

Use of cation-stabilized conditions to improve compatibility of CdTe and HgTe molecular beam epitaxy

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Reflection high-energy electron diffraction (RHEED) dynamic studies are used to reveal the strong differences in growth kinetics of CdTe and HgTe grown by molecular beam epitaxy. These differences arise from the stronger Cd—Te bond compared to the Hg—Te bond. Surface migration activation barriers for Cd and Hg migration on (100) Te-stabilized surfaces were estimated from the RHEED dynamic studies to be 0.72 and 0.45 eV, respectively. These differences result in a large disparity in the ideal growth temperature for two-dimensional layer-by-layer growth of the two material systems. However, by altering the growth conditions (i.e., going from anion stabilized to cation stabilized), the disparity in temperatures is shown to vanish. Consequences for this important heterostructure system are discussed.

The band tailoring potential of HgCdTe—CdTe heterostructures has given impetus to considerable work in the molecular beam epitaxy (MBE) growth of this system.¹⁻⁴ However, the same properties that allow the remarkable band tailoring capabilities, i.e., very small Hg—Te bond energy and large Cd—Te bond energy, cause serious difficulties in the surface/interface quality of these heterostructures. In MBE growth, atoms/molecules impinge randomly on the growing substrate and must be able to migrate large distances (≥ 100 Å) to be incorporated at step sites for growth to occur in a step-edge two-dimensional (2-D) propagation mechanism.^{5,6} For most semiconductors one thus expects a window of ideal growth, below which the surface migration is too low and above which migration is too high and may cause entropy driven disorder (e.g., interface roughness, defects). For HgTe—CdTe one expects large differences in this ideal growth temperature window based on their large dissimilarity in bond strength.⁷ This letter reports on studies that clarify the growth kinetics of the two components and offers a possible alternate to low-temperature CdTe growth.

The experiments were performed on a Riber 2300 MBE system. The system and growth procedures employed here have been described previously.^{8,9} Real-time growth measurements were carried out by reflection high-energy electron diffraction (RHEED) intensity oscillation measurements.⁸⁻¹⁰ (100) CdTe substrates misoriented 0.47° toward the (110) (determined by x-ray measurements) were used. Assuming that the CdTe surface relaxes to its minimum energy, namely, that it breaks into monoatomic steps with precise low-index terraces and edges, an average CdTe terrace width of about 395 Å was calculated. The acceleration voltage of the electron gun was 10 keV, and the electron beam was aligned along the [001] azimuth. The incident electron beam was chosen at a grazing angle which satisfied the off-Bragg condition [about 1° for (100) CdTe], resulting in a high sensitivity to step behavior.¹¹ RHEED intensity oscillations were visible to the unaided eye, but were, however, detected on the phosphor screen by focusing the RHEED

specular beam spot onto a photomultiplier for maximum intensity. The substrates were chemically polished using a solution of 0.5% Br/methanol, mounted on a 2 in. substrate holder (molyblock), introduced into the ultrahigh vacuum system, and heated to about 320 °C for about 5 min. To improve the surface smoothness, a thin CdTe (~ 2000 Å) buffer layer was then grown at 300 °C. The growth temperature was measured with a chromel-alumel thermocouple in contact with the molyblock. This method was calibrated using an indium melting point (~ 156.2 °C) determination and gave a stable, accurate, and reproducible temperature measurement (± 1 °C) from run to run.

RHEED intensity oscillation growth studies of CdTe were carried out using two Knudsen cells that contained elemental cadmium and tellurium. Similarly, Knudsen cells containing elemental mercury and tellurium were used for growth studies of HgTe. Cd and Hg evaporate as elements but tellurium evaporates as a molecule (Te_2). Relative beam fluxes were measured with an ion gauge at the substrate growth position and were corrected for ionization efficiency and molecular weight.

