PHYSICAL REVIEW B VOLUME 44, NUMBER 8 15 AUGUST 1991-II

Phase transitions in CdTe/ZnTe strained-layer superlattices

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(Received 20 September 1990)

In CdTe/ZnTe strained-layer superlattices under hydrostatic pressure, the CdTe phase transition does not occur until around 60 kbar, compared with the bulk CdTe value of 35 kbar. This dramatic superpressing cannot be explained by the model proposed to explain superpressing in unstrained (Al,Ga)As superlattices [Weinstein *et al.*, Phys. Rev. Lett. **58**, 781 (1987)] but can be accounted for by consideration of a probable microscopic mechanism of the phase transition, by shear on (111) planes. The results show that most semiconductors may be superpressed.

Strained-layer superlattices (SLS's) are among the synthetic crystal materials made possible by recent advances in crystal-growth methods such as molecular-beam epitaxy (MBE). They are made of alternate layers of a few atomic monolayers of nonlattice-matched cubic semiconductors, elemental (Si/Ge), or compound (III-V or II-VI). The cubic symmetry of the bulk materials is lifted in SLS's both by the two-dimensional electronic potential and by the biaxial elastic strains in the layers. The lattice mismatch between CdTe and ZnTe is about 6.4%, and this allows large strain-induced valence-band splittings.[1,2] Hydrostatic pressure is an invaluable tool for the study of the electronic properties of such structures. Furthermore, the phase transitions that occur under high pressure in superlattices have revealed unexpected structural properties of these crystals.[3-5]

Phase transitions in bulk tetrahedral semiconductors have been extensively studied.[6] In the zinc-blende (B_3) materials, a variety of structures have been found above the phase-transition pressure P_t. Mostly, however, they are a sixfold-coordinated metal, with the rocksalt (B_1) or β-tin (A_5) or similar structure. The volume is reduced by 15–20 %, corresponding to a reduction in the lattice constant of about 6%. On release of pressure, either the zinc-blende phase or a metastable phase may be recovered.[7] The phase transitions can be a problem in high-pressure studies since they limit the range of the experiments. The results we report here indicate that most semiconductors can be superpressed well above their usual phase-transition pressures.

We have studied the photoluminescence (PL) of CdTe/ZnTe SLS's under high pressure, in a miniature diamond-anvil cell (DAC).[8] The results confirmed the values of strain and layer thickness expected from the growth (for details, see Ref. 8). However, PL was observed to pressures around 60 kbar; this was unexpected because the established phase-transition pressure for CdTe, P_t^{CdTe}, is about 35 kbar (Ref. 10) [or 41 kbar (Ref. 11)]. The design and growth of the samples have been described elsewhere;[9] we studied samples 206-40 [$(\mathrm{CdTe})_8(\mathrm{ZnTe})_{11}$] and 120-17 [$(\mathrm{CdTe})_7(\mathrm{ZnTe})_6$] of that paper. Both these samples are "free-standing" structures; that is, the lattice constant of the SLS is determined solely by the relative thicknesses of the CdTe and the ZnTe layers. The SLS is externally unstrained, while the CdTe layers are under compressive biaxial stress and the ZnTe layers are under a balancing tensile biaxial stress[1,9,12] (Table I).

At pressures where PL is still observed, no phase transition can have occurred. However, the quenching of the PL is not definitive evidence for a phase transition, since there are other mechanisms for quenching. Thus the PL gives lower limits only for P_t^{SLS}. PL is expected to remain quenched after release of pressure, even when the transition is reversible, because of defect creation. Consequently, direct observation is necessary, both to determine P_t accurately and to observe whether the phase transition is reversible.

In order to observe the phase transition directly, samples were removed from their substrates by etching with a 7% aqueous solution of NaOCl, which dissolves the

TABLE I. Bulk material parameters.

	CdTe	ZnTe
Unit cube side (Å)	6.481	6.103
Shear modulus G (kbar)	105	158
Phase transition (kbar)	35	93
$\Delta W = \Delta P \Delta V$ (meV/cell/kbar)	31	
Strain energy E (meV/cell)	$71.4f^2$	$90f^2$

GaAs substrate but not the II-VI compounds. The resulting ~2-μm-thick flakes of SLS's were cleaved to pieces ~50 μm square for loading in the DAC together with a piece of ruby to serve as the pressure gauge. Without the low-band-gap GaAs substrate, the phase transition could be observed directly by the blackening of the transparent SLS at P_t. In these samples the phase transition is thus identified positively.

