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Epitaxial overgrowth of II–VI compounds on patterned substrates

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Abstract

The selected area epitaxial overgrowth of narrow gap HgTe as well as wide gap CdTe and ZnTe on CdTe/GaAs substrates, which had been structured by dry etching techniques, has been investigated. A plasma etching process using a barrel reactor with CH_4–H_2 gases has been employed to prepare stripes with a width of about 1 μm with anisotropic as well as isotropic etching profiles. It has been found, that the selected area HgTe overgrowth takes place with a high local selectivity to the low index planes of the patterned surface. In contrast, the selected area overgrowth of the wide gap CdTe and ZnTe is controlled by anisotropic growth kinetics provided that the substrate temperature is not lower than 220°C and the starting surface consists of well developed low index crystallographic planes.

1. Introduction

The epitaxial overgrowth on patterned substrates has been studied in the last decade to our knowledge entirely for III–V compounds. It is of technological importance for the fabrication of index of refraction guided injection lasers [1] as well as for the synthesis of low dimensional structures [2] which could form the basis for novel device applications. The basic idea of a "true" selected area epitaxy (SAE) is (i) to adjust the pattern dimensions of the substrate surface to correspond to the diffusion length of the adatoms and (ii) to exploit the anisotropy of the growth kinetics. If the dimensions of the structures in the pattern are of the order of the surface diffusion length of the adatoms, then the adatoms can migrate to planes with lower surface energies and condense there. Therefore a peculiar feature of growth on patterned substrates is a position dependent growth rate across the surface which provides the possibility to induce localized condensation and thereby to generate laterally defined structures. The MBE growth kinetics of II–VI compounds is not uniform. The sticking coefficients of cations and anions of wide gap II–VI compounds are comparable over a wide temperature range and therefore the minority flux determines the growth rate [3]. But growth

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regimes are known, where a self-regulation behaviour takes place, e.g. the chalcogen atom sticks only in the presence of a metal atom, similar to the III–V semiconductors [4]. On the other hand, the sticking coefficients of the narrow gap II–VI compounds containing Hg differ by at least two orders of magnitude and show an unusually strong dependence on the growth direction [5]. The purpose of the present work is to study the SAE growth mechanism of wide gap as well as narrow gap II–VI compounds on structured surfaces in general and to determine the possibility of direct preparation of as-grown nanometer structures on micrometer scaled surface structures.

2. Experimental setup

The CdTe/GaAs substrates used in the following SAE experiments consist of approximately 30 μm of CdTe grown on (100) GaAs by hot-wall epitaxy [6]. These CdTe/GaAs substrates are referred to as CdTe substrates in the following. The CdTe layers were etched using a CH_4–H_2 plasma in a barrel reactor. Details of this process are described elsewhere [7]. Both the anisotropic and isotropic etch regimes, were used to generate periodically corrugated CdTe surfaces as shown in Figs. 1a and 1b, which are scanning electron microscopy (SEM) images of cross sections of an isotropically etched and an anisotropically etched stripe pattern, respectively. Characteristic dimensions of the investigated patterns are a stripe width of 1 μm, a stripe height of 0.8–1.5 μm and a stripe to stripe distance of 10–100 μm. All stripes were oriented parallel to [110] directions with a {100} surface plane. Electrical measurements were conducted on contact areas of about 300×500 μm, which were placed on both ends of the stripes.

The epitaxial overgrowth of HgTe and CdTe was carried out in a Riber 2300 MBE system, which was adapted to the special requirements of Hg as described elsewhere [8]. The patterned CdTe/GaAs substrates were cleaned with standard solvents and etched with HCl in order to remove oxygen from the surface. The substrates were then mounted on a molybdenum holder with a graphite solution. All substrates were thermally cleaned in vacuum at 350°C for 2 min. Before overgrowth a homoepitaxial buffer layer of 500 Å was grown to ensure the reproducibilty of the nucleation process. The HgTe layers were grown at a temperature of 180°C and the CdTe layers at 230°C. Some of the experiments, in particular the ZnTe overgrowth, were carried out in a hot wall beam epitaxy (HWBE) system. The principle of the HWBE has been described elsewhere [9]. The ZnTe growth rate was varied between 0.4 and 2.7 μm/h in order to investigate

