# Molecular beam epitaxial growth of (100) $Hg_{0.8}Cd_{0.2}Te$ on $Cd_{0.96}Zn_{0.04}Te$

L He†, C R Becker, R N Bicknell-Tassius, S Scholl and G Landwehr

Physikalisches Institut der Universität Würzburg D-8700 Würzburg, Federal Republic of Germany

**Abstract.** The molecular beam epitaxial growth of (100) $Hg_{0.8}Cd_{0.2}Te$ epilayers has been systematically investigated in order to optimize the growth parameters and in particular the Hg/Te flux ratio. Both the pyramidal hillock density and the mobility depend on the Hg/Te flux ratio. A minimum in the hillock density correlates well with the largest mobilities. As is well known, electrical properties are strongly influenced by structural defects. Structural defects due to non-stoichoimetry, i.e. vacancies and antisites, can be largly reduced by optimizing the Hg/Te flux ratio. It is shown that an optimum Hg/Te flux ratio exists within a narrow range between 270 and 360 at the growth temperature of 180 °C, in contrast with the larger range of the Hg/Te flux ratio over which single-crystal growth could be maintained. The $x$ values of the $Hg_{1-x}Cd_xTe$ epilayers were determined from the $E_0$ gap dependence as well as from the $E_1$ gap dependence. The difficulties encountered in determining the $x$ value from normal transmission curves, i.e. from $E_0(x)$, due to the Burstein–Moss shift are discussed.

## 1. Introduction

The molecular beam epitaxial (MBE) growth of narrow gap $Hg_{1-x}Cd_xTe$ has a number of potential advantages such as a more homogeneous $x$ value and in situ device processing. However, structural twining defects, namely pyramidal hillocks, are a severe problem encountered in the MBE growth of (100) $Hg_{1-x}Cd_xTe$ [1, 2]. It has previously been reported that the formation of hillocks is closely related to improper growth conditions [3–5], an Hg overpressure or Hg clusters, which are believed to play an important role in hillock formation. Structural defects are a source of noise in long wavelength infrared $Hg_{1-x}Cd_xTe$ photodiodes, and they cause a reduction in breakdown voltage in metal–insulator–semiconductor capacitors [5]. However, no detailed results of how Hg flux affects the structural and electrical properties have been reported, and no information concerning the correlation of the structural and electrical properties is available.

In this paper we present results of a systematic investigation of MBE growth conditions, e.g. the effects of Hg flux on pyramidal hillock density and on the electrical properties for the (100) orientation.

## 2. Experimental details

Epitaxial growth was carried out in a Riber-2300 MBE system, which was modified to allow the molybdenum substrate holder to be rotated and still be in physical contact with the thermocouple. This allowed the substrate temperature to be controlled with an accuracy of $\pm 2$ °C during rotation. The temperature of the molybdenum substrate holder was routinely calibrated at the melting point of indium. The system has been described elsewhere [6].

All samples were grown on lattice-matched (100)$Cd_{0.96}Zn_{0.04}Te$ substrates. Substrate preparation included standard cleaning, chemo-mechanical polishing techniques and thermal cleaning in vacuum prior to growth [6]. First a CdTe buffer layer of about 1500 Å was grown at 300 °C. In order to minimize conduction band bending in the interface region [7, 8] due to the large conduction band offset between $Hg_{1-x}Cd_xTe$ and the CdTe buffer layer, a second buffer consisting of the intermediate gap $Hg_{0.3}Cd_{0.7}Te$ with a thickness of 300 Å was grown.

A series of $Hg_{1-x}Cd_xTe$ epilayers were grown at 180 °C with Hg/Te flux ratios between 183 and 550. The substrate was rotated at 8–12 RPM and the Hg pressure (loosely referred to in this paper as flux), which was held constant to better than $\pm 2\%$, was monitored and recorded by means of an ion gauge at the top of the growth chamber during growth. A Te flux of $6 \times 10^{-7}$ Torr was employed for all samples. In order to obtain the same $x$ value of about 0.20 in the narrow gap $Hg_{1-x}Cd_xTe$ epilayer, the CdTe/Te flux ratio was maintained at 0.3 with two exceptions. 13 of the 15 epilayers that were grown with this CdTe/Te flux ratio had an $x$ value of $0.206 \pm 0.005$. The other two had an

† Permanent address: Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, People's Republic of China

$x$ value of about 0.19. The growth rate was 3.1 Å s$^{-1}$, and the sample thicknesses were between 2 and 6 $\mu$m.