Pictures of the samples removed from their substrates and loaded in the DAC under pressure at 300 K are shown in Fig. 1. In these photographs, the upper sample is the $(CdTe)_8(ZnTe)_{11}$ superlattice; in the center the clear ruby crystal is seen, and at the bottom is the $(CdTe)_7(ZnTe)_6$ sample (which has cracked). In Fig. 1 (upper left) at low pressure, both samples are black, as their band gaps are in the near infrared. At about 20 kbar (Fig. 1, upper right), both samples are red, as the band gaps are opened up but the phase transitions have not yet occurred. At about 51 kbar, the $(CdTe)_7(ZnTe)_6$ blackens abruptly, as seen in Fig. 1 (center left), which was taken at about 55 kbar. The $(CdTe)_8$ $(ZnTe)_{11}$ goes black at 64 kbar. It has just started to transit from a few nucleation points around the edge in Fig. 1 (center right), and has completed the transition in Fig. 1 (bottom left), which was taken at about 70 kbar. In most cases, the transition swept across the sample in under a second, but in one case it stuck halfway and required a small increase in pressure to complete it. On subsequent reduction of pressure, the samples became red again at about 35 kbar, so the phase transition is reversible. Figure 1 (bottom right) shows the samples at about 25 kbar after reducing the pressure from above the phase transition. On further cycling of the pressure, the phase transition occurred at about 47 kbar when increasing and about 35 kbar when decreasing pressure. Thus there is about 30 kbar of hysteresis the first time, reducing to some 10 kbar of hysteresis after a few cycles. Damage occurs as the transition is cycled, shown by the dark patches on the lower sample in the last picture.

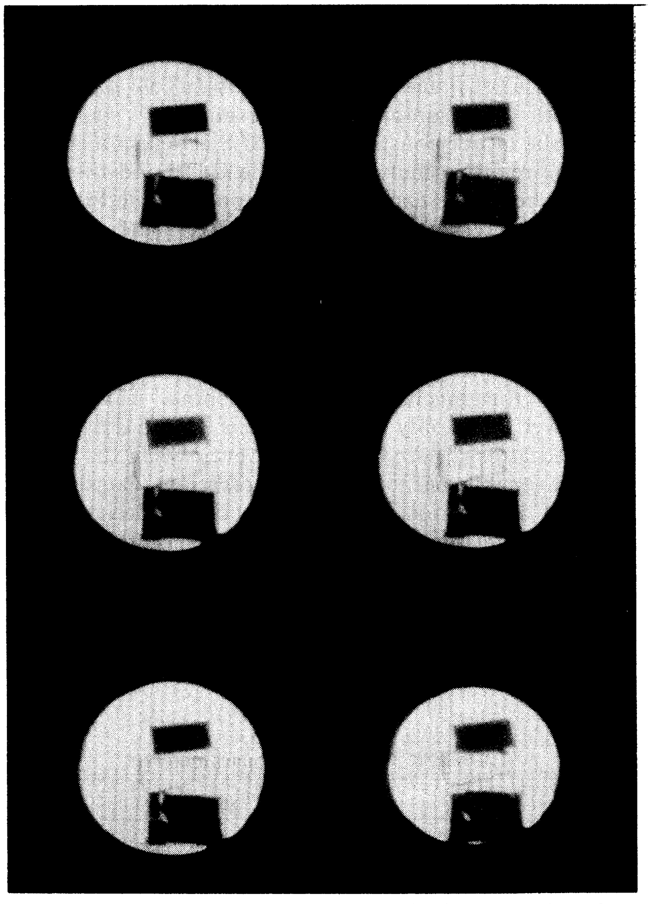

FIG. 1. The two CdTe/ZnTe superlattices detached from their substrates are seen loaded in a DAC together with a piece of ruby for pressure calibration. The pressure is increased through the series of pictures and decreased again in the last. For details, see the text.

