

Self-Organized Formation of Compositionally Modulated $\text{ZnSe}_{1-x}\text{Te}_x$ Superlattices

S. P. Ahrenkiel,¹ S. H. Xin,² P. M. Reimer,³ J. J. Berry,³ H. Luo,² S. Short,² M. Bode,¹ M. Al-Jassim,¹ J. R. Buschert,³ and J. K. Furdyna²

¹National Renewable Energy Laboratory, Golden, Colorado 80401

²Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

³Turner Precision X-ray Laboratory, Goshen College, Goshen, Indiana 46526

(Received 12 April 1995)

We report the observation of periodic compositional modulation in $\text{ZnSe}_{1-x}\text{Te}_x$ alloys grown by molecular beam epitaxy on vicinal (100) GaAs substrates. The period is highly regular, with typical values between 18 and 32 Å, and is long range in character. X-ray diffraction indicates that the composition varies approximately sinusoidally, resulting in superlattices that are expected to have unique physical properties.

PACS numbers: 68.65.+g, 68.55.Bd, 78.66.Hf

During the process of growing $\text{ZnSe}_{0.50}\text{Te}_{0.50}$ alloys by molecular beam epitaxy (MBE) on vicinal (001) GaAs substrates, we have observed spontaneous formation of compositionally modulated $\text{ZnSe}_{1-x}\text{Te}_x$ superlattices, with a highly regular periodic variation of x along the growth direction. The period of the observed composition modulation depends on the growth conditions, but is typically very well defined for any one growth. The spatial extent of such superlattices has a remarkably long range, generally extending throughout the entire epitaxial specimen.

Spontaneous departures from a purely random composition are well known in MBE and metal-organic chemical vapor deposition (MOCVD) of III-V alloys. The formation of atomic superlattices along various crystallographic directions, phase separation, and other forms of nonrandom segregation have been observed and studied in practically all III-V ternary and quaternary alloys [1]. In contrast to this, little is known in this area in II-VI alloys. Some indications of atomic ordering have been reported for ZnSeTe [2,3], and clear evidence of phase separation has been observed in three other II-VI systems (ZnSeS [4], ZnMgSeS [4], and ZnCdTe [5]). In addition, atomic ordering has been observed in the nonisovalent II-VI alloy ZnFeSe [6].

Because of the similarities and differences between the III-V and II-VI alloys [7], the observation of spontaneous segregation phenomena in the II-VI family—apart from signaling the formation of systems that are new and interesting in their own right—is likely to increase our understanding of these phenomena in general (i.e., in II-VI, III-V, and mixed group-IV alloys). We have therefore launched a systematic investigation of the growth and the resulting microscopic morphology in $(AC)_{1-x}(BC)_x$ and $(AC)_{1-x}(AD)_x$ alloys with $x \approx 0.5$, where A, B stand for different group-II elements (cations), and C, D represent different group-VI elements (anions).

During this investigation the system $\text{ZnSe}_{1-x}\text{Te}_x$, when grown on miscut (vicinal) GaAs(001) substrates, revealed a remarkably interesting property—the spontaneous formation of superlatticelike modulation of composition x along the growth direction—and we will be focusing on

this phenomenon here. The observed effect is illustrated in the dark-field transmission electron microscopy (TEM) micrograph shown in Fig. 1. As seen in the figure, the superlattice shows a remarkably well defined period, which, in the case illustrated, is 27.4 ± 1 Å. The period is remarkably constant over a macroscopically large region, usually spanning the entire epilayer.

The $\text{ZnSe}_{1-x}\text{Te}_x$ ($x \approx 0.5$) specimens were prepared in a Riber 32 R&D dual-chamber MBE machine in the form of epilayers (1 to 2 μm thick) grown on vicinal GaAs(001) substrates with various miscut angles between 2° and 10° , at various substrate temperatures, and with various flux ratios. We have only observed the spontaneous modulation phenomenon in cases where the miscut was greater than 2° , and only when the miscut surface was tilted either toward the $[111]a$ or $[111]b$ direction, with the optimum miscut angle being about 4° . It is significant that we have seen this in *every* growth involving a 4° miscut

