Dislocation formation from a surface step in semiconductors: an ab initio study

Julien Godet, Sandrine Brochard, Laurent Pizzagalli, Pierre Beauchamp, Jose M. Soler

▶ **To cite this version:**

Julien Godet, Sandrine Brochard, Laurent Pizzagalli, Pierre Beauchamp, Jose M. Soler. Dislocation formation from a surface step in semiconductors: an ab initio study. Physical Review B: Condensed Matter and Materials Physics (1998-2015), 2006, 73 (9), pp.092105. 10.1103/PhysRevB.73.092105 . hal-00170873

HAL Id: hal-00170873
https://hal.science/hal-00170873

Submitted on 10 Sep 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Dislocation formation from a surface step in semiconductors: an *ab initio* study

J. Godet,[1,*] S. Brochard,[1] L. Pizzagalli,[1,†] P. Beauchamp,[1] and J. M. Soler[2]

[1]*Laboratoire de Métallurgie Physique, UMR 6630, Université de Poitiers, B.P. 30179, 86962 Futuroscope Chasseneuil Cedex, France*

[2]*Dep. de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

(Dated: September 11, 2007)

The role of a simple surface defect, such as a step, for relaxing the stress applied to a semiconductor, has been investigated by means of large scale first principles calculations. Our results indicate that the step is the privileged site for initiating plasticity, with the formation and glide of 60° dislocations for both tensile and compressive deformations. We have also examined the effect of surface and step termination on the plastic mechanisms.

PACS numbers: 61.72.Lk, 07.05.Tp, 02.70.Ns, 68.35.Gy
Keywords: dislocation; silicon; simulation; surface step

hal-00170873, version 1 - 10 Sep 2007

The plasticity of semiconductors has been extensively studied for the last decades in both fundamental and applied research, leading to significant progresses in the understanding of the key mechanisms involved. Several issues remain unsolved, however, one of the most essential being the formation of dislocations in nanostructured semiconductors such as nano-grained materials, or nanolayers in heteroepitaxy, systems extensively used in devices. While in bulk materials the few native dislocations are able to multiply via Frank-Read type mechanisms to ensure plasticity, the situation is different in nanostructured materials where dimensions are too small to allow dislocation multiplication [1]. The presence of dislocations in these materials appears to be more controlled by nucleation than by multiplication processes. It has been proposed that surfaces and interfaces, which become prominent for small dimensions, play a major role. Several observations support this assumption, especially for strained layers and misfit dislocations at interfaces [2, 3, 4]. The formation at surfaces is also relevant where large stresses exist, like near a crack [5, 6, 7, 8, 9].

Since *in situ* experimental observations of dislocation nucleation is not yet possible due to the very small dimensions and short observation timescales, the formation of dislocations at surfaces has been mainly investigated theoretically, particularly with continuum models and elasticity theory [10, 11, 12]. However, in these approaches, the predicted activation energy is very large, in disagreement with experiments. It has been proposed that surface defects, such as steps, help the formation by lowering the activation energy. This is supported by experimental facts in the context of dislocation nucleation at or near crack fronts, with dislocation sources located on the cleavage surface and coinciding with cleavage ledges [13, 14, 15, 16]. In addition, it has been shown that, in a stressed solid, a surface step is a source of local stress concentration [17, 18, 19], although not as efficient as a crack tip. Therefore, a number of continuum models have been developed, taking into account the energy gain associated to the step elimination in the process of dislocation nucleation [20, 21, 22, 23]. Atomistic calculations have also been performed for characterizing the energetics, the processes involved, and the role of surface defects [24, 25, 26, 27, 28, 29, 30].

These studies led to a better knowledge of the dislocation formation from surface steps or cleavage ledges, but we are still far from a complete understanding of the phenomenon. Furthermore, studies were mostly focussed on ductile materials, such as metals, using empirical potentials. In contrast, there is a certain lack of knowledge regarding semiconductors, for which a different behavior is expected. Also, the role of the step has not been identified. Another point of concern is the interatomic potential for modeling dislocations. While sufficiently reliable potentials have been developed recently for some metals, the same is not yet true for a model semiconductor such as silicon [31, 32].

