Selective Growth of CdTe on Si and GaAs Substrates using Metalorganic Vapor Phase Epitaxy

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Epitaxial lateral overgrowth (ELO) is a new technique to grow low-defect-density thin films on lattice-mismatched substrates. For the ELO growth of CdTe and HgCdTe on Si substrate to be successful, the first requirement is that the growth should be selective. To that end, we have used several mask materials, and several growth conditions in order to obtain selective growth. A number of growth-experiments have been carried out, with temperatures in the range from 380°C to 550°C, and pressures in the range from 380 torr to less than 20 torr. Perfectly selective growth of CdTe has been achieved on Si and GaAs substrates using Si_3N_4 as the mask layer. Successful lateral epitaxial growth of CdTe was also achieved.

Key words: Epitaxial lateral overgrowth, MOCVD, CdTe, semiconductor thin films

INTRODUCTION

Hetero-epitaxial growth of CdTe on Si has been actively studied by molecular beam epitaxy[1] (MBE) and metalorganic vapor phase epitaxy (MOVPE)[2,3] for the development of large area substrates suitable for HgCdTe growth. Si substrates will eliminate the thermal mismatch problems encountered when a silicon readout chip with signal processing electronics is bonded to detector arrays in hybrid focal plane array technology. Additionally, if high quality HgCdTe can be grown on Si, the infrared sensors in HgCdTe and the signal processing electronics of the focal plane array can be integrated in the same wafer. The key problem, of course, is the ~19% lattice mismatch between HgCdTe and Si which results in dislocation densities $\geq 2 \times 10^6$ cm^{-2}. As a first step to grow low-defect-density HgCdTe, high quality CdTe and CdZnTe layers of suitable orientation have to be grown on Si substrates.

Recently, a new growth technology known as Epitaxial Lateral Overgrowth (ELO) has been used to grow high quality GaN on sapphire and SiC substrates.[4–6] This technique resulted in markedly improved epitaxial GaN material on these lattice-mismatched substrates. In this technique, narrow slits were opened up in a silicon dioxide layer deposited on previously deposited GaN on SiC or sapphire. In these openings, GaN was selectively nucleated and grown up and over the SiO_2 masks. The growth temperature and the reactor conditions are chosen such that the GaN does not grow on the SiO_2 mask. In the region over the masks, the GaN grows without strain and apparently with fewer defects. There were no coalescence lines where the two growth fronts met as the effective overall strain was a very small fraction of 1% and this strain can easily be accommodated without misfit dislocations. This ELO technology has also been applied previously to various other semiconductors, both Si and compound semiconductors. For example, it has been applied to the growth of Si on insulator[7] (SOI) and cleavage of lateral epitaxial films for transfer (CLEFT) process.[8] Several growth techniques have also been used to realize ELO including low pressure and atmospheric pressure MOVPE,[9] halide VPE,[10] and MOMBE.[11] Therefore, the ELO technique is generally applicable for a wide variety of semiconductors and for a wide variety of growth techniques.

If it is possible to successfully apply ELO crystal growth technology for the synthesis of large area very low defect density CdTe or HgCdTe on silicon wafers, then the pay-off in the long wavelength IR detector performance and cost will be significant. Generally, selective growth process can be enhanced by the proper use of growth temperature and reactor pressure and the reaction precursors. Higher temperature favors selectivity, and adding chlorine-containing species also enhances desorption of unwanted species from the masked region. The choice of the

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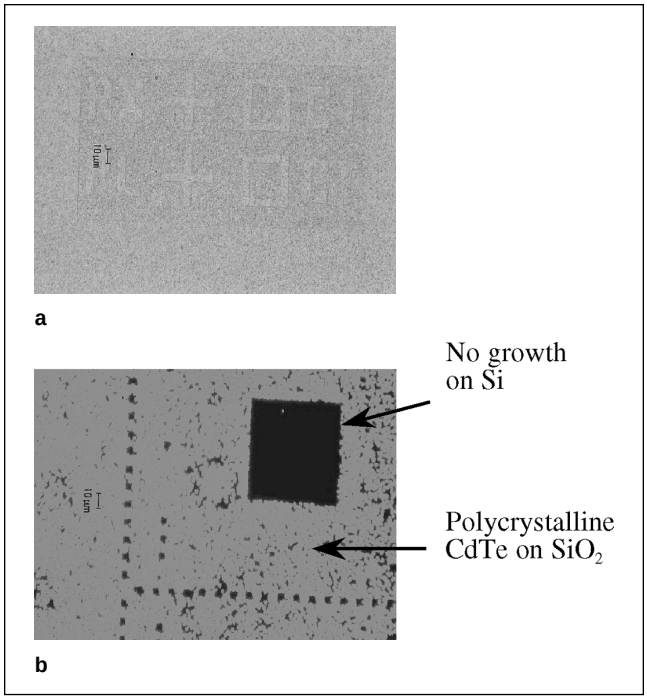