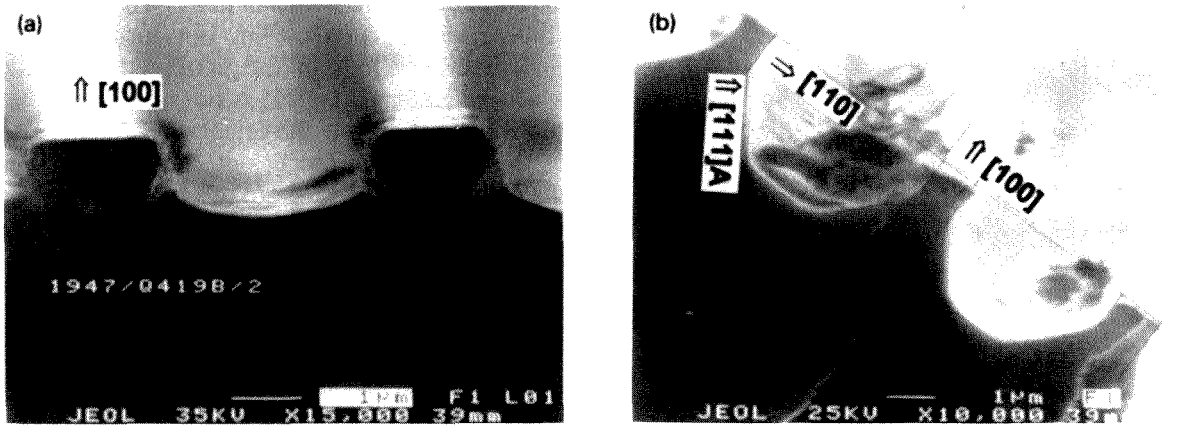

Fig. 1. (a) SEM image of the cross section profile of an isotropic etched CdTe stripe pattern. (b) SEM image of the cross section profile of an anisotropic etched CdTe stripe pattern.

the influence of the growth rate as well as the growth temperature on the selected area growth mechanism.

3. Results and discussion

The epitaxial HgTe overgrowth was carried out on patterned CdTe/GaAs in order to investigate the influence of the crystal orientation on the HgTe growth rate. A scanning electron microscopy image of a (100) surface, which was overgrown with a 0.2 μm thick epilayer of HgTe, is shown in Fig. 2. The image was made in the Hg-sensitive compositional-contrast mode and shows the lateral distribution of HgTe after the growth process. It can be seen, that HgTe has grown only on the (100) oriented surface plane, i.e. on top of the smooth surface of the stripes as well as on the rough surface between the stripes, as indicated by the uniform gray color. No growth was observed on the {111} planes on both sides of the stripes or on the {110} oriented sides of the stripes, which is indicated by the darker color. It has been experimentally shown that the HgTe growth rate and hence the Hg sticking coefficient S is orientation dependent according to the following relationship [7]:

$$S(111)\mathrm{B} > S(100) > S(111)\mathrm{A} > S(110).$$

Apparently overgrowth has been performed in a

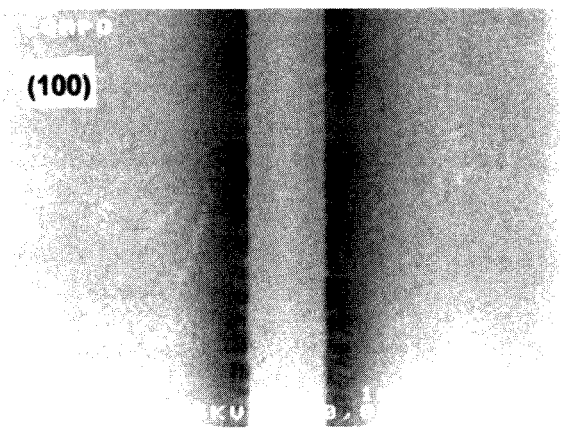

Fig. 2. SEM compositional contrast image of HgTe selected area epitaxy.

