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Effects of the orientational superlattice on the electronic and vibrational properties of CuPt ordered GaInP alloys

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A brief review is given of studies on a new semiconductor superlattice — an orientational superlattice — observed recently in spontaneously ordered III–V alloys GaInP. New experimental data, including band edge optical transitions and Raman transitions, are presented to illustrate the unique and intrinsic properties of orientational superlattices. Copyright © 2001 John Wiley & Sons, Ltd.

INTRODUCTION

It is well known that CuPt ordering tends to occur spontaneously in many III–V alloys when they are grown epitaxially by metal–organic chemical vapor deposition (MOCVD).[1] Among all the III–V systems, the $Ga_xIn_{1-x}P$ ($x \approx 0.5$) alloy is the best studied material for the effects of the ordering on various properties. The so-called CuPt ordering involves the formation of a monolayer superlattice with alternating Ga-rich and In-rich layers, $Ga_{x+\eta/2}In_{1-x-\eta/2}P$ and $Ga_{x-\eta/2}In_{1-x+\eta/2}P$ layers, along one of the [111] directions, where η is the order parameter. In fact, CuPt ordering has so far only been observed in the two $[111]_B$ directions. In the past few years, it has been realized that by tilting the substrate towards one of the $[111]_B$ directions one can enhance one particular ordered variant and suppress the other, which has resulted in a significant improvement in sample uniformity.[2] More important, the availability of single-variant ordered samples has made it possible to study the intrinsic properties of CuPt ordering.[3] For an extended period of time, the ordered structure grown on the exact (001) substrate or $[111]_A$ tilted substrate with two $[111]_B$ ordered variants co-existing has been treated as equivalent to a single-variant ordered structure but with poor quality, although quasi-periodically stacked micro-domain twins along the growth direction [001] had been observed and analyzed for double-variant ordered GaInP alloys in structural studies.[4,5]

The implication for the existence of such a quasi-periodic structure has recently been discussed theoretically in terms of a new type of superlattice termed an orientational

superlattice (OSL)[6–8] or anti-phase boundary superlattice.[9] An OSL is defined generally as one for which the constituent layers within a superlattice period are related to each other by certain symmetry operations (that do not belong to the symmetry group of the constituent layer).[6,7] For the double-variant ordered GaInP alloy that resembles an OSL, the structure has periodically stacked micro-ordered-domain twins with a typical period of ~40 Å.[4,5] An increase in the bandgap is expected with respect to the pure CuPt ordered structure for an OSL that has the same order parameter η for the constituent layers.[6–9] In addition to the band structure modification, the change in the crystal symmetry is expected to result in changes in the selection rules for optical transitions.[7,10] Indeed, the correlation between the microscopic structure and the electronic properties for the double-variant ordered GaInP has been demonstrated experimentally.[10,11] It is clear that the ordered GaInP showing structures resembling the OSL behavior, distinctly different from the pure CuPt ordered GaInP in two major respects:[11] (1) The functional dependence of E_g (bandgap) versus E_{vbs} (valence band splitting) and (2) optical anisotropy between the [110] and $[\bar{1}10]$ (the projection of the ordering direction $[\bar{1}11]$). Other unusual optical effects have also been observed in double-variant ordered GaInP samples,[12–15] although the specific structural information was not given to correlate the optical data with the OSL-type structure. An optical transition near 2.18 eV was observed in presumably double-variant ordered GaInP,[12,13] and was tentatively identified as being associated with the folded X-point as the result of Y_2 ordering (the so-called Y_2 ordering is referred to as a two monolayer superlattice along a $\langle 110 \rangle$ direction).[13] A phase shift between the two band edge transitions was observed in polarized electroreflectance for an ordered GaInP grown on an exact (001) substrate, and the results were explained in the framework of the CuPt ordering.[14] In fact, it has been found

that such an phenomenon occurs only for the double-variant ordered samples and not for the single-variant ordered samples (Y. Zhang and A. Mascarenhas, unpublished work). An new phonon mode at 219 cm^{-1} in double-variant ordered GaInP samples has recently been reported and assigned to folded LA(X) phonon due to the periodic structure of very thin (a few monolayer) ordered domain twins in the [001] direction.[15] However, for these double-variant ordered samples, the most prominent CuPt ordering induced Raman mode at 354 cm^{-1} was not observed.[15]

In this paper, we present the results of a comparative study of pure CuPt ordered GaInP and CuPt ordered GaInP with the two ordering variants forming the OSL-type structure. With the newly developed modeling method (J. H. Li, J. Kulik, V. Holy, Z. Zhong, S. C. Moss, Y. Zhang, S. P. Ahrenkiel, A. Mascarenhas and J. Bai, *Phys. Rev. B* 63,155310 (2001)), for a double-variant ordered samples not only the order parameter but also the average layer thickness for each order variant can be determined by analyzing x-ray diffraction data. We can now decisively distinguish the difference in electronic and vibrational properties between two types of samples with the same order parameter.