Fig. 1. Selective growth of CdTe on Si substrate with different mask layers. (a) Growth of CdTe on both Si and SiO_2 when T<450°C and P>50 torr, (b) Polycrystalline CdTe growth on masked SiO_2 region, but no growth on Si surface when T>450°C and P<50 torr.

mask materials depends on the type of materials to be grown. Additional factors play significant roles as well, such as anisotropy in the growth rates along different orientations, and the direction of the openings in the masks. Rather little is known in detail concerning the selective growth mechanism of CdTe and HgCdTe. In this work, we investigated the possibility of applying ELO technique to grow low-defect-density CdTe and the effects of growth conditions on the selective growth of CdTe.

EXPERIMENTAL

Thin SiN_x and SiO_2 mask layers of about 1000Å thick were deposited by plasma-enhanced chemical vapor deposition (CVD) on Si, GaAs and CdTe/Si substrates. A mask was designed with groups of different widths, spaces and orientations of stripes to study the selectivity of different growth processes. Standard photolithography process was used to pattern the SiO_2- and SiN_x-covered substrates. MOVPE of CdTe films on patterned substrates were carried out in a low-pressure vertical quartz MOVPE reactor using bubblers of dimethylcadmium (DMCd) and diethyltelluride (DETe) kept at 0°C and 20°C respectively. H_2 was used as the carrier gas and the H_2 flow rates for Cd and Te precursors were 50–200 sccm and 300–800 sccm, respectively. The deposition temperatures were controlled in the range from 400°C to 550°C and the deposition pressures were between 380 torr to less than 20 torr. Substrates were dipped in dilute HCl to remove the native oxide immediately prior to loading into the reaction chamber. The selectivity, the thickness and the morphology of as-deposited films were investigated by both the optical microscope and the scanning electron microscope (SEM).

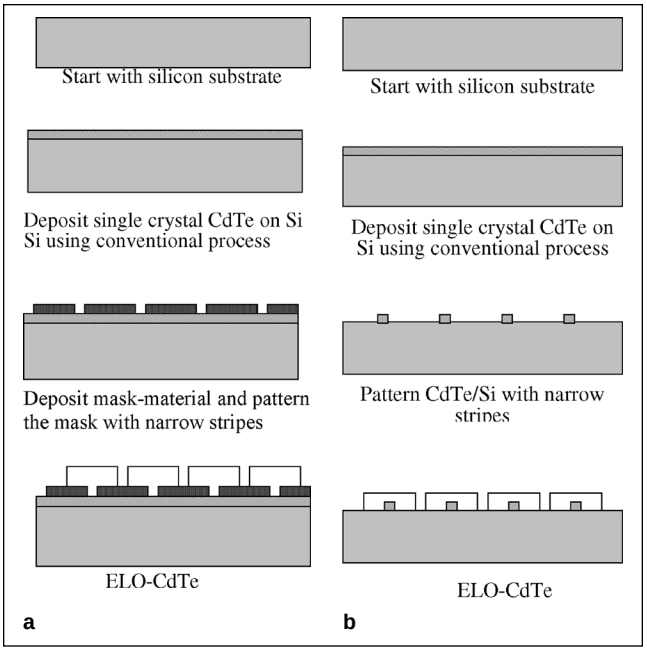


Fig. 2. Schematic diagram of process steps to get high quality ELO-CdTe on silicon substrate. (a) A conventional process, (b) an alternative process.