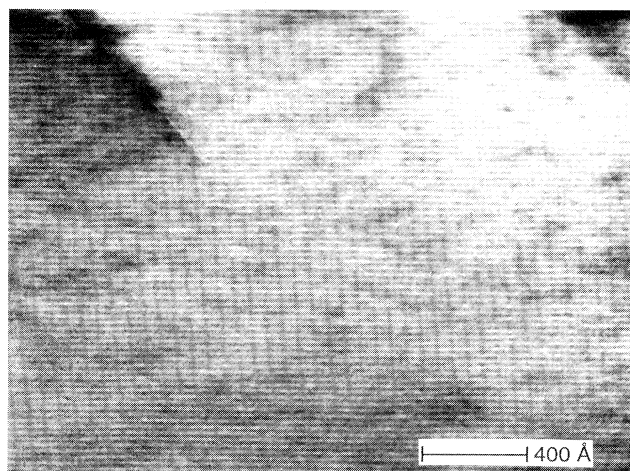


FIG. 1. Dark-field TEM image of a ZnSeTe epilayer grown on a vicinal GaAs(001) substrate, miscut by 4° toward the $[111]b$ direction. The view is taken along the $[110]$ direction, the growth direction being vertical in the figure. Note the clear and regular formation of a superlattice. The period of the superlattice is 27.4 ± 1 Å. The sample was grown at 285°C .

angle toward one of the [111] directions (a total of over 15 such specimens), either directly on GaAs “epiready” substrates, or on epitaxial GaAs buffers, which were deposited on the commercial substrates, or on epitaxial GaAs buffers, which were deposited on the commercial substrate before the $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ growth [8]. The occurrence of the spontaneous composition modulation only on substrates with a certain minimum tilt with respect to the (001) plane suggests that the formation of the superlattice is somehow linked to the atomic steps, which characterize vicinal surfaces.

We have observed differences in the superlattice period with various samples, ranging from 18 to 32 Å, but the period was remarkably constant in any one specimen. Our growths were carried out at temperatures between 275 and 350 °C and at growth rates between 2.5 and 3.5 Å/sec, but at this point we do not have sufficient data to systematically correlate any given property of the superlattices with the growth rate or temperature.

The periodic structure of these spontaneous superlattices is confirmed by transmission electron diffraction (TED) measurements, shown in Fig. 2. Note that satellites in the TED patterns are points rather than streaks, confirming the conclusion already drawn visually from the TEM pictures that the superlattice period is quite well defined. TED data also provide additional information: A careful analysis of the orientation of the TED satellites indicates that they are slightly tilted relative to the $\text{ZnSe}_{0.50}\text{Te}_{0.50}$ crystallographic planes, i.e., that the wave vector of the superlattice is not exactly parallel to the [001] crystallographic direction of the ZnSeTe epilayer, but is normal to the macroscopic sample surface. In certain cases the superlattice layers were not completely flat, but slightly “wavy” within the layer plane, but even in those instances the *period* itself

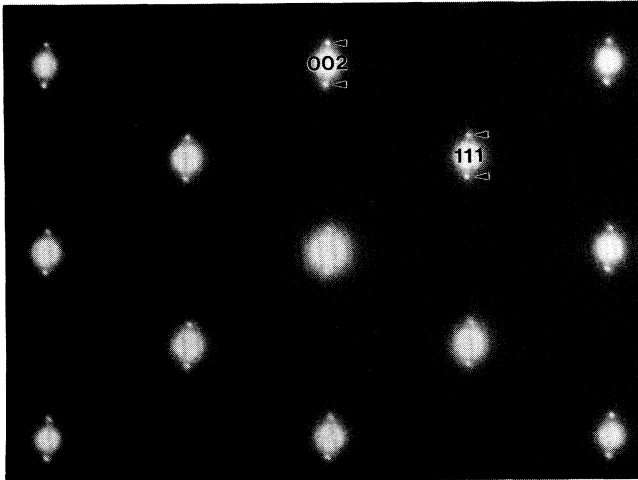


FIG. 2. [110] transmission electron diffraction (TED) pattern for the same sample as in Fig. 1, with superlattice diffraction spots. Close inspection reveals that the spots are very slightly tilted relative to the crystallographic orientation [001], indicating that the planes of the superlattice are not exactly coincident with the (001) crystallographic planes of $\text{ZnSe}_{1-x}\text{Te}_x$.

remained the same at every point. In general, in our still very limited experience the flatness of the superlattice layers has been considerably better in specimens grown on GaAs epilayer buffers than in those grown directly on commercial GaAs substrates.

