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Congruent evaporation temperature of molecular beam epitaxy grown GaAs (001) determined by local droplet etching

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The congruent evaporation temperature T_c of GaAs (001) is critical for many technological processes and is fundamental to the control and stability of Ga droplets for quantum structure fabrication. We apply the technique of local droplet etching (LDE) to measure T_c for technologically important molecular beam epitaxy (MBE) grown GaAs (001). Below T_c, Ga droplets deposited on the surface shrink and form nanoholes via LDE and thermal widening. Above T_c, droplets grow by capturing excess Ga. From the transition between both regimes, we determine $T_c = 680 \pm 10\,°C$. Additionally, we find that the nanohole/droplet densities follow an Arrhenius-type temperature dependence with an activation energy of 1.31 eV. The method probes the stability of pre-existing droplets formed by deposition and so avoids the complication of nucleation barriers and readily allows the measurement of T_c for technologically important planar GaAs surfaces in any standard MBE system. © *2015 AIP Publishing LLC*.
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The congruent evaporation temperature of GaAs (001) is a fundamental property which has been extensively studied due to its scientific and technological importance.[1–6] When GaAs evaporates into a vacuum (Langmuir evaporation), the Ga and As fluxes leaving the surface are equal, provided that the temperature T is below the congruent evaporation temperature T_c. Compound stoichiometry is therefore preserved. However, above T_c, As preferentially evaporates, leaving behind Ga-rich liquid droplets.[7,8] T_c plays a crucial role in the stability[6] and motion[9] of Ga droplets, which are the basis of fabricating quantum structures via the droplet epitaxy technique.[10] It is therefore important to measure T_c for technologically relevant molecular beam epitaxy (MBE) grown material which is the purpose of this letter.

Measurement of T_c for GaAs (001) has received significant attention over the years.[1–4] However, the reported values are widely spread. For instance, $T_c = 690\,°C$ has been measured using mass spectrometry during evaporation from a Knudsen cell,[1] $T_c = 660\,°C$ using modulated beam mass spectrometry in a MBE chamber,[2] *in situ* low energy electron microscopy under ultra-high vacuum (UHV) conditions[3] scaled temperature measurements under As flux to the literature value of $T_c = 625\,°C$,[5] and $T_c = 663\,°C$ obtained with mass spectrometry in UHV.[4]

These experiments have primarily focussed on rough surfaces where the oxide has been thermally desorbed[1–3] or the surface cleaned by sputtering.[4] Furthermore, in each case, the samples were necessarily subjected to different background As pressures due to the different experimental arrangements employed. Recently, however, it has been shown that T_c depends on both surface morphology[11] and the As flux impinging on the surface.[3] This might explain discrepancies in T_c measurements made on different sample morphologies under different conditions and defines the need to measure T_c for smooth MBE grown material which is relevant to droplet epitaxy. In this letter, we utilise the visibility of nanoholes formed by local droplet etching (LDE) to map the temperature regime where $T < T_c$. Above T_c, droplets increase in size, and no nanoholes are present. This allows us to estimate T_c from the transition between these two regimes using atomic force microscopy (AFM).

Our samples are fabricated using solid-source MBE with a valved cracker cell for As evaporation. First, the surface oxide was thermally desorbed by slowly increasing the temperature of the epi-ready (001) GaAs wafer up to the oxide desorption temperature of 582 °C,[12] as observed in the reflection high energy electron diffraction (RHEED) pattern. The samples are then annealed at $T = 620\,°C$ for 30 s followed by MBE deposition of 100 nm of GaAs at an As flux corresponding to a beam effective pressure of $P_{As} = 1.5 \times 10^{-5}$ Torr. Subsequently, the surface was annealed at 650 °C for 300 s under a minimal As background pressure of $P_{As} < 10^{-7}$ Torr, which is reduced by two orders of magnitude compared with typical GaAs MBE growth conditions. This is therefore a technologically relevant minimum characteristic pressure of a typical MBE system in which an MBE prepared surface can be annealed for droplet epitaxy or etching experiments. We note this is nearly 100 times larger than the background pressure associated with UHV imaging systems.[3,9]

