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Surface energy and stability of stress-driven discommensurate surface structures

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A method is presented to obtain *ab initio* upper and lower bounds to surface energies of stress-driven discommensurate surface structures, possibly nonperiodic or exhibiting very large unit cells. The instability of the stressed, commensurate parent of the discommensurate structure sets an upper bound to its surface energy; a lower bound is defined by the surface energy of an ideally commensurate but laterally strained hypothetical surface system. The surface energies of the phases of the Si(111):Ga and Ge(111):Ga systems and the energies of the discommensurations are determined within ±0.2 eV.

In the present paper we show how surface energies of discommensurate surface reconstructions, which exhibit extraordinary large unit cells or are not periodic at all, can be determined with an accuracy of a few tenths of an eV using *ab initio* calculations of much simpler structures. The method is applied to the Si(111):Ga and Ge(111):Ga systems, which display several discommensurate reconstructions.

Reconstructed surfaces can be classified according to their driving force, which is most frequently chemical.[1] When the chemistry is satisfied, surfaces can still be unstable towards rearrangements on a larger scale driven by other factors like entropy[2] or surface stress.[3-5] Stress-driven discommensurate surface structures can be found for clean surfaces, like Au(111),[6] and adsorbate systems. A rich phenomenology has been found for metals adsorbed on (111) surfaces of Si (Ref. 7) and Ge (Ref. 8) for coverages in the monolayer range.

An instability towards discommensuration arises when the parent structure (the structure prior to discommensuration) is under a sufficient compressive (tensile) surface stress.[3] A domain superstructure appears at the surface. Within domains the surface partially relaxes its stress by expanding (contracting) the surface lattice. The structure within domains resembles that of the parent structure whereas the domain walls, which allow the adjustment to the subsurface periodicity, represent defects. They are also considered as excitations if the discommensurability occurs during a commensurate-incommensurate phase transition.[2]

The discommensurate structures of adsorbates on semiconductor surfaces studied here display several characteristic differences with respect to the better-known physisorbed, discommensurate systems, like noble gases physisorbed on graphite,[9] which are understood in terms of the Frenkel-Kontorova model,[10] or with respect to the case of Au(111), which is also understood in those terms and considerations of continuum elasticity theory.[4,5] The main differences are as follows: (i) The adsorbate chemisorbs mediated by covalent, i.e., directional bonds, which represents a dramatic change of the energy scale. (ii) The chemistry changes drastically at the domain walls. (iii) The coexistence of two discommensurate phases at certain coverages suggests a first-order phase transition as function of coverage[11] [see Fig. 1(a)]. These differences indicate the need for a new qualitative understanding. As a first step, we analyze the energetics of these complicated systems.

First-principles studies of reconstructed surfaces are always computationally demanding. However, the situation for discommensurate structures is worse since the surface periodicity is lost (or the unit cell is very large) and the geometry and bonding at domain walls may not be well characterized. Here we show how to obtain surface energies of stress-driven discommensurate surface structures, using only information obtained from commensurate structures of the system. We demonstrate this for the Si(111):Ga and Ge(111):Ga systems. Each system shows two stable discommensurate phases, γ and β, very close in saturation coverages but with quite different structures [cf. Fig. 1(a)]. Both systems are very similar, i.e., $\gamma_{\rm Si}$ is very similar to $\gamma_{\rm Ge}$, and $\beta_{\rm Si}$ very similar to $\beta_{\rm Ge}$.[7,8] However, they differ substantially in the fact that a commensurate $\sqrt{3}\times\sqrt{3}R30^\circ$ phase ($\sqrt{3}$ hereafter) is stable for Si(111):Ga but not for Ge(111):Ga. This rich scenario makes these systems very interesting on their own, but is also very illustrative of the usefulness of our approach.