The surprisingly long range of the phenomenon makes it amenable to characterization by x-ray diffraction. Figure 3 shows a typical radial (θ - 2θ) x-ray scan through the (004) Bragg reflection. The x-ray measurements presented in this Letter were made on a double-axis diffractometer equipped with a single-crystal Si[111] monochromator, using $\text{Cu } K\alpha_1$ radiation (1.54 Å) from a fixed tube source. The scan in Fig. 3 shows two clearly defined superlattice satellites, corresponding (for that specific sample) to a superlattice period $\Lambda = 25.9 \pm 1$ Å, as discussed below.

In addition to signaling the existence of compositional modulation, x-ray diffraction can provide other information on the structural details of these new multilayer systems. It is particularly interesting to know how the composition x varies along the growth direction in the modulated $\text{ZnSe}_{1-x}\text{Te}_x$ structure. We will discuss this aspect in some detail, since the compositional profile of these spontaneous superlattices turns out to be quite unique, distinguishing them from *man-made* short-period superlattices.

The diffracted x-ray scattering intensity is proportional to the square of the Fourier transform \mathcal{F} of the electron density $\rho(r)$ in the scattering system, i.e.,

$$I(q) \propto |\mathcal{F}[\rho(r)]|^2.$$

The observed x-ray scattering can therefore be used for the purpose of mapping the Fourier components necessary to describe the distribution of electrons (and, by extension, the compositional distribution) in the sample. Thus, if a given superlattice consists of abrupt, discontinuous steps

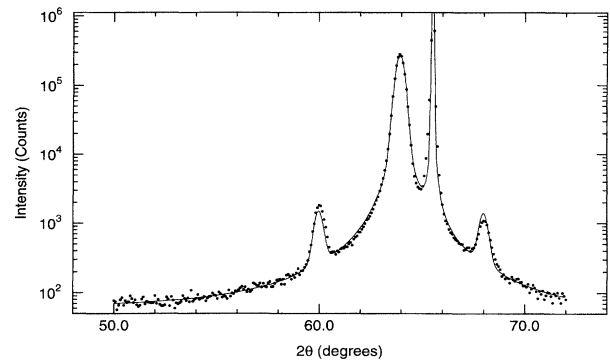


FIG. 3. X-ray θ - 2θ scan through the (004) Bragg reflection for a $\text{ZnSe}_{1-x}\text{Te}_x$ spontaneous superlattice grown on a GaAs(001) substrate miscut by 4° toward [111] b , showing a single pair of clearly defined satellite reflections. The solid line is the best fit to the data assuming sinusoidal composition modulation (single Fourier component), in which the modulation period and the amplitude are free parameters. The fit yields a superlattice period of 25.9 ± 1 Å. The layer was grown at 335 °C, indicating little effect of the growth temperature on the period (compare with data of Fig. 1). The sharp peak near 66° is the GaAs substrate (004) reflection.

in its composition, with sharply defined interfaces, one will require a large number of Fourier components to describe $\rho(r)$, and a large number of x-ray satellites will be observed in the θ - 2θ scan. (See, for example, recent x-ray diffraction observed on GaInP/GaAs superlattices [9], which show many satellite pairs corresponding to a harmonic series of modulations with fundamental period Λ .) A sinusoidal modulation of the composition, with a single, well defined period Λ , will, on the other hand, give rise to only one *pair* of satellite peaks about each Bragg peak, the latter corresponding to the average (or unmodulated) lattice.

We now return to Fig. 3. The most intense, narrow peak in the figure (near 65.5°) is due to the GaAs substrate, and the next most intense, broader peak (near 64°) is the (004) reflection from the average $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ zinc blende lattice [10]. Indeed, the lattice spacing deduced from this (004) reflection corresponds closely to the average of the lattice spacings of ZnSe and ZnTe. In addition, we see *only* two satellites equally spaced above and below the average $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ peak. Careful scans at much higher sensitivity revealed the presence of no other peaks, strongly suggesting that the electron distribution is sinusoidal (or very close to sinusoidal) along the growth direction, as discussed above. In contrast, intentionally grown ZnSe/ZnTe superlattices with periods comparable to the spontaneously modulated structures (30 Å/30 Å, 30 Å/20 Å, and 30 Å/10 Å), prepared for the purpose of comparison, invariably showed a large number of satellites (four or more on either side) in both the x-ray scans and TED images.