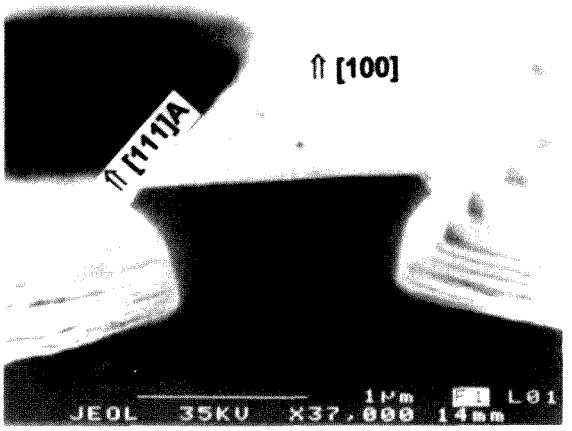

Fig. 3. Cleaved cross section of a single CdTe stripe overgrown with HgTe.

regime where the basic condition for epitaxial growth,

$$K_{\mathrm{HgTe}}(T_{\mathrm{substrate}}) > p_{\mathrm{Hg}}\{hkl\}p_{\mathrm{Te}}^{1/2},$$

was fulfilled only for the {100} planes. Here $K_{\mathrm{HgTe}}(T_{\mathrm{substrate}})$ is the temperature dependent equilibrium coefficient of condensation, $p_{\mathrm{Hg}}\{hkl\}$ is the Hg partial pressure (concentration of physisorbed Hg) and p_{Te} is the partial pressure of tellurium (concentration of physisorbed Te). The orientation dependence of the Hg sticking coefficient implies that the concentration of physisorbed Hg is also dependent on the orientation of the growth surface. The substrate temperature and flux intensities chosen for this experiment, have enabled hetero-nucleation of HgTe for the {100} oriented surfaces but not for the other surface orientations of the patterned substrate, which we assume are {111} A surfaces. This result confirms qualitatively the orientation dependence of the Hg sticking coefficient and demonstrates that it should be possible to use this behavior for local selectivity of epitaxial overgrowth. High resolution X-ray diffraction has shown for all experiments that the full width at half maximum of the corresponding rocking curves was significantly smaller after the epitaxial overgrowth with typical values of about 200 arc sec. Fig. 3 shows a cleaved {110} cross section SEM image of a single CdTe stripe after HgTe overgrowth. It can be seen, that on top of the stripe a faceted structure has formed

with two {111} side surfaces and a {100} top surface. This indicates, that the growth rate R of HgTe for the {111} surfaces must be smaller than for the {100} surface. Tellurium determines the growth rate in the MBE growth of HgTe, which took place at a very low substrate temperature (180°C), and therefore, the migration anisotropy of the rate determining species should be rather low. The growth rates on {100} and {111} in this case are mainly influenced by the ratio of effective incident fluxes F:

$$F\{111\}\mathrm{A} = F\{100\}\cos(54.7°).$$

This results in the formation of a truncated pyramid on top of the stripes. The measured growth rate ratio $Q(\mathrm{HgTe}) = R\{111\}\mathrm{A}/R\{100\}$ is shown in Table 1 and confirms that this growth rate relationship is reproducible; therefore it seems possible to reduce the width of the top {100} HgTe surface from 1 μm down to a few tens of nanometers, and thus to fabricate quantum wires which are in an as-grown state. The principal advantage of the selected area overgrowth on top of a mesa-type pattern, demonstrated in this work, is that epitaxy takes place on surfaces which are almost in an as-grown state and not damaged by the plasma. In order to determine the electrical properties of the 200 nm thick HgTe overgrowth stripes, Shubnikov–De Haas (SdH) measurements were performed. The contact areas were bonded with gold/indium contacts and the transverse magneto-resistance was measured. From the positions of the oscillations a donor concentration of 6×10^{15} cm^{-3} and a mobility of 3.2×10^4 cm^2 V^{-1} s^{-1} at 4.2 K were determined. This is comparable with data of good quality MBE grown HgTe layers as reported in the literature [10] and clearly demonstrates the possibility of growing epitaxial HgTe layers of sufficient quality on top of CdTe stripes.

