ELECTRONIC AND OPTICAL PROPERTIES OF ORIENTATIONAL SUPERLATTICES IN GaInP ALLOYS

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ABSTRACT

We demonstrate the formation, and the electronic and optical properties of a novel type of semiconductor superlattice in spontaneously ordered GaInP alloys. The most frequently observed ordered structure in MOCVD grown GaInP has CuPt symmetry where the ordering directions occur in the two $[111]_B$ directions, corresponding to two distinct ordered variants. A new type of superlattice, termed an orientational superlattice, emerges as the ordered domains are stacked in a sequence whereby the ordering direction switches alternatively from the $[\bar{1}11]$ direction in one domain to the $[1\bar{1}1]$ direction in the next domain. The novelty of this type of superlattice lies in that there is neither a band-gap nor an effective mass discontinuity along the superlattice axis. When the GaInP epilayer is grown on an exact (001) or $[111]_A$ tilt GaAs substrate, the two ordered variants are equally favorable. Thus, ordered domain twins appear in ordered GaInP epilayers. We present a comparitive study between the single-variant ordered structure and the double-variant ordered superlattice structure, using TEM and time-resolved differential absorption. We show that for a same order parameter, the band-gap of an orientational superlattice is higher than that of a single-variant ordered structure, and the in-plane optical anisotropy between the $[\bar{1}10]$ and [110] directions is greatly enhanced due to the superlattice effect. The experimental results are explained in terms of the band structure of the orientational superlattice.

INTRODUCTION

MOCVD grown GaInP alloys are known to exhibit CuPt ordering with two order variants, i.e., the $[\bar{1}11]$ variant and the $[1\bar{1}1]$ variant. The appearance of one variant or the other or both simultaneously depends on growth conditions, mainly the substrate misorientation used for the growth. Properties of CuPt ordered GaInP have been extensively studied in the past 10 years. These studies have included ordering induced changes in the crystal structure,[1] electronic and optical properties (e. g., band-gap reduction,[1,2] valence band splitting,[3-5] optical anisotropy,[3] pyroelectricity,[6] birerefringence,[7] second harmonic generation,[8] conductivity anisotropy,[9] and Raman scattering[10]), and the functional dependence of these phenomena on the order parameter.[11-15] The above investigations have focused on the intrinsic properties of a CuPt ordered structure, i.e., the properties of single-variant ordered samples. However, during the early phase of ordering research, it was not unusual that double-variant ordered samples were studied assuming they were single-variant ordered samples, despite the fact that quasi-periodically stacked micro domain twins or antiphase domain boundaries had been observed and analyzed in ordered GaInP alloys by structural studies.[16,17] Not until recently, possible superlattice effects in the double-variant ordered structure have been explored and modeled in terms of various polytypes of orientational superlattices.[18,19] An orientational superlattice (OSL) is defined as that for which within a superlattice period, the constituent layers are related to each other by certain symmetry operations (that do not belong to the symmetry group of the constituent layer). A periodic stacked domain twin structure is a typical example of such a

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superlattice. Subtle symmetry related changes in various optical properties, beside the modification in the band structure, are expected upon the formation of the orientational superlattice in ordered III-V alloys.[18,19] Experimentally demonstrated superlattice effects in double-variant ordered GaInP samples that were verified to have domain structures resembling an OSL have included the changes in the band structure and the optical anisotropy near the fundamental band gap[19,20] as well as in the selection rule for second harmonic generation,[21] as compared to the simple CuPt ordered structure. Additional above band gap transitions in electroreflectance[22] and new Raman features[23] have also been observed in double-variant ordered samples, which might also be attributed to the superlattice effect. An interesting optical effect related to the ferroelastic nature[18] of the ordered domain twins was observed in a large domain double-variant ordered sample.[24] First-principles approaches have been used for the band structure calculation of such superlattices with sizes of a few monolayers.[25,26] An "interpolation" scheme was given in Ref.[26], which makes it possible to obtain the energies of the conduction and valence band edges for an arbitrary size period using the first-principles results, and to deduce the order parameter in the superlattice structure.

In this work, we present a comparison study between a single-variant CuPt ordered GaInP and a double-variant ordered sample whose TEM picture shows the structure of an OSL along the [001] growth direction. The two samples are deliberately chosen to have nearly a same order parameter η that is determined by comparing the spectroscopy data with the theoretical curves calculated using Ref.[26]'s interpolation scheme. We can decisively verify the theoretical predictions about the band structure changes due to the superlattice effect. We also present a simple picture that explains why a large change in the optical anisotropy whereas only a relatively small change in the band-gap energy occurs in an OSL.