A typical surface morphology obtained by this deposition procedure is shown in Fig. 1(a). The oxide desorbed surface has been smoothed by MBE growth of a 100 nm GaAs layer yielding a nearly atomically flat surface with low step-density and areal route mean square roughness r_{RMS} of only 0.23 nm measured over a $3 \times 3\ \mu m^2$ area. Two monolayers (MLs) of Ga was then deposited on the surface at 650 °C with $P_{As} < 10^{-7}$ Torr to form droplets in Volmer-Weber growth mode,[13] as shown in Fig. 1(b). The Ga flux

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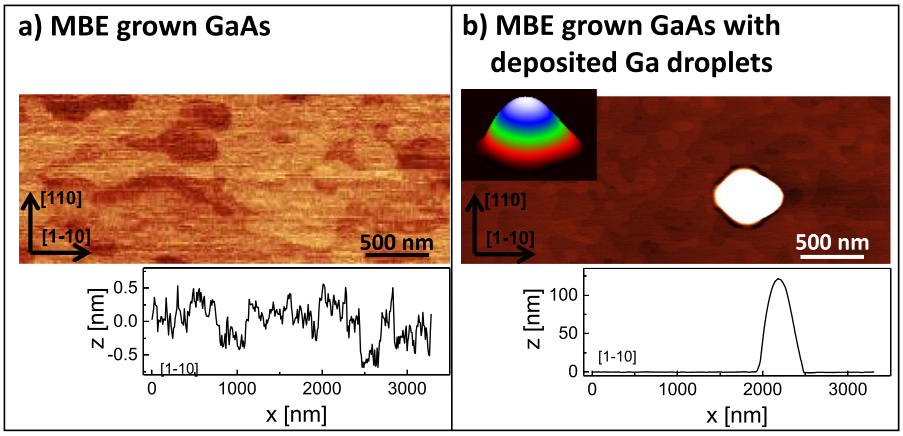

FIG. 1. Initial surfaces used for the evaporation experiments. (a) GaAs surface after oxide desorption, 100 nm GaAs deposition with MBE, and annealing at 650 °C for 300 s. (b) GaAs surface from (a) with Ga droplets after deposition of 2.0 ML of Ga.

corresponds to a GaAs growth rate of 0.8 ML/s, and the Arsenic-cell valve and shutter as well as the main shutter in front of the sample surface are closed to reduce P_{As}. Further details of the droplet formation procedure are described in Refs. 14 and 15.

To determine the congruent evaporation temperature, samples containing surface droplets were annealed at a temperature T for a time t under low As background pressure conditions ($P_{As} < 10^{-7}$ Torr). The same temperature is used for Ga droplet material deposition and heating. Temperature is determined using a thermocouple calibrated by the GaAs oxide desorption temperature visible in RHEED and an infrared pyrometer. Samples were subsequently quenched and the surface morphology analysed using atomic force microscopy (AFM) in tapping mode.

Our method for determining T_c depends on the thermodynamics of Ga droplets and the GaAs surface. During congruent evaporation, Ga and As evaporate at equal rates from the surface so that the Ga surface chemical potential μ_{Ga} attains a steady-state value. With increasing temperature, μ_{Ga} will increase to make As and Ga evaporation rates equal but eventually reaches the Ga liquidus value μ_L which defines the upper limit $T = T_c$ for congruent evaporation. Above T_c, $\mu_{Ga} > \mu_L$ so that excess Ga can collect as droplets

