New Long-Range Atomic Order and Heteroepitaxy of Single-Crystal Zn_3As_2

G. Pangilinan and R. Sooryakumar
Department of Physics, The Ohio State University, Columbus, Ohio 43210

B. Chelluri and T. Y. Chang
AT&T Bell Laboratories, Holmdel, New Jersey 07733
(Received 25 March 1988)

We report evidence of a new long-range order in single-crystal Zn_3As_2 grown epitaxially on lattice-mismatched InP and GaAs. The Raman activity of the layers confirm, in contrast to the bulk C_{4v}^{12} symmetry, a space group of D_{4h}^{15} for the epilayers. Thermodynamic considerations show that the dependence of the free energy on the lattice parameters may be sufficient to account for the stability of the new structure in the epilayer.

PACS numbers: 68.55.Nq, 61.50.Em, 78.30.Hv, 81.30.Hd

There is growing evidence for the occurrence of long-range order (LRO) in several III-V and IV-IV semiconductor alloys grown epitaxially on bulk substrates.[1-5] The new order often takes the form of a monolayer superlattice along specific crystallographic directions. The substrates are found to play a vital role in this periodic compositional modulation and the phenomenon has been observed in strained superlattice[2,4] and in layers whose bulk lattice parameters are matched to those of the substrate.[1,3,5] Strain in the vicinity of the interface has been identified as a mechanism to stabilize the LRO.[2-4,6,7] Recently,[1] reductions in the band gap of the ordered lattice have been reported, indicating changes to the electronic structure. Several studies suggest that the ordering is an equilibrium state with a free energy lower than, but close to, that of the disordered state.[5-7]

In this paper, we report evidence of a modified atomic ordering that leads to the preferential stability of a *new* LRO in nonalloy epilayers, i.e., in a system where there is preexisting long-range order. In contrast to the popular III-V, IV-IV, and II-VI covalent semiconductors, the II-V unit cell is characterized by the presence of a large number of ordered vacancies.[8] The different occupancy in these available cation sites hence makes the II-V's particularly attractive for investigating the more universal nature of the novel ordering transitions of the type observed in alloy epilayers. The focus of our investigation is the single-crystal II-V binary Zn_3As_2 grown epitaxially on InP and GaAs.

Raman scattering is used in the present study as an excellent means to determine the crystal symmetry and atomic locations in the supported Zn_3As_2 epilayers. These measurements unambiguously establish for the layers grown by molecular-beam epitaxy (MBE) a lattice that possesses the D_{4h}^{15} symmetry which is different from the known equilibrium bulk structures. Estimation of free-energy changes based upon a phenomenological model shows that lattice-constant differences may be sufficient to account for the observed preference for stabilizing a new order. The structural modifications consist of relocation of specific atoms of the bulk to neighboring sites with concurrent changes in the lattice parameters.

It is documented[8-10] that bulk Zn_3As_2 exists in three polymorphic modifications:

$$\alpha\,(C_{4v}^{12}) \xrightarrow{457\ \mathrm{K}} \alpha'\,(D_{4h}^{11}) \xrightarrow{945\ \mathrm{K}} \beta\ (\mathrm{fcc})\,.$$

In the body-centered α phase the As sublattice is, barring a slight tetragonal distortion, composed of fcc cells [Fig. 1(a)]. The Zn sublattice is similar to that of fluorine in CaF_2 with 25% vacant Zn sites and these cation vacancies are ordered within the lattice. Each As is surrounded by eight tetragonal cavities of which six are occupied by Zn atoms, while two are vacant. Therefore, every Zn is tetrahedrally bonded to four As atoms, while each As is sixfold coordinated to Zn. This 160-atom C_{4v}^{12} unit cell can equivalently be viewed (Fig. 1) as a stacking of pseudo cubic blocks which, except for the small distortion noted above, are fluorite or zinc-blende unit cells. The α' phase is obtained if atoms on the $3c_0/4$ and $7c_0/8$ planes in Fig. 1(a) are replaced by those at $z = c_0/4$ and $3c_0/8$. In the β phase, the As ions remain fcc with the Zn randomly distributed on cation sites.