EXPERIMENT

Two ordered GaInP samples used in this study were grown on GaAs substrates by MOCVD epitaxy under nominally same conditions, except one was on a 6^{O} B tilt and the other on an exact (001) substrate. The Ga compositions were measured by x-ray to be x = 0.512 and x = 0.511, respectively. For the (001) sample, a high resolution cross-sectional TEM picture and a diffraction pattern analysis have revealed an orientational superlattice structure along the [001] growth direction with an average period of 44 Å and a relatively large fluctuation of ~ 12 Å. The details of the microscopic studies will be published separately.[27] Fig.1 shows a typical section of the TEM pictures for the two samples. The ordering induced band-gap reduction (δE_g) and the valence-band splitting (δE_{VBS}) were measured by time-resolved pump-probe technique. Experimental details have been given previously.[14]

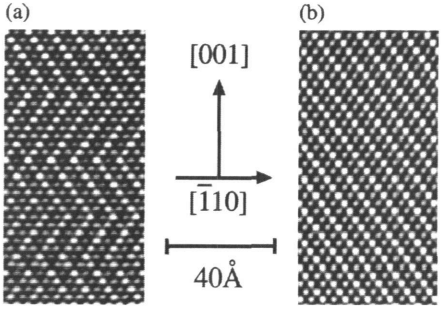

Figure 1. High-resolution cross-sectional TEM pictures of (a) a double-variant ordered and (b) a single-variant ordered GaInP alloys.

RESULTS

Fig.2 shows polarized differential absorption spectra for the two samples measured at 5 K. For the CuPt ordered sample, as shown in Fig.2(a), we have δE_g = 115 meV and δE_{VBS} = 21 meV. For the superlattice sample, as shown in Fig.2(b), we have δE_g = 84 meV and δE_{VBS} = 23 meV. The band-gap reduction is refereed to $E_g(x = 0.52, \eta = 0) = 2.003$ eV.[14] The third transition at ~ 120 meV above the band-gap is a transition associated with the spin-orbit split-off band. Because of the relatively large fluctuation in the layer thickness, the linewidths in Fig.2(b) are somewhat larger than those in Fig.2(a). Comparing the two samples, we have two major observations: (1) the band-gap of the superlattice sample is significantly higher; and (2) the optical anisotropy between the [110] and [-110] is much larger. The results for these two samples are qualitatively similar to those we reported earlier.[20] There, only the correlations between the band-gap reduction and the valence band splitting were found to be different for the superlattice samples and the bulk CuPt-ordered samples. The order parameters for the superlattice samples were not determined.

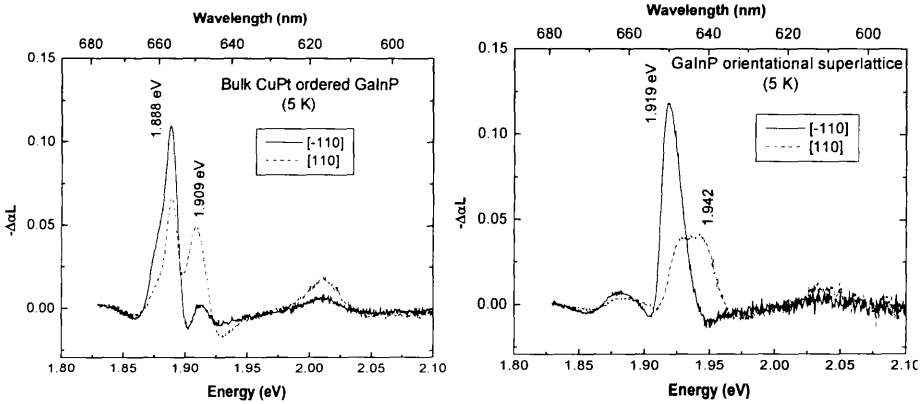

Figure 2. Polarized differential absorption spectra for two ordered GaInP samples: one single variant ordered (left) and one double-variant ordered (right), with nearly the same order parameter and average composition.

Fig.3 shows the variations of band edge energies of the conduction and valence bands with changing the layer thickness or number of monolayers for an [001] OSL without any antiphase domain boundaries. The dotted line are calculated using the interpolation scheme described in Ref.[26], and the solid line is the result of the k.p envelope function calculation.[19] The results shown in Fig.3 are for the case of the order parameter η = 1 in each layer. If the layers that form the superlattice are partially ordered (i.e., $\eta < 1$), the energies should be scaled approximately by a factor of η^2.[11]. The order parameter can thus be estimated using $\eta^2 = \delta E_g(\eta)/\delta E_g(\eta=1)$. With the band-gap reductions given above, we find that the order parameters for both the bulk CuPt ordered sample and the orientational superlattice sample are η = 0.58 (after calibrating for a small strain induced band-gap change of ~ 6meV). We have taken $\delta E_g(\eta=1)$ = 320 meV for a fully ordered bulk CuPt structure,[4] and $\delta E_g(\eta=1)$ = 235 meV for a superlattice with fully ordered CuPt layers and a layer thickness of 22 Å from Fig.3. The above

analysis shows that these two samples have practically the same order parameter but with a band gap difference of 31 meV. It was found by Friedman et al[28] that for a sample grown on an (001) substrate under nominally the same conditions as those samples used for this study, the band-gap of ordered GaInP epilayer decreased with increasing epilayer thickness by an amount of ~ 40 meV between 1 and 10 μm, and this variation was attributed to the variation of the order parameter with film thickness during growth. Our TEM studies[27] have indicated that the ordered domains in a sample of this type evolved from a vertically stacked micro-twinned structure to a laterally arranged super-twinned structure (i.e., the domain sizes were in the order of μm), and most of the evolution was found to occur after 2 μm. Thus, the part of the sample close to the substrate is expected to behavior like the superlattice (with a larger band gap) and the upper part of the sample should behavior like the bulk ordered alloy (with a lower band gap).

