A mechanism of inhibition of phase transitions in nano-grained close-packed Pd thin films

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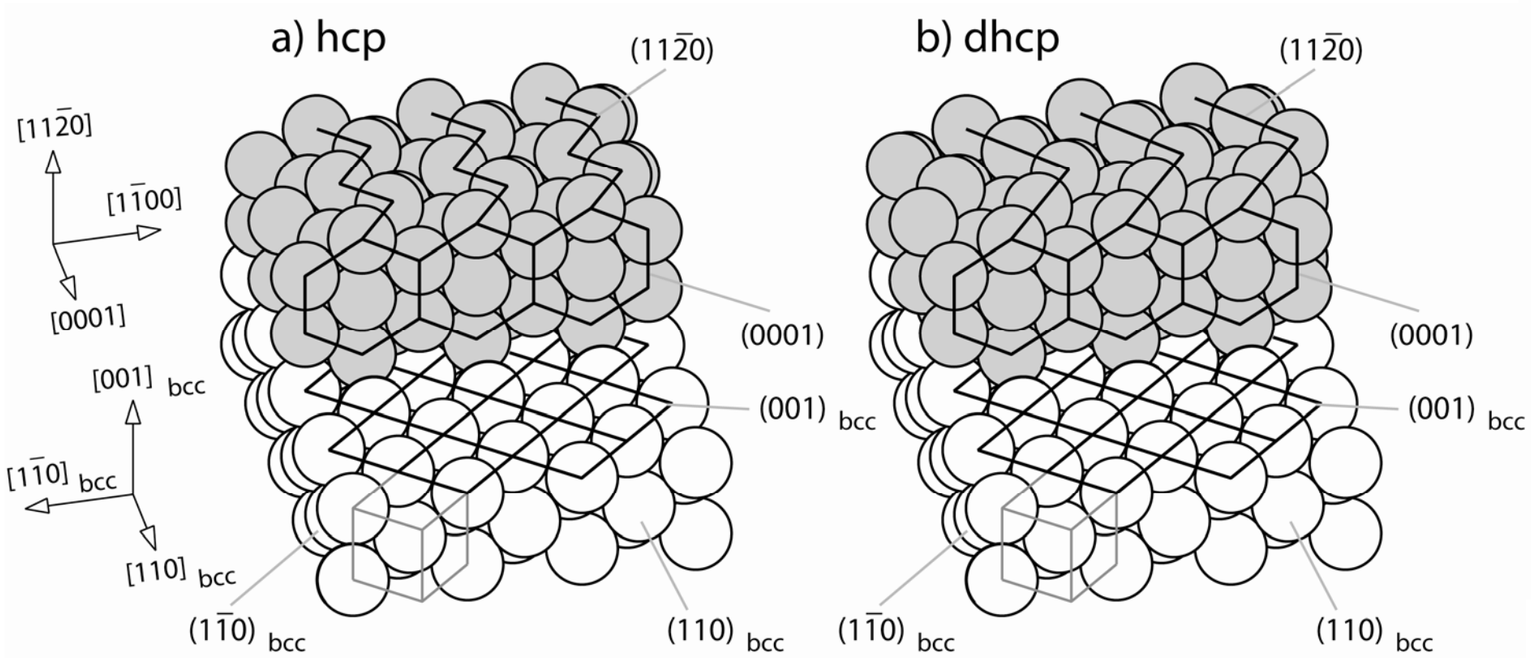
Motivation

Mechanical behavior of materials can be tailored by introducing microstructural obstacles (such as grain boundaries) to dislocation motion [1]. In some cases, such obstacles may even inhibit a phase transformation from a higher-energy configuration back into the ground-state phase [2-4]. Here we explain how a grain boundary network can block the change of the crystal structure inside Pd nanograins [4].
In nanocrystalline materials, both higher-temperature phases at low temperature and lower-temperature phases at high-temperature have been observed. The obstacles (of any kind) may increase the energy barrier inhibiting the transformation.