In this work, we report investigations of the dislocation formation from a surface step in a stressed semiconductor, here silicon. An *ab initio* approach has been employed because of the insufficient reliability of empirical potentials for modeling the rearrangement of atomic bonds that occurs during the formation and propagation of dislocations. Our calculations clearly indicate that a step is a privileged site for initiating plastic deformation. Indeed, a 60° dislocation forms from the step both in compression and traction simulations. We also show the importance of surface and step termination, finding that the dislocation forms below the surface when the surface and the steps are passivated.

Our calculations use density functional theory, in the local density approximation, and norm-conserving pseudopotentials [33]. We have used the SIESTA method [34, 35] with a basis set of atomic orbitals. In order to simulate the largest possible systems, we searched carefully the least expensive basis, able to accurately model the dislocation formation. We used a minimal basis of optimized orbitals with a maximum range of 6 Å . The grid for numerical integration in real space has an energy cutoff of 150 Ry. Two or four special k-points [36] were

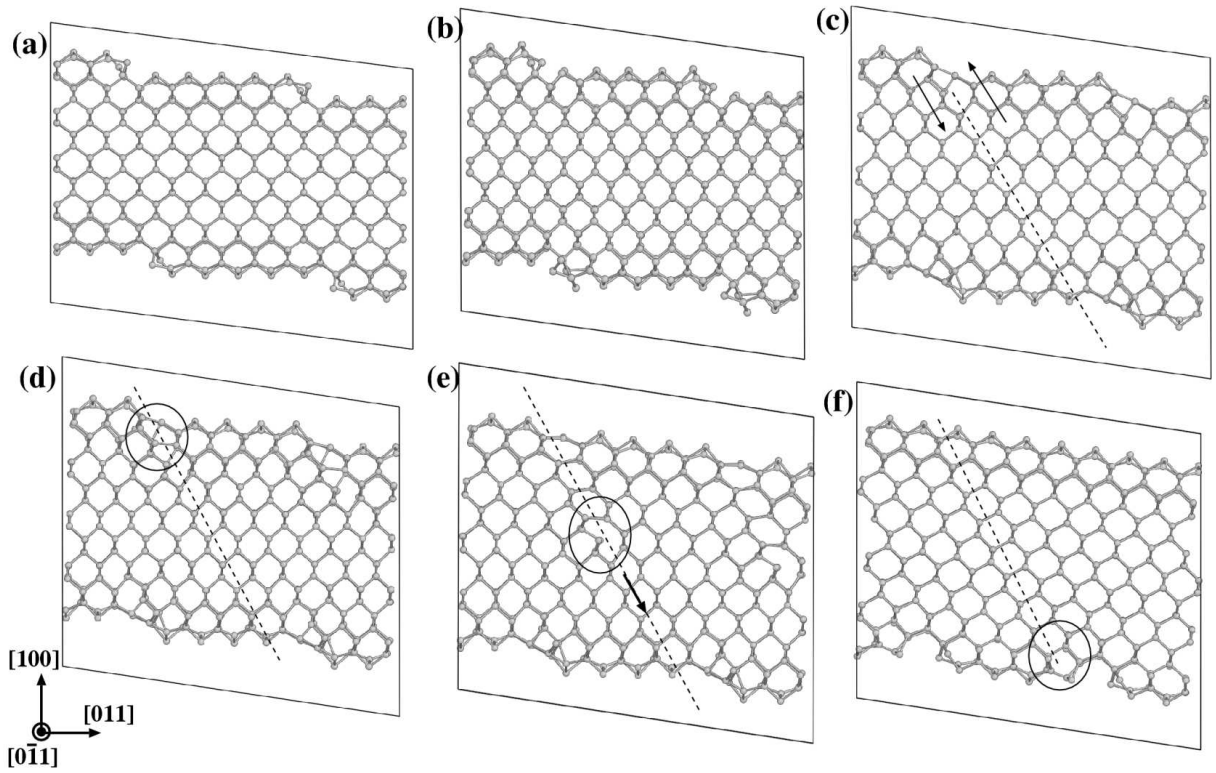

FIG. 1: Different stages of the compression process for a 196 atoms unit cell: (a) Unstrained system, (b) strain of −10.4%, (c) strain of −11.5%, (d-f) strain of −13.6%. The dashed line shows the shuffle plane where the dislocation glides. Two unit cells are drawn for clarity.

