Microscopic View of a Two-Dimensional Lattice-Gas Ising System within the Grand Canonical Ensemble

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A reversible 2D critical transition is observed on the GaAs(001) surface and modeled as a lattice-gas Ising system. Without depositing any material, 2D GaAs islands spontaneously form. The order parameter, *four* critical exponents, and coupling energies are measured from scanning tunneling microscope images of the microscopic domain structure and correlation functions as a function of temperature and pressure. Unprecedented insight into the domain structure of a 2D Ising system through the critical point and a complete Hamiltonian for modeling the GaAs(001) surface are presented.

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The epitaxial techniques used in manufacturing compound semiconductor device structures have demanded insight into the physical process undergone when atoms are deposited on top of a single crystal surface. This insight is of both fundamental and technological importance and modeling these surfaces is challenging due to their two-component nature. Much success has been achieved using various techniques, such as first-principles theory [1], kinetic Monte Carlo simulations [2], rate equations [3], and thermodynamics [4].

On single component surfaces, one of the oldest and simplest approaches to modeling is the celebrated two-dimensional (2D) lattice-gas Ising model [5]. Clever researchers have been able to artificially create 2D systems with a fixed, submonolayer amount of one material deposited on a host surface made of a different material, and successfully applied the 2D lattice-gas Ising model [6–10]. These studies advance our understanding of phase transitions while illuminating the nature of interactions between atoms on surfaces, since the 2D Ising model has been theoretically studied in rigorous detail [11,12]. The above types of experiments are within the canonical ensemble (i.e., fixed number of particles) and therefore, they can fit their data to Onsager's exact solution similar to some 2D Ising-like magnetic phase transitions (i.e., fixed number of spins) that have been observed by neutron scattering [13–15]. The lattice-gas Ising model was originally framed within the more general context of the grand canonical ensemble, where the number of particles is free to fluctuate as it exchanges with a reservoir. This is unlike the ferromagnetic case where the number of spins is fixed. To the best of our knowledge no experimental test of the general solution to the 2D lattice-gas Ising model within the grand canonical ensemble exists.

In this Letter, we discovered a single crystal surface where the surface atoms can exchange with the substrate in a reversible manner consistent with the general solution 2D lattice-gas Ising model within the grand canonical ensemble. Surprisingly, the system is the technologically important two-component GaAs(001) compound semiconductor surface. This experiment is performed by imaging individual domains on a scale comparable to its constituents (i.e., the atoms) with scanning tunneling microscopy (STM), giving unprecedented insight into the microscopic domain structure of a 2D Ising system through the critical point. Equally exciting, this study provides a complete 2D Ising Hamiltonian for modeling the equilibrium and nonequilibrium properties of the GaAs(001) surface.

Experiments were carried out in an ultrahigh vacuum (UHV) multichamber facility [$(5 - 8) \times 10^{-11}$ Torr throughout] which contains a molecular beam epitaxy (MBE) chamber (Riber 32P) that includes a substrate temperature determination system accurate to $\pm 2\,^{\circ}\mathrm{C}$ [16] and a surface analysis chamber with a custom integrated STM (Omicron) [17]. Commercially available, "epi-ready," $n+$ (Si doped $10^{18}/\mathrm{cm}^3$) GaAs(001) $\pm 0.1^{\circ}$ 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 ratio of 15 and a growth rate of 1.0 μm/h as determined by reflection high-energy electron diffraction oscillations.

The spontaneous formation of islands on this surface occurred after each sample was annealed for 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), resulting in an exhaustive study of the accessible parameter space. 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 [18]. 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, a sample bias of -3.0 V, and a demanded tunneling current of 0.05–0.1 nA.

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The thermodynamic behavior of the lattice-gas Ising model was simulated as a function of temperature and fugacity [19] using Metropolis Monte Carlo simulations [20] on a 2D lattice with 100×100 sites, or larger.

A typical STM image of a sample annealed at 560 °C and under a 0.03 μTorr As_4 flux is displayed in Fig. 1(a), and shows the spontaneously formed islands on multiple terraces, where each terrace is shown as a separate grey level. Notice how the edge of each terrace affects the formation of islands by not allowing double-height steps to form. A smaller scale STM image of a sample annealed at 540 °C and under a 0.03 μTorr As_4 flux is displayed in Fig. 1(b). This annealing condition shows a surface half covered with islands. These and all other STM images show either a flat surface or one that has flat terraces covered by only one-monolayer-high (0.28 nm) GaAs islands. Notice how the domains are elongated in the $[1\bar{1}0]$ direction. To quantify this domain geometry a site-site correlation function is computed from the STM image shown in Fig. 1(b) and displayed in Fig. 1(c). The correlation function is elongated in the same direction as the islands and a cross section taken at $1/e$ of the maximum is an ellipse with an aspect ratio of 3.0 (see inset). This is a measure of the average radial island geometry.

