Comparison of band structure calculations and photoluminescence experiments on HgTe/CdTe superlattices grown by molecular beam epitaxy

M. M. Kraus, M. M. Regnet, C. R. Becker, R. N. Bicknell-Tassius, and G. Landwehr
Physikalisches Institut d. Universität Würzburg, D-8700 Würzburg, Germany

(Received 21 October 1991; accepted for publication 25 February 1992)

We have grown HgTe/CdTe superlattices by molecular beam epitaxy; barrier thicknesses were in the range from 15 to 91 Å and the well thickness was maintained at a constant value of 30 Å. The infrared photoluminescence was investigated by means of Fourier transform infrared spectroscopy in the temperature range from 4.2 to 300 K. All superlattices showed pronounced photoluminescence at temperatures up to 300 K. To gain more detailed insight into the band structure of the HgTe/CdTe superlattices, band structure calculations were performed. The concept of the envelope function approximation was followed. Employing the transfer matrix method, the calculations were completed taking into account an eight band **k·p** model. An important parameter in these calculations is the natural valence band offset (VBO) between the well and barrier materials. As a general trend, the value for the direct gap decreases with increasing VBO. The experimentally determined energies of the band gap are in reasonable agreement with the values obtained by the theoretical calculations. A comparison between theory and experiment shows that the observed transition energies are closer to calculations employing a large offset (350 meV) as opposed to a small VBO (40 meV).

I. INTRODUCTION

More than ten years ago HgTe/CdTe superlattices were said to have interesting physical properties and possible advantages as material for infrared detector applications.[1] Since the first successful fabrication of these superlattices by Faurie *et al.*,[2] one of the most stimulating questions concerning this material system is the magnitude of the valence band offset. Early experimental results and the "Common-Anion" rule suggested a small valence band offset (VBO) of around 40 meV [3,4] and later x-ray photoelectron spectroscopy (XPS) experiments[5–7] revealed a large value for the VBO of around 350 meV. However, recent infrared (IR) magnetoabsorption measurements by Choi *et al.*[8] can only be consistently interpreted under the assumption of a small VBO of 40 meV. Although a large variety of experiments have been performed to study the electronic transport properties of this system, data on the photoluminescence of HgTe/CdTe superlattices are still rare and not too well understood. In this paper we compare the experimental results from IR photoluminescence and x-ray diffraction on HgTe/CdTe superlattices with theoretical calculations based on the envelope function approximation.

II. THEORY

The underlying framework for the theoretical band structure calculations employed is the transfer matrix method developed by Ram-Mohan *et al.*[9] This method is an implementation of the well known envelope function approximation. A full eight-band Hamiltonian was used, taking into account $J = \pm\frac{3}{2}$ heavy hole (hh) band, the $J = \pm\frac{1}{2}$ light hole (lh) band, the $J = \pm\frac{1}{2}$ spin-orbit split-off band, and the Γ_6 conduction band.

As input into the band-structure calculation, the well and barrier dimensions obtained by the x-ray diffraction rocking curve experiments were used. The temperature dependence is introduced in our calculation by taking into account the change of energy gap of HgCdTe with temperature. For the well (HgTe), the standard relationship as given by Hansen *et al.*[10] was used. As the barrier material is on the Cd-rich side, the relationship from Laurenti *et al.*[11] was used, which is more appropriate for $Hg_{1-x}Cd_xTe$ with higher x values. The value of the natural VBO between the HgTe and the $Hg_{0.30}Cd_{0.70}Te$ barrier layers was used as a free parameter in the calculations. Over the last few years there has been considerable controversy as to the value of the VBO. Experiments have suggested either a small (40 meV) or a large (350 meV)[3–7] offset. The influence of the VBO on the band structures was investigated by varying the VBO in the calculations, while holding the other parameters constant.

From the theoretical calculations the positions of the valence and conduction bands at the Γ point were obtained and are plotted in Fig. 1 versus the VBO for a $HgTe/Hg_{0.30}Cd_{0.70}Te$ superlattice with 30 Å barriers and wells. While the hh1 valence band remains at a rather constant position, the $c1$ conduction band shifts strongly to lower energies. This results in a band gap decrease with increasing VBO in the structures under consideration. This is consistent with the calculations of Johnson *et al.*[12] for a superlattice with a 100 Å well thickness. However, due to our small well thicknesses, a crossover of the conduction band with the topmost valence band is not observed, and no semimetallic regime is observed. The calculations also show that the effective mass parallel to the growth direction increases for the hh1 valence band significantly with an increase of the VBO.

