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Electronic and optical properties of periodically stacked orientational domains in CuPt-ordered $GaInP_2$

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Abstract

Orientational domain twins that are periodically stacked in the growth direction are frequently observed in spontaneously ordered $GaInP_2$ alloys grown under special conditions. We present experimental evidence showing that the electronic and optical properties of such structures are altered from those of the uniform Cu–Pt ordered alloy.

Orientational domain twins consist of two spatially connected domains with identical crystal structures but different spatial orientations, and are frequently observed as planar defects in many categories of crystalline materials (semiconducting, metallic, superconductiong, ferroelectric, ferromagnetic and ferroelastic). In this article, we present experimental evidence for the electronic properties of a semiconductor superlattice that is formed by periodically stacking domain twins. The structure studied here is generated spontaneously in a CuPt-ordered $GaInP_2$ alloy [1] that results from a disorder–order structural phase transformation. A single unit of such a superlattice is a domain twin consisting of two ordered domains each of which orders along one of the two $[111]_B$ directions of a cubic crystal, respectively. In such a structure, there is neither a band offset nor an effective mass discontinuity along the superlattice axis, but an orientation change of the symmetry axis as one moves across a domain boundary. In the well-studied conventional superlattices, the band offset and/or the effective mass discontinuity are responsible for the superlattice effect [2]. The effects caused by the alternating spatial modulation of domain orientations are relatively unknown, except for a few recent theoretical studies [3–5] where idealized periodic structures, termed as orientational superlattices [4,5] (OSL's), were considered. Although the stacking sequence in the structures which we studied does not exhibit a well defined period, the domain size is always much less than that of the de Broglie wavelength and hence we refer to them as superlattice. We use polarized photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy to show how the electronic band structure and the associated optical properties are modified in such structures.

Single-variant CuPt-ordered $GaInP_2$ is a monolayer superlattice, i.e., $(Ga_{x+\eta/2}In_{1-x-\eta/2}P)_1/(Ga_{x+\eta/2}In_{1-x+\eta/2}P)_1$, along a $[111]_B$ direction, where the parameter $(0 < \eta < 1)$ is defined as the order parameter. Changes in the electronic [1,6,7] and optical properties [8,9] (e.g., band-gap reduction, valence-band splitting and optical anisotropy) caused by the CuPt ordering in $GaInP_2$ have been extensively investigated. In contrast, although double-variant CuPt-ordered structures where the ordering axis alternates

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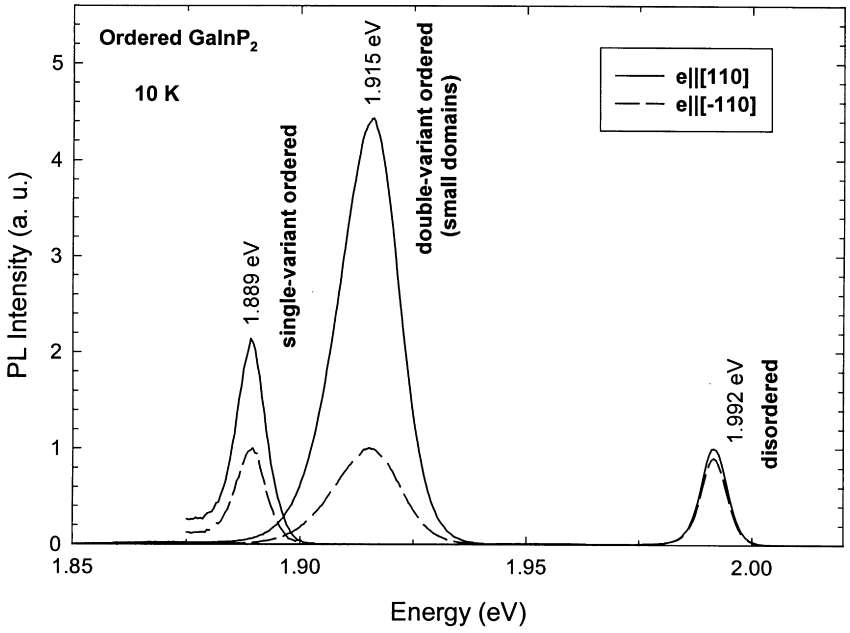

Fig. 1. Polarized PL spectra measured for disordered, single-variant ordered, double-variant ordered (large domain) and double-variant ordered (small domain) samples of $GaInP_2$.

between the two $[111]_B$ directions have been observed earlier in microscopic studies [10,12], the implication that such structures could lead to new types of superlattices was unnoticed until recently [4,5].