EXPERIMENTAL

The results primarily from two pairs of ordered GaInP samples are presented in this paper. The first pair, MA912−6°A and M1639d−6°B, were grown on a 6°A and 6°B tilt (001)−GaAs substrate, respectively. An x-ray study of MA912-6°A reveals the OSL structure along the growth direction, with an identical average layer thickness of 12 monolayers and order parameter $\eta = 0.50 \pm 0.05$ for both order variants (J. H. Li, J. Kulik, V. Holy, Z. Zhong, S. C. Moss, Y. Zhang, S. P. Ahrenkiel, A. Mascarenhas and J. Bai, *Phys. Rev. B* 63,155310 (2001)). The composition for this sample was determined as $x_{Ga} = 0.507$. Similarly, M1639d−6°B is shown to be a single variant ordered sample with $x_{Ga} = 0.523$ and $\eta = 0.50 \pm 0.02$.[16] The second pair, K518−0° and K782−6°B, were grown under identical conditions, except one was on an exact (001) and the other on a 6°B tilt GaAs substrate. The Ga compositions were measured by x-ray spectrometry to be $x = 0.511$ and 0.512, respectively. K518−0° is a double-variant ordered sample and exhibits the [001] OSL structure with an average period of 44 Å, and K782−6°B is a single-variant ordered sample, which were observed in high resolution cross-sectional TEM measurements.[10]

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at 10 K with the sample mounted in a closed-cycle cryostat. Differential absorption spectra were measured at 5 K by the time-resolved pump–probe technique.[3] Raman measurements were performed at either room temperature or 8 K in the backscattering geometry on the (001) growth plane of the samples, using either a 514.5 or a 532 nm laser.[17]

RESULTS

Electronic properties

Figure 1 shows two typical high-resolution cross-section TEM pictures of ordered GaInP.[10] These two pictures are representative for areas that have a well-defined phase for each ordered variant[5] (J. H. Li, J. Kulik, V. Holy, Z. Zhong, S. C. Moss, Y. Zhang, S. P. Ahrenkiel, A. Mascarenhas and J. Bai, *Phys. Rev. B* 63,155310 (2001)). Figure 1(a) is from a small selected area of sample K518−0°. A 'zigzag' stacking sequence of two ordered variants is clearly shown. A picture of larger area would have many lateral anti-phase domain boundaries (APBs). Here an APB is specifically referred to the out-of-phase arrangement of Ga and In-rich atomic planes within a single ordered variant,[5] although sometimes the boundary of two ordered variants was also referred to as an APB.[9,15] In general, APBs (as defined here) also exist in single-variant ordered samples, and their density depends strongly on the growth conditions.[18] Figure 1(b) is typical for a single-variant and single-phase CuPt ordered domain.

Figure 2 compares polarized PL (dotted lines) and PLE (solid lines) spectra of MA912−6°A and M1639d−6°B for [110] and [$\bar{1}$10] polarizations. If the ordering directions
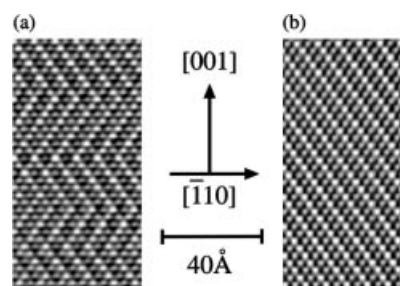

Figure 1. High-resolution cross-sectional TEM pictures of (a) double-variant ordered and (b) single-variant ordered GaInP alloys.
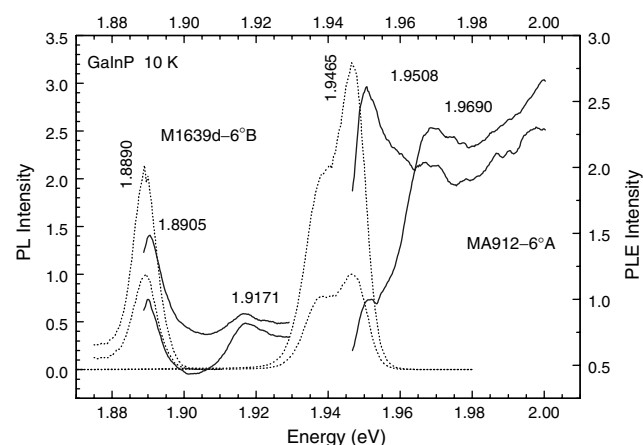

Figure 2. Comparison of polarized PL and PLE spectra between a single-variant CuPt ordered and a double-variant CuPt ordered GaInP with the same measured order parameter.

are defined as being along the $[\bar{1}11]$ or $[1\,\bar{1}\,1]$ directions, the PL or PLE intensity is found to be stronger in [110] polarization. It is apparent that the OSL sample always shows stronger optical anisotropy than the pure CuPt ordered sample, as reported previously.[10,11] For approximately the same order parameter $\eta = 0.5$, the bandgaps differ by 60 meV (from PLE spectra) for these two samples, owing to the OSL effect for MA912−6°A. If the effects due to the composition deviation are taken into account, the bandgap difference will be even larger (~15 meV larger estimated by considering the composition difference and epitaxial strain).