Table 1
Growth rate ratio Q (R [111]/R [100]) for overgrown layers

Sample No.	Overgrown layer	Growth rate along [100] (μm/h)	Q(HgTe)	Q
Q419a	HgTe/CdTe	0.65	0.52	0.26
Q419b	HgTe/CdTe	0.65	0.58	0.51
Q419c	CdTe	0.45	–	0.34
1866-4	HgTe/CdTe	0.35	0.64	0.38
1866-6	HgTe/CdTe	0.35	0.63	0.38
1866-8	ZnTe	0.45		0.27
1866-10	ZnTe	2.75		0.61

The overgrowth behavior of wide gap II–VI compounds was investigated with a series of growth experiments with CdTe and ZnTe. The starting surface was the same as that used in MBE overgrowth of HgTe, i.e. CdTe/GaAs was dry etched to generate mesa shaped stripes along the [110] direction. The overgrowth of CdTe was carried out after the surface was thermally cleaned and the buffer layer was grown as described above. The substrate temperature was decreased to 230°C and the CdTe overlayers were grown using an additional Cd source, in order to maintain a more stoichiometric growth. In some cases, HgTe layers were overgrown on top of the CdTe overgrowth, which reproduces the features discussed above. Fig. 4a shows a SEM image of a cleaved cross section of such a structure. The starting surface profile was isotropically etched as shown in Fig. 1a. It is easily recognized, that the CdTe overgrowth on the stripe starts also with the formation of two {111} facets on both sides of the stripe but obviously now with {111}B polarity. Because of the incident flux relationships, the growth rate of these two {111} facets is smaller than that of the {100} growth plane. The stripe width becomes larger as the overgrowth proceeds which implies the {111}B polarity of the surface. When the HgTe overgrowth is started, the cross section profile changes immediately; the HgTe forms {111} facets with the opposite polarity and the stripe width becomes smaller as discussed above. The mechanism behind the formation of the opposite type {111} facets is not fully understood at the present. If we consider the surface profile between the stripes, we observe the formation of "lips" near the stripes. The measurement of the overlayer thickness between the stripes results in a constant value of 1.5 μm, which indicates that in the case of an isotropically etched substrate profile the surface diffusion is less efficient and the selectivity of the growth rate is suppressed. The formation of "lips" is therefore caused by a shadow effect from the stripes

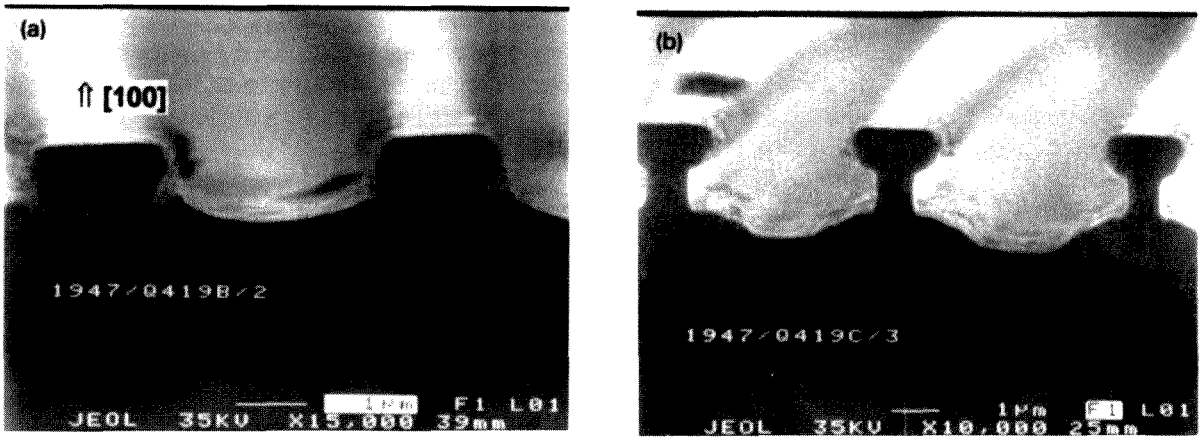

Fig. 4. (a) Selected area growth of HgTe/CdTe on isotropically etched stripe pattern. (b) Selected area epitaxy of CdTe on anisotropically etched stripe pattern.