Similar effects have been reported recently in unstrained GaAs/AlAs superlattices. Bulk AlAs transits (undergoes its phase transition) to a rocksalt structure at about 90 kbar, compared with 180 kbar for GaAs. Weinstein *et al.*[3-5,13] observed up to 40-kbar superpressing in the AlAs layers, and explained it in terms of a model similar to the models of critical thickness in strained-layer growth.[14] The GaAs and AlAs are lattice matched when they are both tetrahedral, and have a lattice mismatch of 5–6% if only one material transits. If the superlattice period and AlAs layer thickness are large, the AlAs layers transit at a slightly higher pressure than usual. A high density of misfit dislocations is required at the tetrahedral-GaAs–rocksalt-AlAs interface, and it is the energy required to create these dislocations that raises P_t. Thinner AlAs layers will transit to a strained state, in biaxial tension. This reduces or eliminates the density of misfit dislocations required, and the increase in P_t is now due to the strain energy.

Our samples are grown as strained layers, with a mismatch between the CdTe and ZnTe of about 6%. If the CdTe alone were to transit, the lattice mismatch to the ZnTe would be essentially eliminated. The strain energy in our structures is thus relieved by the phase transition of the CdTe alone. This is the opposite situation to that studied by Weinstein. The phase-transition pressure should be *reduced* below the bulk CdTe value. We observe an *increase,* so the critical thickness model cannot apply. Furthermore, the thinner CdTe layers would be expected to suffer the greater effect, our data show a smaller effect in the thinner layers (Table II).

Instead, we are obliged to look at the phase transition from a microscopic point of view, in order to identify the mechanism that blocks the CdTe phase transition. The values of P_t^{SLS} that we observe are close to the weighted means of P_t^{CdTe} and P_t^{ZnTe} (see Table I and Refs. 10 and 15), and so the superlattices are behaving rather as the corresponding alloys would, despite having periods of 13 and 19 atomic layers. The inhibition of the CdTe phase transition must be due to the energy of the "4-6" interface between the low-pressure tetrahedral phase and the high-pressure rocksalt phase. We may estimate the energy involved in the superpressing, by considering both the PV terms and the elastic energy in the biaxial strain. The

TABLE II. Superlattice parameters.

	$(CdTe)_7(ZnTe)_6$	$(CdTe)_8(ZnTe)_{11}$
Experimental phase transition pressure P_t (kbar)	51	64
Weighted mean P_t (kbar)	62	69
CdTe biaxial strain f	−0.0338	−0.0404
ZnTe biaxial strain f	0.0262	0.0196
$\Delta W = \Delta P \Delta V$ (eV/SL cell)	1.67	3.6
Strain energy E (eV/SL cell)	0.473	0.655
Total energy $W+E$ (eV/interface atom)	0.53	1.06

work done by the high pressure at the phase transition is

$$W = P\Delta V$$

and for a superpressure of ΔP the extra work is

$$\Delta W = \Delta P \Delta V \ .$$

For $\Delta V = 18\%$ this gives 18 $\mathrm{J\,cm^{-3}\,kbar^{-1}}$, which corresponds to 31 $\mathrm{meV\,kbar^{-1}}$ per unit cell (cube of side 6.48 Å). The values for our two samples are given in Table II. The strain energy in each layer is given by

$$E = 2G(1-\nu)(1+\nu)^{-1} f^2 d \ ,$$

where G is the shear modulus, ν is the Poisson ratio (taken to be 1/3 for both CdTe and ZnTe), d is the layer thickness, and f is the biaxial strain. We obtain f by dividing the misfit strain between the two layers so as to have a free-standing superlattice. The parameter values for each material are given in Table I, and the resulting strain energies for the two samples are given in Table II. The total excess energy available for the creation of a 4-6 interface, if the CdTe were to transit alone, is $\Delta W + E$ per SLS unit cell. This energy has to be divided between two interfaces, each with two atoms per unit square, giving 0.53 and 1.06 eV/atom for the two samples (Table I).

This result is to be compared with the energy of a 4-6 interface. Martin[4] calculated this energy for a (111)-oriented interface and found it to be small but positive (0.35 eV/atom). Clearly, this is insufficient to account for the superpressure that we observe in the $(CdTe)_8(ZnTe)_{11}$ sample, although it could account for the superpressure in the $(CdTe)_7(ZnTe)_6$.