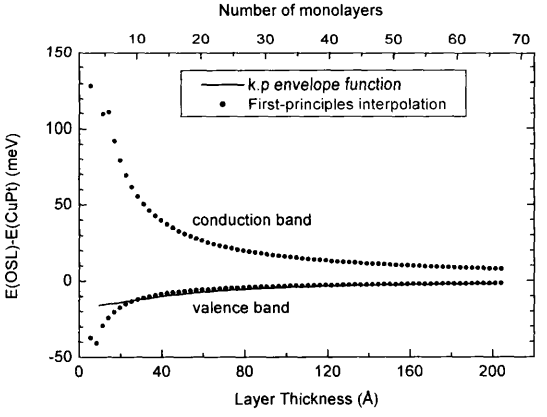

Figure 3. The band edge energies of the conduction and valence band with changing the layer thickness or number of monolayers for an [001] orientational superlattice with fully ordered layers.

DISCUSSIONS

A major difference between a conventional superlattice and an OSL is that the former tends to give rise to a large change in the band-gap energy as a result of quantum confinement, whereas the latter tends to show a large change in optical anisotropy. This difference can be comprehended in terms of the difference in the mechanisms for forming the superlattices: spatial modulations in potential energy versus orientation of the symmetry axis.[18,19] It is found that[13] the optical anisotropy for a bulk ordered alloy is practically independent of the order parameter. However, for a merely ~ 30 meV band-gap energy difference of the two samples shown in Fig.2, we find that the polarization ratio changes drastically from 1.7 to 12.6. The smaller energy difference is understandable, since there is no band offset but an ordering direction change between the two constituents. For the same reason, the orientational superlattice structure is less sensitive to the fluctuation in the layer thickness, as compared to conventional superlattices.

The polarization selection rules can be understood intuitively in a simple way. For the single-variant ordered structure, the $(\bar{1}11)$ ordering plane is an isotropic plane. The [110] polarization (which lies within the ordering plane) is fully allowed for the dipole transition, while the $[\bar{1}10]$ polarization is at an angle between the forbidden $[\bar{1}11]$ direction and the allowed $[\bar{1}1\bar{2}]$ direction (in the $(\bar{1}11)$ plane). Thus, the $[\bar{1}10]$ polarization is a partially allowed transition. The polarization ratio is given by $1/\cos^2(\theta) = 3$, where θ is the angle between the $[\bar{1}10]$ and $[\bar{1}1\bar{2}]$ directions. In fact, this number posts a limit for the possible in-plane

anisotropy in a simple CuPt ordered structure, and this theoretical limit has never been exceeded experimentally.[13] Therefore, the OSL structure has the potential to give much higher in-plane polarization for device applications. For the OSL structure, the only direction not subjected to any modulation is the [110] direction, while along either one of the other two principle axes, the [001] and [$\bar{1}$10] directions, there exists a modulation. Thus, the [110] direction is the only fully allowed polarization for the dipole transition. More specifically, the polarization selection rules can be explained by considering the symmetry of the valence band states. If the spin-orbit coupling is ignored, the CuPt ordering causes a valence-band splitting. The topmost valence band states are double degenerate states of (|X> + |Y>)-like and (-|X> + |Y> - 2|Z>)-like, and the other singlet state is (-|X> + |Y> + |Z>)-like (where |X>, |Y> and |Z> are the three p-like band-edge states in the zinc-blende structure). Upon the formation of the OSL, the double degeneracy of the topmost valence band is removed by the [001] modulation. However, one of them, the (|X> + |Y>)-like, which corresponds to the topmost valence band, remains unchanged. This result indicates that in the OSL the [-110] polarization becomes fully forbidden and, so a 100% polarization can be expected between the [110] and [-110] direction. The numerical calculation with the spin-orbit coupling taken into account[19] showed that the [-110] polarization is in fact weakly allowed, which qualitatively explains the strong polarization we observed experimentally.

CONCLUSIONS

We have showed the formation of orientation superlattices in double-variant CuPt ordered GaInP by high resolution cross sectional TEM. We have demonstrated that the formation of the superlattice increases the band-gap and the in-plane optical anisotropy, as compared to those for a single-variant CuPt ordered sample with the same order parameter. The experimental results are explained in terms of the band structure properties of the superlattice.

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