As the Cd concentration in the barriers is also experimentally subject to some uncertainty, the influence of this quantity on the calculated band energies was also studied. The calculations show that the Cd concentration in the

 0021-8979/92/115610-04$04.00

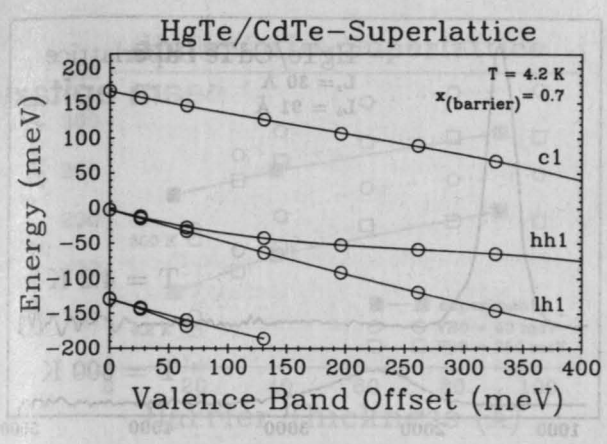

FIG. 1. Theoretical predictions for the positions of the valence bands and the conduction band at the Γ point vs the valence band offset between pure CdTe and HgTe for a temperature of 4.2 K. The barrier x value was assumed to be 0.7.

barrier has a strong influence on the fundamental $c1$-hh1 transition. In Fig. 2 the $c1$-hh1 transition energy is plotted versus the barrier x value. Both VBO discussed here are included. This plot demonstrates that if there is an uncertainty in the barrier x value of $\pm 5\%$, a variation in the calculated energy gap of approximately 20 meV is introduced. This amount of variation is comparable with the differences in the band gaps calculated using small and large valence band offsets. Thus if one is going to try to estimate the offset in this system very careful attention must be paid to the determination of the barrier x values.

III. EXPERIMENTAL DETAILS

Epitaxial growth was carried out in a four chamber RIBER 2300 molecular beam epitaxial (MBE) system which has been modified to permit the growth of Hg based materials. The vacuum in the growth chamber is better than 6×10^{-10} Torr when no Hg has recently been admitted. Three MBE cells were employed, two of which were commercial cells and which contained high purity CdTe

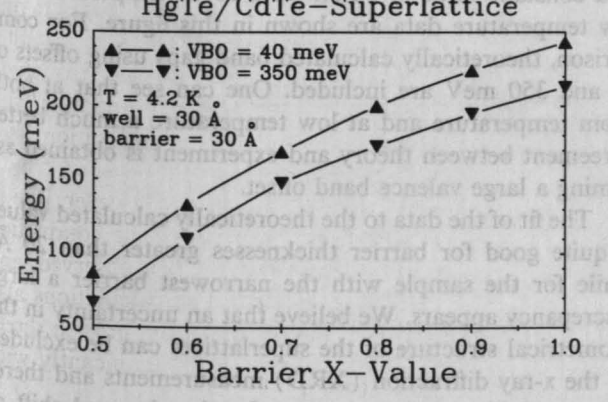

FIG. 2. Theoretical predictions for the band gap in $HgTe/Hg_{1-x}Cd_xTe$ superlattices with a thickness 30 Å for both the barrier and the well. The x value in the barriers is varied, both a small VBO (upper line) and a large VBO (lower line) are considered.

and Te. The third cell is a self designed and constructed stainless-steel cell for Hg which can be refilled without breaking the vacuum. The flux of the latter cell is stable to within $\pm 1.5\%$ and $\pm 3\%$ over a period of 2 and 30 h, respectively. The CdTe-HgTe superlattices were grown on (110) CdZnTe substrates which had been chemomechanically polished for several minutes, degreased, etched in a weak solution of bromine in methanol, and rinsed in methanol. Immediately prior to loading the substrates into the MBE system, they were rinsed in de-ionized water, briefly dipped in hydrochloric acid, and then rinsed in de-ionized water so as to remove all of the original oxide and carbon from the substrate surface. This is accomplished by heating the substrates at temperatures up to about 350 °C while being monitored by reflection high energy electron diffraction (RHEED) as described elsewhere.[13]

The infrared photoluminescence was measured with a commercial Fourier transform infrared (FTIR) spectrometer, which has been extended to enable the collection of luminescence light. A KBr beamsplitter was used along with a CMT detector cooled to 77 K. A Nd:YAG laser was employed as the excitation source. To separate the photoluminescence light from the background radiation, a double modulation technique was used with phase sensitive detection. The lower detection limit of 100 meV was imposed by the cutoff energy of the mercury cadmium telluride detector. The samples were mounted in a helium gas-exchange cryostat equipped with ZnSe windows and cooled to temperatures ranging from 4.2 to 300 K.

