A lattice gas model of II–VI(001) semiconductor surfaces

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Abstract

We introduce an anisotropic two–dimensional lattice gas model of metal terminated II–VI(001) semiconductor surfaces. Important properties of this class of materials are represented by effective NN and NNN interactions, which result in the competition of two vacancy structures on the surface. We demonstrate that the experimentally observed transition from dominant $c(2\times2)$–ordering of the CdTe(001) surface to a local (2×1) arrangement of Cd–atoms can be explained as a phase transition in thermal equilibrium. The model is studied by means of transfer–matrix and Monte Carlo techniques. The analysis shows that the small energy difference of the competing reconstructions determines to a large extent the nature of the different phases. Possible implications for further experimental research are discussed.

Two–dimensional lattice gases have served as models of atoms adsorbed on a singular crystal surface, or the terminating layer of such a surface itself, respectively. The interplay of attractive and repulsive short range interactions can result in highly non–trivial features, see e.g. [1, 2, 3, 4, 5, 6] and references therein. For instance, square lattice systems with infinite NN–repulsion (*hard squares*) and NNN–attraction display tricritical behavior [7, 8, 4]. At low temperatures a dense, $c(2\times2)$ ordered phase coexists with a disordered phase of low coverage. Here we will investigate a particular model with highly anisotropic attractive and repulsive interactions, which result in a $c(2\times2)$ groundstate, as well. However, this ordering competes with a (2×1) structure which can prevail locally in the disordered regime.

The model parameters are chosen to represent certain properties of metal terminated II–VI(001) semiconductor surfaces. This class of materials has attracted considerable attention due to their potential technological relevance in the development of optoelectronic devices, for a recent overview see [9]. Frequently, (001) surfaces serve as substrates for the growth of II–VI crystals [10] by means of Molecular Beam Epitaxy or Atomic Layer Epitaxy, for instance. Surface reconstructions play an important role in this context and have been the target of experimental studies [10, 11, 12]. In contrast to most III–V materials, II–VI(001) surfaces exhibit a fairly small number of possible reconstructions, which are less complex than their III–V counterparts, in general.

In the following we will mainly address the CdTe(001) surface, see [10] for a detailed discussion. Apparently, only Cd–terminated (001) surfaces are observed in vacuum [13, 14]. The underlying, complete Te half–layer provides potential Cd–sites which form a simple square lattice. Electron counting rules [15] and similar considerations [16] show that the simultaneous occupation of NN–sites in the $[1\bar{1}0]$–direction (termed the y–direction in the following) is excluded in the terminating Cd–layer, whereas NN–neighbors along the [110]–direction (or x–axis, for short) are possible. Therefore, unless excess Cd is deposited, the surface is characterized by a vacancy structure with a maximum Cd–coverage of $\theta = 1/2$.

Figure 1 (a) illustrates the structure of the two relevant configurations which satisfy this constraint at $\theta = 1/2$. The $c(2\times2)$ reconstruction is characterized by a staggered (*checkered*) occupation of the square lattice sites. In the (2×1) structure, Cd–atoms arrange in rows along the x–direction which alternate with rows of vacancies. In principle, the configurations can be transformed into one another by shifting every other column of Cd–atoms by one lattice site.

Density functional (DF) calculations have shown that the surface energies of the two competing structures at $\theta = 1/2$ and $T = 0$ differ only by a small amount ΔE, with the $c(2\times2)$ reconstruction having the slightly lower energy. In [17] it is argued, that this preference can be unterstood qualitatively in terms of electron Coulomb interactions, as the distances of neighboring metal atoms are smaller in the (2×1) arrangement. For ZnSe, a value of $\Delta E \approx 0.03eV$ per potential Zn–site is given in [17, 18, 19]. According to [20], the energy difference is even smaller ($\Delta E \approx 0.016eV$) for the CdTe(001) surface.

This factor should play a crucial role in a phase transition which has been studied for CdTe [10, 11, 12]: in vacuum at temperatures below a critical value of about $T_c = 270^oC \pm 10^oC$, the surface displays a mixed $c(2\times2)$–(2×1) structure with a clear prevalence of the checkered configuration close to (but below) T_c. Above T_c, a local (2×1) arrangement of Cd–atoms dominates the surface. The observed coverage is in the vicinity of $\theta \approx 0.4$ in both regimes [12]. The situation is complicated by the fact that the material begins to sublimate significantly at about the same temperature T_c. However, it has been argued that sublimation through step flow would not hinder the surface to achieve an effective equilibrium configuration on terraces [12].