Pd nanograins on W(001)

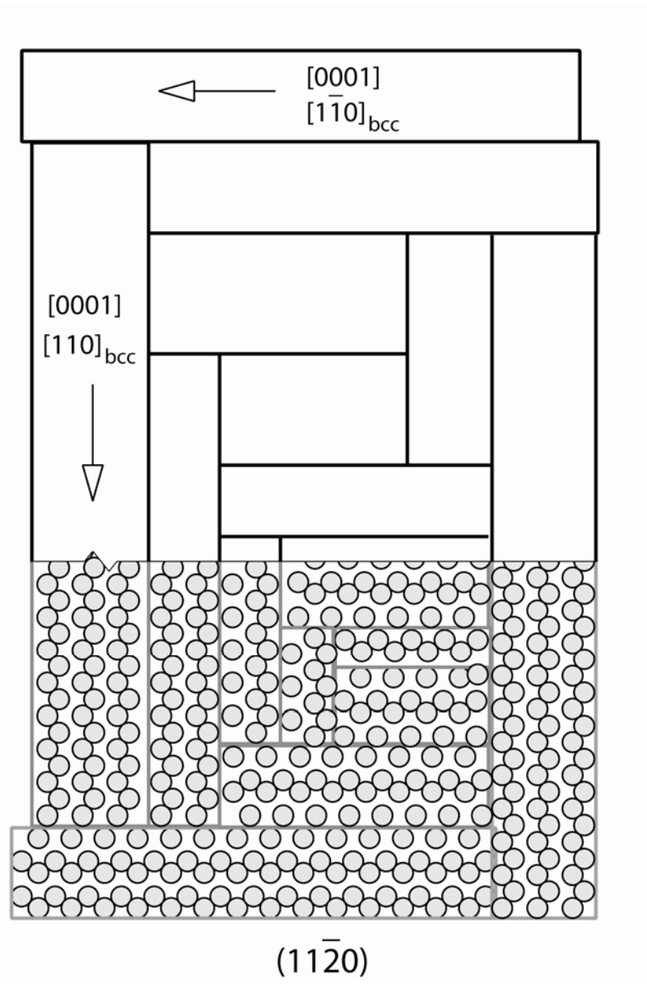
First stage of their growth is pseudomorphic with the bcc W substrate. Then hcp islands of Pd appear. They further grow in the form of an orthogonal set of rectangular domains. After annealing the Pd film at 400 K the initial hcp structure changes to dhcp [5]. The hcp and dhcp structures are higher-energy phases, while the fcc structure is ground-state structure of Pd



Epitaxial relationship of Pd films on W(001) cubic substrate:

hcp $(11\bar{2}0)$ || bcc(001) and hcp[0001] || bcc⟨110⟩ (top)

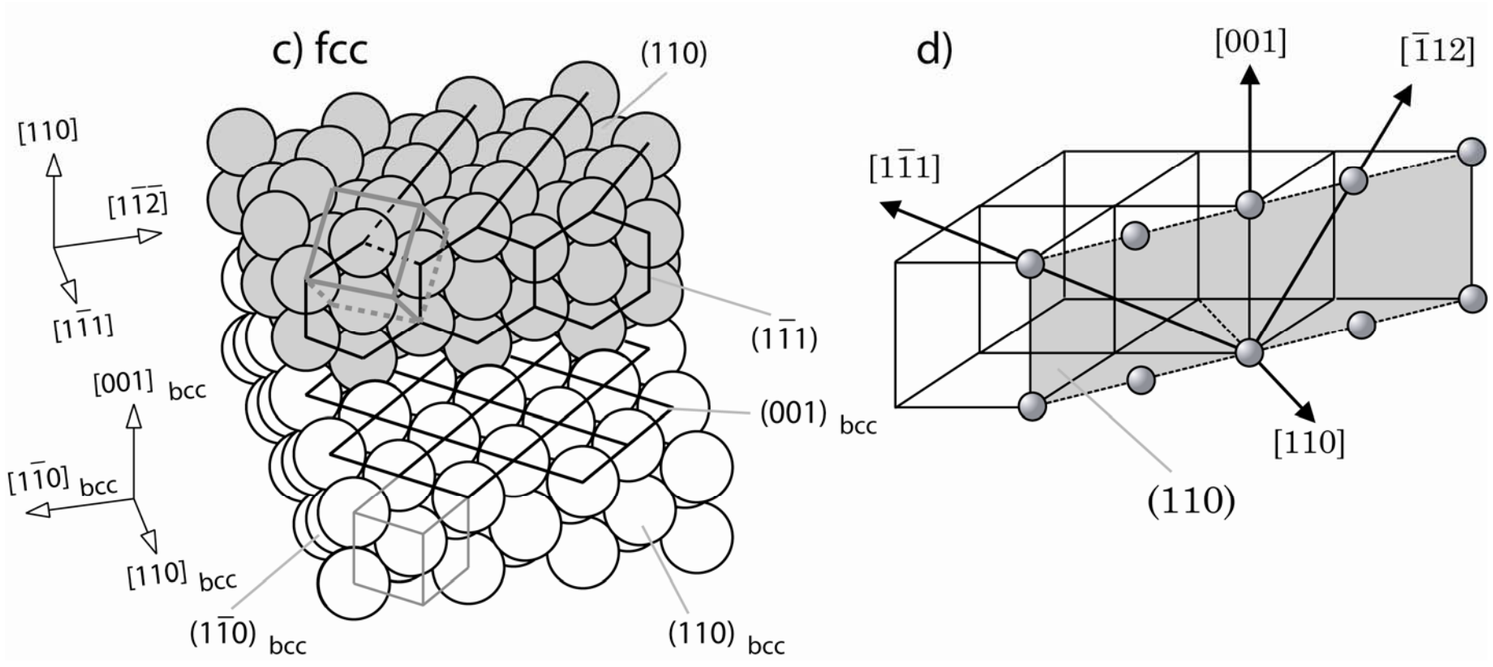
The Pd close-packed planes lie perpendicular to the substrate