Single-crystal Zn_3As_2 was grown by MBE with the tetragonal axis along [001] on InP and GaAs as described elsewhere.[11] The lattice mismatch between bulk Zn_3As_2 and InP is 0.35%, while there is a 4% mismatch with GaAs. Layers of about 2 μm thick were found to grow commensurately on InP. For growth on GaAs thicknesses of only about 1000 Å were achieved before their quality observably deteriorated. Electron diffraction in the interface region shows evidence of incommensurate growth for layers on GaAs, while high-resolution lattice images of Zn_3As_2 on InP confirm the absence of any significant density of dislocations.[11] The Raman spectra at 5 K were taken in backscattering mode with 150 mW of 5308-Å radiation. The results are

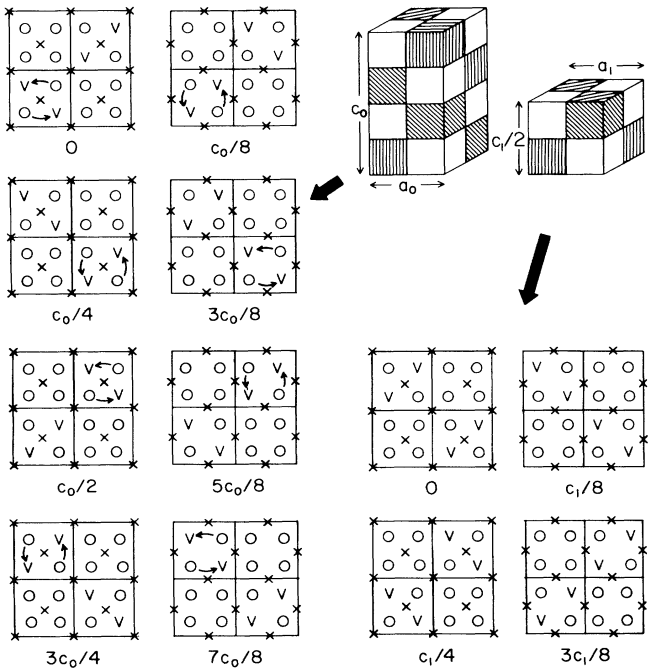

FIG. 1. The atomic positions in (a) C_{4v}^{12} and (b) D_{4h}^{15}. ×, As on plane; v, vacancy on Zn sites; o, Zn at $c_0/16$ above plane in C_{4v}^{12} and $c_1/16$ above plane in D_{4h}^{15}. These structures are also shown as a stacking of fluorite (unhatched) and zinc-blende (hatched) unit cells. The vertically hatched cell (type A) differs from the diagonally hatched block (type B) by a $\pi/2$ rotation about the c axis. The arrows in (a) indicate one possible way by which a correlated reordering of a few Zn ions (with simultaneous change in a_0, c_0) could lead to the D_{4h}^{15} symmetry.