used for the Brillouin zone sampling, depending on the size of the system. These parameters lead to accurate values for the lattice parameter and elastic coefficients. Another test was the energy variation when bulk silicon is strained along the {111} dense planes in the ⟨110⟩ direction, the direction of Burgers vector dislocations in the diamond cubic structure [37]. The calculated shear strength is 28% larger than the one obtained with another basis, more accurate but much more expensive, but it is reached for the same shear strain [32]. Therefore we expect that the minimal basis set is adequate to study the mechanisms of dislocation formation.

A typical model used in our simulations is shown in Figure 1-a. The slab includes two (100) surfaces, with a p(2×1) reconstruction of asymmetric dimers. Steps lying along the [0$\bar{1}$1] directions, which correspond to the intersection of {111} slip planes and the (100) surface, are placed on both surfaces. We have used double layer steps, as formed by the emergence of a perfect dislocation at the surfaces [38]. Tilted periodic boundary conditions are applied normal to the step direction, in order to have only one step on each surface. For the periodic boundary conditions along the step line direction [0$\bar{1}$1], four atomic planes are considered, allowing the p(2×1) reconstruction. The total number of atoms in the system ranged from 124 to 508, depending on the number of layers along [100] and [011], the normals to the step line. We impose an increasing uniaxial stress contained in the surface and making an angle α with the step normal [011], by applying a strain. We have shown previously from Schmid factor analysis and empirical potential calculations that $\alpha = 22.5°$ was the easiest orientation to form dislocations [38], then unless explicitly stated the results presented here are for this stress orientation. After each stress increment of 1.5 GPa ($\sim 1\%$ deformation), the atomic positions were relaxed with a conjugate gradient algorithm until the atomic forces were lower than 0.04 eV/Å. The relaxed configurations are then relevant for a crystal at 0 K.

The short period along the step direction allows only for the formation of straight defects, no half-loop dislocations or even kinks can form. However, there is no *a priori* restriction on the type of straight dislocation, either perfect or partial, in the shuffle set or the glide set [39]. These simulations are representative of the low temperature behavior.

For a D_B non rebonded step [40], we found that the 196 atoms system behaves elastically up to a compressive strain of −13.6%, which corresponds to a linear stress of 19.5 GPa= $0.16G$, G being the shear modulus (Fig. 1). This is lower than the theoretical shear strength calculated using the same method, $0.21G$. At

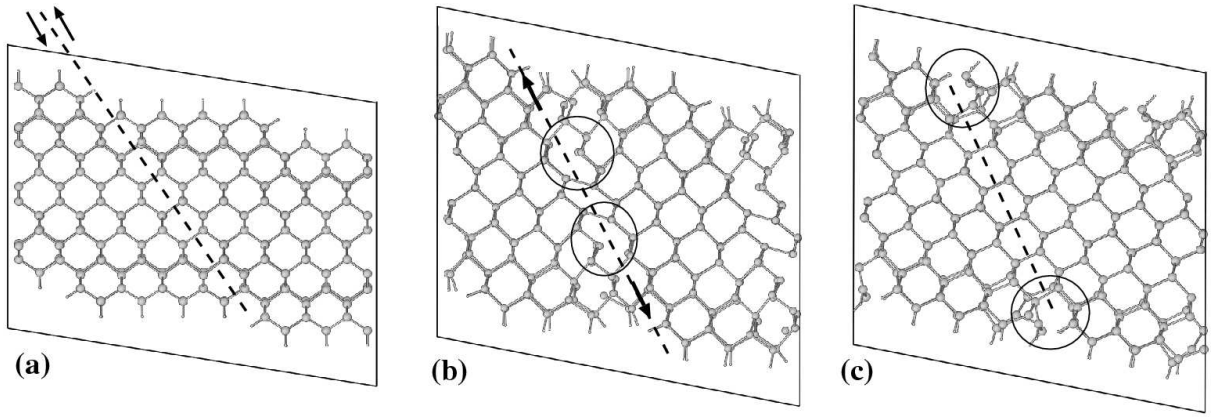

FIG. 2: Different stages of the compression process for a 128 atoms system, with surfaces passivated with hydrogen atoms (white balls). (a) Unstrained system projected along $[0\bar{1}1]$, (b-c) -16.7% of strain, formation and glide of a dislocation dipole in bulk associated with the shear strain of the (111) shuffle set plane crossing the steps. Two unit cells are drawn for clarity.