The epitaxial misfit can control the Pd structure during growth

The *expected* epitaxial relationship of ground-state fcc Pd film on W(001) cubic substrate is
fcc(110) || bcc(001) and
fcc ⟨111⟩ || bcc⟨110⟩. (right).

This configuration is, however, not experimentally observed in Pd thin films on cubic substrates. Why?



Calculational methods

We have used the full-potential Linearized Augmented Plane Waves (FLAPW) method implemented in the WIEN2k code. For exchange-correlation energy. both local density approximation (LDA) and generalized gradient approximation (GGA) were used. They both yield similar results for Pd structures.

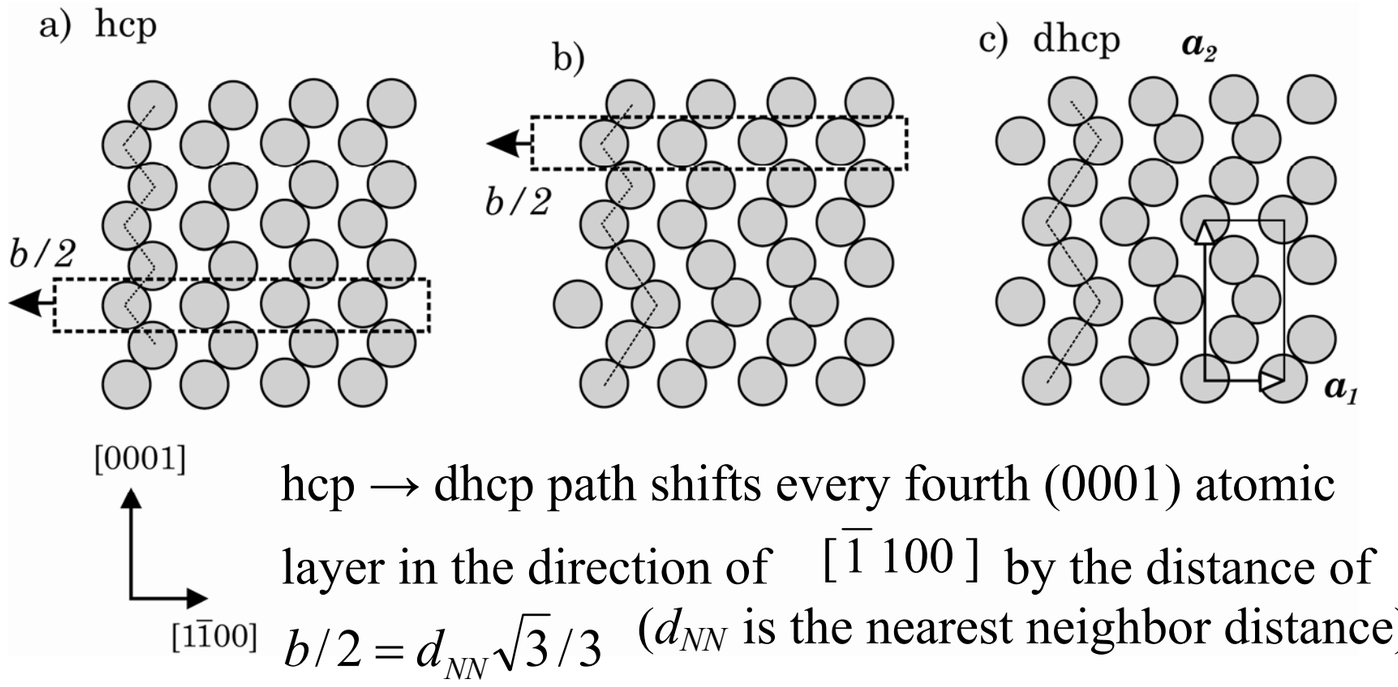
Proposed transformation paths:

hcp → dhcp (path 4)
hcp → fcc (paths 1-3)
The paths are described using bulk primitive unit cell. This cell is deformed (hcp → fcc paths 1-2) or remains fixed in space (hcp → fcc path 3, hcp → dhcp path)

Transformation path hcp → dhcp

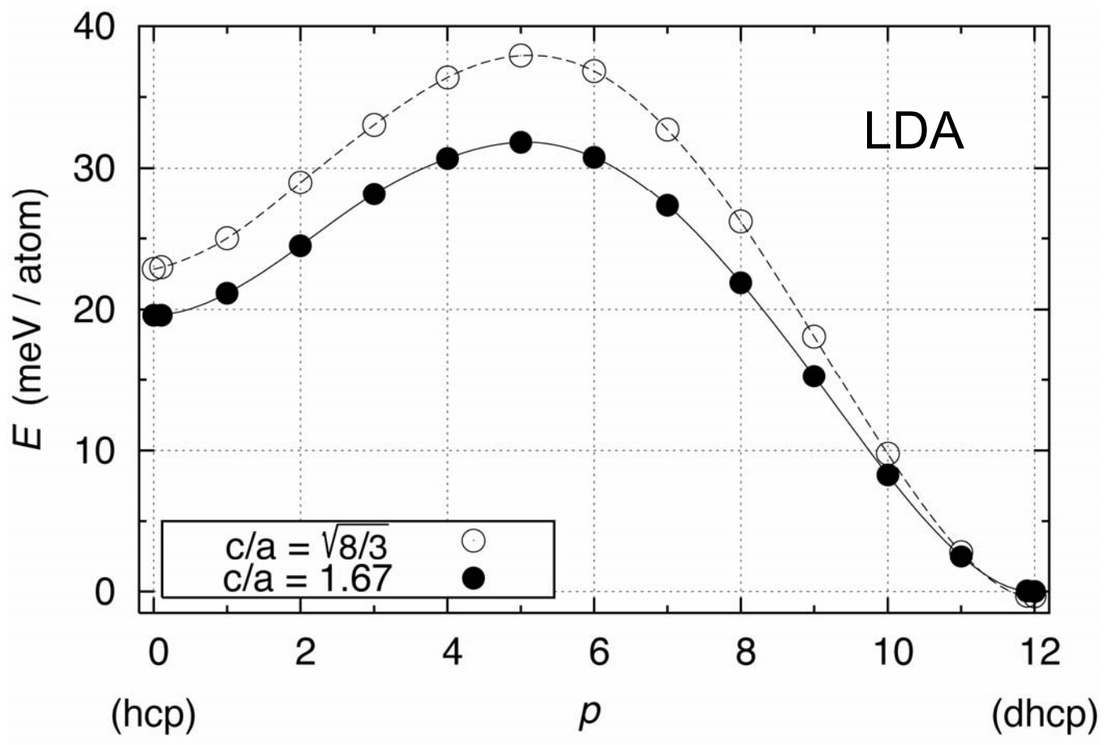
Figs. (a) - (c) show $(11\bar{2}0)$ atomic planes of the Pd adsorbate.