RHEED observations demonstrated that single-crystal growth of $Hg_{1-x}Cd_xTe$ for the (100) orientation can be maintained over a wide range of Hg/Te flux ratio. Well defined RHEED patterns with short streaks were exhibited and remained unchanged during the growth for Hg/Te flux ratios higher than 215 and lower than 517. At the lowest and highest Hg/Te flux ratios studied, 183 and 550, the RHEED pattern was indicative of single-crystalline growth during the initial stages of growth, and then after about one hour additional dots appeared in the RHEED pattern, indicating either the onset of polycrystalline growth or the presence of twins.

Transmission and reflection measurements in the wavelength ranges of the middle IR and the visible were carried out with a Fourier transform spectrometer, IFS88, from Bruker. The epilayer thickness was determined from the interference pattern in the reflection spectrum, which was confirmed by a direct measurement of the layer with a depth profiler by using a contact mask on several samples. The electrical properties were determined using the standard van der Pauw method for the Hall effect at 0.3 T for temperatures between 300 and 4.6 K. The electrical contacts were placed on the edges of the samples whose dimensions were 5 and 10 mm. These data were analysed with a one-charge-carrier model. A standard Hall structure with dimensions of 200 and 300 $\mu$m was etched onto six samples. Standard Hall effect measurements as well as Shubnikov–de Haas (SdH) oscillation experiments were conducted for these six samples at 4.2 K. Pyramidal hillocks on the surface of every sample were observed with a microscope with a Nomarski filter. The measured hillock density is the average of hillock densities from various surface regions. It should be mentioned that higher hillock density regions normally existed on the edges or corners of the epilayers, whose total area was < 3% of the surface. These high density regions are substrate-related, and were therefore not included in the calculations of hillock densities.

## 3. Results and discussion

### 3.1. Optical measurements

Optical transmission spectra in the wavelength region near the energy gap $E_g$ (or $E_0$) are generally used to estimate the $x$ value [9] because of the non-destructive nature and simplicity of this method. However, there are several problems when applying this method to thin epitaxially grown n-type samples. One major problem is the influence of the Fermi level position, which can cause a shift of the apparent absorption edge to shorter wavelengths, i.e. the Burstein–Moss shift. In an attempt to estimate the magnitude of this shift we calculated the Fermi level position as a function of electron concentration using the Kane model [10] for non-parabolic degenerate bands, and then compared the results with

the intrinsic concentrations $n_i$ [11] at different $x$ values [12]. The results for $x = 0.21$ and a carrier concentration of $7 \times 10^{17}$ cm$^{-3}$ demonstrated that the shift of the apparent absorption edge would correspond to an error of 10% in $x$. An additional complication is the presence of interference fringes. Because these epilayers are thin, the absorption edge of a MBE-grown sample is much less steep than that of bulk material. Consequently the absorption edge is more strongly influenced by the widely spaced interference fringes, resulting in larger uncertainities in the absorption coefficient $\alpha$ and thus in the $x$ value.

Because of these difficulties in determining the $x$ value from the absortion coefficient, we have also determined the $x$ value of the $Hg_{1-x}Cd_xTe$ epilayers from the $E_1$ energy gap (L6–L4,5) [13] by means of reflection measurements in the visible region. Since the $E_1$ gap is much larger than the $E_0$ gap, the effects of degeneracy and interference fringes are essentially eliminated. The $E_1$ gap was determined from the peak position of the reflection curve. Because of discrepancies between $x$ values as determined from the $E_0$ gap and those obtained from the $E_1(x)$ relationship according to the literature [14–17], we calibrated this relationship again. A MBE-grown HgTe layer, a bulk p-type $Hg_{0.702}Cd_{0.298}Te$ sample and a CdTe substrate were employed. The $Hg_{0.702}Cd_{0.298}Te$ sample was provided by the AEG company in Heilbronn, Federal Republic of Germany. Its $x$ value was determined using the absorption coefficient method. The results are given by

$$E_1(\text{eV}) = 2.070 + 0.568x + 0.662x^2. \qquad (1)$$

The $x$ values were determined from the $E_0$ gap using the standard criterion of $\alpha = 1000$ cm$^{-1}$ [18] as well as from the $E_1$ gap using equation (1). The discrepancy between $x$ values is within experimental uncertainity ($\pm 0.002$ and $\pm 0.004$ for $E_1$ and $E_0$, respectively) if the electron concentration is less than $4 \times 10^{17}$ cm$^{-3}$. However, this discrepancy increases exponentially for samples with electron concentrations higher than $4 \times 10^{17}$ cm$^{-3}$. A discrepancy of about 23% was observed for a sample with an electron concentration of $1.7 \times 10^{18}$ cm$^{-3}$.