In this study, double-variant ordered $GaInP_2$ samples were grown on exact (001) or 6°-$[111]_A$ tilted GaAs substrates, and single-variant ordered samples on 6°-$[111]_B$ tilted substrates, using metal–organic vapor–phase epitaxy. The variation in the order parameter was obtained by varying the growth conditions (growth temperature and growth rate). With optimized growth conditions, the band-edge excitonic emission peak in PL and the excitonic absorption peaks of the two topmost valence bands in PLE are observed in all the samples grown on 6°A or 6°B-tilted substrates, indicating good structural uniformity.

The interface between the two ordered variants that constitute a domain twin is an orientational domain boundary. This study focuses on one of several distinct orientational domain boundary structures that are possible in CuPt-ordered $GaInP_2$ [4,5], where the superlattice axis is oriented along the [1001] growth direction. Periodically stacked domain twins are observed by using various techniques of transmission electron microscopy (TEM): electron diffraction pattern, high-resolution cross-sectional TEM and dark-field image. However, we should note that such a spontaneously generated stacking sequence has a significant deviation from the idealized periodic structure considered in Ref. [6]. The size of the domain twin is typically < 50 Å. The domain size fluctuation can be as large as a factor of 2 in certain areas, which is very similar to the observations of Refs. [11,12]. These twinned structures are formed spontaneously during epitaxial growth. The domain size and size distribution can be controlled to some extent by varying the growth conditions. An optimized substrate orientation, 6° tilted toward a $[111]_A$ direction, yields a somewhat more uniform domain size and, thus, narrower spectral linewidth in PL and PLE measurements. The detailed results of the microscopic study will be presented elsewhere.

Although changes in the electronic band-structure induced by single-variant ordered $GaInP_2$ have been extensively studied, OSL effects in double-variant ordered $GaInP_2$, where the period of alternation of domains is of the order of the de Broglie wavelength of the electron and hole, have only recently been