For sinusoidal modulation of composition along the [001] direction, it is readily shown that the angular positions of the (004) peak for the average composition ($2\theta_0$), the high-angle satellite ($2\theta_+$), and the low-angle satellite ($2\theta_-$) are related as follows [11]:

$$\sin\theta_{\pm} = \sin\theta_0 \pm \lambda/2\Lambda,$$

where λ is the wavelength of the xrays, and Λ the modulation period. The solid line in Fig. 3 is the best fit to the data assuming a lattice with a simple sinusoidal modulation of electron density (a single Fourier component), in which the period and the amplitude are free parameters. As already mentioned, this gives a period of 25.9 Å for the data in Fig. 3. In all, we have carried out x-ray (and TEM) observations on thirteen $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ samples grown on vicinal GaAs substrates, with periods ranging from 18 to 32 Å. X-ray θ - 2θ scans for all the specimens examined indicated only two satellites, in close similarity to the behavior seen in Fig. 3.

The modulation of electron density that manifests itself via x-ray scattering satellites can arise from two causes: a *strain* modulation, and a *chemical* modulation. Pure strain modulation would arise in a sample with identical atoms at every site, in which the lattice spacing is modulated (in our case, along the growth direction) about some average value. Pure chemical modulation consists of modulating the relative concentrations of atoms with different x-ray

scattering powers (in our case, the Se and Te atoms) in a lattice with a perfectly uniform lattice spacing. Each of these effects taken separately would result in a pair of equal intensity satellites, such as those in the solid-line fit in Fig. 3. When both are present simultaneously (as is the case in most real systems, since the two effects are causally related), the strain wave and the composition wave will interfere, and the high-angle and low-angle satellites will no longer have exactly the same intensity [11]. Close inspection of the data in Fig. 3 does reveal that the low-angle satellite peak is indeed slightly stronger than the higher-angle satellite. Quantitative analysis of the satellite intensity ratios relative to the central $\text{ZnSe}_{0.5}\text{Te}_{0.5}$ peak [12] and to one another should in principle allow one to disentangle the strain and chemical contributions, and to establish the modulation amplitude of x along the growth direction [10]. Such analysis must, however, also take into account the small tilt of the superlattice planes with respect to the crystallographic planes (pointed out in connection with Fig. 2), and we do not yet have sufficient data to do this reliably.

While we have established the formation of the superlattice structures phenomenologically, we have not at present pinpointed the mechanisms that lead to this rather remarkable form of spontaneous ordering. We have eliminated some “mundane” causes, such as the possibility that the superlattice forms due to the rotation of the substrate stage during growth, since the phenomenon is observed whether or not the stage is rotated. The phenomenon also differs from commonly observed phase separation whose wave vector is *parallel* to the growth surface (referred to as “lateral” phase separation in Ref. [1]), where the effect may be linked to the process of reconstruction at the original surface, at which it nucleates. There exist reports of compositional segregation along the growth direction in some III-V antimonides [13,14], and the present phenomenon may possibly be related to that. It should be remembered, however, that the phenomena observed in the antimonides (referred to as “vertical” phase separation in Ref. [1]) have so far been observed with a much longer period (typically 300 Å or more) than what we see, and the alternation of composition appears to be abrupt, with sharp (on nearly monolayer scale) interfaces between distinct phases [13,14], in contrast to the sinusoidal behavior that we observe.

It is important to emphasize that the $\text{ZnSe}_{1-x}\text{Te}_x$ superlattices described here persist for many *hundreds* of periods. The absence of direct contact with the original substrate after the formation of the n th period (for large n) implies some form of self-organized behavior in the growth dynamics. The interplay between spinodal decomposition characteristic of alloys involving different bond lengths [1], together with the building up of (successively compressive and tensile) strain as the composition periodically deviates from stoichiometry, the nonequilibrium nature of MBE growth and, of course, the role of atomic steps on the vicinal surfaces, must all be considered in

future studies in identifying the physical mechanism of the observed spontaneous superlattice formation.

Although the mechanism of forming the superlattices described in this paper is at this point far from clear, their high quality and empirical reproducibility suggest that it is not premature to speculate on their band structure and the corresponding optical properties. We note especially that, unlike the *atomic* ordering [1] observed in some III-V structures (whose period is on the scale of monolayers) or phase separation [1] (whose period is typically in several hundreds of angstroms, and is generally quite irregular), the structures described here have dimensions corresponding to quantum wells, and thus appear ideally suited for electron confinement.