The optical thickness $nd$ was obtained from the difference in frequency of the interference fringes in the reflection spectra in the long wavelength region [9], i.e. below the $E_0$ gap. A calibrated value for the refractive index $n$ was determined by measuring the thickness of an epilayer grown on a substrate with a contact mask using a depth profiler. A refactive index $n = 3.50$ was obtained for $x = 0.208$ at a wavelength of 12 $\mu$m, which is in good agreement with the literature [9].

### 3.2. The influence of the Hg/Te flux ratio on structural defects

The hillock density depends strongly on Hg pressure as shown in figure 1, and hillock size increases with increasing epilayer thickness. In addition, careful examination revealed that the size was the same for the majority of
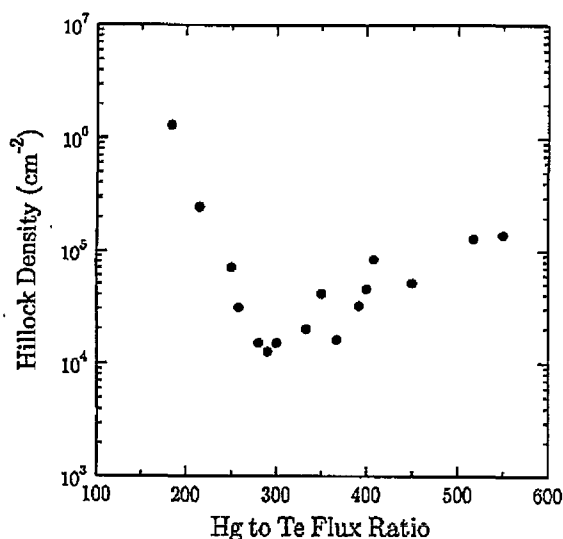
**Figure 1.** Hillock density against Hg/Te flux ratio for all $Hg_{1-x}Cd_xTe$ samples.



**Figure 2.** Electron concentration against Hg/Te flux ratio for the $Hg_{1-x}Cd_xTe$ epilayers with an $x$ value of $0.206\pm0.005$. The Hall effect results at 300 and 10 K are shown as full triangles and circles respectively. The electron concentrations as calculated from SdH oscillations at 4.2 K are displayed as open circles.

hillocks on each sample and that high density regions usually occurred near the edges of the epilayer. At both the lowest and highest Hg/Te ratios, hillock density are very high, $1.3 \times 10^6$ cm$^{-2}$ and $2.9 \times 10^5$ cm$^{-2}$, respectively. The best surface morphology with the lowest hillock density of $1.5 \times 10^4$ cm$^{-2}$ was obtained with a HgTe flux ratio of 280. Of particular significance is the fact that the hillock density depends more dramatically on the Hg pressure at lower values of the Hg/Te flux ratio than at higher values, as shown in figure 1.

The fact that all hillocks on each epilayer have nearly the same size indicates that they are generated during the first stage of epitaxial growth, where twins occur near or at the interface between the epilayer and substrate, and then propagate during growth to form pyramidal hillocks [1]. These twins can originate either from the substrate [2] or from the epilayer only during the initial stage of epitaxial growth if all the growth parameters are held constant over the entire growth period. It has been reported [4, 5] that excess Hg pressure strongly influences twin formation, which explains the behaviour of the hillock densities in the higher Hg flux region. The mechanism of the hillock density dependence in the lower Hg flux region is not clear, but is possibly due to the occurrence of antiphase twins caused by excess Te [4] or Te precipitates, or the effects of a rough surface caused by very low Hg pressures.

As discussed above, pyramidal hillocks are related either to the substrate surface or to its preparation, or to the growth conditions. They can be reduced to a substrate-limiting value by optimizing the growth conditions. Our best result of $1.5 \times 10^4$ cm$^{-2}$ was obtained with a Hg/Te flux ratio of 280 for the growth temperature of 180 °C.