and not influenced by surface kinetics. The same surface profiles were obtained for low growth rates of about 0.5 μm and high growth rates of 2.5 μm. For comparison, CdTe overlayers were grown on anisotropically etched surfaces which are shown in Fig. 1b. Fig 4b shows the resulting cross section surface profile after deposition of 0.9 μm of CdTe with the same growth parameters as described above. One can see that a completely different profile of the surface between the stripes results without the presence of "lips". In analyzing this behavior, we have measured the thickness distribution, considering that the Cd and Te flux densities arriving at the {111} and {100} planes is different from geometrical reasons. Without sufficient surface migration we would expect a relationship for the growth rates on {100} and {111}, analogous to the situation for the low temperature HgTe growth, i.e. $R\{111\} = R\{100\}\cos(54.7°)$. Hence, if the measured ratio $Q = R\{111\}/R\{100\}$ is significantly greater or smaller than 0.57, the surface kinetics and in particular the migration of adatoms influences the growth velocity of the adjacent planes. The measured ratio in the experiment discussed here is

$$Q = R\{111\}/R\{100\}$$
$$= 0.15\ \mu\text{m/h}/0.45\ \mu\text{m/h} = 0.34.$$

This means that the growth velocity of the {111} facets is reduced due to a net flow of the rate determining species from the {111} facet to the adjacent {100} plane. Such a net flow can only occur if the mobility of the adatoms on the {111} facets is sufficiently high and exceeds the mobility at the {100} plane. In this context, one can explain the abscence of "lips" in all experiments with anisotropically etched surfaces. The large surface diffusion compensates local inhomogenities in the incident fluxes, i.e. shadows. Table 1 summarizes the measured growth rate ratio Q for HgTe as well as CdTe and ZnTe overgrowth on anisotropically etched starting surfaces.

4. Summary and conclusions

Selected area epitaxial overgrowth of narrow gap HgTe and wide gap CdTe and ZnTe on dry etched CdTe/GaAs substrates has been investigated. A plasma etch process using a barrel reactor with CH_4–H_2 gases has been employed to prepare stripes with dimensions of about 1 μm and with anisotropic as well as isotropic etched profiles. It has been found, that HgTe grow with a reduced growth rate anisotropy because of the low mobility of the rate determining Te adatoms at substrate temperatures of 180°C. A significant

anisotropic behavior of the growth rate is influenced only by the geometry of the facets and planes which form the initial surface. On the other hand, the selectivity of the epitaxial overgrowth of Hg compounds is rather high, due to the strong orientation dependence of the Hg sticking coefficient. The initial width of the substrate stripes can be reduced by HgTe selected area overgrowth and opens the possibility of directly preparing low dimensional structures during the epitaxial growth process. It can be expected that the crystalline perfection of such quantum wires is sufficiently high, because of the non-damaged starting surface on top of the CdTe stripes. In comparison, the selected area overgrowth of wide gap compounds, as demonstrated here for the examples of CdTe and ZnTe overgrowth, can be carried out with kinetically determined growth rate anisotropy, provided that the substrate temperature is not lower than 220°C, the starting substrate surface consists of anisotropically etched low index planes and the growth rate in the [100] direction does not exceed 0.6 μm/h. It has been found that the epitaxial overgrowth of HgTe and CdTe starts with the formation of {111} facets of different polarity. The reasons are unknown at the present; however, experimental investigations using transmission electron microscopy have been started.

5. Acknowledgments

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