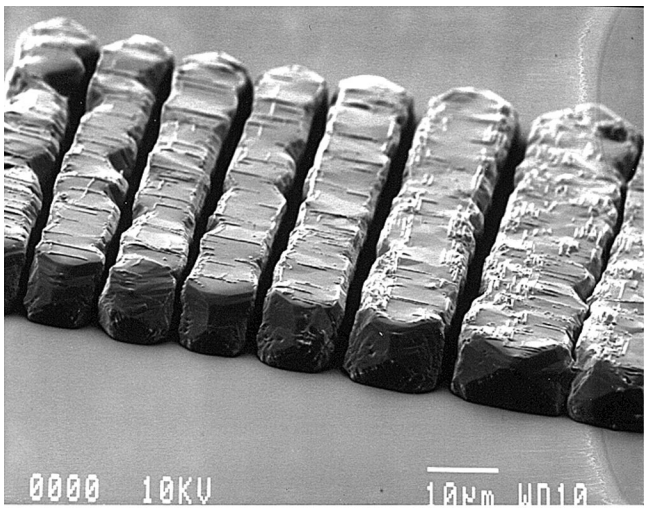
RESULTS AND DISCUSSIONS

Selective Growth of CdTe Thin Films

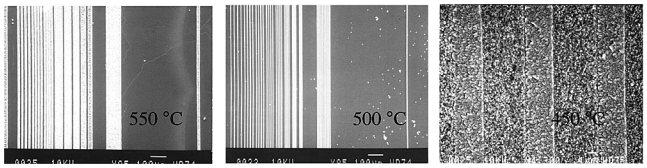
Selective growth relies on establishing reactor conditions, which permit the efficient deposition of precursor molecules on the surface of the substrates, while producing negligible interaction with the masked regions. In principle, this can be achieved in various ways. The simplest is for the precursors to exhibit negligible sticking probabilities on the mask material. Alternatively, the adsorbed entity, reaction intermediates or reaction by-products could be lost from the masked surface either by desorption into the gas phase or by diffusion from the masked region into the growth windows. For the later to occur, the distance between the opening in the mask should be less than the mean free path of precursor molecule on the surface. Thus, selective growth can be enhanced by adjusting the spaces between the growth windows on the mask layer. The choice of the mask materials depends on the type of materials to be grown.

The selectivity of the growth is mainly influenced by the growth temperature, pressure, substrate and mask materials. Generally the selectivity can be improved by increasing the growth temperature and by reducing the growth pressure. Further improvements can be achieved by chlorine assisted epitaxy.[12] In order to establish growth conditions that promote perfect selective growth of CdTe on Si and GaAs substrates, different mask materials were investigated in this study.

SiO_2 mask layer was first investigated on Si substrates. CdTe grew on both the Si and SiO_2 surfaces



a



b

Fig. 3. Selectivity of the growth of CdTe at different temperatures on (a) GaAs(100) substrate with SiN_x mask layers, (b) CdTe (211)B/Si substrate with SiN_x mask layers.

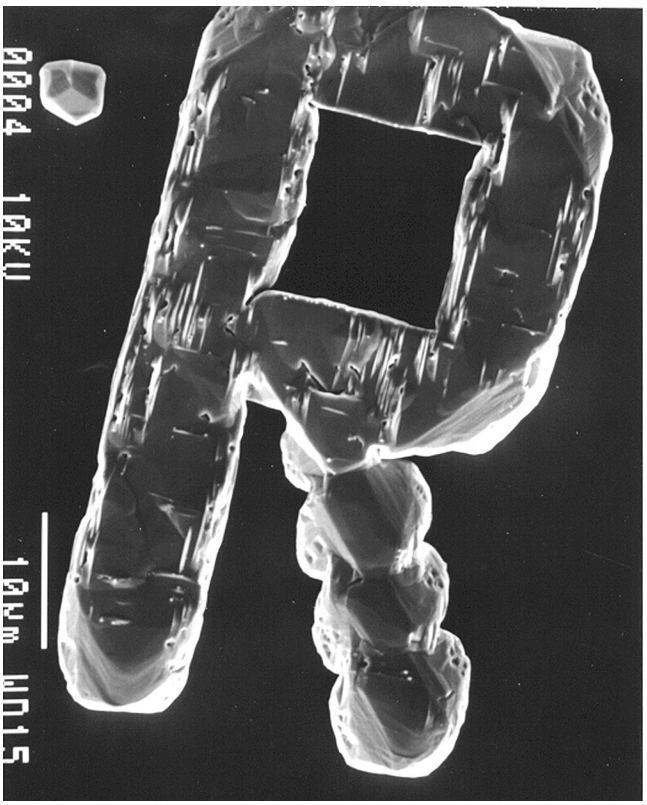


Fig. 4. Selective growth of CdTe on GaAs (100) using SiN_x as the mask. The letter R shows the importance of aligning the edges of openings to one of the major axis.