### 3.3. The influence of the Hg/Te flux ratio on electrical properties

All the samples under consideration were n-type. The electron concentration as determined by the van der
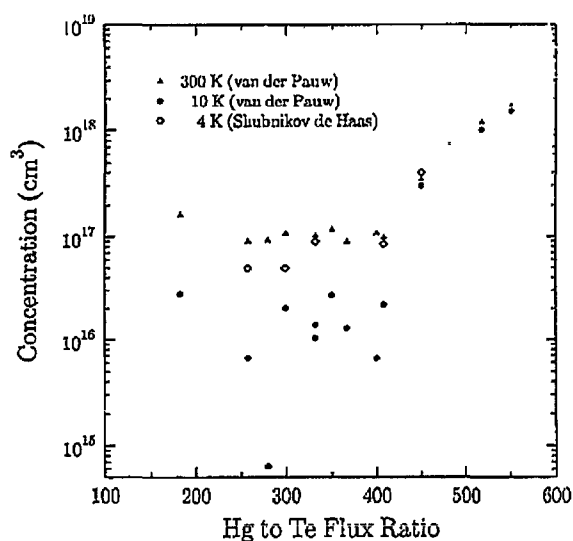
Pauw method is in good agreement with the value obtained using the standard Hall geometry. The electron concentration was also calculated from the SdH oscillations assuming a spherical Fermi surface. The resulting electron concentrations are larger than the Hall effect results by a factor of 1.6–10, even though the assumptions involved should result in a discrepancy of at most a factor of 2. The SdH oscillations were shown to be three-dimensional and hence not due to an interface effect. Furthermore, reducing the thickness of the Hall geometry of one of the samples by etching with a solution of Br in ethylene glyocol, resulted in no measurable change in the electron concentration as determined by both the Hall effect and the SdH oscillations. Therefore, in spite of the discrepancy in the electron concentration, which is not yet understood, both the Hall effect and the SdH oscillations appear to result from the same three-dimensional electrons in the epilayer. The electron concentration as determined by the Hall effect at both 300 and 10 K is shown as a function of the Hg/Te flux ratio in figure 2. Here only epilayers with an $x$ value of $0.206\pm0.005$ are included. At room temperature the concentration is nearly independent of the Hg/Te flux ratio with the exception of an appreciable increase in concentration at Hg/Te flux ratios above approximately 450, where the $Hg_{1-x}Cd_xTe$ epilayers are degenerate. The behaviour of the electron concentration at 10 K is similar except that the values scatter by more than an order of magnitude for Hg/Te flux ratios between 250 and 420. The concentration as calculated from the SdH oscillations for five of these samples seems to scatter much less, as can be seen in figure 2.

The electron mobility as determined from the Hall effect results at both 300 and 10 K is a function of the Hg/Te flux ratio as shown in figure 3, where only epilayers with an $x$ value of $0.206\pm0.005$ are included. Three
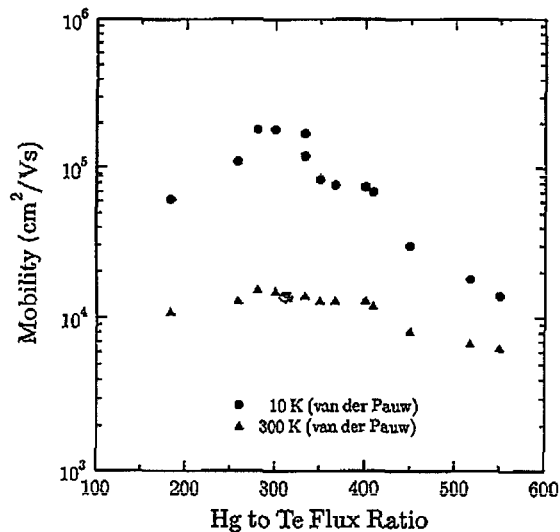
**Figure 3.** Electron mobility against Hg/Te flux ratio for the $Hg_{1-x}Cd_xTe$ epilayers with an $x$ value of $0.206\pm0.005$. The mobilities at 300 and 10 K are shown as full triangles and circles respectively.

samples with a slightly smaller $x$ value are included in the plot of hillock density versus Hg/Te flux ratio but not in the plots of mobility and concentration versus Hg/Te flux ratio. At room temperature, the mobility does not vary appreciably at lower Hg/Te flux ratios and then decreases moderately for Hg/Te flux ratios above a value of 400.

It is also shown in figure 3 that at low temperatures the mobility increases with deceasing Hg/Te flux ratio and either reaches a plateau at a Hg/Te flux ratio of about 360 or peaks between 280 and 360. It should be noted that such a mobility dependence cannot be explained by the small deviation in the $x$ value of these samples. A variation in mobility due to an uncertainity in the $x$ value was estimated using an empirical expression [19] for mobility versus $x$ at 4.5 K for an electron concentration of $1 \times 10^{15}$ cm$^{-3}$. This estimate predicts that the deviation in $x$ values of the samples employed in this comparison, i.e. $x = 0.206 \pm 0.005$, results in a variation in mobility of less than 15%. By comparing figure 3 with figure 1, an optimum range for the Hg/Te flux ratio between 280 and 360 is apparent, i.e. the hillock density displays a minimum between 280 and 360, and the mobility has either a plateau at a Hg/Te flux ratio above approximately 360 or peaks at a Hg/Te flux ratio between 280 and 360. The maximum values for the electron mobilities at 300 and 10 K are approximately $1.5 \times 10^4$ and $2 \times 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. These values compare well with published values for $Hg_{0.8}Cd_{0.2}Te$ with similar electron concentrations [19, 20].