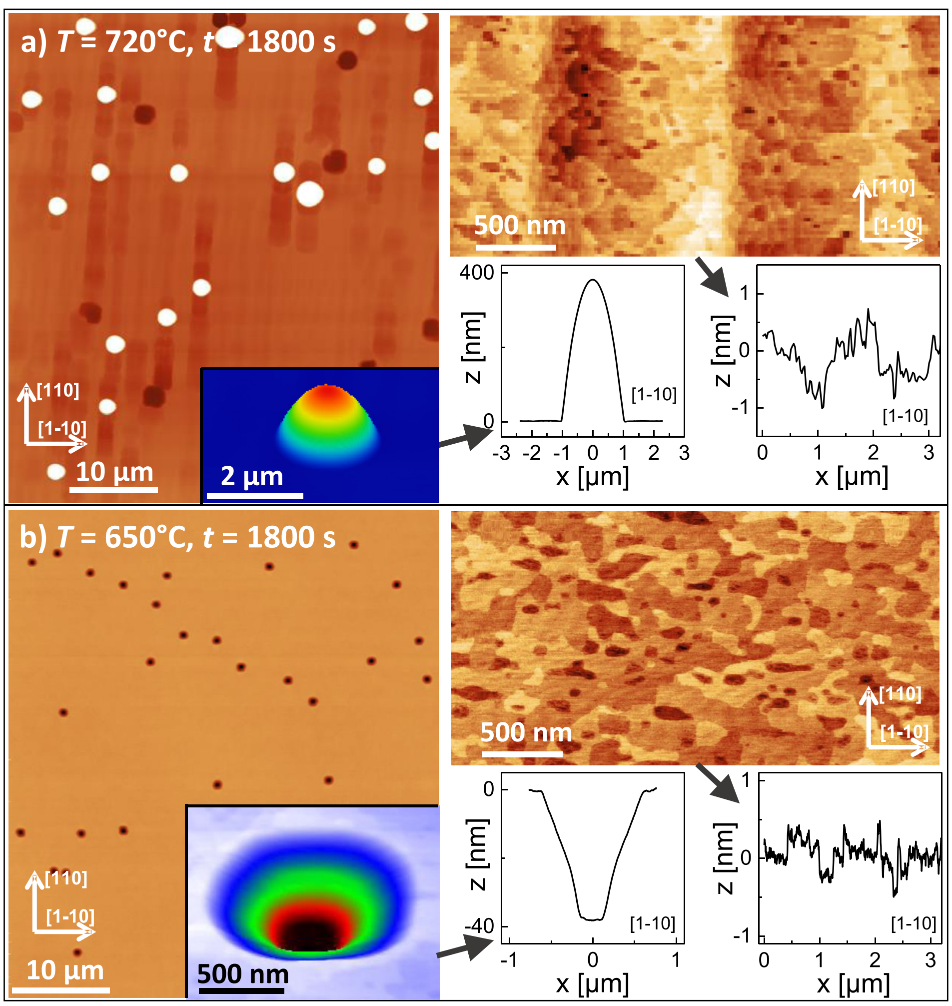

FIG. 2. GaAs surfaces with deposited Ga droplets after annealing (a) at $T = 720$ °C for $t = 1800$ s and (b) at $T = 650$ °C for $t = 1800$ s. AFM micrographs with different scales are shown with associated linescans.

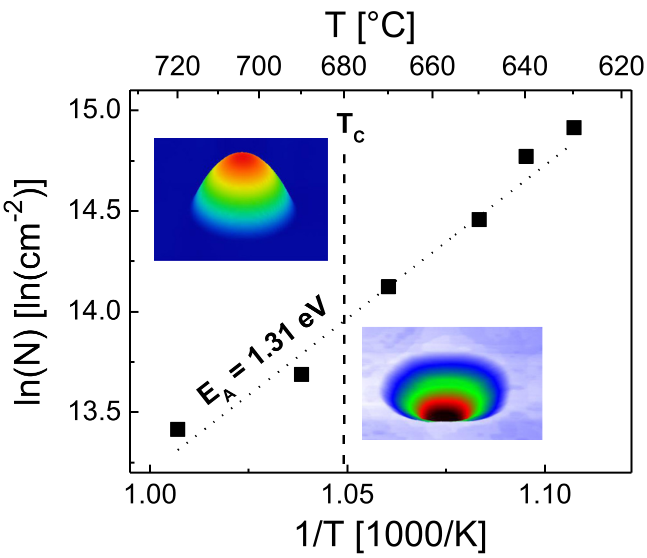

FIG. 3. Density N of large holes and droplets as function of anneal temperature T. Holes are formed for $T < T_c \simeq 680\,°C$ and droplets for $T > T_c$. An Arrhenius-type analysis of the data yields an activation energy of $E_A = 1.31$ eV.

which are assumed to remain close to liquidus composition in equilibrium with the GaAs substrate. The droplets therefore act as sinks for surface Ga adatoms which pins μ_{Ga} close to μ_L. This prevents the increase in Ga so that above T_c, As evaporates more rapidly than Ga and the Ga droplets grow.