when the depositions were carried out at temperatures lower than 450°C and pressures higher than 50 torr, as shown in Fig. 1a. For higher temperatures, and lower pressures, CdTe grew only on the SiO_2 surface and there was no detectable growth of CdTe on Si surface. Figure 1b shows the polycrystalline growth of CdTe only on the SiO_2 masked region. Perfect selectivity was achieved on feature sizes as large as 50 μm × 50 μm. These deposition results reveal that SiO_2 might not be a good mask material for the selective growth of CdTe on Si substrates. However, a more important result is that CdTe does not "wet" Si substrate at temperatures higher than 450°C. This fact that CdTe does not nucleate on silicon at higher temperature can be used for selective growth of CdTe. For example, when a patterned CdTe/Si wafer is used for CdTe growth, deposition will be seen only on CdTe, but not on silicon. This offers an alternative approach for ELO of CdTe on Si substrates. The schematic diagrams in Fig. 2 outline the routes to obtain ELO-CdTe by the conventional ELO process and the proposed alternative process. The new process proposed here does not require the mask layer and thus can simplify the process. We will investigate the lateral growth of CdTe using this approach in our future works.

SiN_x layers were also studied as the mask material for GaAs and CdTe/Si substrates. Perfect selective growths of CdTe films were achieved at temperatures higher than 525°C. Growth temperature is an imported growth parameter for the selective growth. Figure 3 shows the perfectly selective growth of CdTe on both GaAs (100) and CdTe(211)B/Si substrates. Also shown are examples of partially selective growth at 500°C and non-selective growth at 450°C. The effects of growth pressure, reactant flow rates and the growth temperatures were studied systematically in this work. The growth rate achieved for CdTe selective growth was as high as 7~8 μm per hour, and this will form the base line process for further ELO-CdTe studies.

Morphology and Anisotropy in Growth Rates

Additional factors also play significant roles in selective growth, such as anisotropy in the growth rates along different orientations, and the direction of the mask openings. The direction of the mask opening plays a significant role in the surface morphology. Rather little detail is known concerning the selective growth mechanism of CdTe and HgCdTe. Figure 4 illustrates the development of CdTe facets and the importance of aligning the edges of openings to one of the major axis for the selective growth. In order to determine the growth anisotropy, we used a mask that contains groups of stripes along different crystallographic directions. The morphology of the CdTe films are determined by the substrate orientation, the alignment of the mask strips, as well as the growth rate and surface cleanliness.

The temperature, pressure, and partial pressures of the precursors affect the vertical growth rates and the lateral growth rates differently. The vertical growth rates of CdTe films increases significantly

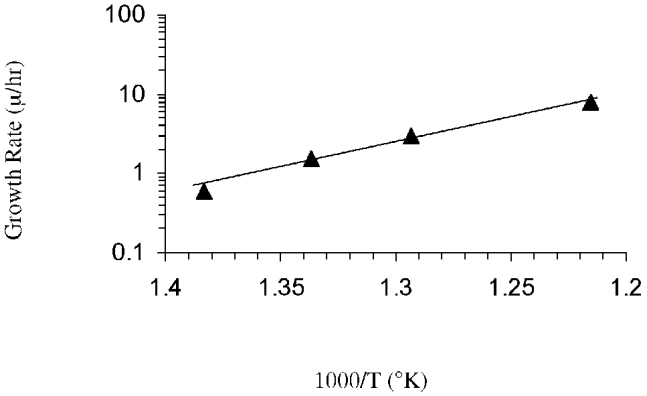


Fig. 5.Vertical growth rate as a function of temperature for CdTe films grown on patterned CdTe (211)B/Si substrate.

