Atomic-Scale Observation of Temperature and Pressure Driven Preroughening and Roughening

Z. Ding, D.W. Bullock, and P.M. Thibado
Department of Physics, The University of Arkansas, Fayetteville, Arkansas 72701, USA

V.P. LaBella
School of NanoSciences and NanoEngineering, University at Albany–SUNY, Albany, New York 12203, USA

Kieran Mullen
Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma 73019, USA
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Preroughening and roughening transitions are observed on the GaAs(001) surface using scanning tunneling microscopy. By tuning the substrate temperature or As_4 pressure the surface morphology can be made free of islands, covered with one monolayer high islands or covered with islands on top of islands forming a wedding-cake–type structure. These three distinct surface morphologies are classified as ordered flat (OF), disordered flat (DOF), and rough within the restricted solid-on-solid model. Here, the DOF phase is macroscopically flat; however, an up-down-up-down step pattern persists across the entire surface. Using this model we have determined the next-nearest-neighbor interaction energy to be about 0.05 eV.

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Phase transitions in two dimensions (2D) exhibit a rich variety of fundamental physics [1–5]. Single crystal surfaces are excellent playgrounds for these 2D phase transitions, and nowhere is it more technologically important to understand these phase transitions than in the family of III-V compound semiconductors. This is because the atomically flat (001)-oriented GaAs surface is the starting point for producing the majority of high-speed optoelectronic devices. In addition, fabrication is carried out using epitaxy where layers of atoms are deposited on top of one another to produce the desired structure.

One well understood 2D surface phase transition is roughening [6,7]. Here it is common for the surface morphology to change from a flat surface directly to one with islands on top of other islands, forming a wedding-cake–type structure. This is predicted by Kosterlitz and Thouless, and is equivalent to a liquid-solid phase transition in 2D [3,5,8,9]. Roughening has also been successfully predicted by using a nearest-neighbor (NN) interaction within the restricted solid-on-solid (RSOS) model [1–3,10]. Many experimental observations of roughening have been made [11–14]. Most studies are on elemental metal surfaces, where the transition from flat to rough is driven by increasing the substrate temperature. The sudden and massive atomic rearrangement that is observed has been instrumental in developing our microscopic understanding of phase transitions.

A less well-known 2D surface phase transition is preroughening [1–3,15–19]. This was first described by Rommelse and den Nijs [1–3] by adding the next-nearest-neighbor (NNN) interaction to the RSOS model. They found that preroughening occurs when thermal fluctuations overcome the local nearest-neighbor interactions but not the longer ranged next-nearest-neighbor interaction, which acts to stabilize an overall flat surface. During the preroughening process, the surface remains macroscopically flat, but on microscopic scale it contains a disordered array of one monolayer high islands giving the surface an up-down-up-down step pattern [1,2,4,16–21]. Then, at higher temperatures the surface roughens completely. Experimental observations of preroughening have used rare gases on solid surfaces [16]. Weichman *et al.* used calorimetry measurements to deduce the various surface phases as a function of temperature.

In this Letter, we report not only the observation of preroughening followed by roughening as a function of temperature, but also that pressure drives the transitions. Furthermore, we provide clear real-space pictures of the various phases, from which we determine the NNN interaction energy for the technologically important GaAs(001) surface.

Experiments were carried out in an ultrahigh vacuum (UHV) multichamber facility [$(5–8) \times 10^{-11}$ Torr throughout], which contains a solid-source molecular beam epitaxy (MBE) chamber (Riber 32P) with a substrate temperature determination system accurate to $\pm 2\,^{\circ}$C [22], and an arsenic cell with an automated valve and controller. The MBE chamber also has an all UHV connection to a surface analysis chamber, which contains a custom integrated STM (Omicron) [23]. Commercially available "epi-ready," $n+$ (Si doped 10^{18} cm^{-3}) GaAs(001) $\pm 0.05^{\circ}$ substrates were loaded into the MBE system without any chemical cleaning.

The surface oxide layer was removed and a 1.5-μm-thick GaAs buffer layer was grown at 580 °C using an As_4 to Ga beam equivalent pressure (BEP) ratio of 15 and a growth rate of 1.0 μm/hr as determined by reflection high energy electron diffraction oscillations.

The samples were then prepared by annealing at a fixed time (between 0.25–33 h), a fixed temperature (between 500–700 °C), and a fixed As_4 flux (between 0.01–10.0 μTorr). To ensure the samples were in equilibrium, the anneal times were successively increased until the surface morphology remained unchanged, which resulted in 33 h anneals for the lowest temperatures. The samples are cooled to room temperature using a procedure that freezes in the surface morphology present at higher temperatures and has been described elsewhere [24]. After the anneal, the samples were transferred to the STM without breaking UHV, and imaged at room temperature. For each sample, 5–10, 1 μm $\times$ 1 μm filled-state STM images were acquired using tips made from single crystal $\langle 111 \rangle$-oriented tungsten wire, with a sample bias of -3.0 V and a tunneling current of 0.05–0.1 nA. To compute the fractional area of the surface covered by the islands, 10–20 regions of 200 nm $\times$ 200 nm are cropped far from steps from 5–10 larger images, and an averaged island coverage is computed, which has a uniform standard deviation of $\sim$5%.

