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Blanket and patterned growth of CdTe on (211)Si substrates by metal-organic vapor phase epitaxy

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1 Introduction

Mercury cadmium telluride ($\text{Hg}_{1-x}\text{Cd}_x\text{Te}$) is the material of choice for high performance infrared focal plane array (FPA) systems used in military applications. Epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ can be conducted on lattice-matched $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ substrates. However, there are several advantages to using Si instead of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ substrates – lower cost, larger substrate sizes and no thermal mismatch with the read-out electronics substrate (also Si) in FPAs [1]. The chief challenge with using Si substrates for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epitaxy is a 19% lattice mismatch between Si and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. This causes misfit dislocations at the interface and threading dislocations (TDs) at the surface of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ device layer. The TDs act as recombination centers and reduce the minority carrier lifetime. Thick (8 μm to 15 μm) CdTe buffer layers are generally used during hetero-epitaxy of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ on Si in order to reduce the TD density. (211)B is the preferred orientation for molecular beam epitaxy (MBE) of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [2]. Hence there is a requirement for high-quality (211)B CdTe buffer layers on Si.

MBE has been the most widely used technique for growth of (211)B CdTe on Si. The etch pit density (EPD) produced using an Everson etch is commonly used to estimate the TD density in (211)B CdTe layers [3]. High-quality thick ($\sim 10 \mu\text{m}$) (211)B CdTe/Si buffer layers with EPD in the mid- 10^5 cm^{-2} to low- 10^6 cm^{-2} range have been reported using MBE [4, 5]. For fabricating long-wavelength infrared (LWIR) $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ photo-diodes, further reduction in TD density of the (211)B CdTe/Si buffer layers is required. MOVPE may offer some advantages over MBE in this respect and hence investigated in this study.

We first investigated the growth of (211)B CdTe on blanket (211)Si substrate by metalorganic vapor phase epitaxy. It is shown that layers comparable in quality to those grown by MBE can be grown on (211)Si substrates using Ge and ZnTe interfacial layers. Once this is achieved, further reduction of threading dislocation density was attempted by using patterned growth technique also called epitaxial lateral overgrowth (ELO) technique since MOVPE growth process is more suitable than MBE for the

ELO process. The ELO technique has been successfully used to reduce the TD density in lattice mismatched hetero-epitaxial systems like GaAs/Si [6, 7], GaN/6H-SiC [8], ZnSe/GaAs [9].

2 Experimental procedure

The CdTe films were grown in a low-pressure vertical cold-wall reactor equipped with a rotating heater/substrate-holder. The starting substrates were 3" Si wafers - (112) off 3° towards $[1\ 1\ \bar{1}]$. These were degreased using organic solvents, followed by a RCA clean [10]. The substrates were then loaded into the reactor and heated up to the Ge growth temperature (525 °C) in hydrogen (H_2) flow. Tertiary butyl arsine (TBAs) was used to provide an As over-pressure, enabling As-passivation of the starting Si substrate. Dilute germane gas (1% GeH_4 in H_2) was used as the precursor to first grow a thin (~300 nm) Ge film. After Ge growth, the substrates were cooled down to the ZnTe growth temperature (350 °C) in the presence of TBAs. A thin (~200 nm) ZnTe film was grown using diethylzinc (DEZn) and diisopropyltelluride (DIPTe), followed by growth of thicker CdTe film (also at 350 °C) using dimethylcadmium (DMCd) and DIPTe. The CdTe growth was interrupted at regular intervals for anneal cycles, the details of the cyclic anneal procedure are reported elsewhere [11].

For studying the efficacy of using patterned growth for defect reduction, the starting substrates were ~10 μm thick MBE grown (211)B CdTe films grown on Si substrates (using intermediate ZnTe layer) provided by Night Vision and Electronic Sensors Directorate (NVESD). The substrates were of high crystalline quality; with (422) X-ray diffraction (XRD) rocking curve full-width-at-half-maximum (FWHM) less than 100 arcs and Everson EPD in the low- $10^6\ cm^{-2}$ range. Si_3N_4 was used as the mask in this study [12]. Plasma enhanced chemical vapor deposition (PECVD) was used to deposit a 200 nm thick Si_3N_4 on the CdTe layer, the Si_3N_4 was then patterned using conventional photolithography and reactive ion etching (RIE) to expose seed windows. The pattern consisted of 2 μm growth windows separated by mask widths of 38 μm . The mask deposition and patterning was conducted by Prof. Schetzina and co-workers at North Carolina State University (NCSSU). CdTe growth by MOVPE was conducted as above except that the growth takes place directly on the patterned CdTe/Si wafers and used diethyltelluride (DETe) instead of DIPTe as the Te source since DETe is found to be a better source for growth at higher temperature. The key step in the process is selective nucleation i.e. the growth process parameters are chosen such that CdTe nucleation occurs in the exposed seed windows but not on the Si_3N_4 mask. After the CdTe layer becomes thicker than the Si_3N_4 film, the CdTe growth progresses in the vertical direction, as well as in the lateral direction over the mask. If the growth process is extended for a long enough time, the growth stripes from adjacent seed windows merge to form a continuous film. The main advantage of this process is