The first-principles method used here is based on the local-density approximation,[12] and is described in detail elsewhere.[7] A repeated slab geometry, 12 layers thick, six layers of vacuum, approximates the semi-infinite geometry of the surface. The surface energy (per surface unit cell Ω) is defined as[13]

$$E_s = (E_{\rm slab} - N_{\rm subs}E^{\rm bulk}_{\rm subs} - N_{\rm ad}E^{\rm atom}_{\rm ad})/2, \qquad (1)$$

where $E_{\rm slab}$ is the energy of the slab system per slab unit cell, $E^{\rm bulk}_{\rm subs}$ is the energy per atom of the substrate (Si or Ge) in its bulk form, $E^{\rm atom}_{\rm ad}$ is the atomic energy of the adsorbate species (Ga), and $N_{\rm subs}$ and $N_{\rm ad}$ are

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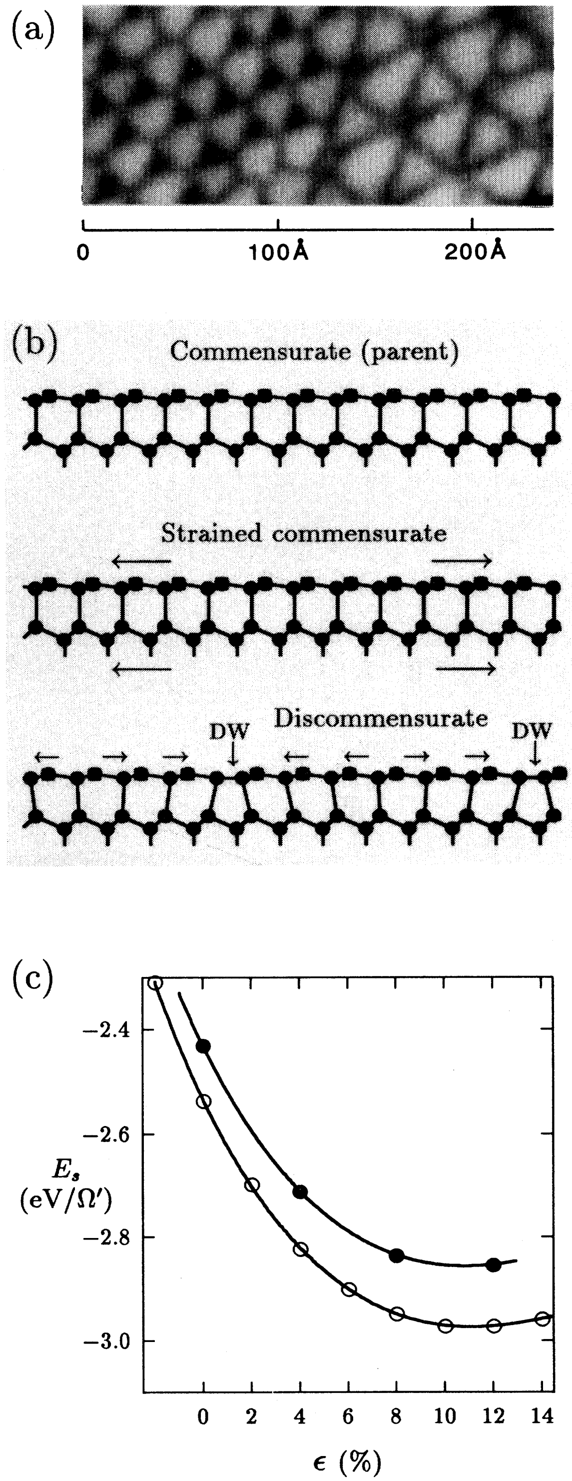

FIG. 1. (a) Scanning-tunneling-microscopy image of the γ (left) and β (right) phases coexisting on Ge(111):Ga (taken from Ref. 11). (b) Commensurate, strained commensurate, and discommensurate structures in side view. (c) Surface energy per *strained* surface unit cell (Ω') versus lateral strain for Ge(111):Ga-(1×1) with Ga substituting the surface layer, with (full circles) and without (empty circles) stacking fault at the surface. DW means domain wall.

the number of atoms of substrate and adsorbate species, respectively, per slab unit cell. The factor 1/2 reflects the presence of two surfaces per slab.

A stress-driven discommensurate structure is stabilized (versus its parent) by the energy released as the surface is allowed to relax laterally within domains. However, the energy gain is reduced by the discommensuration energy, $E_{\rm dis}$, which is always positive. Two terms contribute to $E_{\rm dis}$: (a) the energy required for creating the domain walls, which represent defects from a chemical point of view, since they disturb the otherwise preferred atomic arrangement at the surface;[14] and (b) the energy necessary to allow for the local shears that appear for a strained surface on an unstrained bulk.[4] While the exact values of these energy contributions are not accessible by current *ab initio* methods, we can calculate upper and lower bounds of the surface energy of such discommensurate systems. We start with the latter.