The (bulk) unit cell is shown in Fig. (c) - vectors $\boldsymbol{a_1}$, $\boldsymbol{a_2}$, (vector $\boldsymbol{a_3}$ is perpendicular to the plane of the figure)



hcp → dhcp path shifts every fourth (0001) atomic layer in the direction of $[\bar{1}100]$ by the distance of $b/2 = d_{NN}\sqrt{3}/3$ (d_{NN} is the nearest neighbor distance)

Total-energy profile of the hcp → dhcp path

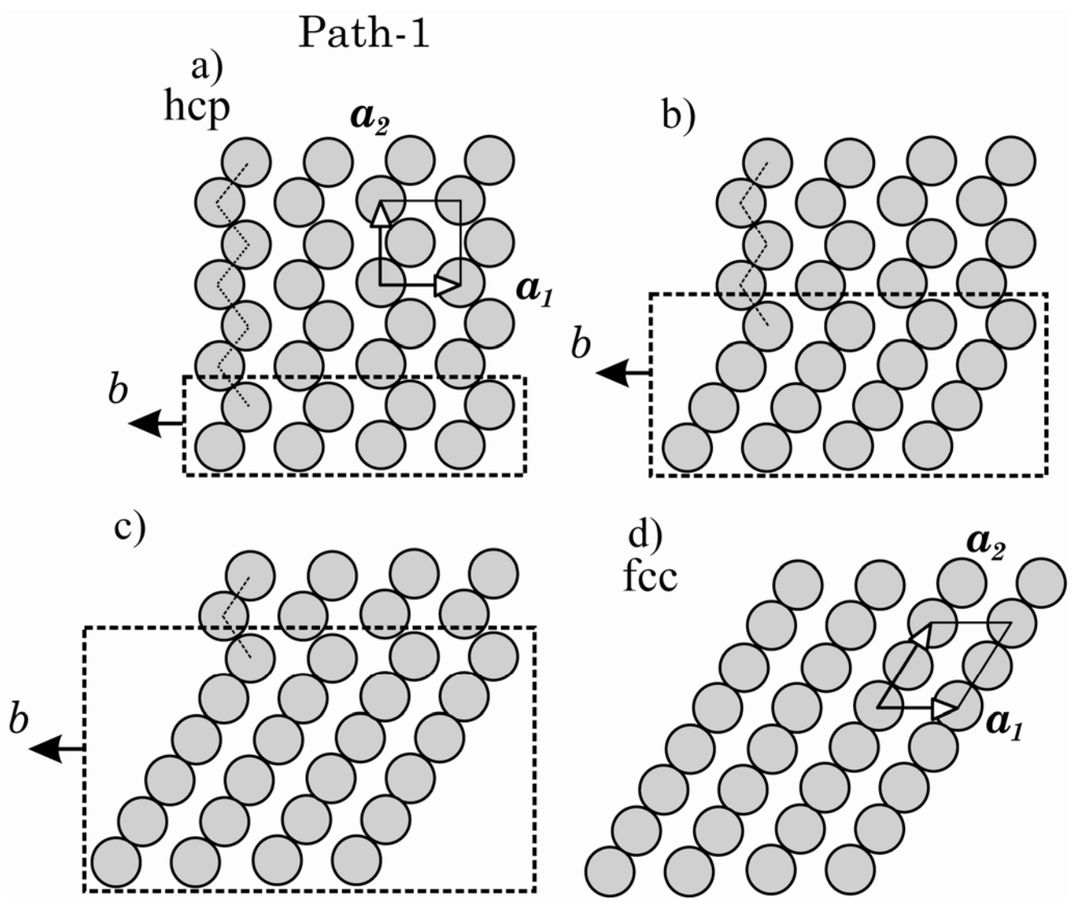


Energy barrier from hcp to dhcp
(at experimental *c/a*) is ΔE =16.8 meV/atom (GGA)
or 12.2 meV/atom (LDA), respectively.
An estimate of the transformation temperature by
$T = \Delta E / k_B$ yields T = 195 K (or 142 K).