Figure 1 shows the RHEED oscillation data taken during the growth of CdTe on the (100) substrate. The growth was carried out under excess anion ($J_{\text{Cd}}/J_{\text{Te}} = 0.81$) flux ratio. In this particular case, the surface reconstruction is (2×1) , with half-order streaks on the [011] azimuth; this diffraction pattern is typical of a Te-stabilized surface.¹² We note that at a growth temperature of 205 °C the oscillations are damped due to lack of cation surface migration and the resulting three-dimensional (3-D) nucleation growth takes place. Long-lasting RHEED oscillations are observed at higher temperatures due to higher migration rates; 2-D nucleation takes place on the terrace, and at 385 °C the oscillations disappear since the cation migration length at this temperature has approached the substrate terrace width (395 Å). Under these conditions, the adatoms on the terrace can reach and nucleate at the steps; a 2-D step propagation growth mode takes place.¹³ The surface step concentration

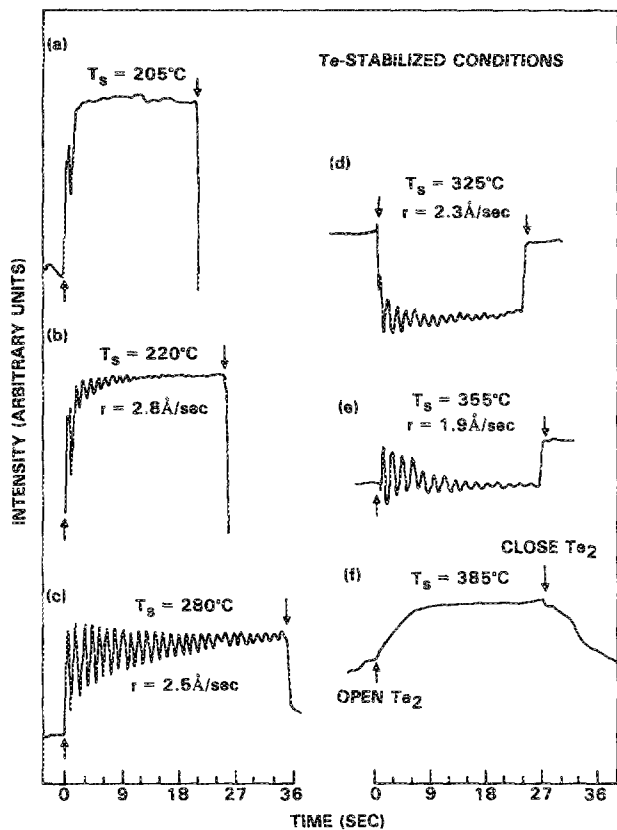


FIG. 1. RHEED intensity oscillations during growth of (100) CdTe, under Te-stabilized conditions as a function of surface temperature: [001] azimuth. (a)–(c) $Te_2 = 270^\circ C$, $Cd = 140^\circ C$, J_{Cd}/J_{Te} ratio = 0.81; (d)–(f) $Te_2 = 285^\circ C$, $Cd = 140^\circ C$, $J_{Cd}/J_{Te} = 0.76$. Growth is initiated and terminated by opening and closing the Te_2 flux, while maintaining the Cd flux on the surface. Growth rate (r) is also illustrated.

during growth is stationary and equal to that before growth. When this happens,⁶ RHEED oscillations are not observed.

Figure 2 shows the first studies of RHEED oscillations on HgTe growth. Due to the much higher migration rates for Hg atoms at the surface, the oscillations, 2-D nucleation on the terrace, were observed at much lower temperatures (as low as $36^\circ C$). In these studies the growth of HgTe was initiated and stopped by opening and closing the Te_2 shutter. A Te-stabilized reconstruction at $160^\circ C$ was observed in this case for the flux ratio (J_{Hg}/J_{Te_2}) of 430. In case of HgTe growth at $160^\circ C$ the migration length approaches the terrace size and once again RHEED oscillations disappear. This temperature is $225^\circ C$ lower than that needed for CdTe growth under Te-stabilized conditions.