To accurately determine the well thickness, superlattice period, and variations in these values, a high resolution five-crystal x-ray diffractometer was employed. From the measured symmetric (002) Bragg reflections the average superlattice period ($\overline{t_p}$), the mean value for the well thickness ($\overline{d}_{\text{Layer}}$), and its deviation, were evaluated. The (004) reflection was measured to determine variations in the average superlattice period.

In this compound semiconductor material system the (002) Bragg reflection shows a rather high reflectivity, in contrast to many other zinc-blende materials. This is due to the sizeable (002) structure factor of the HgTe layers. Therefore, the envelope of the (002) SL satellites represents simply the single-slit function corresponding to the HgTe layers in the superlattice structure. The angular difference between the first-order zero points of this envelope ($\delta\omega_{\text{ZP}}$) can then be used to calculate the thickness of the HgTe layers very accurately. The angular difference of the SL satellites ($\Delta\omega_P$) represents the average superlattice period. From the broadening of the satellites with increasing order number ($\delta\omega_{\text{Sat}}$), the deviation of the HgTe layer thicknesses can be obtained.

The following equations[14]

$$\overline{t_P} = \frac{\lambda|\gamma_H|}{\Delta\omega_P \sin(2\theta_B)}, \tag{1}$$

$$\frac{\delta t_P}{t_P} = \frac{\delta\omega_{\text{Sat}}\overline{t_P}\sin(2\theta_B)}{\lambda|\gamma_H|}, \tag{2}$$

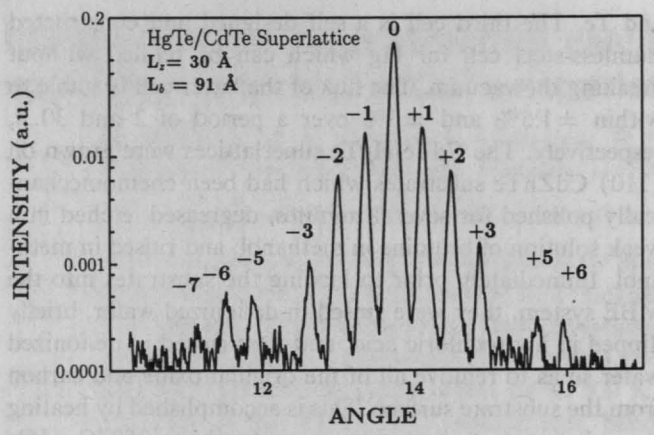

FIG. 3. X-ray rocking curve of the (002) Bragg reflection obtained with a four-crystal diffractometer. The large number of maxima indicate the excellent structural quality of the superlattice.

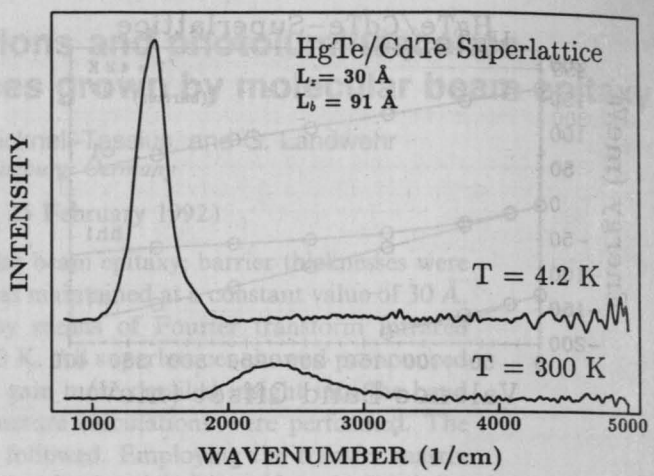

FIG. 4. FTIR photoluminescence spectra at the indicated temperatures from a $HgTe/Hg_{1-x}Cd_xGe$ superlattice. The curves are shifted vertically for clarity, while the scale of the signal is maintained constant.