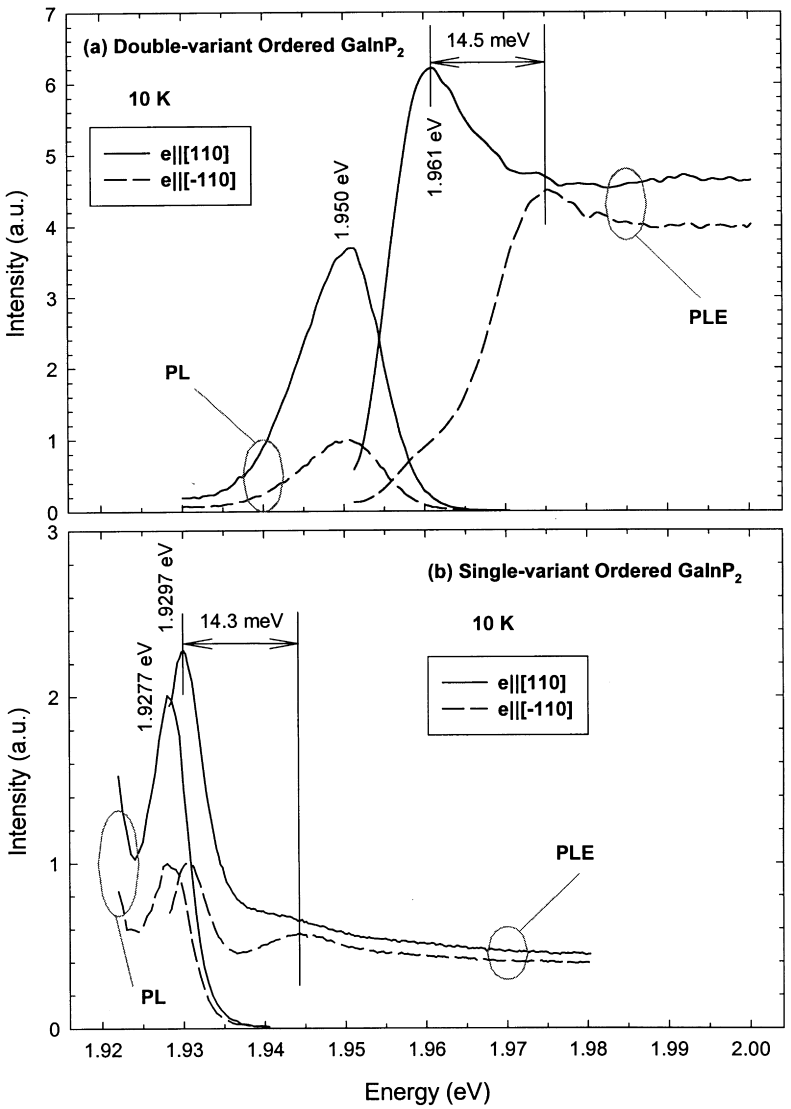

Fig. 2. Polarized PL and PLE spectra of a double-variant (small domain) and a single-variant ordered $GaInP_2$ with nearly the same value of the valence-band splitting.

predicted [4,5]. One of these effects is an increase in the band-gap of the OSL as compared with the single-variant ordered structure. Another is an increase in the polarization anisotropy of band-edge optical transition intensities, which is determined by the anisotropy in the transition matrix elements of the band-edge states. Despite the apparent irregularity in the domain size, we indeed observe major changes in the electronic and optical properties in these twinned structures.

Fig. 1 contrasts the PL emission spectra measured at 10 K for disordered, single-variant ordered, and double-variant ordered (with an average domain size of $\sim$ 50 Å) samples of $GaInP_2$. The emission for the disordered ordered alloy is essentially unpolarized, whereas that from the single-variant ordered alloy occurs about 103 meV lower in energy and exhibits a polarization anisotropy $R = 2.1$ These results are typical of those obtained from extensive studies [6–9]

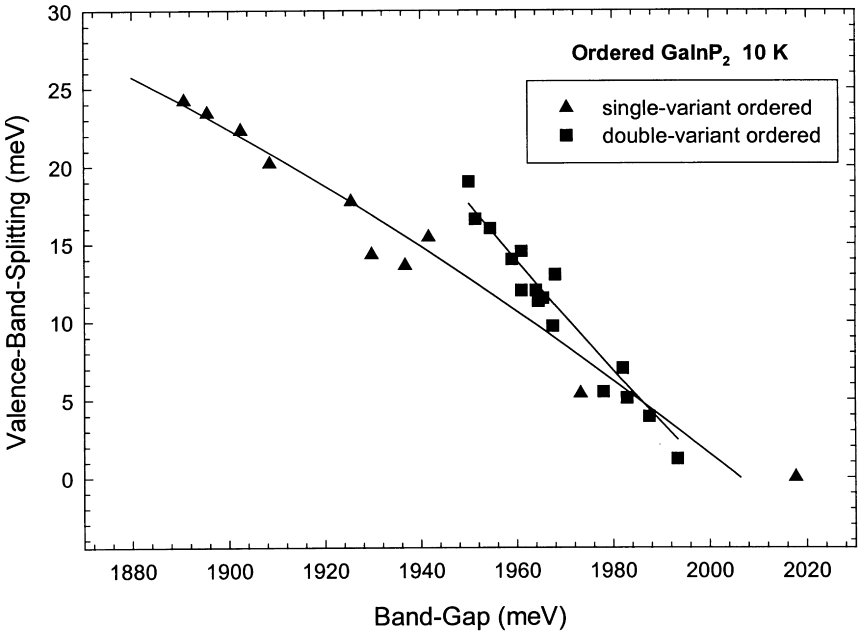

Fig. 3. A comparison of the functional dependence of the valence-band splitting versus the band-gap between singe-variant and double-variant (small domain) ordered $GaInP_2$ samples.