This transformation is experimentally observed

Three proposed hcp → fcc paths: Path-1 (right)

The hexagonal (0001) double layers are shifted by the distance of $b = 2d_{NN}\sqrt{3}/3$ in the $[\bar{1}100]$ direction.

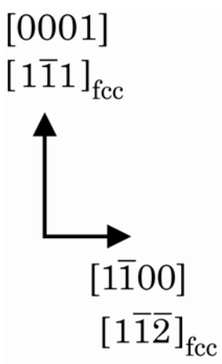


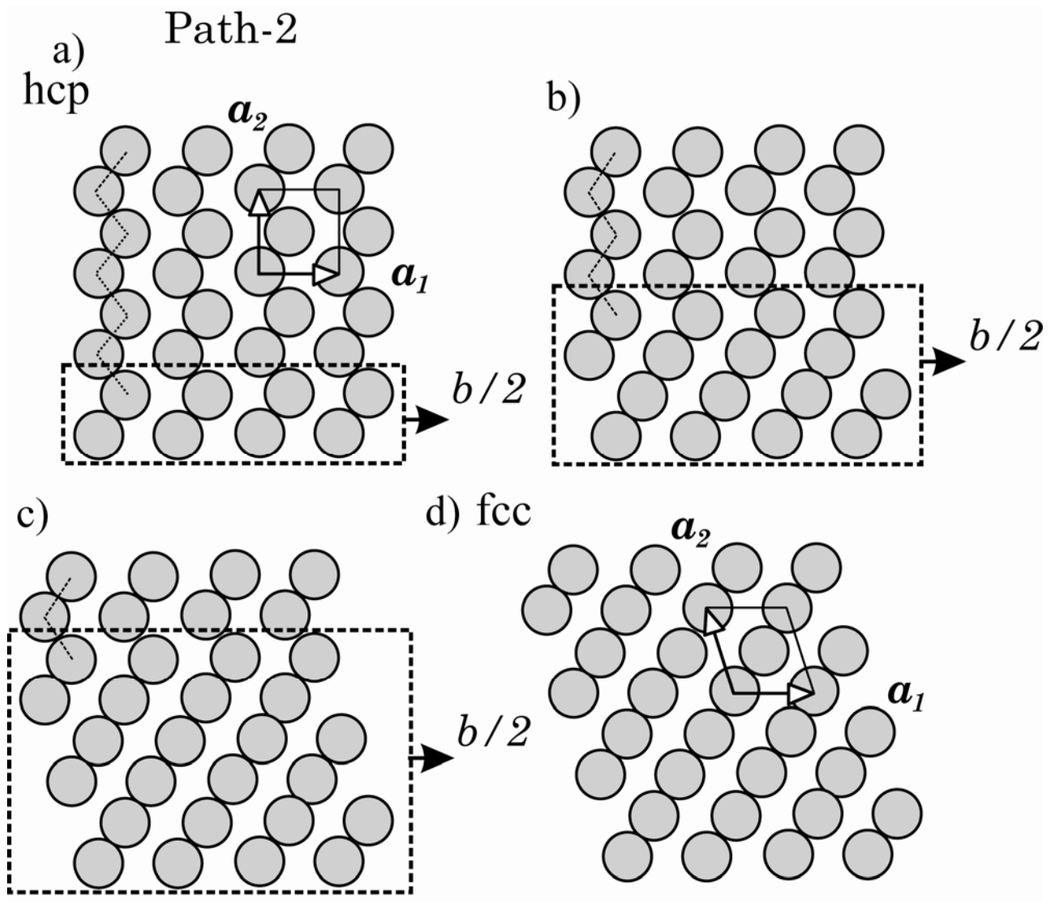
Proposed hcp → fcc paths: Path-2 *(right)*

