kelvin probe force microscopy (SKPFM) (Ref. 13) for probing of the electrical potentials in the GaInP epilayer.

Three sets totaling eight partially ordered GaInP samples are used in this study. They were grown by atmospheric-pressure OMVPE. The basic structure is doped-GaAs substrate/GaAs buffer/GaInP. The compositions of the GaInP epilayers were determined by x-ray diffraction. Both buffer and epilayer are nominally undoped, but typically found to have $\sim 10^{16}$ cm^{-3} n-type background doping, measured by secondary-ion-mass spectroscopy or C-V. The thickness of the buffer is ~0.5 μm, and the epilayer is 1–1.5 μm. They differ in the following aspects: (1) grown on either 6°-A or 6°-B tilted substrates, which results in double- and single-variant ordering, respectively; (2) on n- or p-type substrates; (3) with or without thin GaAs caps. The first set of samples are on 6°-B tilted n^+- or p^+-substrates with caps (labeled as S1–6B-n and S1–6B-p), the second set on 6°-A tilted n^+- or p^+-substrates (S2–6A-n and S2–6A-p) without caps, and the third set on both 6°-A and 6°-B tilted and n^+- or p^+-substrates, under the same nominal growth conditions as the first set but with no caps (S3–6B-n, etc.). They were characterized by polarized low temperature photoluminescence to assess the general quality of the samples and estimate their order parameters.[7] The samples were grown under optimized conditions such that small linewidths of the excitonic bandgap luminescence are obtained at low temperature: <5 meV for the single-variant ordered samples grown on 6°-B substrates, and <10 meV for double-variant ordered samples grown on 6°-A substrates.[7,11]

Figure 1(a) shows room temperature ER spectra in two polarizations of light, [1,1,0] and $[\bar{1},1,0]$, for S1–6B-n ($x=0.5238$). They exhibit Franz–Keldysh oscillations (FKOs) due to the built-in electric field in the GaInP epilayer. The spectra can be fit to a generalized FKO lineshape function with a broadening parameter,[14] assuming that there are two critical points because of the ordering induced valence band splitting. The fitting yields $E_{g1}=1.7955\pm0.0007$ eV,

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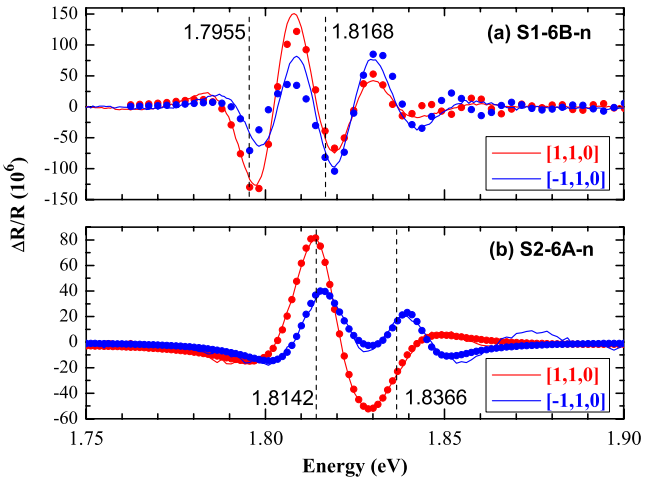

FIG. 1. (Color online) Polarized ER spectra (solid lines) for sample S1–6B-n and S2–6A-n. Solid points are the fitting results with the bandgap energies denoted by dashed vertical lines.

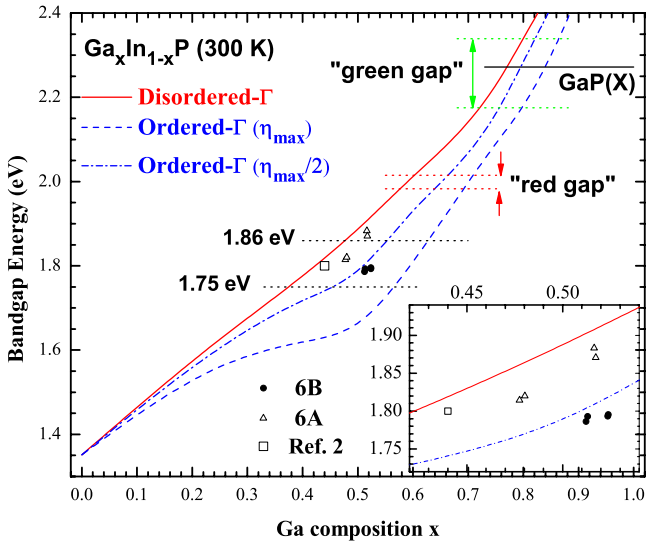

FIG. 2. (Color online) Bandgap energy of GaInP alloy vs Ga composition at room temperature. Symbols are the experimental data, the solid line is the Γ-like bandgap for the disordered alloy, the dashed line is the Γ-like bandgap for maximum order parameter $\eta_{\max}$, the dotted dash line is the bandgap with $\eta_{\max}/2$, and the solid horizontal line is the *X* point bandgap of GaP.