$$\overline{d}_{\text{Layer}} = \frac{2\lambda|\gamma_H|}{\Delta\omega_{ZP}\sin(2\theta_B)} \tag{3}$$

have been employed to obtain these values, where θ_B is the Bragg angle of the substrate, and $\Delta\omega_P$ the angular difference between the SL satellites. γ_H is $\mathbf{k}_H \times \mathbf{n}$, where $\mathbf{k}$ is the unity wave vector of the scattered beam and $\mathbf{n}$ is the normal unit vector to the surface.

In Fig. 3 is displayed the rocking curve of the (002) reflection of a HgTe/CdTe superlattice. The appearance of seven orders of satellites from this structure attests to the high structural quality of the superlattices that have been investigated. The almost complete suppression of the ± 4 satellites in this spectrum allows for an accurate determination of the HgTe layer thickness in this structure, as described above.

While the superlattice period and the well thickness can be determined rather accurately using x-ray diffraction methods, the Cd concentration in the barriers is subject to some uncertainty. The x value was not determined for each sample individually but was estimated by carefully comparing numerous control samples which have been grown under the same conditions as the barriers during superlattice growth. The x value of these control samples was determined using room temperature transmission and x-ray photoelectron spectroscopy. In this way, the cadmium concentration in the barrier was determined to be 70%.

IV. RESULTS AND DISCUSSION

Typical FTIR luminescence spectra of a $HgTe/Hg_{0.30}Cd_{0.70}Te$ superlattice at temperatures of 4.2 and 300 K is shown in Fig. 4. The spectrum at 4.2 K consists of one nearly symmetric line, its peak occurring at an energy of 181 meV. The full width at half maximum (FWHM) of this low temperature line is 32 meV, again indicating the high quality of the superlattices that were investigated.

Interpretation of the low temperature photoluminescence is not a straightforward problem. Earlier work has assigned the observed luminescence transition to a band-band recombination for the whole range of temperatures studied.[15] After careful consideration of data available in the literature and a comparison of the IR photoluminescence spectra with transmission data we have concluded that at low temperatures the observed recombination is most likely through a bound state. This assignment is consistent with previous work on bulk HgCdTe alloys, where low temperature recombination is assigned to donor-acceptor and other bound recombination mechanisms.[16,17] Thus at low temperatures the high energy side of the luminescence peak was assigned to the band gap of the superlattice and at room temperature, where band-to-band recombination is most likely, the low energy side of the luminescence peak was assigned to the band gap.

Knowing the barrier and well thicknesses as well as the band gap (as determined by the IR photoluminescence measurements) we are able to plot the variation of the superlattice band gap versus barrier thickness. The result is shown in Fig. 5 where the band gap for a series of $HgTe/Hg_{0.30}Cd_{0.70}Te$ superlattices as a function of barrier thickness is shown. In this series the well thickness is held at a constant value of 30 Å. Both room temperature and low temperature data are shown in this figure. For comparison, theoretically calculated band gaps using offsets of 40 and 350 meV are included. One can see that at both room temperature and at low temperature a much better agreement between theory and experiment is obtained assuming a large valence band offset.

The fit of the data to the theoretically calculated values is quite good for barrier thicknesses greater than 20 Å, while for the sample with the narrowest barrier a large discrepancy appears. We believe that an uncertainty in the geometrical structure of the superlattices can be excluded by the x-ray diffraction (XRD) measurements and therefore cannot be used to account for the observed shift of photoluminescence energy. However, it was shown above that the barrier x value, which is deduced from control samples grown under nominal identical growth conditions,

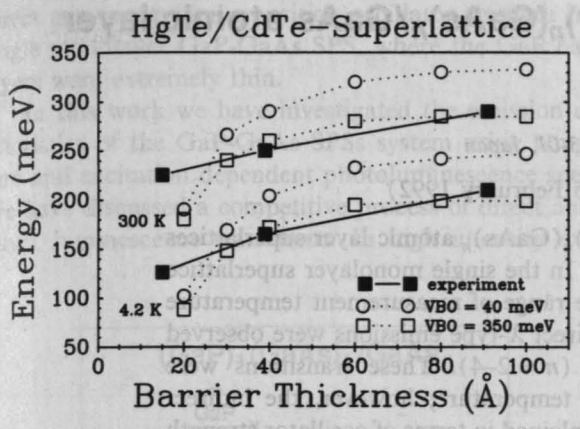

FIG. 5. Comparison between theoretical and experimentally determined band gaps at 4.2 and at 300 K. Closed symbols indicate the position of the band gap as determined by FTIR photoluminescence. Open symbols are the results from the theoretical calculations.