Figure 3 compares the differential absorption spectra of K518−0° and K782−6°B. The order parameters for these two samples have not yet been measured by the x-ray te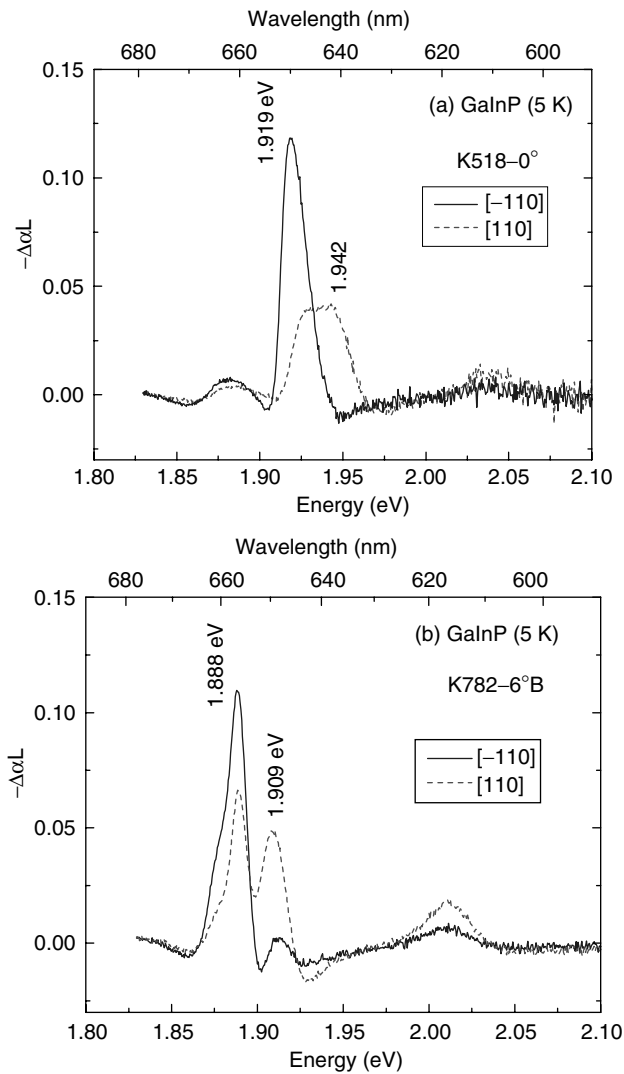chnique. However, they were estimated to have the same order parameter $\eta = 0.58$ by comparing their bandgap reductions with the theoretical values.[10] Again, the bandgap of the sample showing the OSL structure (K518−0°) has a 31 meV larger bandgap than the pure CuPt ordered sample (K782−6°B). Also, the polarization ratio for the band edge transition differs by 640% (12.6 vs 1.7). The OSL effects are indeed very pronounced for K518−0°.

Vibrational properties

So far, three CuPt ordering induced new Raman peaks at ~60, ~205 and 354 cm^{-1} have been clearly observed in single-variant ordered samples.[17,19,20] In double-variant order samples, an extra peak at ~219 cm^{-1} has been observed and explained as a folded LA(X) phonon due to the OSL effect.[15] However, the 354 cm^{-1} peak was not seen in the double-variant ordered samples studied in Ref. 15.

Figure 4 shows [001] backscattering Raman spectra for samples K518−0° and K782−6°B. For K782−6°B, in addition to the 381 cm^{-1} GaP-like LO_{Γ}, the 364 cm^{-1} InP-like LO_{Γ} and the ~330 cm^{-1} InP-like TO_{Γ} phonons, the 354 cm^{-1} CuPt ordering induced folded LO mode is clearly seen.[17,19,20] For