The aim of our theoretical investigation is to clarify whether the nature of the above discussed transition can be explained within a thermodynamic equilibrium framework at all, or if non–equilibrium effects should play a crucial role.

The modeling of reconstructions which are characterized by displacement of atoms from their regular lattice positions, usually requires continuous two– or three-dimensional degrees of freedom. A prominent example is the description of W(100) surfaces by XY–models, see e.g. [21] and references therein. Here, however, reconstruction occurs via the rearrangement of atoms in vacancy structures and a description in terms of occupation variables is appropriate.

We present here a lattice gas model which takes into account important features of the above discussed II–VI(001) surfaces. We will loosely speak of Cd–atoms in the following, without claiming to reproduce particular properties of CdTe faithfully. In fact, the basic structure of the model would be the same for other II–VI(001) surfaces. In our simplifying picture we consider only the terminating Cd–layer, represented by a square lattice of sites (x, y) which can be either occupied ($n_{x,y} = 1$) or empty ($n_{x,y} = 0$). The influence of the underlying crystal structure is accounted for by effective pairwise interactions of atoms. In the y–direction, an infinite repulsion excludes the simultaneous occupation of NN–sites, i.e. $n_{x,y} = 1$ always implies $n_{x,y\pm1} = 0$. In the x–direction, an attractive interaction favors the occupation of NN–pairs, the strength of which is denoted by $\epsilon_x < 0$. A competing attractive interaction of diagonal neighbors (NNN) $\epsilon_d < 0$ tends to stabilize the $c(2\times 2)$ arrangement of atoms. The total energy of the system is given by

$$H = \sum_{x,y} n_{x,y} \left(\epsilon_d \, [n_{x+1,y+1} + n_{x+1,y-1}] + \epsilon_x \, n_{x+1,y} - \mu \right), \tag{1}$$

where the sum is over all lattice sites and the (effective) chemical potential μ controls the mean coverage $\theta = \langle n_{x,y} \rangle \leq 1/2$. Without loss of generality we can choose $\epsilon_d = -1$ and thus fix the energy scale. Then ϵ_x controls the energy difference ΔE (in units of $|\epsilon_d|$) between a perfectly ordered $c(2\times 2)$ and a perfect (2×1) arrangement at $\theta = 1/2$: $\Delta E = |2 + \epsilon_x|/2$ (per lattice site). The groundstate of the system is a $c(2\times 2)$ ordered configuration with $\theta = 1/2$, whenever $\epsilon_x > -2$ (and $\mu > -2$).

The free energy of the system is obtained from the partition function $Z = \sum_{\{n_{x,y}\}} e^{-\beta H}$, where the temperature $T = 1/\beta$ is also measured in units of $|\epsilon_d| = 1$. The sum is restricted to configurations $\{n_{x,y}\}$ which obey the NN–exclusion in y–direction. We have applied standard transfer matrix (TM) techniques [22] to evaluate the logarithm of Z_L, the partition sum of a system with $M = L \times N$ lattice sites in the limit $N \to \infty$. Strips of width L with periodic boundary conditions were aligned with the x-axis. Hence, only even L allow for the perfect $c(2\times 2)$ ordering of the groundstate. Note that the TM is of dimension $2^L \times 2^L$, but with a much smaller number 3^L of non–zero elements due to the anisotropic repulsion. This allows for the sparse representation of the TM in the numerical treatment.

As a first example we consider the model with $\epsilon_x = -1.96$. Figure 1 (b) shows results for strip width $L = 10$ at different temperatures and constant chemical potential $\mu = -1.96$. We have evaluated the coverage $\theta = \langle n_{x,y} \rangle = \sum_{x,y} n_{x,y}/M$ as well as the correlations

$$c_d = \frac{1}{2} \langle n_{x,y} \, (n_{x+1,y+1} + n_{x+1,y-1}) \rangle \quad \text{and} \quad c_x = \langle n_{x,y} n_{x+1,y} \rangle. \tag{2}$$

These measure the probabilities of finding an occupied NN–pair (c_x) or NNN–pair (c_d) of Cd–atoms, i.e. the contribution of (2×1)– or $c(2\times 2)$– dominated regions in the system. Coverage and correlations can be obtained from proper derivatives of $\ln Z_L$, or, as in the case of θ and c_x, directly from the relevant eigenvector of the TM [3, 4].