-11.5% there is first a formation of bonds between the atoms of the step edges and those of the lower terraces (Fig. 1-c). Then at -13.6%, as relaxation continues, a defect is formed which, through successive breaking and formation of bonds, glides from the top to the bottom surface (Fig. 1-d,e). Finally, a new step forms on the bottom surface, leaving a now perfect top surface (Fig. 1-f). An analysis revealed that a perfect 60° dislocation formed and slipped on the {111} shuffle plane that passes through the step edge of the top surface. The process removes almost all of the applied stress, with only 1.5 GPa remaining. This stress value corresponds roughly to the deformation increment of 1%. It is likely that this remaining stress could be reduced by using smaller increments.

Qualitatively, we found quite similar results for traction. Plasticity occurred at 21.9% (31.5 GPa= $0.26G$) with several atomic rearrangements in the vicinity of one step, leading to a locally disordered crystal. Then, a 60° dislocation formed from this area and slipped in a shuffle plane toward the opposite surface. Therefore, our results clearly indicate that surface steps facilitate the formation of dislocations in covalent materials. As a consequence, the elastic limit is lowered, compared to the bulk or to the perfect surface. The step breaks the surface symmetry and facilitates the nucleation of plastic events in its vicinity. This effect may be attributed either to a stress concentration or to a local reduction of elastic constants. A deeper analysis is difficult, since both contributions are intimately linked.

In order to check whether the step geometry has an effect on the kind of formed dislocation, a calculation with a D_B rebonded step has also been carried out. This step can be thought as formed by the emergence at the surface of a perfect dislocation located in a glide set plane, followed by surface reconstruction. In that case a 60° perfect dislocation is also nucleated in the shuffle set plane near the step, but for a larger strain (16.7%), as already observed with classical empirical potentials calculations for $\alpha = 0°$ [44]. Thus this suggests that for all step geometries, a 60° perfect dislocation is nucleated in a shuffle set plane for this stress orientation. Such a result may be surprising, since it is known that plasticity of silicon deformed at high temperature is governed by dissociated dislocations located in the glide set. In that case, dislocations move with the formation and migration of double kinks. However, it has been shown that in the low temperature/high stress regime, the plasticity is dominated by perfect dislocations located in shuffle planes [7, 41, 42]. Also, theoretical investigations suggest that the Peierls stress is lower for a shuffle than for a glide dislocation [43]. Our results are then in agreement with experiments and with bulk calculations.

The influence of system size was checked by performing additional simulations with 124 and 508 atoms. For the smaller size the elastic limit was slightly larger, -14.6%, whereas it remains at -13.6% for the larger size. These results are consistent with the trend obtained from potential calculations, the elastic limit being larger for smaller systems [38]. However, this effect is very small and there were no noticeable differences on the dislocation formation process, suggesting that 196 atoms are enough. The suitability of the minimal basis was checked by performing simulations with the smaller system and the more accurate basis, leading to similar results. We also investigated the influence of the relative positions of the steps on the top and bottom surfaces. In figure 1, the two step edges belong to two distant shuffle planes, what results in two opposite steps on the bottom surface after relaxation. We built a 128 atoms system with steps lined up in the same shuffle plane. Under similar conditions, we found the same behavior than with the 124-atom system, though with a slightly larger elastic limit of -15.6%. Thus, both the effects of system size and

step location appear to be negligible for the process of dislocation formation.

In a previous study, using classical potentials, we had investigated the influence of several parameters such as the step height and the orientation of the applied stress [38]. We found that the step height has only a quantitative effect, a higher step lowering the elastic limit. Such an investigation implies several simulations with larger systems, and is beyond the scope of the present work. However, we expect this conclusion to remain valid in our case. Regarding stress orientation, it has been shown that a perfect 60° dislocation is nucleated for a wide range of stress orientations, in agreement with a Schmid factor analysis [38]. However, an intriguing case is $\alpha = 45°$, for which the Schmid factors are equal for screw and 60° dislocations. We have performed the simulation in compression for this orientation, finding that plasticity occurs at -20.2%. The analysis of atomic displacements is difficult in this case. Some atoms are displaced according to the formation of a 60°, and others according to the formation of a screw dislocation. However, we were unable to clearly identify dislocations segments.