Figure 3. Polarized differential absorption spectra for two ordered GaInP samples with nearly the same order parameter and average composition: (a) for a double-variant ordered and (b) for a single variant ordered sample.
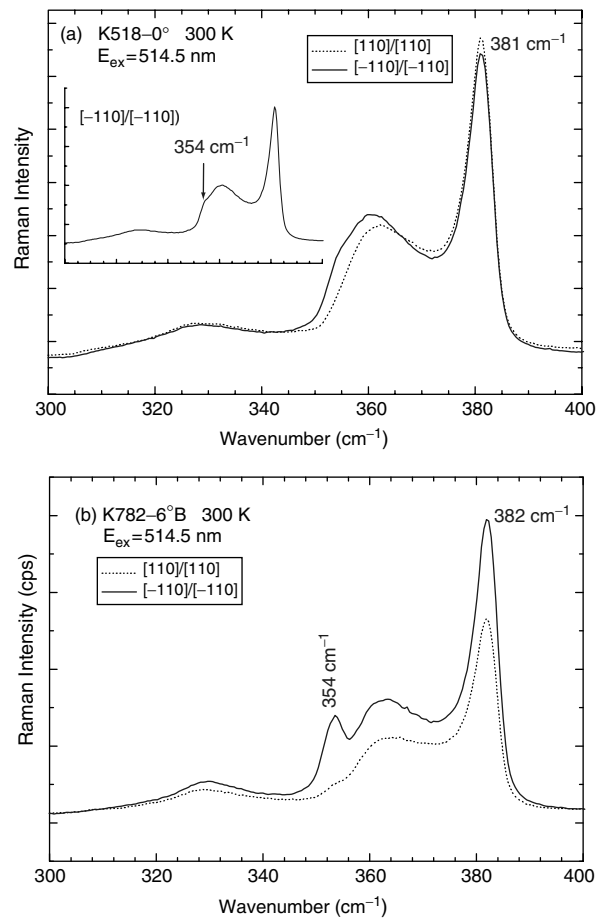
Figure 4. Comparison of the 354 cm^{-1} feature in the Raman spectra between a double-variant ordered (K518−0°) and a single-variant ordered (K782−6°B) GaInP.

K518–0°, the 354 cm^{-1} mode remains although not well resolved [it is clearer in the inset in Fig. 4(a) measured with a higher resolution]. In fact, such a weakened 354 cm^{-1} transition has been observed in other samples that were grown under similar conditions to those for K518–0°. However, this peak is not observable for the other OSL sample MA912–6°A. There are at least two possible reasons for the weakening of the folded LO phonon mode: the vertical OSL and the lateral APBs. Further investigations are needed to probe the impact of these effects on Raman transitions of the ordered structure.

Figure 5 shows [001] backscattering Raman spectra for K518–0° and K782–6°B and also an additional sample MA582–6°B measured at low temperature and using a 532 nm laser. It is clear that all of these three samples have a transition at ~222 cm^{-1} in addition to the 211 cm^{-1} transition. The 211 cm^{-1} peak has frequently been observed in CuPt ordered structures,[17,19,20] but the 222 cm^{-1} peak has only been seen in double-variant ordered samples.[15] Hence this 222 cm^{-1} peak was associated with the OSL structure in the [001] direction.[15] Now this peak has been observed in single-variant CuPt ordered samples that do not show any OSL type structure but, as usual, have APBs. Not only do both K782–6°B and MA582–6°B behave like a single-variant ordered sample in the optical measurements (e.g. PL, PLE, differential absorption), but this also was confirmed by TEM measurements.[21,22] Similarly to the observations in Ref. 15, we found that the relative strength of the 222 cm^{-1} peak with respect to the 211 cm^{-1} peak depends strongly on the excitation energy or temperature (the temperature variation effectively changes the resonant condition). Since this feature is not 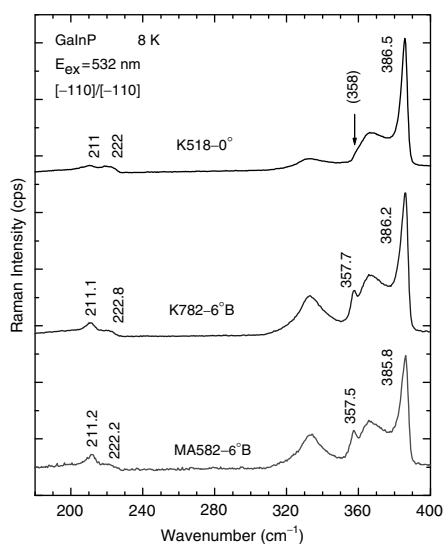uniquely related to the OSL structure, other mechanisms (e.g. the APBs) should be considered in understanding the origin of this transition.

CONCLUSION

We have briefly reviewed recent studies on a derived superlattice structure, termed an orientational superlattice, observed in CuPt ordered III–V alloys. More experimental results on the optical and Raman measurements have been presented to illustrate further the unique and intrinsic properties of this novel superlattice.

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Figure 5. Comparison of 222 cm^{-1} feature in the Raman spectra between single- and double-variant ordered GaInP.