In addition, Figure 1 (b) displays results of grand canonical Monte Carlo simulations of a system with $M = 64 \times 64$ sites. In order to achieve reasonably fast equilibration we have applied a rejection-free algorithm [23] which, at any given time, represents all possible changes of the system in a binary search tree and chooses a particular one according to the respective rate. The results are in good agreement with the TM–calculation. In addition to the correlations (2) we determine order parameters which are associated with a perfect $c(2\times 2)$ or (2×1) structure on one of the sublattices:

$$m_{2\times 1} = \frac{1}{M} \sum_{x,y}^{y \text{ even}} n_{x,y} \quad \text{and} \quad m_{2\times 2} = \frac{1}{M} \sum_{x,y}^{(x+y) \text{ even}} n_{x,y} \tag{3}$$

Large values ($\leq \theta$) of these quantities indicate long range order, whereas a homogeneously disordered occupation of the lattice would yield $m_{2\times 2} = m_{2\times 1} = \theta/2$. For the sake of breaking the sublattice symmetry, we have initialized the system with $m_{2\times 2} = \theta$ for the equilibration dynamics. We have refrained from determining the order parameters within the TM–approach

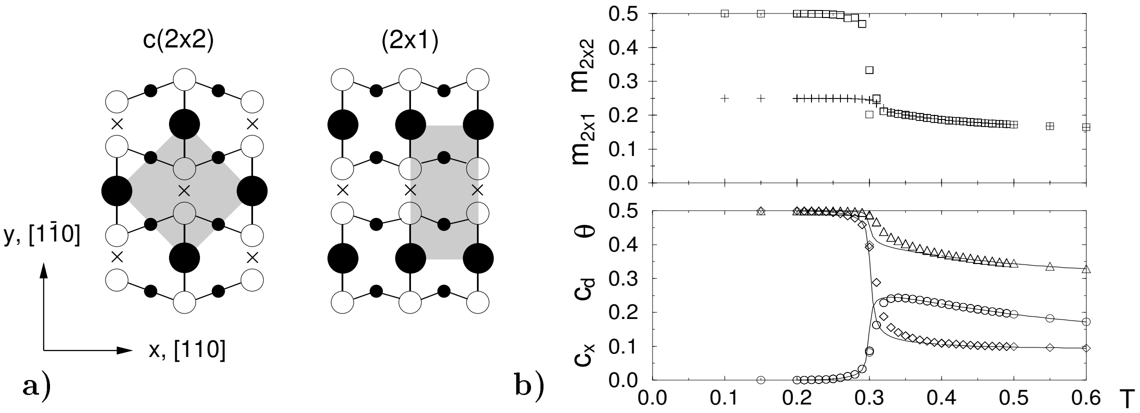

Figure 1:
a) Structural model of the $c(2{\times}2)$ and $(2{\times}1)$ reconstructions of the CdTe(001) surface [11, 12]. Shaded areas mark the corresponding primitive unit cells. Large filled circles represent Cd–atoms at the surface, open circles correspond to Te in the underlying half–layer, and small filled circles to the next, completed half–layer of Cd. Crosses represent empty sites in the simplifying lattice gas model. Note that the Te–atoms are dislocated according to the Cd–positions in the respective reconstruction.
b) The phase transition at constant chemical potential $\mu = -1.96$ for $\epsilon_x = -1.96$. The lower panel displays results of the TM–calculation for $L = 10$ (solid lines) and MC–simulations (64×64 sites, single run): coverage θ (triangles), correlations c_d (diamonds) and c_x (circles). The upper panel shows $m_{2\times2}$ (squares) and $m_{2\times1}$ (crosses) for the same temperature range.

which would require the introduction of additional staggered fields to the energy function (1). The TM–formalism offers a more suitable method to localize the phase transition [4].