An important factor in the process of dislocation formation is the surface and step termination. In fact, in compression, the formation of bonds between the step atoms and the lower terrace leads to an easier nucleation, starting from the step edge. In traction, dislocation formation also occurred in the vicinity of the step. Therefore, surface and step termination are expected to play a key role in realistic surfaces. We have then simulated a system of 128 Si atoms, whose surfaces and steps were passivated with hydrogen atoms (Fig. 2). In that case, the dimers of the p(2×1) surface reconstruction are symmetric. The system is elastically strained up to -16.7%, so that the shuffle plane passing through the step edge is increasingly sheared. In that case, however, the hydrogen atoms prevent the formation of bonds between step edge atoms and the terrace, and plasticity first occurred inside the slab with the formation of a dislocation dipole, each dislocation moving progressively towards one surface. Thus, the relaxation mechanism clearly depends on the surface and step state, with or without hydrogen atoms. However, it is noteworthy that the calculated elastic limits remain very similar.

In this work, we have considered a (100) surface. For the cubic diamond structure, another important surface orientation is (111). A simple Schmid factor analysis suggests that larger applied stresses would be required for forming dislocations. In addition, the same analysis suggests that a screw dislocation would be nucleated for the (111) surface instead of a 60° dislocation.

In conclusion, we have investigated the process of dislocation formation from surface steps in a stressed covalent solid, using first principles calculations. Our study has been restricted to two-dimensional systems, in the context of athermal nucleation at 0K. It has been shown that a simple surface defect, such as a step, facilitates the formation of dislocations, by lowering the elastic limit and initiating the plastic deformation. For the orientations considered, perfect 60° dislocations were nucleated, in agreement with a previous analysis [38]. It has also been shown that, with passivated steps and surfaces, the formation mechanism is different but occurs for similar applied strains. Overall, the elastic limits are reached for very large applied stresses, much higher than expected in experiments. However, it is very likely that thermal activation and higher defects will considerably decrease these stresses, while preserving the formation mechanisms. Performing *ab initio* finite temperature molecular dynamics for these systems remains presently a huge task, but it is obviously the next goal to attain in the future.

Acknowledgements

The authors thank the Psi-K network for financial support of this work, and J. Junquera and E. Anglada in the SIESTA group for providing localized orbitals basis.

* Current address: EPFL, IRRMA, Bât. PPH 332 (CRPP), Station 13, CH - 1015 Lausanne, Switzerland
† Electronic address: Laurent.Pizzagalli@univ-poitiers.fr

[1] A. Moulin, M. Condat, and L. P. Kubin, Phil. Mag. A **79**, 1995 (1999).
[2] J. Dunstan, J. Mater. Sci.: Materials in Electronic **8**, 337 (1997).
[3] S. C. Jain, A. H. Harker, and R. A. Cowley, Phil. Mag. A **75**, 1461 (1997).
[4] R. X. Wu and G. C. Weatherly, Phil. Mag. A **81**, 1489 (2001).
[5] Y. Q. Wu and Y. B. Xu, Phil. Mag. Lett. **78**, 9 (1998).
[6] C. Scandian, H. Azzouzi, N. Maloufi, G. Michot, and A. George, Phys. Stat. Sol. A **171**, 67 (1999).
[7] J. Rabier, P. Cordier, J. L. Demenet, and H. Garem, Mater. Sci. Eng. A **A309-A310**, 74 (2001).
[8] P. Pirouz, J. L. Demenet, and M. H. Hong, Phil. Mag. A **81**, 1207 (2001).
[9] P. Pirouz, A. V. Samant, M. H. Hong, A. Moulin, and L. P. Kubin, J. Mar. Res. **14**, 2783 (1999).
[10] F. C. Frank, in *Symposium on plastic deformation of crystalline solids* (Carnegie Institute of Technology, Pittsburgh, 1950), p. 89.
[11] S. V. Kamat and J. P. Hirth, J. Appl. Phys. **67**, 6844 (1990).
[12] G. E. Beltz and L. B. Freund, Phys. Stat. Sol. (b) **180**, 303 (1993).
[13] A. George and G. Michot, Mater. Sci. Eng. **A164**, 118 (1993).
[14] G. Michot, H. Azzouzi, N. Maloufi, M. L. de Oliviera, C. Scandia, and A. George, in *Multiscale Phenomena in plasticity*, edited by J. Lépinoux, D. Mazière, V. Pontikis, and G. Saada (Kluwer Academic Publishers, Dordrecht,