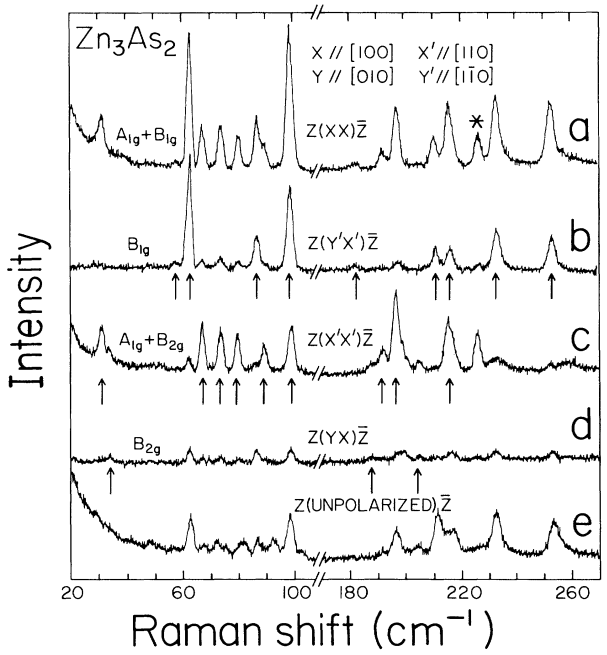

FIG. 2. Raman spectra of Zn_3As_2 epilayers. (a) d-polarized scattering from single crystal on InP. (e) Unpolarized spectra of single crystal on GaAs. Arrows under (b), (c), and (d) identify, respectively the B_{1g}, A_{1g}, and the weak B_{2g} phonons. Incomplete polarizer suppression allows very weak leakage between spectra. One peak (*) of apparent A_{1g} symmetry is anomalous. As evident from (e), this particular mode is absent from the layers on GaAs. Further, in contrast to the other phonons this Raman mode fails to appear at an exciting frequency of 6471 Å. The origin of this peak is presently unknown.

shown in Fig. 2.

The most striking aspect of the data is their simplicity. A few first-order phonons are observed, and their number and symmetries (identified in Fig. 2) do not agree with mode assignments presented in the next paragraph for the bulk C_{4v}^{12} phase. Films grown on GaAs displayed spectra [Fig. 2(e)] similar to those on InP. The sharpness of the Raman lines, particularly from Zn_3As_2/InP, is consistent with the high epitaxial quality achieved in the growth of this II-V compound.

Zone-center phonons of the bulk C_{4v}^{12} structure can be classified in terms of their irreducible representations. They are $\Gamma_{ir}=61E+28A_1$ and $\Gamma_{Raman}=61E+28A_1+29B_1+29B_2$ with $29A_2$ modes being silent. This multitude of 147 Raman phonons expected from the bulk α phase results from the specific arrangement of Zn (or equivalently the vacancies) leading to the large unit cell and low C_{4v} symmetry. The observation of only a fraction of the predicted phonons and their incompatibility with the vibrational symmetries for the C_{4v}^{12} structure provide direct evidence of a new LRO with higher symmetry and/or smaller unit cell in the supported Zn_3As_2 epilayers.

Any structural modifications arising from epitaxial growth must lower the overall free energy. To first order, such changes need only be a weak perturbation to the total energy and the new structure would then retain the same nearest neighbors as in the original lattice. In this situation, atoms further removed would be susceptible to the new order. The lattice that satisfies these criteria, i.e., having the same neighbor atoms in the C_{4v}^{12} α phase and possessing higher structural symmetry, is the structure shown in Fig. 1(b). This lattice crystallizes in the D_{4h}^{15} space group with 40 atoms/cell. The reordered structure accounts for the measured Raman activity in the epilayers.

The Raman-active phonons supported in the D_{4h}^{15} structure are $\Gamma_{Raman}=16E_g+9A_{1g}+10B_{1g}+4B_{2g}$. For backscattering along [001], 23 modes (A_{1g},B_{1g},B_{2g}) are expected and all but two (B_{1g} and B_{2g}) are identified in Fig. 2. More importantly, polarized scattering (Fig. 2) shows that the symmetry of the observed phonons is in

complete agreement with the new LRO, thus confirming the new symmetry.

We now consider the feasibility of stabilizing the D_{4h}^{15} structure during epitaxial growth. While minimization of the Gibbs free energy provides the basis for such considerations, a quantitative analysis would require lattice parameters of *bulk* unstrained Zn_3As_2 in the D_{4h}^{15} symmetry—a state that does not exist. We therefore evaluate $\Delta F(a,c)=F(C_{4v}^{12})-F(D_{4h}^{15})$, the difference in Helmholtz free energies of the C_{4v}^{12} and D_{4h}^{15} atomic arrangements, as a function of the lattice parameters a and c. We show within a simplified model that it is possible for ΔF to change sign when the lattice constants are altered from the bulk (a_0,c_0) to epilayer (a_1,c_1) values, and hence establish that the strain-driven ordering may provide the necessary constraints to favor the new LRO in the supported MBE layers.