$E_{g2}=1.8168\pm0.001$ eV, averaging over the two polarizations. The modulation signal is stronger for the [1,1,0] polarization near the first band edge, and the polarization is reversed near the second band edge, as expected based on the calculated interband transition matrix elements for a moderate strength of ordering,[15] which is the case for this sample. The spectra for S1–6B-p ($x=0.5236$) are very similar to those shown in Fig. 1, with fitting results of $E_{g1}=1.7934\pm0.0005$ and $E_{g2}=1.8127\pm0.001$ eV. The bandgaps for these samples represent a major reduction, ~120 meV, from the bandgaps of the disordered alloys.

Figure 1(b) shows the ER spectra for S2–6A-n ($x=0.4775$), and the spectra for S2–6A-p ($x=0.4803$) are qualitatively similar. There are two significant differences between the 6B and 6A samples: (1) the modulation peaks of the two polarizations are nearly in phase across the energy range of the two band edges for the 6B samples, whereas they become out of phase for the 6A samples for energy higher than the fundamental bandgap. (2) The anisotropy near the fundamental bandgap is stronger for the 6A samples. The reason for these differences is that the anisotropy in the interband transition matrix element is enhanced for the double-variant ordered structure that is observed in the 6A sample, as a result of the formation of an "orientational superlattice."[11,16] The spectra of the 6A samples are found to fit better with the lineshape function for low electric field,[17] with results of $E_{g1}=1.8142\pm0.0001$ and $E_{g2}=1.8366\pm0.0041$ eV for S2–6A-n, and $E_{g1}=1.820\pm0.002$ and $E_{g2}=1.831\pm0.003$ eV for S2–6A-p. The bandgap reductions for these samples are ~45 meV from the corresponding disordered alloys.

The four samples of the S3 set were grown simultaneously with intent of having compositions closer to $x_0=0.516$ and thus examining the effects of the substrate orientation on the ordering. Their ER spectra are qualitatively similar to those of S1 and S2. The fitting yields $E_{g1}=1.8832$ eV for S3–6A-n ($x=0.5165$), 1.8704 eV for S3–6A-p ($x=0.5173$), 1.7863 eV for S3–6B-n ($x=0.5122$), and 1.7929 eV for S3–6B-p ($x=0.5130$). The results of this set of samples clearly indicate that the electronic structure of the ordered alloy depends quite sensitively on the domain structure that can be modified by changing the orientation of the substrate miscut. Although the order parameters for these samples are not measured, the results are qualitatively consistent with those from previous studies,[11,18] which have shown that for the same order parameter, the double-variant ordered structure tends to have a significantly smaller bandgap reduction than the single variant ordered one. In principle, the double-variant ordered superlattice can provide superior carrier transport yet without the large bandgap reduction in the single-variant ordered structure, because on the one hand ordering generally decreases the alloy fluctuation and on the other hand the ordering induced valence band splitting lessens the alloy scattering by reducing the density of the states for the hole.

Figure 2 shows the bandgaps of the eight samples within the full accessible range of $Ga_xIn_{1-x}P$ alloys, which is approximately defined by three curves. $E_{g\Gamma\text{-}d}(x)$ for the Γ-like bandgap of the disordered alloy, $E_{g\Gamma\text{-}o}(x)$ for the Γ-like bandgap of the ordered structure with maximum order parameter $\eta_{\max}=\min[2x,2(1-x)]$, and the $E_{gX\text{-}d}(x=1)$ for the *X* point bandgap of GaP. $E_{g\Gamma\text{-}d}(x)$ and $E_{g\Gamma\text{-}o}(x)$ are plotted for 300 K, which are obtained by applying a temperature shift of $[70(1-x)+115x]$ meV (Ref. 19) to the calculated results for 0 K.[5,8] The theoretical curves are for the strain-relaxed alloys that can be obtained by growing the epilayer on a composition-graded buffer.[2,3] However, the samples used in this work are coherently strained to GaAs substrates. For the two proposed optimal triple junction solar cells that require the bandgaps of the top GaInP layers to be either 1.86 or 1.75 eV,[3] from Fig. 2, we find the usable composition ranges to be 0.477–0.628 and 0.375–0.566, respectively, depending on the strength of the ordering and the substrate orientation. Also shown in Fig. 2 are the energy ranges of the "red-gap" and "green-gap" identified for "ultraefficient" white-light LEDs.[4] A metamorphic GaInP epilayer with ordering could be used to address the material challenges for these applications.