The three distinctly different surface morphologies of the GaAs(001) surface are displayed in Figs. 1(a)–1(c). These surfaces were prepared under different annealing conditions. The flat surface was prepared by annealing at 510 °C and 0.03 μTorr As_4 BEP and shows 1 μm wide terraces [cf. Fig. 1(a)]. This image is shown as a gray scale where each color change represents a one monolayer height change (i.e., 0.3 nm). Notice the large terraces are nearly free of islands and pits and no double-height steps are formed. Also, at higher magnifications (not shown), the surface structure is a well-ordered (2 $\times$ 4) reconstruction [24]. Within the RSOS model this surface is called ordered flat (OF), because no islands exist on the surface [1,2].

The surface showing only 2D islands was prepared by annealing the sample at 565 °C and 0.03 μTorr As_4 BEP [cf. Fig. 1(b)]. This image also shows large terraces without any double-height steps. One convenient and insightful way to characterize this surface is to notice that the pattern for step height changes is up-down-up-down, etc. That is, as one moves across a terrace, the step height change goes up one monolayer then down one monolayer as an island is traversed. This pattern is repeated across the entire terrace. Within the RSOS model this surface is called disordered flat (DOF) [1,2]. It is interesting to also notice that the surface favors 2D island formation and not pit formation. This has been understood and modeled previously by assigning an energy difference to islands which have outside corners and pits which have inside corners [2].

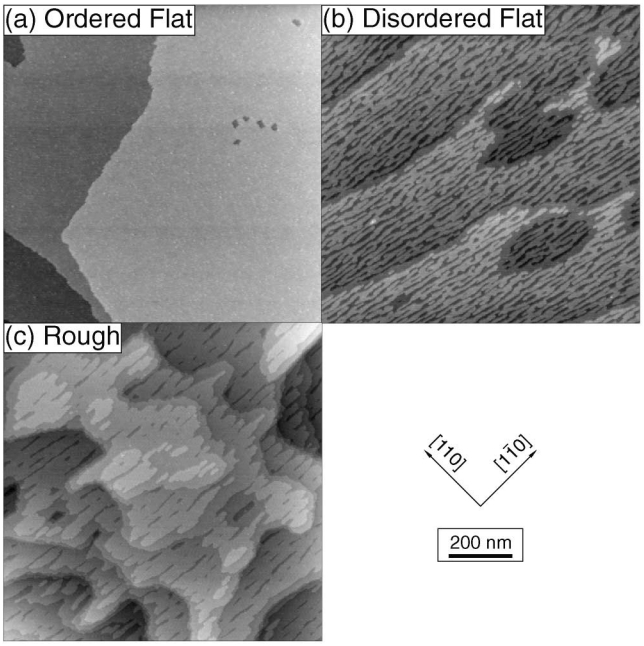

FIG. 1. (a)–(c) Three 1 μm $\times$ 1 μm filled state STM images of the GaAs(001) surface prepared under different annealing conditions. (a) 510 °C and 0.03 μTorr As_4, (b) 565 °C and 0.03 μTorr As_4 showing single level islands, (c) 605 °C and 0.03 μTorr As_4 showing multilevel islands.

The surface showing 2D islands on top of other 2D islands was prepared by annealing at 605 °C and 0.03 μTorr As_4 BEP [cf. Fig.e 1(c)]. Again, notice that no double-height steps exist, but more interestingly notice that the up-down-up-down step pattern is now broken. Here as one moves across the surface several up steps will occur before a down step occurs. Within the RSOS model this surface is called rough [1,2].

After an exhaustive search of the accessible parameter space, the transitions between the three distinct morphologies have been determined as a function of substrate temperature and As_4 BEP as shown in Fig. 2. At low temperatures and high As_4 BEP, the surface is free of all islands (OF) and appears similar to the image shown in Fig. 1(a). As the temperature is increased or the As_4 BEP is decreased, the surface transitions (black line with squares) to one containing only one monolayer high islands (DOF) and appears similar to the image shown in Fig. 1(b). Finally, at even higher temperatures or lower As_4 BEPs the surface transitions again (black line with circles). This time the surface contains 2D islands on top of other 2D islands (rough) and appears similar to the image shown in Fig. 1(c).