So far, we have only carried out elementary photoluminescence (PL) characterization of these structures. The PL peaks observed in various specimens occur between 2.08 and 2.15 eV at 10 K, with linewidths (FWHM) of 60–75 meV, and are unusually intense, especially for a type-II structure [15]. Recalling that the energy gap for *random* ZnSe_{1-x}Te_x alloys exhibits a remarkably pronounced bowing [16,17] with x , with a minimum of 2.22 eV at $x \approx 0.66$ at low temperatures, it is significant that the positions of the observed PL peaks are much below this minimum value for the random alloy of any composition.

While it would be premature to discuss these limited optical data in detail, one should note that *intentionally grown* short-period (ca. 20 Å) ZnSe/ZnTe superlattices [16–18] (fabricated because of their promise for application as bright light emitters) show very similar photoluminescence behavior (i.e., very bright photoluminescence at about 2.1 eV, with a linewidth of ca. 60–70 meV). Although the optical behavior of these structures is often discussed in terms of isoelectronic Te centers [18–20], the mechanism of the observed strong photoluminescence in ZnTe/ZnSe short period superlattices (and, of course, in our systems) still remains an open question. Here the similarities between the spontaneous and “artificial” superlattices discussed above (short period, and the strength and position of photoluminescence) and differences (the composition in our system varies sinusoidally) may prove valuable in pinpointing the physical mechanisms responsible for the observed optical properties.

In summary, we have observed a remarkably regular long-range modulation of composition, with the modulation period in the range of tens of angstroms, which occurs spontaneously in the MBE growth of ZnSe_{1-x}Te_x alloys (with $x \approx 0.50$) on vicinal GaAs(001) substrates miscut toward the [111] direction. The optimal miscut for the formation of such spontaneous superlattices, identified in our as yet limited experience, is about 4°. The orientation of the superlattice layers is parallel to the vicinal surface, rather than to the [001] direction of the ZnSe_{1-x}Te_x crystal. The highest superlattice quality (very flat interfaces, with a minimum of waviness) is observed in structures grown on GaAs epilayer buffers. While the mechanism of formation of these structures grown on GaAs

epilayer buffers. While the mechanism of formation of these structures is at present not understood, their reproducibility holds promise for optical and electrical phenomena that are quite unique because of the sinusoidal (or at least near-sinusoidal) modulation of the superlattice composition along the growth direction.

The authors are grateful to G. Yang for insightful comments. This work was supported by the U.S. Department of Energy through OER/BES Contract No. DE-AC36-83CH10093.

-
- [1] For an up-to-date comprehensive review of atomic ordering, phase separation, and related phenomena in III-V alloys, see A. Zunger and S. Mahajan, *Handbook on Semiconductors*, edited by T. S. Moss (Elsevier, Amsterdam, 1994), Vol. 3, Chap. 19, pp. 1399ff.
 - [2] H. Luo *et al.*, J. Vac. Sci. Technol. B **12**, 1140 (1994).
 - [3] B. Freytag *et al.*, Solid State Commun. **94**, 103 (1995).
 - [4] G. C. Hua *et al.*, J. Cryst. Growth **138**, 367 (1994).
 - [5] R. D. Feldman *et al.*, J. Vac. Sci. Technol. B **5**, 690 (1987).
 - [6] K. Park *et al.*, Appl. Phys. Lett. **61**, 2302 (1992).
 - [7] Both alloy families are tetrahedrally coordinated, but the II-VI are somewhat more polar than the III-V, their covalent bonds are weaker, and (except for the III-V nitrides) the range of energy gaps spanned by the II-VI is greater. In the bulk, some II-VI form in the wurtzite structure (e.g., CdS, CdSe) or as polytypes (ZnS). And the II-VI readily accommodate some nonisovalent atoms to form ternary alloys (e.g., Mn, Fe, Mg, Co) to a surprisingly high atomic fraction.
 - [8] We should add parenthetically that, although so far we have only investigated ZnSe_{1-x}Te_x with average $x \approx 0.5$, we do not expect the observed phenomenon to be restricted to that composition.
 - [9] X. G. He *et al.*, Appl. Phys. Lett. **65**, 22 (1994).
 - [10] In this Letter we only discuss scans for which the scattering vector \mathbf{q} and the wave vector of the modulation are both approximately parallel to the [001] direction of the crystal lattice (i.e., the growth direction).
 - [11] A. Guinier, *X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies* (W. H. Freeman, San Francisco, 1963), Chap. 8.
 - [12] If only chemical modulation is assumed, the fit in Fig. 3 indicates that the composition along the growth direction oscillates sinusoidally between ZnSe_{0.82}Te_{0.18} and ZnSe_{0.18}Te_{0.82}. Inclusion of strain in the analysis is expected to reduce the amplitude of compositional modulation.
 - [13] T. Ferguson *et al.*, Appl. Phys. Lett. **59**, 3324 (1991).
 - [14] A. G. Norman *et al.*, Semicond. Sci. Technol. **8**, S9 (1993).
 - [15] In analogy with ZnSe/ZnTe conventional superlattices, the present system is expected to have a type-II band alignment, in the sense that wells in the conduction and the valence band are expected to occur in different layers.
 - [16] J. E. Bernard and A. Zunger, Phys. Rev. B **36**, 3199 (1987).
 - [17] M. J. S. P. Brasil *et al.*, Appl. Phys. Lett. **58**, 2509 (1991).
 - [18] J. J. Davies, Semicond. Sci. Technol. **3**, 219 (1988).
 - [19] H. Ozaki *et al.*, J. Cryst. Growth **127**, 361 (1993).
 - [20] N. Takojima *et al.*, J. Cryst. Growth **138**, 633 (1994).