In the considered example, one observes a sudden drop of the coverage at $T \approx 0.3$ when $\mu = -1.96$ is held constant. Simultaneously, the system loses its long range order as indicated by values $m_{2\times2} = m_{2\times1} = \theta/2$ in the simulations. This is also signaled in the properties of the relevant eigenvector in the TM-analysis [4]. The behavior is consistent with a first order transition, as it was investigated for similar models with isotropic or anisotropic interactions, see e.g. [1, 2, 3, 4, 5] and references therein.

Here, however, also the NNN–correlation c_d decreases rapidly at the coverage drop, while c_x displays a sudden increase and $c_x > c_d$ in the high temperature regime. This indicates that the phase transition also affects the short range correlations in the system: atoms order in rows of the (2×1)–type without long range order. For $\theta = 1/2$ the $c(2 \times 2)$ ordering is always preferred energetically. At small coverages, however, the local rearrangement of atoms in rows along the x–direction can be favorable compared to a partial occupation of NNN–sites with many broken bonds of type ϵ_d. Indeed, the degree of the prevalence of c_x over c_d depends strongly on the actual coverage as will be discussed below.

We have followed the prescription outlined by Bartelt et al. [4] for estimating the coverage discontinuity and phase boundaries for $L \to \infty$ from three different strip widths. The results as obtained from $L = 6, 8, 10$ are shown in Figure 2 for the models with $\epsilon_x = -1.90$ and $\epsilon_x = -1.60$, i.e. $\Delta E = 0.05$ and 0.2, respectively. At low temperatures (III), an ordered phase with $\theta \approx 1/2$ coexists with a disordered phase of low coverage. At higher temperatures, the system becomes homogeneously disordered (II) or ordered (I) depending on the coverage. For $T \to \infty$, we expect the phase boundary (I/II) to approach the $\theta = 1/2$ axis. In this limit

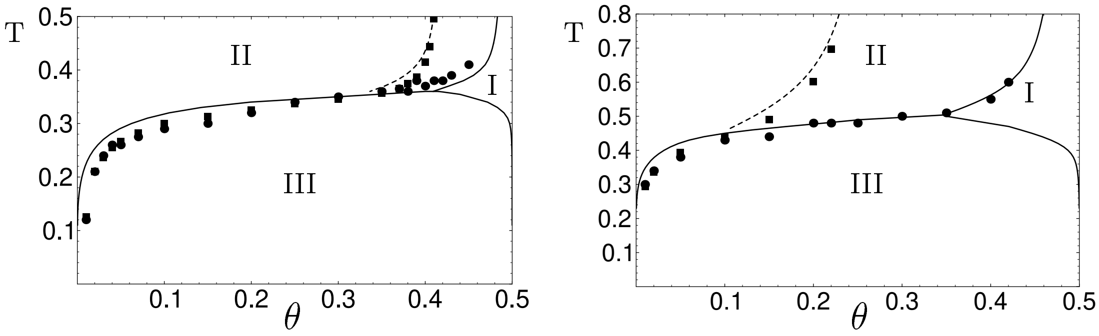

Figure 2: Phase diagram of the model with $\epsilon_x = -1.90$ (left panel) and $\epsilon_x = -1.60$ (right panel), note the different temperature scales. Phase I is homogeneously ordered, in region II the system is homogeneously disordered, and in III the high and low coverage phases coexist. Solid lines represent the TM–extrapolation and symbols (circles) correspond to the results of Monte Carlo Simulations ($M = 128 \times 128$) at constant coverage. The additional dashed lines (squares, respectively) indicate the values of (θ, T), where $c_x = c_d$, hence it separates the region of $c(2 \times 2)$–prevalence from the one where the (2×1) structure dominates. Statistical errors would be on the order of 0.05 for all the simulation data.

the infinite repulsion should be the only relevant interaction, columns of lattice sites decouple and the system is always disordered. This is in contrast to hard square models with isotropic NN–repulsion, where an extended regime (I) persists for arbitrary temperature [3, 4].

As an additional characteristics of the system we have determined the line $T(\theta)$ where $c_x = c_d$ and extrapolated for $L \to \infty$. Right of the dashed lines in Figure 2, the $c(2 \times 2)$–structure is prevalent and vice versa. For small coverage, this characteristic line coincides with the boundary (II/III) of the coexistence region. Hence, for a range of coverages, the transition into disorder is accompanied by a simultaneous and discontinuous change of local ordering from $c(2 \times 2)$ to (2×1) arrangement of Cd–atoms.