Figure 3 shows the distributions of the electrical potentials along the growth direction for all the eight samples, measured by SKPFM from the (110) cleaved edge. The po-

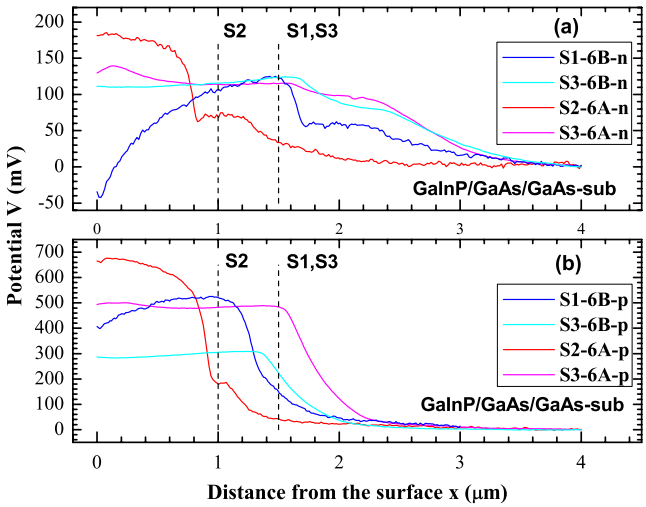

FIG. 3. (Color online) The potential profile of GaInP/GaAs heterostructure that is the average of the cross-sectional EFM image at a given distance. (a) For samples grown on *n*-type substrates, and (b) for *p*-type substrates. Dashed vertical lines indicate the approximate junction positions of the GaInP/GaAs heterostructures.

tential curves reveal that there is a strong electric field in the GaAs buffer layer when the structure is grown on the *p*-type substrate, as shown in Fig. 3(b) with a potential step close to 0.5 V or the bandgap difference between GaAs and GaInP for some samples. This large field is manifested as strong FKO signals from the GaAs buffer layer (not shown). For the samples grown on the *n*-type substrate, as shown in Fig. 3(a), the potential change across the whole structure is understandably much smaller, because all the layers are n-type. There is one very interesting difference between the 6A and 6B samples, that is, the potential slope dV/dx tends to be negative in the GaInP epilayer for the 6A samples, but positive for the 6B samples. Because all the GaInP epilayers are residual *n*-type, the effect of surface depletion should always result in $dV/dx>0$, which is indeed the case for all the 6B samples studied in this work, although the magnitude of the slope varies with the doping level and depends on the surface capping. However, the reversed slope $dV/dx<0$ observed in these 6A samples is abnormal. For the 6A sample, the slope seems to sensitively depend on the residual doping level, and the variation, which could not be controlled accurately in the growth, can in fact reverse the sign of the slope (in other samples measured but not included in this work). The abnormality occurring in the 6A samples could be related to the spontaneous polarization or pyroelectric effect that is anticipated in the CuPt ordered structure, based on the symmetry consideration. From the computed electric field in a (disordered-GaInP)/(fully ordered-GaInP) superlattice,[20] we arrive at an estimate of the spontaneous polarization $|P_0|=0.0265\ \mathrm{C/m^2}$,[21] which is comparable to that of GaN.[22] An unusual charge modulation has been reported in a laterally stacked alternating double-variant ordered GaInP epilayer with large ordered domains of micron size (but not in a single variant ordered structure).[23] An important difference from this early work is that the domain sizes are much smaller (only a few nanometers) and stacked vertically for the 6A samples studied here.[16] The observed abnormal band bending could be potentially useful for designing the electronic properties of the heterostructure, although further study is needed to understand the exact mechanism.

In summary, we have demonstrated an alternative way to tailor the electronic and electrical properties of a GaInP alloy by engineering the domain structure of the two $CuPt_B$ ordered variants. The superstructure exhibits an enhanced optical anisotropy, an unusual potential profile, and additional flexibility for achieving a desirable bandgap, compared to the simple alloy or single-variant ordered structure.

We thank R. Reedy for SIMS and M. Young for *C-V* measurements and J. M. Olson, S.-H. Wei and W. Metzger for helpful discussions. This work was supported by the DOE-OS-BES under Contract No. DE-AC36-08GO28308 to NREL.

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