The fraction of the surface that these islands occupy is plotted versus temperature and As_4 flux and shown in Fig. 2. To minimize the influence of steps on the computed coverage, 10–20 200 nm $\times$ 200 nm regions are cropped far from terrace edges from 5–10 larger images, and then thresholded to compute an average coverage, which has a uniform standard deviation of ~5%. A series of these thresholded 200 nm $\times$ 200 nm images is shown in Figs. 2(b)–2(d), which visually demonstrates the increase in coverage from 0.05 to 0.2 to 0.7, respectively, with increasing anneal temperature under a constant 0.03 μTorr As_4 flux. A best fit Fermi function is drawn over each series of samples annealed under the same As_4 flux to highlight the trend of the data. The dashed lines indicate the experimentally inaccessible region. In addition, it has been determined that any one surface structure can be reversibly transformed into any other structure by annealing it at the corresponding temperature and As_4 flux.

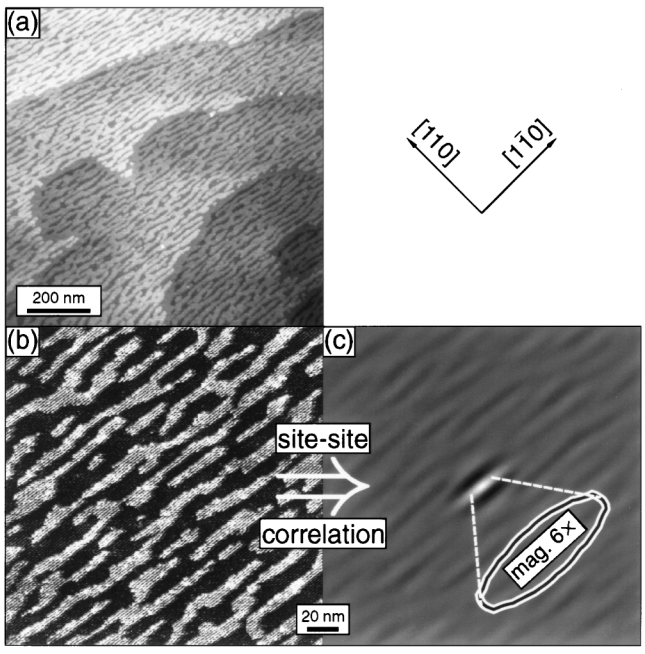

FIG. 1. (a) A 1 μm $\times$ 1 μm STM image of the spontaneously formed GaAs islands annealed at 560 °C under a As_4 flux of 0.03 μTorr. (b) A 200 nm $\times$ 200 nm STM image of the spontaneously formed GaAs islands annealed at 540 °C under a As_4 flux of 0.03 μTorr. (c) A correlation function computed from image (b) shows the average geometry of the islands. (inset) Ellipse taken at $1/e$ of the maximum showing an aspect ratio of 3.0.

The fractional coverage is the order parameter for the 2D Ising system. It is computed from the Monte Carlo simulations of the lattice-gas Hamiltonian and displayed in Fig. 2(a) as a function of a reduced fugacity parameter ζ which spans several decades [5]. The fugacity of a gas z is related to its pressure through an equation of state, which in this system is the Ga pressure as will be discussed later [4]. The curve calculated with the critical fugacity, $\ln(z_c) = 2\epsilon/k_B T_c$ (i.e., $\zeta = 1$), shows the coverage jumping from low to high occupation at T_c. For fugacities greater than z_c, the coverage jumps from one side of the coexistence curve (Onsager solution) to the other as the temperature is increased. As the fugacity is decreased below z_c, the change in the coverage with temperature decreases, and stays low even for high temperatures. This thermodynamic behavior is mimicked in the behavior of the data. The series of samples annealed under the lowest As_4 flux of 0.01 μTorr has the sharpest increase in the coverage of the islands as a function of temperature. From this series the critical temperature T_c is estimated to be 527.5 $\pm$ 2 °C and the coexistence curve (Onsager solution) is plotted along with the critical fugacity curve from the Monte Carlo simulations. The rest of the samples annealed under larger As_4 fluxes have higher onset temperatures for the lowest coverage, slower rates of increase, and saturate at lower coverages.