We obtain also a rough estimate of the phase diagram from additional Monte Carlo simulations at constant coverage. For this purpose, we apply a non–local algorithm which exchanges empty with occupied sites according to Kawasaki–like rates [23]. The system is again initialized in an ordered $c(2 \times 2)$-configuration for equilibration, and a rapid decrease of $m_{2\times2}$ with increasing T marks the transition into the homogeneously disordered phase. Figure 2 shows in both diagrams the results for $M = 128 \times 128$, which are in good agreement with the TM–prediction. Within error bars, we obtain the same results by searching for a pronounced maximum in the fluctuations of order parameters, correlations, or energy. Note that this method is not suitable for detecting the transition into the homogeneously ordered region (I): simulations slow down considerably at almost maximal coverage and, furthermore, (I) and (III) become virtually indistinguishable in small systems. The transition between (I) and (II) is continuous in terms of $m_{2\times2}$ and should be Ising like, details will be published elsewhere.

Figure 2 demonstrates the crucial role that the energy difference ΔE plays for the nature of the phase transition. With increasing ΔE, the tricritical point shifts to smaller coverage and higher temperature. Even more so does the line which separates $c(2 \times 2)$ from (2×1) prevalence. This feature might offer a qualitative explanation for the remarkable fact that the transition from $c(2\times2)$– to (2×1)–prevalence, which was investigated for CdTe in great detail, has not been found in ZnSe, so far. There, ΔE is expected to be significantly larger than for CdTe and the region of noticeable (2×1)–dominance should indeed be smaller. Experimental data indicates that the (2×1) ordering is restricted to rather small domains and provides no evidence of long range ordering of this type [12].

In summary, our model offers an interpretation of the transition from $c(2\times 2)$– to (2×1)–dominance in CdTe(001) as a concomitant phenomenon of an equilibrium phase transition. At medium coverage the transition is, with increasing T, from a coexistence regime into a homogeneously disordered phase. For small enough energy difference ΔE, the phase transition is accompanied inevitably by a rearrangement of the vacancy structure from $c(2\times 2)$– to local (2×1)–ordering.

Of course, some of the detailed experimental findings cannot be accounted for in our simple model, see for instance [12] for particular phenomena related to the relaxation of surface strain. For a more quantitative comparison with experiments, additional information is needed. A precise measurement of θ as a function of the temperature is difficult, but would reveal the path on which the system enters the (2×1)–dominated region in the phase diagram.

In a naive attempt to interpret our results quantitatively one would identify the dimensionless critical temperature (in units of $\mid \epsilon_d \mid = 1$) with $T_c \approx 270^o C$, thus setting the scale for expressing the energy difference $\mid 2+\epsilon_x \mid /2$ in physical units. For example, the model with $\epsilon_x = -1.94$ exhibits the desired transition with $\theta \approx 0.4$ at a temperature $T \approx 0.3$. This would translate into $\Delta E \approx 0.005 eV$ which is significantly smaller than the value $(0.03 eV)$ given in [17, 18, 19]. DF–calculations yield ΔE at $T=0$ and the precise effect of higher temperatures on the relation of (free) energies is unknown. Furthermore, recent calculations have shown that the DF–results are very sensitive (up to a factor of about 2) to the number of atomic layers considered in the calculation [24]. Hence, a serious quantitative matching is not feasible unless more reliable estimates of ΔE become available.

Another open question is, how our results for small values of θ can be interpreted in the experimental context. Terminating layers of metal atoms with very low coverage are unstable in vacuum and the next (metal) layer is uncovered, see e.g. [10, 13, 14]. However, the presence of excess group VI atoms might stabilize an effective equilibrium situation with small metal coverage. As a test for this hypothesis we suggest to search for the structural transition of the ZnSe(001) surface under mildly Se–rich conditions.

Our model also opens the possibility to study the shapes and sizes of domains, e.g. the regions of local (2×1)–dominance in the disordered phase. Experimental data is available for the pronounced anisotropy of such domains [10]. Furthermore, we will study the equilibrium shape of isolated *islands* of atoms and its dependence on the temperature. This should allow for further comparison with experimental results as reported in [14], for instance.

Acknowledgment: We would like to thank S. Gundel for fruitful discussions. M. Ahr was supported by the Deutsche Forschungsgemeinschaft.

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