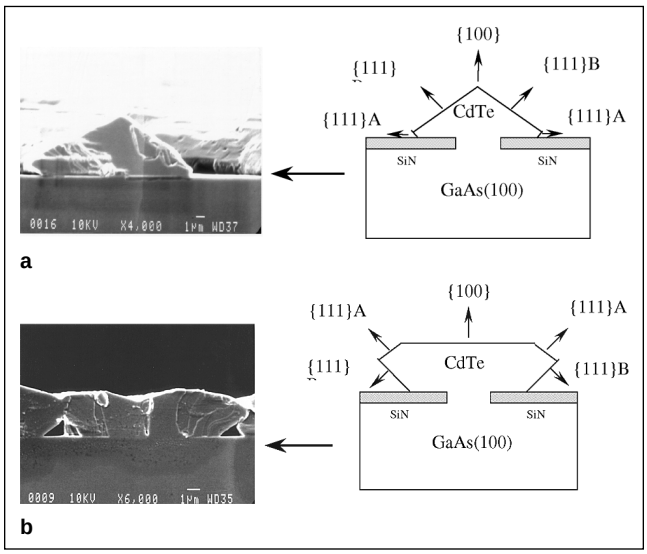


Fig. 6. SEM and corresponding schematic cross section of CdTe grown on GaAs (100) substrate at 550°C. (a) Growth window aligned to the [011] direction, 3 μm wide window with 20 μm spacing, (b) Growth window aligned to the [01$\bar{1}$] direction, 5 μm wide window with 6 μm spacing.

with the increase of the growth temperatures. Figure 5 shows the influence of the temperature on the vertical growth rate on (211) substrates. A few experiments were conducted to understand the growth rates of CdTe when the mask openings were aligned along different directions, such as (100), (111), and (110). The experimental results demonstrate clearly the anisotropy of the growth in different directions. Figure 6 shows the cross sections of the CdTe ridges grown on (100) GaAs when the mask openings were aligned along two orthogonal directions. The slowest growing crystallographic planes will terminate the growth structures. Figure 6 also shows the schematic diagram illustrating different crystallographic planes that are possible if the mask openings were aligned as shown. Even though the schematic diagram closely matches the real cross sectional shapes of the CdTe ridges, actual alignment seems to be rotated by 45 degrees based on the orientation data supplied by the wafer vendor. Selective growth of CdTe on CdTe (211)B/Si substrate shown in Fig. 7 confirms that the

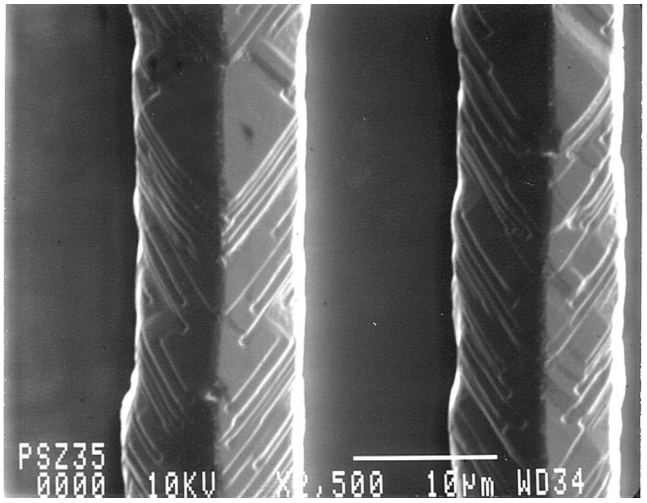


Fig. 7. Selective growth of CdTe on CdTe (211)B/Si substrate in the window stripe oriented along [011] direction at 550°C. The width and spacing of growth windows are 3 μm and 20 μm, respectively.

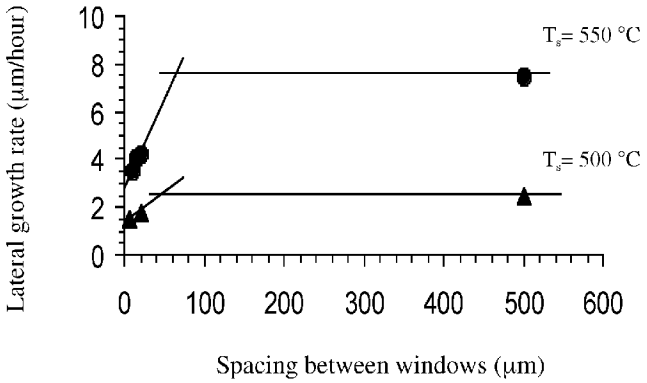


Fig. 8. Lateral growth rate as a function of the spacing between mask opening for two different growth temperatures.