When the whole parent system, bulk included (the slab in this case), is strained laterally by ϵ [Fig. 1(b)], the energy of the system increases, but the surface energy $E_s^{\rm par}(\epsilon)$ decreases towards a minimum [Fig. 1(c)] at a strain value very close to the one observed experimentally within domains, $\epsilon_{\rm dis}$. In the β phases half of the domains show a stacking fault at the surface, the other half do not.[7,8] In this case $E_s^{\rm par}(\epsilon_{\rm dis})$ is half of the sum of the surface energies of both strained parent structures (with and without stacking fault). Energies are obtained from first principles by relaxing the geometry up to the fifth layer for each value of the strain.[7,8] Note that $E_{\rm subs}^{\rm bulk}$ in Eq. (1) is the energy of the substrate bulk under the same strain. Since the energies shown in Fig. 1(c) refer to the surface unit cell of the strained system Ω' they have to be corrected by the ratio of areas of Ω and Ω', giving $E_s^{\rm low} = E_s^{\rm par}(\epsilon_{\rm dis})/(1+\epsilon_{\rm dis})^2$.

The lower bound is more precisely adjusted by taking into account the small change of adsorbate coverage at the domain walls $\delta\theta_w$ (negative in the case of light walls as for Si:Ga and Ge:Ga). This is done by adding the term $E_s^{\rm par}(\epsilon_{\rm dis})\delta\theta_w/\theta_{\rm par}$, where $\theta_{\rm par}$ is the Ga coverage of the parent structure. Since $1/(1+\epsilon_{\rm dis})^2 = (\theta_{\rm dis} - \delta\theta_w)/\theta_{\rm par}$, where $\theta_{\rm dis}$ is the Ga coverage of the discommensurate structure, we obtain the following lower bound:

$$E_s^{\rm low} = E_s^{\rm par}(\epsilon_{\rm dis})\frac{\theta_{\rm dis}}{\theta_{\rm par}}. \qquad (2)$$

The energy of a discommensurate phase χ is then expressed as

$$E_s^{\chi} = E_s^{{\rm low},\chi} + E_{\rm dis}^{\chi}. \qquad (3)$$

For Si:Ga (Ref. 7) the coverages[15] are $\theta_\gamma = 0.8$ ML and $\theta_\beta = 0.9$ ML, and $\theta_\gamma = 0.7$ ML and $\theta_\beta = 0.8$ ML for Ge:Ga.[8] For the strain we use $\epsilon_{\rm dis} \approx 10\%$, similar to the experimentally observed value[7,8] and in accordance with the minima in Fig. 1(c).

Upper bounds are obtained by an analysis of the surface energy as a function of adsorbate coverage, using the fact that the unstrained, commensurate parent structures are not observed experimentally. The stability of the different phases is shown by the *convex-hull* criterion:[16] in the graph of energy versus coverage the lines joining the points representing stable, saturated surface phases define a convex curve. This treatment is strictly equivalent to the analysis based on the grand-canonical free energy as a function of adsorbate chemical potential,[17] both analyses at zero temperature. Required for this analysis and observed experimentally are well-defined saturation coverages for all the phases involved.

The only variable-coverage Ga phase that grows on the (111) surfaces of Si and Ge is bulk Ga in the form of clusters. Assuming bulklike, large clusters, their internal energy per Ga atom $\mu_{\rm Ga}$ can be approximated by the corresponding value in bulk Ga, $\mu_{\rm Ga}^{\rm bulk}$.[17] This quantity has been calculated for the stable (orthorhombic) bulk Ga phase using the same technique and approximations as for the surface calculations, giving $\mu_{\rm Ga}^{\rm bulk} = -3.45$ eV/atom ($\mu_{\rm Ga}^{\rm atom} = 0$). In the plot of surface energy versus coverage, the cluster phase appears as a straight line with slope equal to $\mu_{\rm Ga}^{\rm bulk}$. The line starts at the point associated with the stable adsorbate phase of highest coverage, since the surface energy as defined in Eq. (1) is now that corresponding to the adsorbate phase plus the cluster energy, which is equal to $\mu_{\rm Ga}^{\rm bulk}(\theta_{\rm tot} - \theta_{\rm ad})$. It should be noted that, depending on the growth conditions, Ga forms *small* clusters for coverages up to a few ML, which may increase the effective $\mu_{\rm Ga}^{\rm clus}$ (a kinetic effect).

