Journal of Crystal Growth 127 (1993) 331–334
North-Holland

Molecular beam epitaxial growth and characterization of (100) HgSe on GaAs

C.R. Becker, L. He [1], S. Einfeldt, Y.S. Wu, G. Lérondel, H. Heinke, S. Oehling, R.N. Bicknell-Tassius and G. Landwehr

Physikalisches Institut der Universität Würzburg, D-W-8700 Würzburg, Germany

In this paper, we present results on the first MBE growth of HgSe. The influence of the GaAs substrate temperature as well as the Hg and Se fluxes on the growth and the electrical properties has been investigated. It has been found that the growth rate is very low at substrate temperatures above 120°C. At 120°C and at lower temperatures, the growth rate is appreciably higher. The sticking coefficient of Se seems to depend inversely on the Hg/Se flux ratio. Epitaxial growth could be maintained at 70°C with Hg/Se flux ratios between 100 and 150, and at 160°C between 280 and 450. The electron mobilities of these HgSe epilayers at room temperature decrease from a maximum value of 8.2×10^3 $cm^2/V\cdot s$ with increasing electron concentration. The concentration was found to be between 6×10^{17} and 1.6×10^{19} cm^{-3} at room temperature. Rocking curves from X-ray diffraction measurements of the better epilayers have a full width at half maximum of 550 arc sec.

1. Introduction

HgSe is a semimetal with many properties similar to those of HgTe. Therefore, many of the physical properties which make HgTe based materials of interest are also of interest in HgSe based materials. Of particular importance is the possibility of an ohmic contact between HgSe and ZnSe comparable to the case of HgTe on CdTe. Recently, blue laser diodes based on ZnSe have been produced by molecular beam epitaxy (MBE); however, the production of good electrical contacts on p-type ZnSe or $ZnS_{1-x}Se_x$ remains one of the major problems in the technology of ZnSe laser diodes [1].

HgSe single crystals have been grown by the Bridgman method and annealed in a broad range of Hg and Se vapour pressures by Kumazaki et al. [2]. These authors have also investigated the electron concentration and mobility as a function of annealing conditions. However, to our knowledge the MBE growth of HgSe has not been reported in the literature.

In this paper, we present results of an investigation of MBE growth conditions, e.g. the effects of substrate temperature as well as Hg and Se fluxes on the growth and on the electrical properties for the (100) orientation.

2. Experimental details

Epitaxial growth was carried out in a four-chamber 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 ±1°C during rotation. The temperature of the molybdenum substrate holder was routinely calibrated at the melting point of indium and tin. The MBE system has been described previously [3].

All samples were grown on (100) GaAs substrates. The substrates were chemo-mechanically polished with a solution of Br in methanol, cleaned with standard solvents and etched with HCl in order to remove the original oxygen from the surface. Some of the substrates were also

[1] Permanent address: Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, People's Republic of China.

etched with a solution of H_2SO_4, H_2O_2 and H_2O with the proportions of 5:1:1. The substrates were then mounted on a molybdenum substrate holder with a graphite solution. The surfaces of some of the substrates were oxidized in air at 150°C. All substrates were then thermally cleaned in vacuum at 585 to 600°C prior to growth without a stabilizing As flux. This process was monitored by RHEED in order to ensure the removal of as much oxygen and carbon as possible from the surface, while minimizing the arsenic depleting on the surface which occurs at temperatures above 420°C.

A series of HgSe epilayers were grown at temperatures between 70 and 180°C with Hg/Se flux ratios between 80 and 450. In this paper the pressure which is measured with an ionization gauge in the growth position is referred to as flux. Some of the substrates were rotated at about 0.5 cps. The Hg flux was held constant to better than $\pm 2\%$ and a Se flux of between 5.2×10^{-7} and 9.0×10^{-7} Torr was employed. The Se flux, F_{Se}, was calibrated by depositing Se on GaAs as well as Si at about 15°C according to:

$$F_{Se} = R_{Se} \frac{\rho_{Se}}{m_{Se}} \frac{1}{S_{Se}}, \qquad (1)$$

where R_{Se} is the growth rate, ρ_{Se} the density of Se (4.79 g/cm^3), m_{Se} the atomic mass of Se and S_{Se} the Se sticking coefficient which is assumed to be one at this temperature. The HgSe growth rate varied between 0.36 and 2.7 Å/s at 180 and 70°C, respectively, and the sample thicknesses between 0.26 and 2.0 μm.