that dislocations can thread from the substrate into the epitaxial layer only through the narrow seed windows, so the film that grows laterally over the mask will have a much lower threading dislocation density compared with the starting substrate.

3 Results and discussion

3.1 Growth of MOVPE CdTe on blanket (211)Si substrates

One of the challenges with using Si starting substrates in a MOVPE reactor used to grow CdTe is that Si is very reactive with any trace amounts of Te present in the reactor. Severe surface degradation of the Si substrates has been observed during pre-growth temperature ramp-up [11]. This problem has been solved by using a TBAs mole fraction of $\sim 4 \times 10^{-4}$ during the temperature ramp-up and temperature stabilization steps. TBAs decomposes and the resulting As passivates the Si surface and prevents surface degradation. Even though direct growth of single crystal CdTe on (211)Si using As passivation is possible, use of Ge and ZnTe interfacial layer enable a gradual grading of the lattice constant from Si (5.431 Å) to Ge (5.646 Å) to ZnTe (6.104 Å) and finally to CdTe (6.481 Å). A cyclic annealing procedure was used during the growth of thick films, details of the anneal process parameters are described elsewhere [12, 13]. Figure 1(a) shows the XRD (422) rocking-curve scan of a 12 μm thick CdTe film. The low FWHM of 64 arcs indicates excellent crystal quality. Figure 1(b) shows the optical microscope image after a 30 s Everson etch of the same film. The low EPD value of $3 \times 10^5\ cm^{-2}$ confirms the excellent crystal quality. These FWHM and EPD values are the best reported for MOVPE-grown CdTe on Si and equal to the state-of-the-art material obtained using MBE. Figure 1(c) shows the Everson EPD obtained for CdTe films of different thicknesses grown in this study. An exponential dependence of EPD on thickness is observed for thinner CdTe films, but the EPD appears to saturate for $\sim 13\ \mu m$ thick CdTe. This indicates that other dislocation reduction techniques like patterned growth or epitaxial lateral overgrowth (ELO) need to be used in combination with thick buffer layers and cyclic annealing in order to further reduce the EPD.

3.2 Patterned growth The patterned growth process involves selective homo-epitaxial growth of (211)B CdTe that does not wet the mask material. For this we used a 10 μm thick CdTe deposited by MBE on (211)Si substrate provided by NVESD. XRD θ -2 θ scans (not shown here) confirm that the CdTe films grown on un-patterned MBE grown (211)B CdTe/Si substrates were single-crystal of (211) orientation. Growth was carried out in the temperature range from 275 °C to the 625 °C temperature range and selective nucleation of CdTe was established only in the growth window regions and not on the Si_3N_4 mask. This enables growth to begin in the window regions and then expand laterally over the mask. High temperatures and low pressures were found to be necessary to obtain

good selectivity. Growth temperatures higher than 500 °C and reactor pressures lower than 25 Torr were found to be essential to obtain selectivity for the precursor mole fractions used (mole fraction of Te $\leq 10^{-3}$, mole fraction of Cd $\leq 6 \times 10^{-4}$) and typical H₂ carrier flow rates in the 1.5 slm–2.5 slm range.