The free energy F is determined by U, the configurational energy of the lattice, and entropy S. It is U, with contributions from the interaction between pairs of atoms, that is critical to our results. We write[12]

$$U=U_0+Nm_am_b\sum_i\alpha_{0i}V_{0i}\,, \tag{1}$$

where U_0 is the configurational energy of a random distribution of atoms and V_{0i} is the ordering energy between sites 0 and i. The effects of mismatch strains that modify the lattice parameters and hence the integration energy between atoms are introduced through V_{0i}. For a binary with ordered vacancies like Zn_3As_2 it is convenient to view the two structures in Fig. 1 in terms of blocks A and B identified in the figure. In evaluating V_{0i} it is hence necessary to deal only with the linear combination $V_{0i}=[(V_{0i}^{AA}+V_{0i}^{BB})/2]-V_{0i}^{AB}$, representing the average change of energy when a pair A,A or B,B is replaced by two unlike blocks A,B at the same positions. The summation over lattice sites in Eq. (1) is approximated by those in the nearest and next nearest blocks of Fig. 1.[13] U_0 and S do not contribute towards ΔF.

Given the C_{4v}^{12} and D_{4h}^{15} symmetries of Zn_3As_2, N (the number of sites), m_A $(=m_B)$ the fraction of type-A (or type-B) blocks of Fig. 1, and α_{0i}, the order parameters,[12] are all known. We hence have $\Delta F\propto V_{0P}-V_{0Q}$. P and Q identify the specific zinc-blende blocks along [101] and [110]. Because of symmetry of the As atom locations, the contributions to V_{0P} and V_{0Q} originate only via interactions among Zn ions. We consider these interactions to arise from an electrostatic repulsion $(\approx E/r)$ and an attractive induced dipole coupling $(\approx D/r^6)$. For simplicity we assume that E and D are constants and thus neglect screening. For given equilibrium lattice parameters a and c, ΔF is hence proportional to $D_1-(t/a^5)D_2$, where t $(=D/E)$ is a measure of the relative strengths of the dipole and Coulomb interactions. D_1 and D_2 can be calculated, and depend only on the tetragonal distortion c/a.

The observed C_{4v}^{12} symmetry for bulk unstrained Zn_3As_2 requires $\Delta F(a_0,c_0)<0$. Adopting the most accurate[8] available a_0,c_0 values, this hence sets an upper bound on t (<79.1 Å^5). The lattice parameters a_1 and c_1 measured from epilayers grown commensurately on InP are $a_1=0.9965a_0$ and a 0.95% mismatch along the tetragonal axis. Hence $\Delta F(a_1,c_1)>0$, the condition needed for a D_{4h}^{15} epilayer to be stabilized, is valid for $t>78.4$ Å^5. We thus find it energetically feasible that the bulk and supported epilayer exhibit different LRO if t for these materials is constrained within this range. Moreover, based upon the measured bulk lattice parameters,[9] similar estimates for ΔF also account for the stability of the α and α'' phases reported in bulk Cd_3As_2.[9] The thermodynamic considerations thus show that lattice-constant changes alone may be sufficient to stabilize the new LRO in Zn_3As_2 when grown epitaxially on InP and GaAs substrates.