RHEED observations and X-ray defraction experiments, which were carried out for the (004) reflection, demonstrated that single crystal growth of HgSe for the (100) orientation can be maintained over a range of Hg/Se flux ratios, see table 1. The RHEED patterns in the [011] azimuth at low temperatures became weaker and sometimes totally disappeared during the initial stages of growth. After 1 to 3 min, weak, elongated spots reappeared. Weak half-order reconstruction was observed in the [010] azimuth which is indicative of a c(2 × 2) Hg-stabilized surface. An extremely weak half-order (2 × 1) reconstruction in the [011] azimuth was observed in some of the samples. At high temperatures the RHEED pattern was initially spotty. Later, weak half-order c(2 × 2) reconstruction was observed for some samples.

Table 1
The range of Hg/Se flux ratios over which single crystalline growth of HgSe could be maintained at various growth temperatures; here single crystalline HgSe is defined as HgSe whose rocking curve has a FWHM of less than 2400 arc sec

Growth temperature (°C)	Hg/Se flux ratios
70	100–150
90	150–260
120	200–400
160	280–450

Transmission and reflection measurements in the wavelength range between 20 and 2 μm were carried out with a Fourier transform spectrometer. 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. These data were analysed with a one-charge-carrier model.

3. Results and discussion

The growth rate of epitaxial HgSe is strongly dependent on growth temperature. It decreases from 2.7 Å/s at a substrate temperature of 70°C to 0.36 Å/s at 180°C for a constant Se flux. For comparison, the growth rates of HgTe and $Hg_{1-x}Cd_xTe$ with a Te flux equal to that of Se are significantly larger at 180°C (approximately 3 Å/s). The Hg/Se flux ratio necessary to maintain epitaxial growth increases at higher temperatures, as shown in table 1. A Hg/Se ratio of between about 100 and 150 is sufficient at 70°C, but a flux ratio between 280 and 450 is required at temperatures above 120°C. This behaviour can be explained as a result of the high vapour pressure of

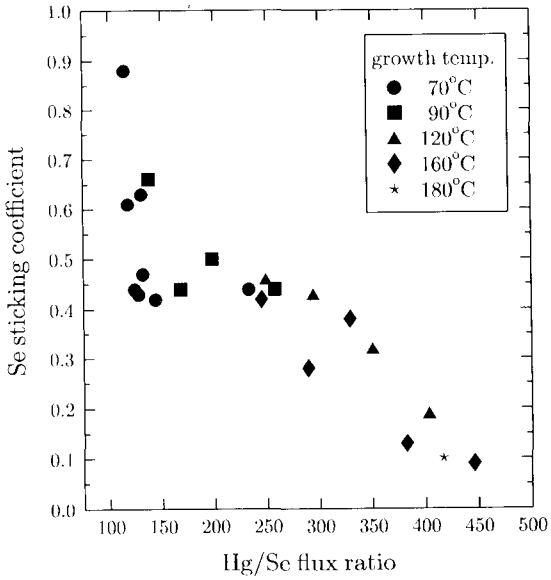

Fig. 1. The Se sticking coefficient versus the Hg/Se flux ratio. The growth temperatures are indicated.

Hg, i.e. the Hg desorption rate dependence on temperature.

The sticking coefficient, which is the inclusion rate of Se divided by the calibrated Se flux, is plotted for various growth temperatures versus the Hg/Se flux ratio in fig. 1. HgSe epilayers, which are polycrystalline according to X-ray rocking curves (FWHM $\geq$ 2400 arc sec), are not included in fig. 1. For a particular temperature above 70°C, the sticking coefficient appears to decrease with increasing Hg/Se flux ratio. Due to the large variation in the data at 70°C no conclusion can be drawn. The dependence on Hg/Se flux ratio at temperatures higher than 70°C is not understood at present. Epitaxial growth at higher temperatures requires a larger Hg/Se flux ratio and results in a lower sticking coefficient, as can be seen in fig. 1.

There is more scatter in these data than one would like. We believe that this is due to substrate preparation as well as to experimental uncertainties in the Se flux and the epilayer thickness. As mentioned above, the substrates are heat treated at 585 to 600°C in vacuum and not in an As environment, which is necessary to prevent varying degrees of As depletion. Heat treatment in an As environment should result in a better defined starting point for MBE growth and consequently more uniform data for the sticking coefficient and electrical properties.

The crystalline quality of HgSe on GaAs which has a lattice mismatch of about 8% does not seem to be dependent on the growth temperature. The two best epilayers, as judged by their rocking curves from X-ray diffraction measurements, which have a FWHM of 550 arc sec, were grown at 160 and 70°C.