also has a large influence on the effective band gap (see Fig. 1). The shift toward higher energy for the superlattice with the extremely thin barrier could indicate that the barrier x value may be larger, due to flux bursts, if the CdTe shutter is opened for only very short periods (in the case of the superlattice with 15 Å barrier ~12 s). A second possible reason could be interface roughness. If each interface of the barriers has one to two monolayers of roughness, it would mean a total of two to four monolayers of thickness variation in a barrier which is only five monolayers thick. In such a case, it would not be surprising to see strong deviations from theoretically calculated values.

V. CONCLUSION

In conclusion, we report on the growth and characterization of HgTe/CdTe superlattices with well widths of 30 Å and various different barrier thicknesses. FTIR photoluminescence experiments have been completed in order to determine the superlattice band gap. High resolution x-ray diffraction techniques have been employed to determine the actual dimensions of both the superlattice period and the HgTe layer thicknesses. The experimentally determined band gap data have been compared with the results obtained from theoretical calculations based on the envelope function approximation. We have shown that there is a much better agreement with the theoretically calculated band gaps and those experimentally measured under the assumption of a large (350 meV) valence band offset.

ACKNOWLEDGMENT

This project was supported by the Bundesministerium für Forschung und Technologie.

[1] J. N. Schulman and T. C. McGill, Appl. Phys. Lett. **34**, 663 (1979).
[2] J. P. Faurie, A. Million, and J. Piaguet, Appl. Phys. Lett. **41**, 713 (1982).
[3] Y. Guldner, G. Bastard, J. P. Vieren, M. Voos, J. P. Faurie, and A. Million, Phys. Rev. Lett. **51**, 907 (1983).
[4] J. P. Faurie, S. Sivananthan, and J. Reno, J. Vac. Sci. Technol. A **4**, 2096 (1986).
[5] S. P. Kowalczyk, J. T. Cheung, E. A. Kraut, and R. W. Grant, Phys. Rev. Lett. **56**, 1605 (1986).
[6] R. W. Grant, E. A. Kraut, J. T. Cheung, and S. P. Kowalczyk, J. Vac. Sci. Technol. A **5**, 3070 (1987).
[7] C. R. Becker, M. M. Kraus, Y. S. Wu, R. N. Bicknell, and G. Landwehr, Semicond. Sci. Technol. **6**, C76 (1991).
[8] J. B. Choi, L. Ghenim, R. Mani, H. D. Drew, K. H. Yoo, and J. T. Cheung, Phys. Rev. B **41**, 10872 (1990).
[9] L. R. Ram-Mohan, K. H. Yoo, and R. L. Aggarwal, Phys. Rev. B **38**, 6151 (1988).
[10] G. L. Hansen, J. L. Schmit, and T. N. Casselman, J. Appl. Phys. **53**, 10, 7099 (1982).
[11] J. P. Laurenti, J. Camassel, A. Bouhemadou, B. Toulouse, R. Legros, and A. Lusson, J. Appl. Phys. **67**, 10, 6454 (1990).
[12] N. F. Johnson, P. M. Hui, and H. Ehrenreich, Phys. Rev. Lett. **61**, 1993 (1988).
[13] Y. S. Wu, C. R. Becker, A. Waag, R. N. Bicknell-Tassius, and G. Landwehr, J. Appl. Phys. **69**, 268 (1991).
[14] M. Quillec "Structural Characterization of Superlattices by X-Ray diffraction," in *Springer Proceedings in Physics* (Les Houches, France, 1986), Vol. 13, p. 121ff.
[15] J. P. Baukus, A. T. Hunter, J. N. Schulman, and J. P. Faurie, J. Appl. Phys. **64**, 283 (1988).
[16] A. T. Hunter and T. C. McGill, J. Vac. Sci. Technol. **21**, 205 (1982).
[17] A. T. Hunter, D. L. Smith, and T. C. McGill, Appl. Phys. Lett. **37**, 200 (1982).