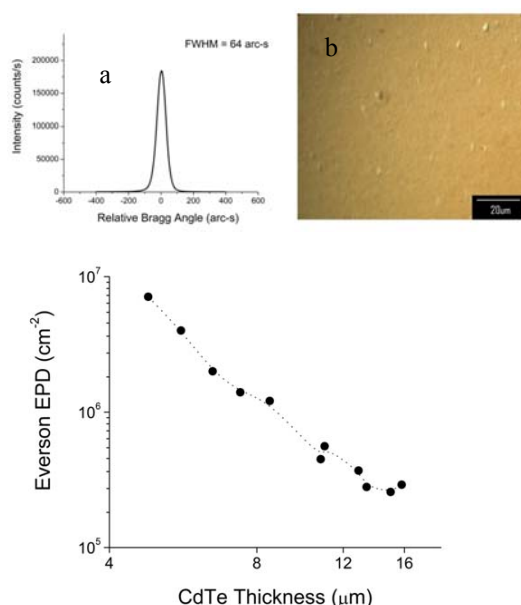


Figure 1 (a) XRD (422) rocking-curve scan of a 12 μm thick CdTe film. (b) Nomarski optical microscope image after a 30 s Everson etch of the same film. (c) Everson EPD obtained for CdTe films of different thicknesses grown in this study.

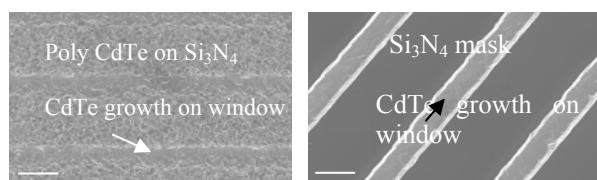


Figure 2 SEM images of CdTe growth on patterned Si₃N₄/CdTe/Si(211) substrates, (a) non-selectivity at growth temperature of 400 °C and reactor pressure of 100 Torr leading to polycrystalline growth on the mask, (b) good selectivity at 500 °C and 25 Torr. Marker represents 20 μm.

Figure 2(a) shows the surface of a CdTe film grown on a patterned substrate using the process parameters developed for blanket homo-epitaxial (211)B CdTe growth. Smooth CdTe surface is observed in the growth windows where the Si₃N₄ mask was etched to expose underlying CdTe. But non-selective nucleation leads to polycrystalline growth over the mask regions. Figure 2(b) shows good selectivity obtained (very little nucleation in the mask regions) using a higher growth temperature of 500 °C and lower reactor pressure of 25 Torr.

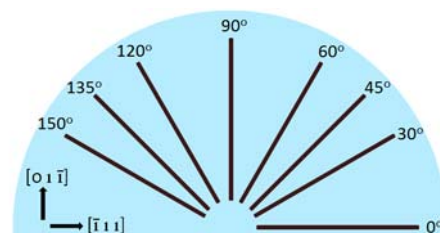


Figure 3 Schematic showing the orientation of the ELO stripes chosen for FIB SEM study from the circular pattern. Stripes on the mask were spaced 0.5° apart.

The quality and surface morphology of ELO-CdTe have been shown to be very sensitive to the orientation of the growth windows [14]. So, choosing the right orientation for the stripe window is essential. The anisotropy during ELO was studied using a circular pattern consisting of 5 μm-wide growth windows arranged at 0.5° angular intervals. The mask width varied from 15 μm in the center of the pattern to 40 μm towards the edge of the pattern. ELO using the circular-patterned substrates was conducted at 700 °C, reactor pressure of 25 Torr and DMCD and DETe mole fractions of 3.6×10^{-4} and 6.3×10^{-4} , respectively. A scanning electron microscope (SEM) equipped with a focused ion beam (FIB) was then used to look at the cross-sections of the ELO-strips. Figure 3 is a schematic showing the orientation of the ELO stripes chosen for the FIB-SEM study from this circular pattern. The orientation of the growth windows was measured with reference to the $[\bar{1}11]$ direction, thus growth windows along $[\bar{1}11]$ and $[01\bar{1}]$ had 0° and 90° mis-orientations respectively with the $[\bar{1}11]$ reference direction. Figure 4 shows the significant anisotropy observed in the geometry of the ELO stripes and the different facets obtained for ELO using growth windows along different orientations. ELO stripes with vertical side-walls and flat top-surfaces are desirable for future device fabrication. Our studies here show that this can be achieved using growth windows oriented along the $[01\bar{1}]$ direction (90° mis-orientation with the $[\bar{1}11]$ reference direction). Subsequent experiments were conducted using a parallel stripe pattern with growth windows along the $[01\bar{1}]$ direction.

The ELO process time was next extended in order to ensure that growth from adjacent windows merged to form a continuous film. The rocking-curve FWHM increased from 85 arcs for the un-patterned (211)B CdTe/Si substrate to 184 arcs for the merged ELO film, indicating no improvement in crystal quality. The rough surface morphology of the ELO-grown CdTe precluded the use of Everson etch pit density characterization in order to estimate the TD density and compare it with the un-patterned starting substrates.