It has been shown by Neave *et al.*⁶ that RHEED studies on misoriented surfaces can be used to estimate the surface migration activation barriers. Their detailed studies have provided a prefactor for the atomic migration for Ga migration in GaAs growth. The activation barrier obtained by them was $\sim 1.3 \pm 0.1$ eV. In an earlier theoretical work, it has been pointed out⁵ that the surface migration activation barrier for a free cation atom on an anion surface should be approximately equal to the energy required to break two cation–anion bonds and two cation–cation second neighbor bonds. This energy is roughly half the surface evapora-

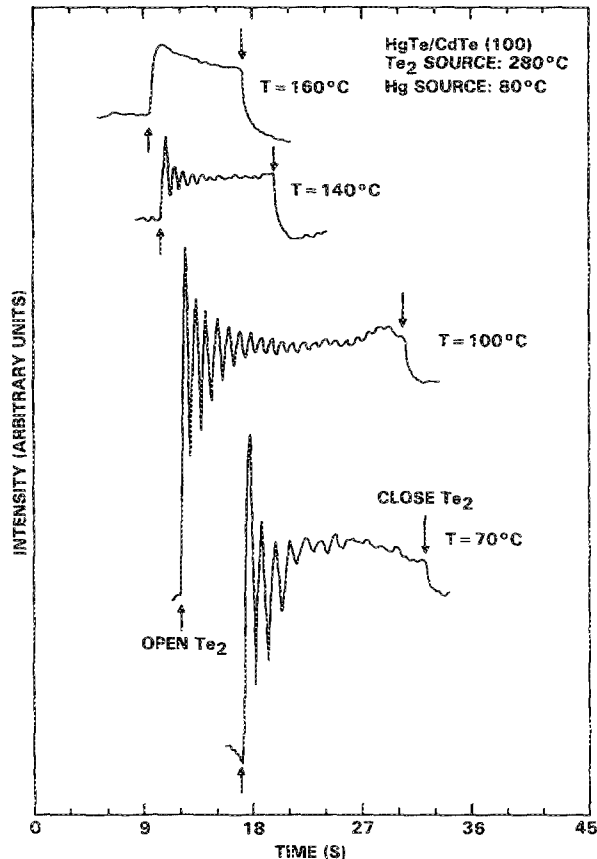


FIG. 2. Temperature dependence RHEED intensity oscillations during growth of HgTe on a (100) CdTe substrate under Te-stabilized conditions. The growth is initiated and terminated by opening and closing the Te_2 flux, while maintaining the Hg flux on the surface; [001] azimuth.

tion energy which can be obtained from the vapor pressure activation energy. Based on this simple model, the activation barriers for surface migration of Cd on Te and Hg on Te should be ~ 0.7 and 0.42 eV, respectively. On the other hand, using the diffusion length estimated above from our RHEED data and using the prefactor given in Ref. 6, we find the activation barriers to be 0.72 and 0.45 eV.

The agreement between the activation barriers obtained by the simple bond-energy counting method and the RHEED data is quite good and points to the universal nature of the growth mechanism in II-VI's and III-V compound growth by MBE. In Table I, we show the temperature

TABLE I. Calculated migration (R_d) and evaporation (R_e) rates for Hg and Cd atoms on a (100) Te-stabilized surface.