To fulfill the convex-hull criterion, the curve that joins the points corresponding to saturation phases and ends in a line of slope $\mu_{\rm Ga}^{\rm bulk}$ has to be convex. It is more convenient to use in the diagrams the reduced energy

$$\mathcal{E}_s = E_s - \mu_{\rm Ga}^{\rm bulk}\theta_{\rm Ga}. \qquad (4)$$

The stability curve remains convex, but the cluster line now has zero slope (inset in Fig. 2). The energies for the clean, reconstructed (111) surfaces of Si (Ref. 18) and Ge (Ref. 19), and $\sqrt{3}$ phases for Si (Ref. 13) and for Ge (Ref. 20) have been taken from the literature.[21]

In Fig. 2 convex-hull diagrams are shown for Si:Ga and Ge:Ga. The bars indicate the energy range of stability for the γ and β phases, without taking into account the experimentally determined (in)stability of the $\sqrt{3}$ phases. The resulting surface energies are $E_s^\gamma = -1.90 \pm 0.32$ eV/Ω and $E_s^\beta = -2.25 \pm 0.32$ eV/Ω for Si:Ga, and $E_s^\gamma = -1.71 \pm 0.23$ eV/Ω and $E_s^\beta = -2.05 \pm 0.22$ eV/Ω for Ge:Ga. The $\pm$ gives the margins of stability for these systems, which are larger than typical errors of full first-principles calculations. However, the margins diminish with increasing domain size, since the strain is smaller. This reduces the difference in energy between parent and strained surfaces, the local shears, and the domain-wall energy per surface atom (lower density of domain walls). Thus, in particular for very large domains, where full first-principles calculations become impractical, the applicability and accuracy of our method improve. Furthermore, the *relative* energies of the discommensurate phases are more precisely defined by the convex hull criterion: $\mathcal{E}_s^\beta$ has to be within $[\mathcal{E}_s^\gamma - \delta, \mathcal{E}_s^\gamma]$, and vice versa; $\mathcal{E}_s^\gamma$ has to be within $[\mathcal{E}_s^\beta, \mathcal{E}_s^\beta + \delta]$, with $\delta \leq 0.08$ eV/Ω in this case.

We obtain important information about the discommensuration energy $E_{\rm dis}$, which is the energy increase of the discommensurate phase compared to the lower bound [cf. Eq. (3)]. As indicated in Fig. 2, $E_{\rm dis}^\gamma > E_{\rm dis}^\beta$ by at least 0.10 eV/Ω for Si and 0.14 for Ge [at most, $E_{\rm dis}^\gamma > E_{\rm dis}^\beta$ by $(0.10 + \delta)$ eV/Ω for Si, and by $(0.14 + \delta)$ eV/Ω for Ge]. This means energy differences of the order of 5–10 eV per domain. Taking into account that the contribution of the local shears to these energies is expected to be larger for β than for γ (larger domains), these results indicate that we have chemically a better bonding situation at the domain walls for β than for γ, for both Si and Ge. This agrees with the experimental