Droplet growth due to excess Ga incorporation can be seen in Fig. 2(a) where droplets have been annealed at $T = 720\,°C$ for 1800 s. Here, the average droplet volume has increased relative to that of the deposited droplets (Fig. 1(b)), indicating that $T_c < 720\,°C$. The AFM image in Fig. 2(a) also reveals droplet traces with depth 6–16 nm indicating droplet motion along [110] directions during annealing. This is consistent with a driving force for motion depending on the disequilibrium between droplet and surface when $T \neq T_c$.[9] The dark depressions of depth 35 ± 5 nm, which are also visible in the image, are the signature of asymmetric coalescence events where a droplet has coalesced with a neighbouring droplet, leaving behind a surface etch pit.[16] The areal roughness r_{RMS} of free areas on this surface is 0.37 nm, which is close to that of the initial MBE grown GaAs layer.

Conversely, when T is below T_c, we have $\mu_{Ga} < \mu_L$ and droplets will lose Ga to the surrounding surface and shrink. During this process, the droplets locally etch the surface creating nanoholes.[14–18] We note that for LDE to occur, there must be some departure from liquidus but this is assumed small. From a technological perspective, these structures are of interest because they can be filled with a different material from the substrate in order to create various types of novel nanostructures.[19–22] For the purpose of this paper, we can utilise such holes as a signature of droplet shrinkage, which can be detected by AFM to establish $T < T_c$. Nanohole formation by droplet etching and thermal widening[23] can be observed in Fig. 2(b) for an annealing temperature $T = 650\,°C$ for 1800 s. Droplets have therefore shrunk and disappeared at this temperature indicating that $T_c > 650\,°C$. The absence of trails evident for $T < T_c$ suggests that LDE rapidly pins the droplets and restricts droplet motion.[16] The areal roughness of free areas on this surface is $r_{RMS} \simeq 0.27$ nm.

To focus in on the congruent evaporation temperature where $\mu_{Ga} = \mu_L$ and the droplets neither shrink nor grow, we have performed a series of annealing experiments to determine the boundary between droplet growth and shrinkage (nanohole formation). This is summarised in Fig. 3 where we determine $T_c = 680 \pm 10\,°C$ for MBE grown GaAs with $P_{As} < 10^{-7}$ Torr.

It should be noted that during droplet etching every deposited droplet is transformed into a nanohole.[14] Thus, the nanohole density at $T < T_c$ is equal to the density of the initial deposited droplets and can be compared to the droplet density at $T > T_c$. The continuous evolution of the hole and droplet densities in Fig. 3 suggests that excess surface Ga is captured by the deposited droplets and no additional droplet nucleation takes place during heating above T_c. An analysis of hole and droplet densities agrees with an Arrhenius-type temperature dependence and yields an activation energy $E_A = 1.31$ eV (Fig. 3). Droplet formation is relatively complicated involving adatom diffusion, droplet nucleation, and growth.[24] While we cannot identify the precise nature of the physical process corresponding to the measured energy barrier, its magnitude provides quantitative insight into the rate limiting process as droplets are formed.

In summary, we have used LDE to measure the congruent evaporation temperature of MBE grown GaAs (001) as $T_c = 680 \pm 10\,°C$. The measurement contrasts with previous experiments undertaken on rough surfaces and applies to a standard MBE system with a background As pressure $P_{As} < 10^{-7}$ Torr. The LDE method utilises the shrinkage/growth of deposited Ga droplets and therefore avoids the possibility of nucleation barriers influencing the measurement of T_c. It can be applied to measure T_c for any MBE system to provide an important reference point for the control and manipulation of droplets for quantum structure fabrication. Since the method relies on determining the transition between droplet etching and droplet growth regimes, it should also be applicable to similar systems such as InAs and GaP as well as other material combinations.

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