Temp. (K)	Hg atoms		Cd atoms	
	R_d (hop/s)	R_e (atom/s)	R_d (hop/s)	R_e (atom/s)
300	2.0×10^3	2.5×10^0
350	2.2×10^4	3.1×10^1
400	1.3×10^5	1.1×10^3	3.0×10^1	5.0×10^{-5}
450	5.5×10^5	1.8×10^4	3.1×10^2	6.0×10^{-2}
500	1.6×10^6	1.7×10^5	2.0×10^3	2.5×10^{-1}
550	9.3×10^3	5.4×10^0
600	3.3×10^4	6.9×10^1
660	9.7×10^4	5.9×10^2
700	2.4×10^5	3.8×10^3

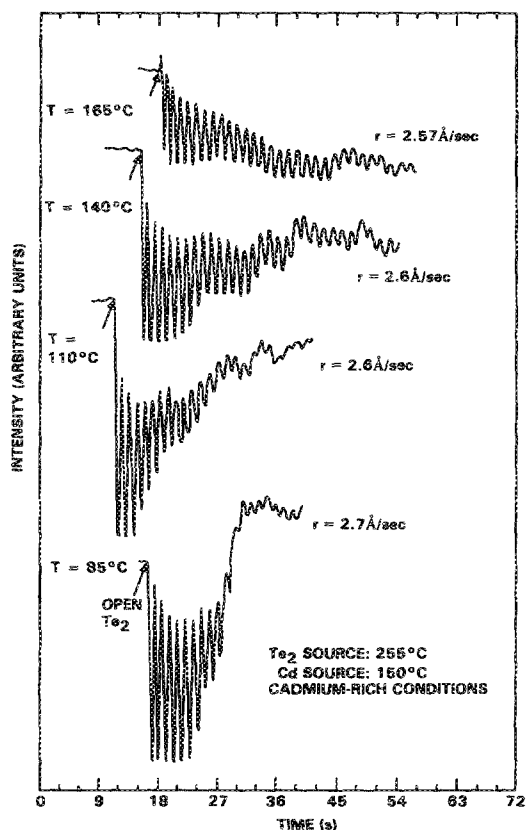


FIG. 3. RHEED intensity oscillations (100) CdTe, under Cd-stabilized conditions ($J_{Cd}/J_{Te} = 2.1$) as a function of surface temperatures; [001] azimuth.

dependence of the surface migration rates using the bond-energy model. The evaporation rates which are also tabulated are based on the vapor pressure data.

Under Te-rich conditions the limiting activation barrier for Cd (or Hg) migration occurs when Cd breaks a bond with the lower Te atom and hops to the next site. This bond is quite strong. If, however, the Cd atom had to hop over a Cd layer, i.e., break a Cd-Cd bond, the activation barrier is expected to be much smaller. These ideas have been used in low-temperature growth of GaAs,¹⁴ where Ga migration rates are known to have been increased by one order of magnitude.¹⁵ Improvements in ZnTe epitaxial layers grown by MBE under cation-rich (Zn) flux ratios at 300–320 °C have also been reported.¹⁶

Figure 3 shows the RHEED oscillation studies of the CdTe growth under cation-stabilized conditions ($J_{Cd}/J_{Te} = 2.1$). The reconstruction now has half-order streaks for the [001] azimuth; this diffraction pattern is typical of a Cd-stabilized surface.¹² Well defined and long-lasting RHEED oscillations are now seen at temperatures as low as 85 °C, clearly showing that Cd surface kinetics are enhanced on a

Cd-stabilized surface. Growth of CdTe below 85 °C under the same flux ratio resulted in polycrystalline material as detected by RHEED. Thus, by altering the normally used growth conditions, CdTe can be grown at low temperatures that are compatible with HgTe growth.

CdTe epilayers grown under Cd-stabilized conditions at temperatures required to produce HgTe/CdTe superlattices with low interdiffusion (~ 160 °C) have high quality structural and optical characteristics, comparable to those previously obtained using a surface temperature of 300 °C. The details of this study will be published elsewhere. It is also important to mention that during growth of HgTe/CdTe superlattices, the CdTe part is grown with the Hg cell open^{17,18} under cation-rich conditions.

In summary, we have carried out detailed studies of the growth kinetics of CdTe and HgTe. We find that while under Te-rich growth conditions a large difference exists between the temperatures required for 2-D growth for the two materials. However, cation-rich growth conditions tend to reduce this difference presumably due to enhanced Cd kinetics.

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