The behavior of the coverage obtained by *increasing* the As_4 flux by 3 orders of magnitude is similar to the Monte Carlo results where the fugacity or pressure is *decreased* over ~3 orders of magnitude. This inverse relationship is expected, because earlier studies by Tersoff, Johnson, and Orr determined that the Ga adatom concentration or pressure is inversely proportional to the arsenic flux [4,21]. On an atomistic level, it is these Ga adatoms that are mobile on the surface at high temperatures, which are then frozen into GaAs islands when cooled to room temperature. The higher arsenic pressure results in terminating the gallium surface [18], thereby lowering the number of mobile Ga atoms. This Ga adatom concentration is related to the Ga

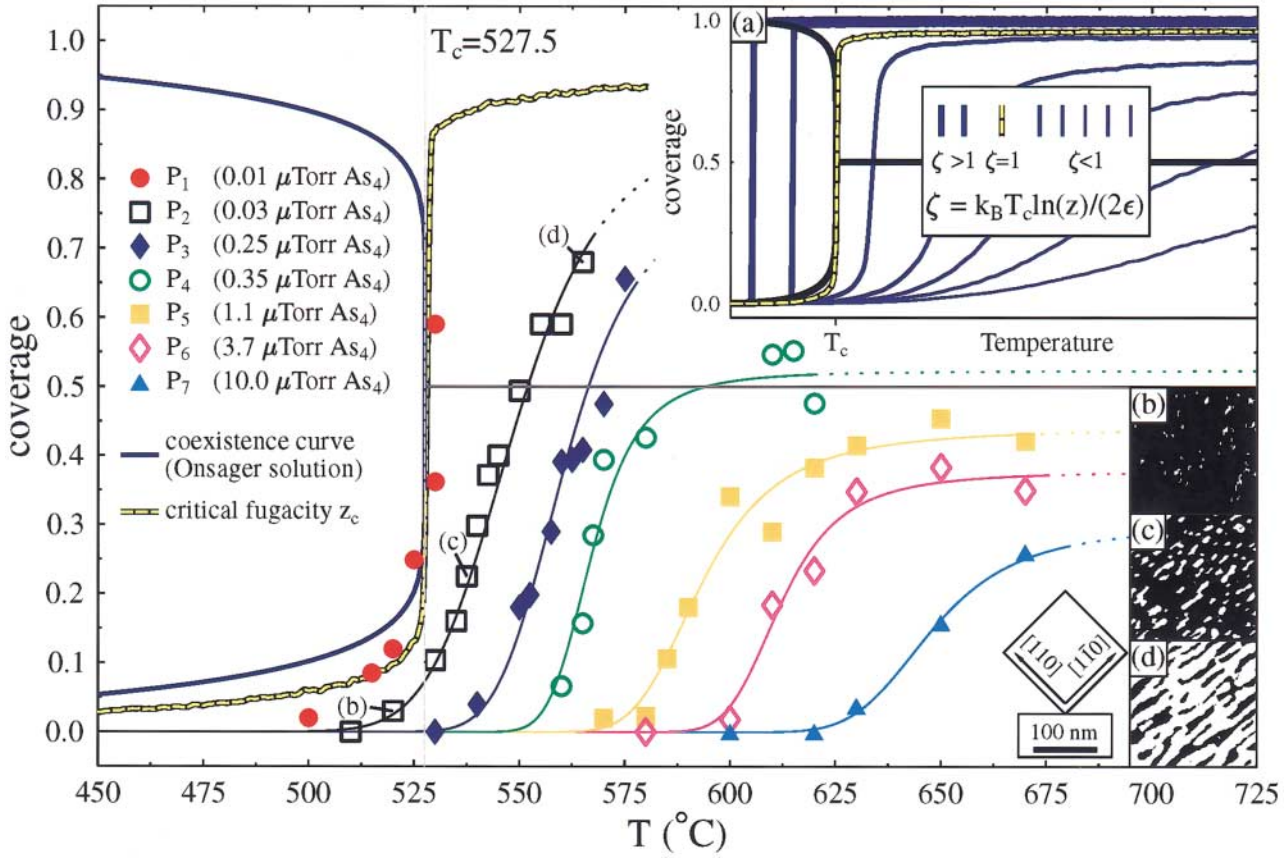

FIG. 2 (color). The fractional coverage obtained from STM images as a function of temperature and applied As_4 gas pressure as well as the coexistence curve and the curve of critical fugacity from the Monte Carlo modeling. The lines drawn through the data are best fit Fermi functions. (a) Behavior of the coverage for the lattice-gas Ising model from the Monte Carlo simulations. (b)–(d) 200 nm × 200 nm thresholded STM images, annealed at the temperatures indicated on the 0.03 μTorr As_4 pressure data series.

fugacity, which directly compares to the fugacity of the lattice-gas simulations.

The STM images of the 2D islands in Fig. 1 and the reduced macroscopic thermodynamic data in Fig. 2 provide strong evidence that this system follows the 2D lattice-gas Hamiltonian. However, quantifying a systems dimensionality and internal degrees of freedom requires the measurement of critical exponents [22]. Because of the large data set acquired as a function of temperature, pressure, coverage, and time, an unprecedented *four* of the seven 2D universal critical exponents are determined and shown in Table I with their functional relationships. All seven exponents can be determined by measuring only two and their interrelationships can be tested by measuring more. The pair correlation critical exponent η is a measure of the average domain size at the critical point. It is measured from the decay of the correlation function shown in Fig. 1(c), and our value is in good agreement with the 2D Ising prediction.