Examining the mechanism of the phase transition in more detail provides a plausible explanation of the superpressing. As Martin[4] pointed out, the low-pressure phase and the likely high-pressure phase are closely related, being simply different stackings of hexagonal-close-packed (111) planes:

$$T_d \ (\text{zinc blende}) \ A\text{--}aB\text{--}bC\text{--}cA\text{-} \ ,$$

$$O \ (\text{rocksalt}) \ A\text{-}c\text{-}B\text{-}a\text{-}C\text{-}b\text{-}A\text{-}$$

in the notation of Ref. 4. It is then very likely that the mechanism of the phase transition is the movement of alternate (111) planes to their new positions (Fig. 2). Here, the atom (b) at $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ has moved to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the other atoms in the (111) planes (b) move similarly. Keeping the center of gravity stationary, one fcc sublattice has moved through $(-\frac{1}{8},\frac{1}{8},\frac{1}{8})$ while the other sublattice has moved through $(\frac{1}{8},-\frac{1}{8},-\frac{1}{8})$. Since our samples are grown in the (001) direction, every (111) plane intersects both the CdTe and the ZnTe layers, and so separate phase transitions in the two components are strongly hindered. Then the phase-transition pressure in each sample will be the weighted mean of the bulk values (Table I). There remains some discrepancy between these and the experimental values; it is possible that this may be due to the effect of the axial strain on the stability of the low-pressure phase. However, we have insufficient data to test this hypothesis.

There are four variants of this mechanisms, since there are four equivalent (111) planes. Depending on how the transition nucleates, there may be regions in the sample that undergo different variants, causing damage at the interfaces between these regions. There is also another possible mechanism, in which shearing on (111) planes occurs in the two directions $(-\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{1}{4},-\frac{1}{4},\frac{1}{4})$. Again keeping the center of gravity stationary, one sublattice has been displaced by $(0,0,-\frac{1}{8})$ while the other

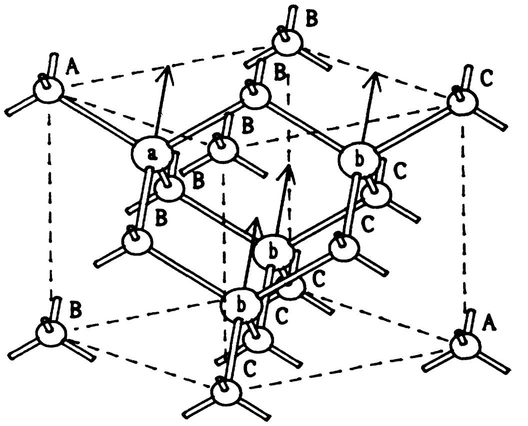

FIG. 2. A diagram of the proposed mechanism of the phase transition discussed in the text. A unit cube of the zinc-blende lattice is shown, with (111) planes labeled as in the text. The new positions for the lower-case (111) planes after the phase transition are shown by the arrows; the upper-case planes do not move.

sublattice has moved through $(0,0,\frac{1}{8})$ and in addition undergone displacement of alternate (111) planes by $(-\frac{1}{4},\frac{1}{4},0)$ and $(\frac{1}{4},-\frac{1}{4},0)$. With so many possibilities, it is not surprising that cycling the transition results in heavy damage to the original single crystal, as seen in Fig. 1 (bottom right).

This model predicts that, in superlattices grown on (111)-oriented substrates, the superpressure will be much reduced, or even negative, according to strain values and layer thicknesses. No experimental information on this point is available, to our knowledge.

The (Al,Ga)As system is unusual in that it is lattice matched, and also in that the compound with the lower atomic weight also has the lower value of P_t. Generally, the trend in the Periodic Table in the group-IV, III-V, or II-VI materials is for a larger lattice constant, a lower P_t, and a lower band gap. In the critical thickness model, (Ga,Al)As is exceptional and most other SLS's would not display superpressing. Our results here show that in fact superpressing *will* generally occur in any (001) superlattice. This is very valuable, since often interesting behavior such as the $\Gamma - X$ crossover in InP is predicted to occur at a pressure above P_t, previously considered to be inaccessible.

Dr. J. Mullins (Durham) provided the recipe for removing GaAs from the II-VI SLS. J. Tyzzer assisted with the photography. J.P.F. thanks DARPA for financial support under contract No. F 4962087-C-0021. D.J.D. and A.D.P. thank the Science and Engineering Research Council (UK) for financial support. Groupe d'Etudes des Semiconducteurs (Montpellier) is the Laboratoire associe au Centre National de la Recherche Scientifique No. 357.

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[1] E. P. O'Reilly, Semicond. Sci. Technol. **4**, 127 (1989).