on single-variant ordered $GaInP_2$ where the lowering of the band-gap has been shown to be a function of the order parameter η [6,7], and the polarization anisotropy to be independent of η ($\eta \sim 0.5$ in this case) [9]. One expects that in the double-variant sample (where the scale of alternation of domains is of the order of the de Broglie wavelength) OSL effects will be manifested. Indeed, we observe that its PL spectra show a much larger polarization anisotropy of $R = 4.6$. As expected, a double-variant ordered sample with a large domain size (in the order of 1 μm [12]) shows a similar polarization anisotropy ($R \sim 2$) as the single-variant ordered sample. It has been shown experimentally that the polarization anisotropy R in single-variant ordered alloys never exceeds a theoretical limit of 3 [9]. Although one can attribute the enhanced polarization anisotropy to OSL effects, it is not possible to do this for the energy difference, since this could as well be attributed to a difference in the order parameter between the single and double-variant ordered samples. F for an OSL structure, the band-gap energy depends not only on the order parameter but also on the geometric parameters of the superlattice.

To eliminate the uncertainty aforementioned, we utilize the fact that for a single-variant ordered alloy there is a unique correspondence between its valence-band splitting and band-gap lowering, which has been carefully investigated and modeled [6,7]. The PL and PLE spectra of a double-variant (small domain) ordered alloy and a single-variant ordered alloy with nearly the same value of the valence-band splitting (14.5 meV versus 14.3 meV) are shown in Fig. 2a and 2b, respectively. It is very important to observe that in PLE the band-gap of the double-variant sample shifts up by 31 meV, compared to the single-variant sample. Also, a significantly larger polarization anisotropy in both PLE and PL is shown for the double-variant sample. It is clear from comparing Fig. 2a and 2b that the modifications to the electronic band structure of the double-variant sample cannot be attributed to CuPt ordering alone, and that the periodic rotation of ordered domains results in an increase in both the band-gap and the polarization anisotropy. Another factor, which may affect the band-gap and the polarization anisotropy, is the deviation of alloy composition from its lattice-matched value and the associated strain effects. However, such a possibility can

definitely be ruled out, since the two sample used in Fig. 2 are closely lattice-matched to the substrate (with an in-plane biaxial strain $< 10^{-4}$) as verified by X-ray rocking curve measurements.

To further verify the superlattice effect, Fig. 3 shows a comparison of the functional dependence of the valence-band splitting versus the band-gap, for single-and double-variant ordered samples. The results clearly indicate that the functional relationship for double-variant ordered samples is distinct from that for single-variant ordered samples. In addition, we observe that the values of the polarization anisotropy R for all double-variant ordered samples shown in Fig. 3 are significantly larger than the limiting value of 3 for the single-variant ordered case, and R lies mostly between 4 and 7, whereas the value for the single-variant ordered samples lies around 2.[9] These experiments clearly demonstrate that distinct modifications to electronic states are induced by the periodic alternation of the ordering axis of the orientational domains, when the scale of alternation is of the order of the de Broglie wavelength of the electron and hole in the semiconductor.

The polarization anisotropy measured for single-variant ordered alloys results from the fact that the ordering direction $[\bar{1}11]$ is a special axis of the unaxial point group C_{3v}. The $[\bar{1}11]$ polarization, which has a projection in the $[\bar{1}10]$ direction, is forbidden for the dipole transition. In the case of double-variant ordered alloys, the crystal structure is described by the biaxial point group C_{2v}, both $[\bar{1}10]$ and $[\bar{1}10]$ correspond to special axes. One can show that the polarization anisotropy between these two directions is larger than that of single-variant ordered alloys. For a 25Å/25Å OSL structure with a typical value of the crystal-field splitting parameter $\Delta_{CF} = 45$ meV ($\eta \sim 0.5$), the predicted band-gap shift is 10 meV and the polarization anisotropy is 22.

Although results of the simple model [4,5] used to calculate the electronic properties of OSLs are qualitatively consistent with the experimentally observed increase in band-gap and polarization anisotropy, the experimental values are significantly different from those predicted theoretically. Clearly, more refined calculations are required to provide a better understanding of the electronic and optical properties of such structures. Moreover, the domain size fluctuation certainly alters the electronic and optical properties from the ideal OSL structure. The significance of the experimental results presented lies in the fact that the domain twins are observed universally in many categories of crystalline materials, but superlattice effects of a periodic stacking of domain twins have never before been observed experimentally.

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