The correlation length critical exponent ν is a measure of how the island size changes with temperature. It is calculated by extracting the width at $\frac{1}{e}$ of the maximum from the correlation functions as a function of temperature assuming that the Ga pressure is constant in the 0.01 μTorr series from 500 to 525 °C. The isotherm critical exponent δ is a measure of how quickly the coverage changes with pressure. It is calculated using pressure and coverage differences and ratios to eliminate unknown coefficients and assumes that the Ga pressure scales with the arsenic pressure from 0.25 to

TABLE I. Measured critical exponents with predicted 2D and 3D values.

Quantity	Scaling Law	Measured Value	2D	3D
Pair correlation function ($T = T_c$)	$G(r) \sim r^{-\eta}$	$\eta = 0.25 \pm 0.05$	0.25	~0.04
Correlation length, $G(r, T < T_c) \sim r^{-\eta} e^{-r/\xi}$	$\xi \sim \lvert\frac{T}{T_c} - 1\rvert^{-\nu}$	$\nu = 1.0 \pm 0.25$	1	~0.638
Critical isotherm ($T = T_c$)	$P - P_c \sim \lvert 2\sigma_n - 1\rvert^{\delta}$	$\delta = 15 \pm 3$	15	5
Compressibility, $K_T(T < T_c) = \sigma_n^{-1}(\partial\sigma_n/\partial P)_T$	$K_T \sim \lvert\frac{T}{T_c} - 1\rvert^{-\gamma}$	$\gamma = 1.74 \pm 0.2$	1.75	1.25

0.01 μTorr at 530 °C. Finally, the compressibility critical exponent γ is a measure of how the compressibility changes with temperature. It is calculated using the 0.01 and 0.03 μTorr series of data between 515 and 525 °C (note interpolated values for σ_n were used). This unprecedented large set of critical exponents, all well within the 2D Ising universality class, is the most rigorous testament to this systems 2D Ising behavior and was achievable because of the microscopic images obtained with STM.

Beyond being a study of a 2D Ising system, this study also demonstrates that the thermodynamics of the technologically important GaAs(001) surface can be understood with the Ising model. To complete this picture, the coupling energies in both the [110] and $[1\bar{1}0]$ directions are needed. At T_c and z_c the system reduces to the zero-field Hamiltonian, where the coupling energies $\epsilon_{[110]}$ and $\epsilon_{[1\bar{1}0]}$ and T_c are related by Onsager's [11] original finding:

$$\sinh(\epsilon_{[110]}/2k_BT_c)\sinh(\epsilon_{[1\bar{1}0]}/2k_BT_c) = 1. \quad (1)$$

Unfortunately, this equation has two unknowns which are the energy differences between an atom having a neighbor or not, and the binding energy at a step edge. One might naively assume that the aspect ratio of the islands is the ratio of the coupling energies, however this is not true. Fortunately, Wu *et al.* calculated the exact correlation function for the 2D Ising model [23]. From that paper, this formula

$$\frac{\sinh(\epsilon_{[1\bar{1}0]}/2k_BT_c)}{\sinh(\epsilon_{[110]}/2k_BT_c)} = (AR)^2 \quad (2)$$

can be derived, where AR is the aspect ratio of the correlation function. Now, for the first time two equations exist relating the two coupling energies. For our system we find $\epsilon_{[1\bar{1}0]} = 250 \pm 25$ meV and $\epsilon_{[110]} = 45 \pm 5$ meV. These coupling energies are the energy cost for forming a step edge on the GaAs(001) surface, thus providing numerical values for testing against theoretical predictions [24]. This also explains why the islands are longer in the $[1\bar{1}0]$ direction. With absolute knowledge of the coupling energies the Hamiltonian is complete and one can solve for equilibrium and nonequilibrium properties using standard methods [25]. This is unlike other 2D Ising studies which measure the ratio of two coupling energies [26].

In summary, the 2D lattice-gas Ising model within the grand canonical ensemble has been successfully applied to the technologically important GaAs(001) surface. Surprisingly, the single component Ising model can successfully describe a two-component system; this is because the Ga atoms are the constituents and the arsenic flux provides an external control of the Ga pressure. Four universal 2D critical exponents were measured, more than any other system. A relationship between the aspect ratio of the 2D site-site correlation function and the asymmetric nearest neighbor coupling energies for a 2D Ising system was developed. This relationship may prove useful in other studies by allowing an estimate of coupling energies simply from images of real space domains. Finally, with complete knowledge of the 2D Ising Hamiltonian a new approach to modeling the GaAs(001) surface is possible.

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