1999), vol. 367 of *NATO ASI Series E: Applied Sciences*, p. 117.
[15] B. J. Gally and A. S. Argon, Phil. Mag. A **81**, 699 (2001).
[16] A. S. Argon and B. J. Gally, Scripta Materialia **45**, 1287 (2001).
[17] D. M. Marsh, *Fracture of Solids* (Interscience, 1963), p. 119.
[18] E. Smith, Int. J. Engng. Sci. **6**, 9 (1968).
[19] A. G. Cullis, A. J. Pidduck, and M. T. Emeny, J. Cryst. Growth **158**, 15 (1996).
[20] K. Jagannadham and J. Narayan, Mater. Sci. Eng. **B8**, 107 (1991); J. Electron. Mater. **20**, 767 (1991).
[21] G. E. Beltz and L. B. Freund, in *Thin Films: Stresses and Mechanical Properties V. Symposium*, edited by S. P. Baker, C. A. Ross, P. H. Townsend, C. A. Volkert, and P. Borgesen. (Mater. Res. Soc, Pittsburgh, 1995), p. 93.
[22] J. Zou and D. J. H. Cockayne, J. Appl. Phys. **79**, 7632 (1996).
[23] N. Junqua and J. Grilh, Phil. Mag. Lett. **75**, 125 (1997).
[24] A. S. Nandedkar, Acta Metall. Mater. **41**, 3455 (1993).
[25] M. Ichimura and J. Narayan, Phil. Mag. A **72**, 297 (1995); Mater. Sci. Eng. B **31**, 299 (1995).
[26] Y.-M. Juan, Y. Sun, and E. Kaxiras, Phil. Mag. Lett. **73**, 233 (1996).
[27] J. A. Zimmerman and H. Gao, Mat. Res. Soc. Symp. Proc. **399**, 401 (1996).
[28] A. Aslanides and V. Pontikis, Phil. Mag. Lett. **78**, 377 (1998).
[29] L. Dong, J. Schnitker, R. W. Smith, and D. J. Srolovitz, J. Appl. Phys. **83**, 217 (1998).
[30] S. Brochard, P. Beauchamp, and J. Grilhé, Phil. Mag. A **80**, 503 (2000); Phys. Rev. B **61**, 8707 (2000).
[31] L. Pizzagalli, P. Beauchamp, and J. Rabier, Phil. Mag. A **83**, 1191 (2003).
[32] J. Godet, L. Pizzagalli, S. Brochard, and P. Beauchamp, J. Phys.: Condens. Matter **15**, 6943 (2003).
[33] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[34] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996).
[35] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[36] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[37] J. P. Hirth and J. Lothe, *Theory of dislocations* (Wiley, New York, 1982).
[38] J. Godet, L. Pizzagalli, S. Brochard, and P. Beauchamp, Phys. Rev. B **70**, 054109 (2004).
[39] There are two inequivalent {111} planes in the diamond cubic structure, the widely spaced shuffle and the narrowly spaced glide [37].
[40] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).
[41] J. Rabier *et al.*, J. Phys.: Condens. Matter **12**, 10059 (2000); Scripta Materialia **45**, 1259 (2001).
[42] T. Suzuki *et al.*, Phil. Mag. Lett. **77**, 173 (1998); Phil. Mag. A **79**, 2637 (1999);
[43] L. Pizzagalli and P. Beauchamp (unpublished).
[44] J. Godet, L. Pizzagalli, S. Brochard, and P. Beauchamp, Scripta Materialia **47**, 481 (2002).