[2] H. Mathieu, J. Allegre, A. Chatt, P. Lefebvre, and J. P. Faurie, Phys. Rev. B **38**, 7740 (1988).

[3] B. A. Weinstein, S. K. Hark, and R. D. Burnham, in *Proceedings of the 18th International Conference on the Physics of Semiconductors, Stockholm, 1986* (World Scientific, Singapore, 1987), p. 707.

[4] R. M. Martin, in *Proceedings of the 18th International Conference on the Physics of Semiconductors, Stockholm, 1986* (Ref. 3), p. 639.

[5] B. A. Weinstein, S. K. Hark, R. D. Burnham, and R. M. Martin, Phys. Rev. Lett. **58**, 781 (1987).

[6] See, e.g., S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. **25**, 49 (1978).

[7] J. M. Besson, E. H. Mokhtari, J. Gonzales, and G. Weill, Phys. Rev. Lett. **59**, 473 (1987).

[8] B. Gil, D. J. Dunstan, J. Calatayud, H. Mathieu, and J. P. Faurie, Phys. Rev. B **40**, 5522 (1989).

[9] G. Monfroy, S. Sivanathan, X. Chu, J. P. Faurie, R. D. Knox, and J. L. Standenmann, Appl. Phys. Lett. **49**, 152 (1986).

[10] D. J. Dunstan, B. Gil, and K. P. Homewood, Phys. Rev. B **38**, 7862 (1988).

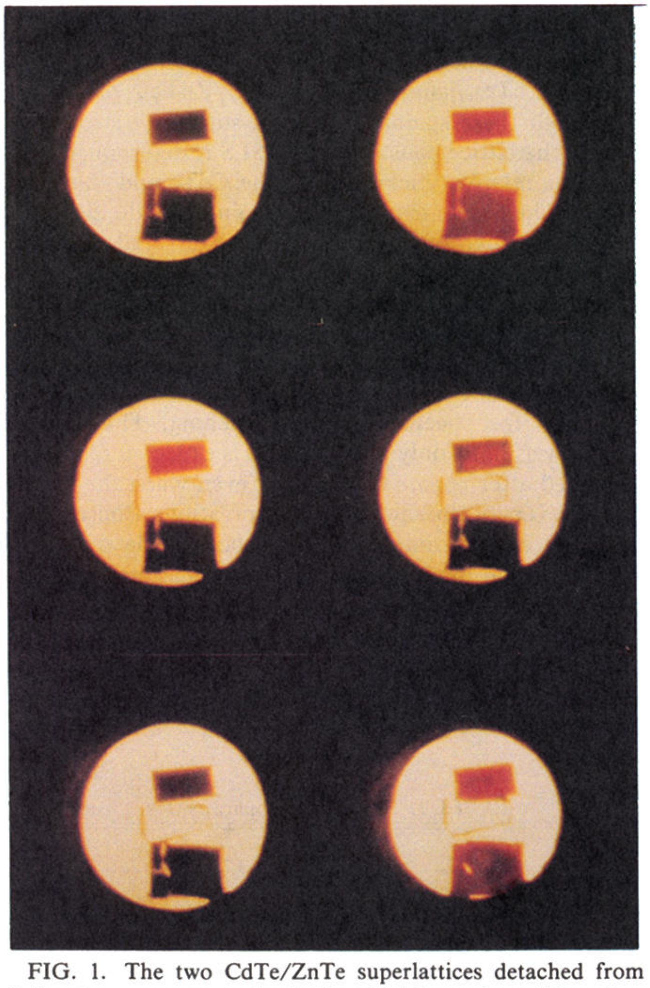
[11] K. Zanio, *Cadmium Telluride, Semiconductors and Semimetals* (Academic, New York, 1978), Vol. 13, p.10.

[12] R. H. Miles, G. Y. Wu, M. B. Johnson, T. C. MacGill, J. P. Faurie, and S. Sivanathan, Appl. Phys. Lett. **48**, 1383 (1987).

[13] B. A. Weinstein, Semicond. Sci. Technol. (to be published).

[14] See, e.g., R. People and J. C. Bean, Appl. Phys. Lett. **47**, 322 (1985).

[15] K. Strossner, S. Ves, Chul Koo Kim, and M. Cardona, Solid State Commun. **61**, 275 (1987).



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