The hexagonal (0001) double layers are shifted by the distance of

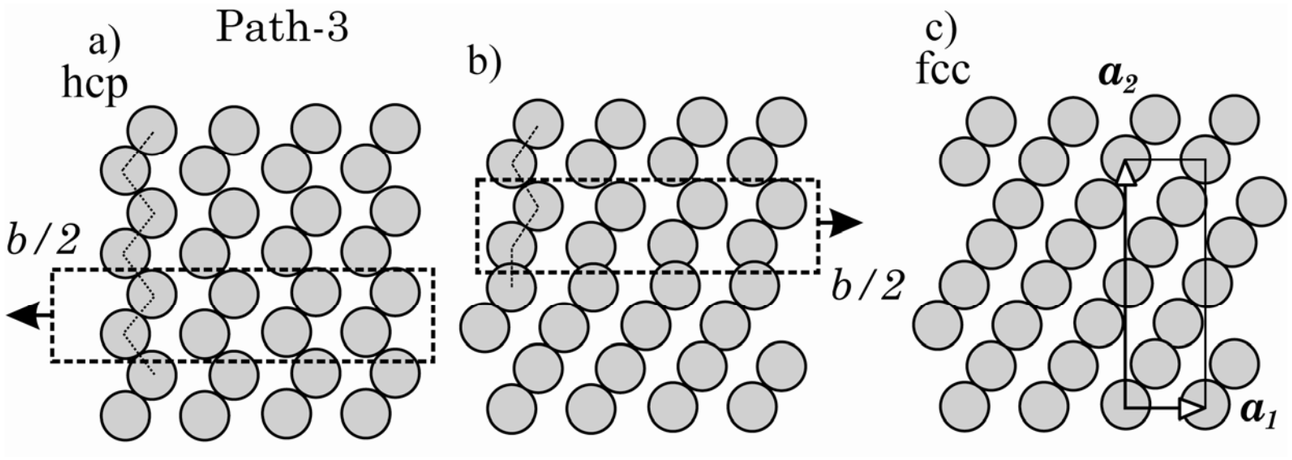
$$b/2 = d_{NN}\sqrt{3}/3$$

in the $[1\bar{1}00]$ direction.