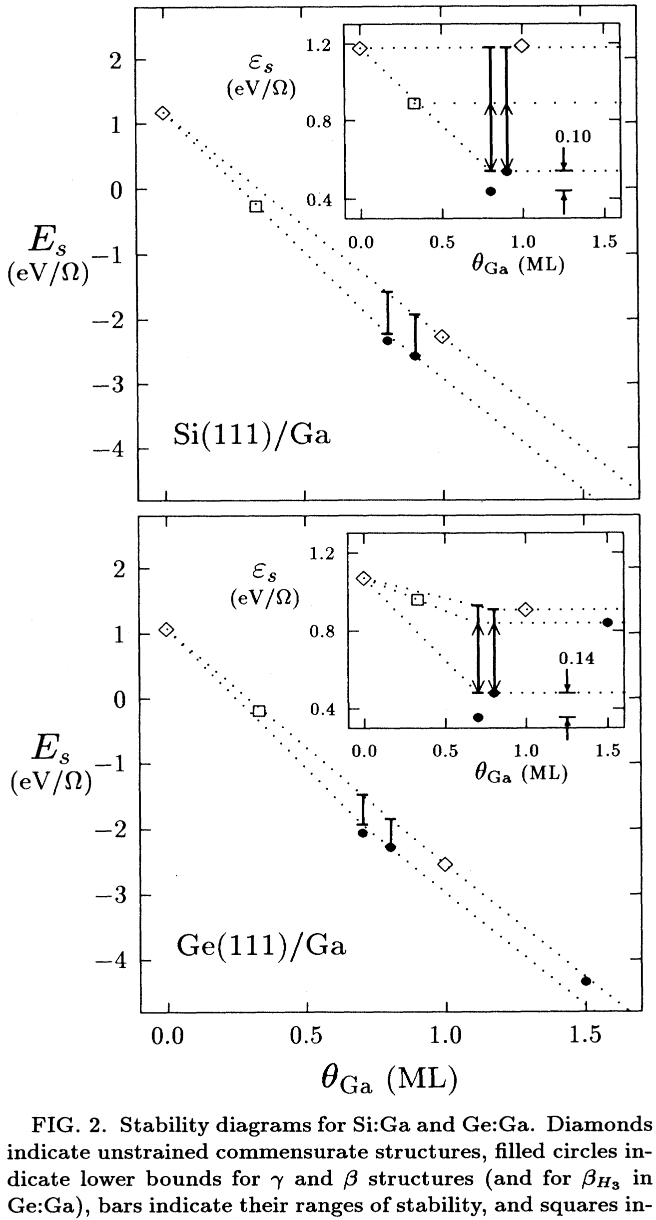

FIG. 2. Stability diagrams for Si:Ga and Ge:Ga. Diamonds indicate unstrained commensurate structures, filled circles indicate lower bounds for γ and β structures (and for β_{H_3} in Ge:Ga), bars indicate their ranges of stability, and squares indicate $\sqrt{3}$ structures. The insets show the diagrams in terms of the reduced energy [cf. Eq. (4)]. Arrows indicate ranges of stability if exploiting the knowledge about the (in)stability of the $\sqrt{3}$ phases.

findings of scanning-tunneling-microscopy measurements for Ge:Ga, showing saturated bonds, i.e., little density of states in the band-gap region at the walls for β but not for γ.[11] This is actually the factor stabilizing the β phase, a phase that is *higher* in energy *within* domains due to the presence of the stacking fault [cf. Fig. 1(c)].

The problem of the (in)stability of the $\sqrt{3}$ phases is also addressed in this analysis.[21] Figure 2 shows that the $\sqrt{3}$ phase in Si:Ga is stable, and that in Ge:Ga it is probably unstable (stable only if the energies for γ and β would be at about their upper limits).[21] Experimentally, the $\sqrt{3}$ phase has been shown to be stable for Si but not for Ge, though it can be prepared for Ge at low temperature on cleaved (111) surfaces.[23]

The surface energies of the discommensurate phases can be restricted to a narrower range if we use the information about the (in)stability of the $\sqrt{3}$ phases as input[21] (insets in Fig. 2). The new surface energies are then $E_s^\gamma = -2.05 \pm 0.18$ eV/Ω and $E_s^\beta = -2.39 \pm 0.18$ eV/Ω for Si:Ga, and $E_s^\gamma = -1.76 \pm 0.18$ eV/Ω and $E_s^\beta = -2.10 \pm 0.18$ eV/Ω for Ge:Ga with the ± giving again the margins.

For Ge:Ga and approximately 1.5 ML Ga coverage, a third discommensurate structure, β_{H_3}, has been characterized experimentally and observed to be metastable.[8] It consists of Ga adatoms covering the β phase at H_3 positions. The lower bound is calculated as for the other structures and is found to be $\mathcal{E}_s^{\mathrm{low},\beta_{H_3}} = 0.84$ eV/Ω. It is just on the limit of stability (see Fig. 2). The surface strain present in the underlying β structure is an essential ingredient for the appearance of β_{H_3} versus other possible adlayer structures (see Fig. 8 in Ref. 8). Its existence can be understood in terms of an energy barrier toward the formation of large Ga clusters (see above) and may furthermore suggest that the energies for γ and β are closer to their upper than to their lower bounds. As discussed in detail earlier,[8] we believe that this structure mediates an easy transition from γ to β.