Other possibilities to explain the discrepancy between the measured and expected Raman spectra in the C_{4v}^{12} symmetry were considered and found inadequate. They included deriving the α-Zn_3As_2 phonons from high-symmetry k points of smaller unit cells to introduce mode degeneracies,[14] the possible presence of the α' and β phases, and a reported large D_{4h}^{20} structure.[15]

The observed ordering is novel and unlike heteroepitaxial growth on specific lattice-parameter-adapted substrates that, in some instances, lead to different orientations of the epilayer.[16] In marked contrast, a change in the symmetry and the concomitant stability of a new crystal structure of this Zn_3As_2 lattice is revealed from the modified order. To achieve the new LRO we suggest as a possible mechanism a process analogous to stress-induced Zener relaxation of specific atoms observed in bulk solid solutions.[17] Our experiments show that the epitaxial layers exhibit a similar structural change that, as in several Zener transitions,[18-20] could have been achieved by a relocation of Zn atoms to available vacancy sites (Fig. 2). In this situation, the strain from the lattice mismatch stabilizes the new LRO.

In summary, our Raman measurements have provided evidence of stabilization of a new LRO—a structure not favored in the bulk—in supported single-crystal epilayers. The Zn_3As_2 films grown on InP and GaAs substrates crystallize in the D_{4h}^{15} space group that retains the same nearest neighbors as in the bulk. The modified order has a profound effect on the Raman spectra which thus becomes a sensitive structural probe of such complex systems. It is shown that strain-induced free-energy changes in this binary system may be sufficient to account for the observed structural modifications. The work also illustrates the possibility to utilize lattice-mismatch strain in developing high-quality heterolayers with novel crystal structures.

We thank C. Jayaprakash for valuable discussions. Work at The Ohio State University was supported by the

NSF under Contract No. DMR-87-03980.

[1]A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. **60**, 2645 (1988).

[2]M. A. Shahid *et al.*, Phys. Rev. Lett. **58**, 2567 (1987).

[3]H. R. Jen, M. J. Cherng, and G. B. Stringfellow, Appl. Phys. Lett. **48**, 1603 (1986).

[4]A. Ourmazd and J. C. Bean, Phys. Rev. Lett. **54**, 201 (1985).

[5]T. S. Kuan *et al.*, Phys. Rev. Lett. **54**, 201 (1985).

[6]G. P. Srivastava, J. L. Martins, and A. Zunger, Phys. Rev. B **31**, 2561 (1985); A. Mbaye, A. Zunger, and D. Wood, Appl. Phys. Lett. **49**, 782 (1986); Jose Luis Martins and Alex Zunger, Phys. Rev. Lett. **56**, 1400 (1986).

[7]C. P. Flynn, Phys. Rev. Lett. **57**, 599 (1986); P. B. Littlewood, Phys. Rev. B **34**, 1363 (1986).

[8]A. D. Izotov, A. Sanygin, and V. F. Ponomarev, Kirstallografiya **23**, 764 (1978) [Sov. Phys. Crystallogr. **23**, 429 (1978)].

[9]A. Pietraszko and K. Lukaswewicz, Phys. Status Solidi (a) **18**, 723 (1973).

[10]*Proceedings of the First International Symposium on the Physics and Chemistry of II-V Compounds, Mogilany, Poland, 1980,* edited by M. Gelton and L. Zdanowicz (Eindhoven University of Technology, The Netherlands, 1980).

[11]B. Chelluri *et al.*, Appl. Phys. Lett. **49**, 1665 (1986), and J. Cryst. Growth **81**, 530 (1987).

[12]J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[13]Evaluating the additional small contribution of including all blocks is, of course, possible though tedious. Moreover, since we are interested in ΔF (and not F) the effects of this approximation to a Madelung sum are expected to be minimal and will not affect the establishment of the feasibility of the new LRO in these layers.

[14]A. Mackinnon, Festkoerperprobleme **21**, 149 (1981), and references therein.

[15]T. A. Zyubina *et al.*, Inorg. Mater. Engl. Trans. **13**, 296 (1977).

[16]J. Hasima *et al.*, J. Cryst. Growth **83**, 466 (1987).

[17]A. S. Norwick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, 1972).

[18]G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).

[19]R. G. Leisure, T. Kanashiro, P. C. Riedi, and D. K. Hsu, J. Phys. F **13**, 2025 (1983).

[20]H. J. Blythe and F. Walz, Phys. Status Solidi (a) **89**, 213 (1985).