The optical thickness, nd, was obtained from the difference in frequency of the interference fringes in the reflection spectra in the long wavelength region, where n and d are the index of refraction and sample thickness, respectively. A calibrated value for the refractive index was determined by measuring the thickness of an epilayer grown on a substrate with a contact mask using a depth profiler. A value of $n \approx 3.45$ was obtained at a wavelength of approximately 4 μm.

All the samples under consideration were n-type. The electron concentration at 300 K falls between 5.8×10^{17} and 1.6×10^{19} cm^3, as shown in fig. 2. Three of the samples with an electron concentration near 1.2×10^{19} cm^3 are polycrystalline according to X-ray rocking curves (FWHM $\geq$ 2400 arc sec). The electron mobility is inversely proportional to the concentration, decreasing from about 8.2×10^3 to 4.0×10^2 cm^2/V·s at 300 K. In other words, the resistivity of these samples is to a first approximation constant. This dependence of electron mobility on concentration differs from the published dependence for bulk HgSe [2,4], i.e. $\mu \propto 1/\sqrt{n}$. The electron concentration of the better MBE samples is smaller than the best as-grown bulk HgSe [2] by approximately a factor of 5. Annealing bulk crystals in Se vapour pressure resulted in comparable electron concentrations, e.g. approximately 4×10^{17} cm^{-3} [2].

The mobility at 77 K decreases from 1.1×10^4 to 4.6×10^2 cm^2/V·s when the concentration increases from 3.4×10^{17} to 1.6×10^{19} cm^3. These values for the mobility at low temperatures are approximately an order of magnitude lower than

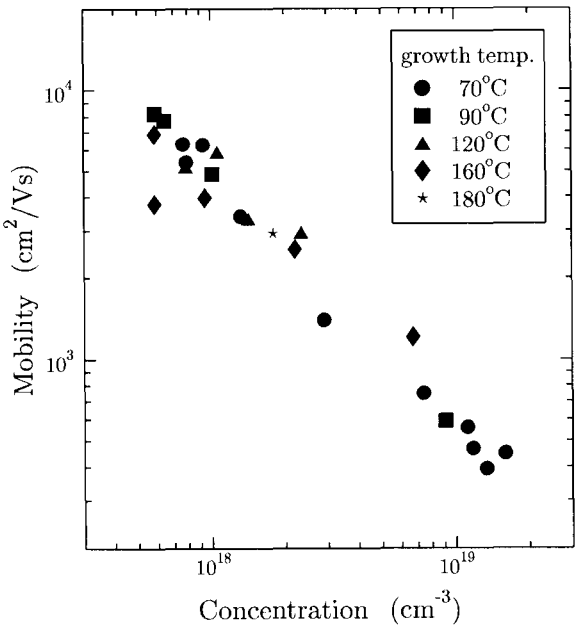

Fig. 2. The electron mobility versus the electron concentration at 300 K.

the values in the literature for HgSe annealed in a Se atmosphere [5] and for $Zn_{0.02}Hg_{0.98}Se$ [4].

4. Conclusions

We have shown that the growth rate and therefore the Se sticking coefficient appears to increase with decreasing Hg/Se flux ratio. The growth rates of HgSe at 180°C are extremely low and the structural quality and electrical properties are not improved compared with samples grown at lower temperatures where the growth rate is much higher. In addition, the Hg/Se flux ratio necessary to maintain single crystal growth, and thus the Hg consumption increases with increasing substrate temperature. However, at 70°C the growth parameters are more difficult to control. According to these considerations, the best growth temperature is between 90 and 120°C.

Acknowledgements

This work was supported by the Bundesministerium für Forschung and Technologie and the Alexander von Humboldt Stiftung. In addition, the authors wish to thank A. Schönteich for maintaining and making the necessary changes in the MBE system.

References

[1] M.A. Haase, J. Qiu, J.M. DePuydt and H. Cheng, Appl. Phys. Letters 59 (1991) 1272.
[2] K. Kumazaki, E. Matsushima and A. Odajima, Phys. Status Solidi (a) 37 (1976) 579.
[3] C.R. Becker, Y.S. Wu, A. Waag, M.M. Kraus and G. Landwehr, Semicond. Sci. Technol. 6 (1991) C76.
[4] N.P. Gavaleshko, P.N. Gorley V.V. Khomyak and V.A. Shenderovskii, Phys. Status Solidi (b) 98 (1980) 463.
[5] K. Kumazaki and N. Nishiguchi, Solid State Commun. 60 (1986) 301.