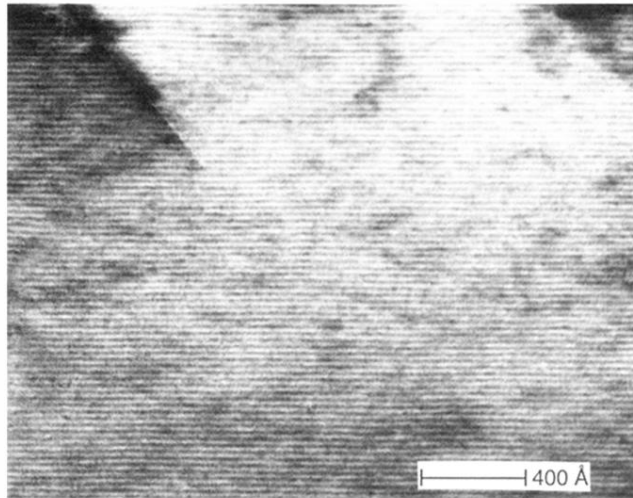


FIG. 1. Dark-field TEM image of a ZnSeTe epilayer grown on a vicinal GaAs(001) substrate, miscut by 4° toward the $[111]b$ direction. The view is taken along the $[110]$ direction, the growth direction being vertical in the figure. Note the clear and regular formation of a superlattice. The period of the superlattice is $27.4 \pm 1 \text{ \AA}$. The sample was grown at 285°C .

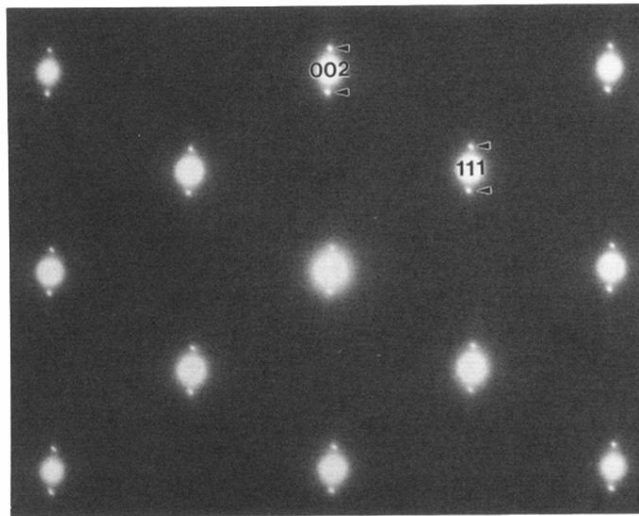


FIG. 2. [110] transmission electron diffraction (TED) pattern for the same sample as in Fig. 1, with superlattice diffraction spots. Close inspection reveals that the spots are very slightly tilted relative to the crystallographic orientation [001], indicating that the planes of the superlattice are not exactly coincident with the (001) crystallographic planes of $\text{ZnSe}_{1-x}\text{Te}_x$.