{111}B planes were the slowest growth planes among the main crystallographic planes. Here, the final surfaces were dominated by the {111}B crystallographic planes. The calculated values of the angle between (211) and (111) is 18.45°. This angle was verified using SEM. The reason for the 45° rotation of the stripe opening direction on (100) GaAs substrate is not understood at present, but will be studied in the future.

This information on the growth anisotropy can be used for determining the orientation of the substrate and the growth window direction to enhance the lateral growth of the CdTe films as well as to improve the morphology. The alignment of the growth window should be such that the sidewall surfaces have relatively high growth rate and the top surface has the lowest growth rate. Besides, the mask density and the feature size will also affect the morphology of CdTe films.

Lateral Growth and Surface Diffusion

The lateral growth of CdTe depends not only on the differences of the growth rates of the crystallographic planes, but also on the surface diffusion of the precursor atoms on the surface of the mask. The mask pattern we used consists of groups of stripes of various

widths and various spaces. This can be used to study the surface diffusion lengths of precursor molecules during the growth, which is essential to determine the growth conditions necessary for ELO.

Based on the principles of surface chemistry, the adatoms at the substrate surface can be assumed to be vibrating at some frequency ν_0. Sometimes, the thermal energy of fluctuations give the atom sufficient energy to leave its initial site and migrate along the surface to become an adatom in a neighboring position of potential energy minimum. This is the simplest picture of the self-diffusion of an adatom on a surface. A real substrate surface contains many defects on the atomic scale and thus has many low-energy sites for the adatoms. The frequency ν with which the adatom can escape from its initial site depends upon the energy barrier ε of the escape:

$$\nu = z\nu_0 \exp\left(\frac{-\varepsilon}{kT}\right) \quad (1)$$

where z is the number of equivalent neighboring sites for the atom. This equation can be combined with a mathematical treatment of an atom executing a random walk for a time t over a mean square distance $<X^2>$:

$$<X^2> = Dt \quad (2)$$

and,

$$D = D_0 \exp\left(\frac{-\varepsilon}{kT}\right) \quad (3)$$

D is normally refereed to as the diffusion coefficient and is expressed in cm^2/second.[13]

During the selective growth of MOVPE, the adatoms on the mask material regions may desorb to the gas phase after a lifetime t if no nucleation can occur on the mask material. Along the growth window openings, a depletion zone will be developed due to the surface diffusion of the atoms towards the growth windows. Adatoms within the depletion zone can migrate to the growth window and adatoms outside the depletion zone will desorb to the gas phase. The length of the depletion zone is equal to the mean square distance X that the atoms can migrate on the mask surface. If the mask openings are closely spaced, then the lateral growth rate will be affected. Figure 8 shows the effect of the spacing between the growth windows on the lateral growth rate. The window spacing of 500 μm is considered as "infinite" spacing here. Based on the depletion zone model we argued above, the growth window stripes with 500 μm all should have the same lateral growth rate because each consumes atoms by surface diffusion only in its depletion zone. When the spacing of the window strips is so small that the depletion zones of the two adjacent windows overlap, the lateral growth rate will be reduced. Thus, we can define a "critical spacing" S_c to be a parameter for the mask patterning. The value of the "critical spacing" under a certain growth condition is equal to twice the depletion zone:

$$S_c = 2X \quad (4)$$

The mean free path X of the surface diffusion can be reduced by a lowering of the growth temperature and or by increasing the reactor pressure. Figure 9 shows the influence of the temperature on the lateral growth under the same reactor pressure and flow rate. Compared to the growth rate for windows with infinite spacing, the lateral growth of the small-spaced windows are more suppressed at 550°C than at 500°C. The critical spacing, or the surface diffusion depletion zone, can be experimentally estimated taking the growth rate of the infinite spacing windows as the equilibrium value. More studies of this are underway.

CONCLUSIONS

Selective growth process can be enhanced by the use of proper mask materials and by optimizing the growth conditions. We have investigated several growth conditions for CdTe, and different mask materials such as PECVD-SiO_2 and SiN_x. Perfect selective growth of CdTe on Si, CdTe/Si, and GaAs substrates were achieved on feature sizes as large as several hundred microns. By suitable choice of the growth conditions, it has been possible to grow CdTe either on Si or on masked region. Growth rates up to 8 μm/hr have been achieved still maintaining the selectivity. The growth rates are different along different crystallographic directions. Proper patterning of the substrates can enhance the lateral growth of CdTe over the masked layer by promoting the surface diffusion of the precursor atoms.

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