At low temperatures ionized impurity scattering is the dominant factor limiting the electron mobility of narrow gap $Hg_{1-x}Cd_xTe$ [21, 22]. The scattering centres are either extrinsic impurities or electrically active structural defects such as twins and non-stoichiometric defects consisting of Hg interstitials and vacancies or Te antisites. Because all the samples were grown in

the same environment with the exception of the Hg flux, the influence of foreign impurities can reasonably be considered to be the same. As mentioned above, a minimum in the hillock density coincides with larger mobilities. It is obvious that optimizing the Hg/Te flux ratio is very important; this improves the structural quality, i.e. reduces the hillock density and the number of defects due to non-stoichoimetry, which should improve the electrical properties.

## 4. Conclusions

We have shown that an optimum Hg/Te flux ratio is essential for the MBE growth of good quality $Hg_{1-x}Cd_xTe$. Both hillock density and electron mobility depend on the Hg/Te flux ratio employed during growth, and a minimum in the hillock density and a plateau or a maximum in the electron mobility correlate well. Structural defects, twins and defects due to non-stoichoimetry can be reduced by optimizing the Hg/Te flux ratio. It is also shown that the optimum Hg/Te flux ratio falls within a narrow range between 270 and 360, at the growth temperature of 180 °C. This is in contrast to the much larger range for the Hg/Te flux ratio over which single crystalline growth can be maintained. In addition an empirical relationship for the $x$ dependence of the $E_1$ energy gap was determined.

## Acknowledgments

## References

[1]   Million A, DiCicio L, Gailliard J P and Piaguet J 1988
      *J. Vac. Sci. Technol.* A6 2813
[2]   Koestner R J and Schaake H F 1988 *J. Vac. Sci. Technol.* A 6 2834
[3]   Harris K A, Myers T H, Yanka R W, Harris K A, Mohnkern L M, Green R W and Otsuka N 1990
      *J. Vac. Sci. Technol.* A 8 1013
[4]   Faurie J P, Sporken R, Sivananthan S and Lange M D 1991 *J. Cryst. Growth* 111 698
[5]   Koestner R J, Goodwin M W, Schaake H F 1991
      *J. Vac. Sci. Technol.* B 9 1731
[6]   Becker C R, Wu Y S, Waag A, Kraus M M and Landwehr G 1991 *Semicond. Sci. Technol.* 6 C76
[7]   Guldner Y, Boebinger G S, Vieren J P, Voos M and Faurie J P 1987 *Phys. Rev.* B 36 2958
[8]   Hoffman C A, Meyer J R, Wagner R J, Bartoli F J, Chu X, Faurie J P, Ram-Mohan L R and Xie H 1989
      *J. Vac. Sci. Technol.* A 8 1200
[9]   Finkman E and Schacham S E 1984 *J. Appl. Phys.* 56 2896
[10]  Kane E O 1957 *J. Phys. Chem. Solids* 1 249

[11]  Hansen G L and Schmit J L 1982 *J. Appl. Phys.* **54** 1639

[12]  Hansen G L, Schmit J L and Casselman T N 1982 *J. Appl. Phys.* **53** 7099

[13]  Katsuki S and Kunimune M 1971 *J. Phys. Soc. Japan* **31** 415

[14]  Ludeke R and Paul W 1966 *J. Appl. Phys.* **37** 3499

[15]  Galazka R R and Kisiel A 1969 *Phys. Status Solidi* **34** 63

[16]  Moritani A, Taniguchi K, Hamaguchi C and Nakai J 1973 *J. Phys. Soc. Japan* **36** 79

[17]  Kisiel A, Podgorny M, Rodzik A and Giriat W 1975 *Phys. Status Solidi* b **71** 457

[18]  Finkman E and Nemirovsky Y 1979 *J. Appl. Phys.* **50** 4356

[19]  Raccah P M, Garland J W, Zhang Z, Chu A H M, Reno J, Sou I K, Boukerche M and Faurie J P 1986 *J. Vac. Sci. Technol.* A **4** 2077

[20]  Higgins W M, Pultz G N, Roy R G and Lancaster R A 1989 *J. Vac. Sci. Technol.* A **7** 271

[21]  Long D 1968 *Phys. Rev.* **176** 923

[22]  Scott W 1972 *J. Appl. Phys.* **43** 1055