Notice that even though the transition from OF to DOF is coincident with island formation, the transition from DOF to rough is more complicated. To illustrate this, the circular data points are also labeled with the coverage reached just prior to roughening. For low As_4 BEPs and low temperatures the surface needs to be 80% covered with islands before roughening. At high As_4 BEPs and

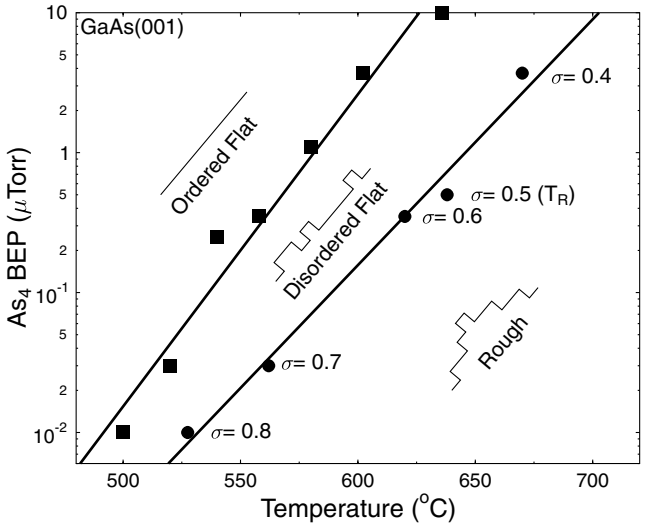

FIG. 2. Three phases GaAs(001) (2×4) reconstructed surface prepared under different annealing conditions. The black line with squares is the boundary of ordered flat and disordered flat phases. To the left of this line, the coverage of island is zero. The black line with circles is the transition boundary between disordered flat and rough phases. For this line the data points are also labeled with the island coverage reached just prior to roughening. Notice that the coverage just before roughening varies from 80% to 40% as the substrate temperature is increased.

high temperatures the surface needs to be only 40% covered with islands before roughening.

It is interesting to consider the question of why the GaAs(001) surface roughens when heated or exposed to a different As_4 BEP, while normally a low-index surface becomes flat when heated. At a fundamental level, entropy is driving the system to form islands. Within this formulation and in order to predict both preroughening and roughening, two different energies must exist. Essentially, one drives the preroughening, while the other drives the roughening. It has been shown theoretically that modeling the surface atoms using NN and NNN interactions provides the minimum number of parameters [2].

Fantastically, the predictions made by den Nijs are played out in our data. Specifically, den Nijs shows in a phase diagram that for a given set of interaction energies the surface will start off in an ordered flat state at low temperatures. Then, as the temperature increases, the surface undergoes a preroughening transition to a disordered flat state. Finally, raising the temperature further he shows the surface will roughen. He further explains that by knowing the roughening temperature T_R, the next-nearest-neighbor interaction energy E_{NNN} can be found. Specifically, the critical point for roughening corresponds to the following condition: $\exp(E_{\mathrm{NNN}}/k_B T_R) = 2$. Even though these calculations are done *without* an external field term, it still shows the full variety of surface morphologies. Since our data are taken in the presence of an external field (i.e., the As_4 pressure), we must tune the As_4 pressure to find the temperature at which the surface roughens when the coverage is 50%. Our experimental data show this happening at 640 °C, which yields a repulsive NNN interaction energy of about 0.05 eV. This energy value compares extremely well with the first-principles total-energy study done by Zhang and Zunger [25]. Experimental determination of the NNN interaction energy compliments the already known nearest-neighbor interaction energies for GaAs(001) [26].

With our ability to change both the substrate temperature and the external pressure, we observe the entire boundary between all three phases, not just a roughening point. Even more interesting, we can see that roughening can happen at either high or low coverages. Since the transition is driven by the NNN interaction energy, we believe the high energy cost for forming double-height steps holds the key to understanding this. Specifically, the interaction of the islands with the terrace edge is what initiates the transition.

The technologically important GaAs(001) surface is a two-component system and the RSOS model, which is mainly used on metal surfaces, is successfully applied. We believe this is because the Ga atoms are the mobile species controlling the roughening just like the elemental metal surface and the arsenic pressure provides an external control over the Ga concentration on the surface [26]. This opens up the opportunity for refining the growth models for III-V compound semiconductors. Specifically, it would be helpful to see calculations done using the model of den Nijs where the field term is included.

Not only does this surface phenomenon contain exciting physics, but since it is happening on the (001) surface of GaAs it has technological implications [27]. By purposely growing quantum-well structures on the rough surface, one may be able to engineer 3D dot structures. Alternatively, a rough surface may deleteriously influence transport or optical device properties via increased scattering centers. This study may also provide insight into why growing GaAs between 580 and 640 °C is best (i.e., due to the presence of numerous nucleation sites at the edges of the islands). This possibility is also confirmed in a study by Tersoff, Johnson, and Orr [28]. They showed that during growth the GaAs(001) surface and added adatoms are very close to equilibrium.

In summary, we observed preroughening and roughening on the atomic scale. The (001) surface of GaAs provides an excellent example for the phase transition of preroughening and roughening because it can be driven by both temperature and pressure. In addition, excellent agreement with both first-principles theory predictions and RSOS theory predictions were reported. The roughening transition temperature was found and used to find the NNN interaction energy of about 0.05 eV.

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