In summary, we have shown how to assess the surface energy of discommensurate surface phases. Based on first-principles calculations of much simpler, commensurate structures and on stability considerations we obtain upper and lower bounds. We have demonstrated this approach for Si:Ga and Ge:Ga. The (in)stability of the $\sqrt{3}$ phases has also been addressed and values for the energies of the discommensurations have been obtained. This information is particularly important for understanding the phase diagram of these systems.

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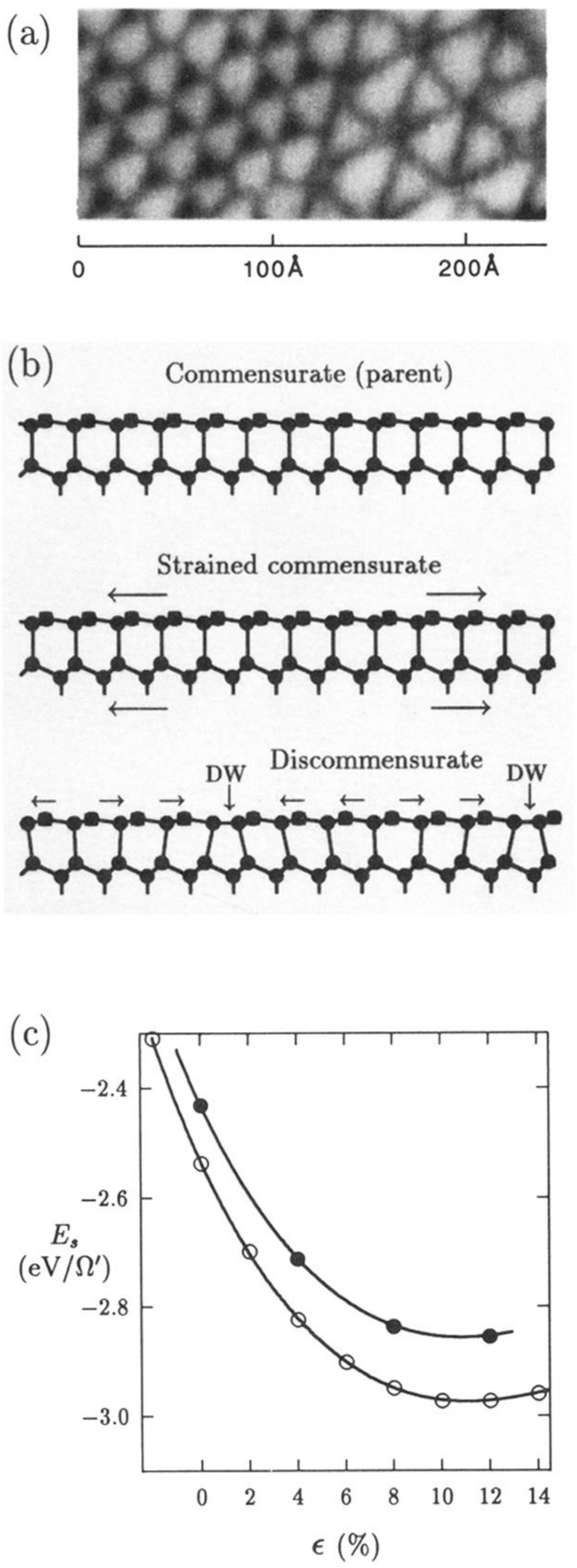

FIG. 1. (a) Scanning-tunneling-microscopy image of the γ (left) and β (right) phases coexisting on Ge(111):Ga (taken from Ref. 11). (b) Commensurate, strained commensurate, and discommensurate structures in side view. (c) Surface energy per *strained* surface unit cell (Ω') versus lateral strain for Ge(111):Ga-(1×1) with Ga substituting the surface layer, with (full circles) and without (empty circles) stacking fault at the surface. DW means domain wall.