Proposed hcp → fcc paths: Path-3 *(bottom)*

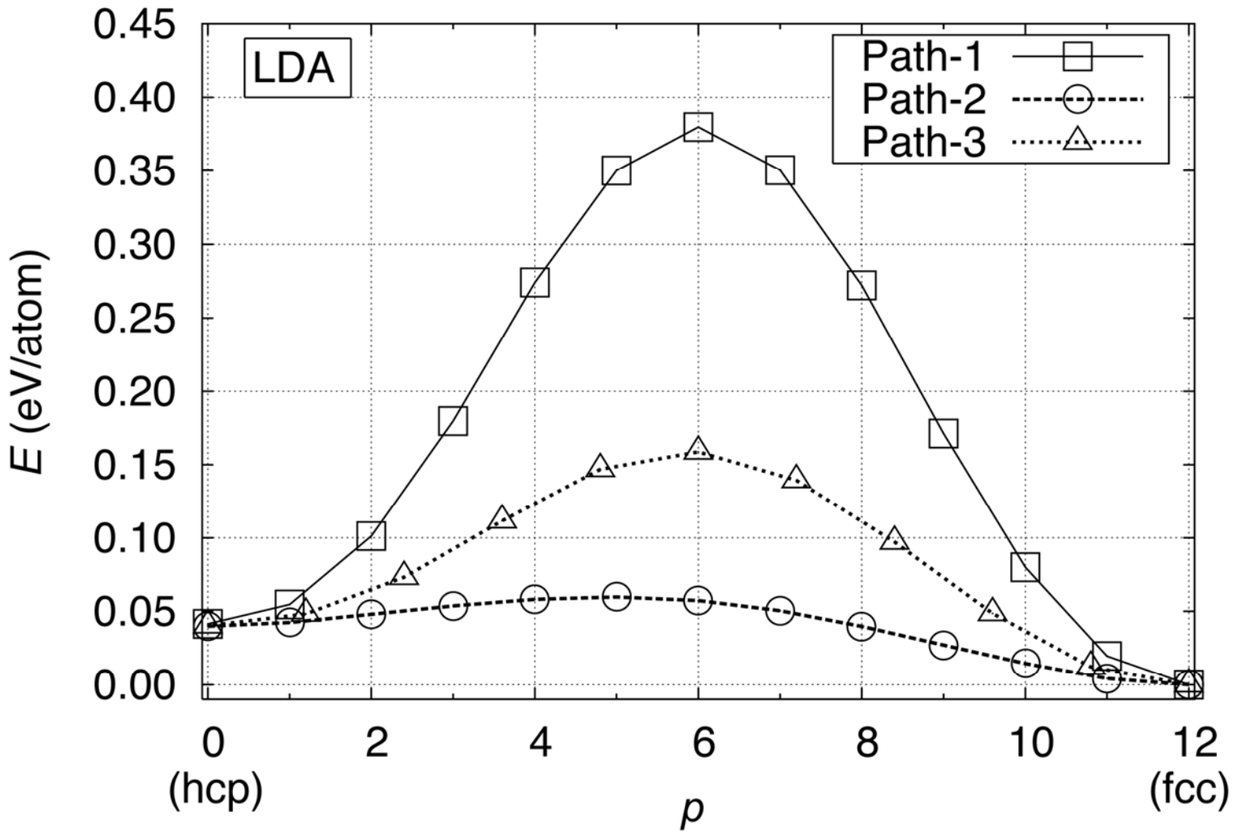


The hexagonal (0001) double layers are shifted by the the distance of

$$b/2 = d_{NN}\sqrt{3}/3$$

in two opposite directions $[\bar{1}100]$ and $[1\bar{1}00]$

Total energy profiles of the hcp → fcc paths (LDA)



The energy barrier of Path-2 from hcp to fcc structure amounts to
25 meV/atom (T = 290 K, GGA) or
20 meV/atom (T = 232 K, LDA),
respectively.

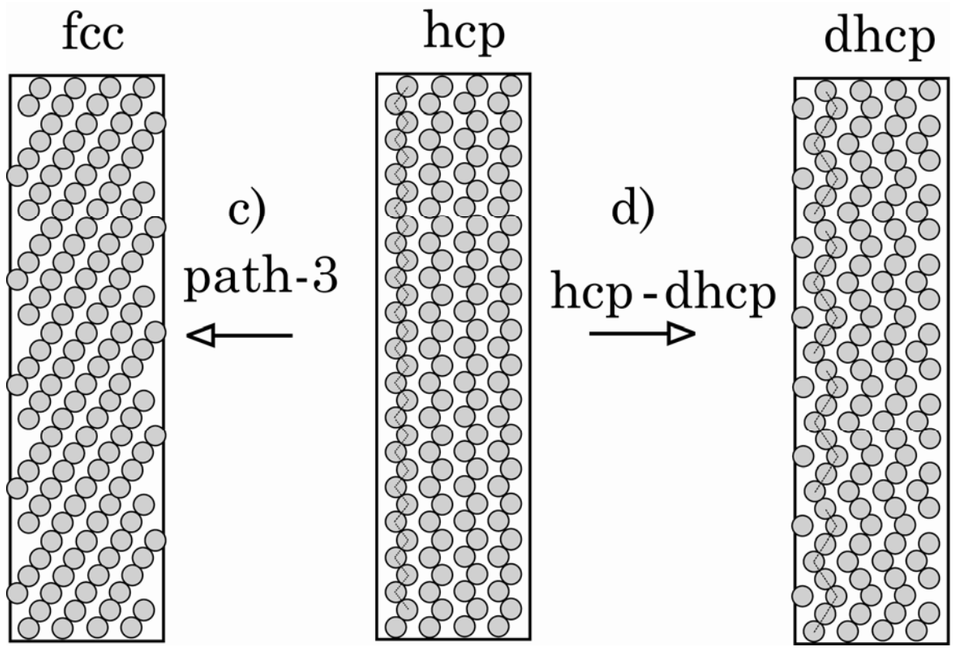
Discussion of the energy profiles

The height of the energy barrier at hcp → fcc path-2 (~ 260 K) is comparable to the energy barrier of the hcp → dhcp path (~170 K), but unlike the hcp → dhcp path, **the transformation via hcp → fcc path-2 was not observed to operate** in Pd films on cubic substrates, even for thick films (more than 100 monolayers and more).

What are the **stabilizing agents** for the hcp Pd structure present in the thin films on cubic substrates?
(i) the need to overcome epitaxial stresses caused by the misfit of the adsorbate and substrate
(ii) the domain topology of the Pd films (they grow in orthogonal set of rectangular domains)

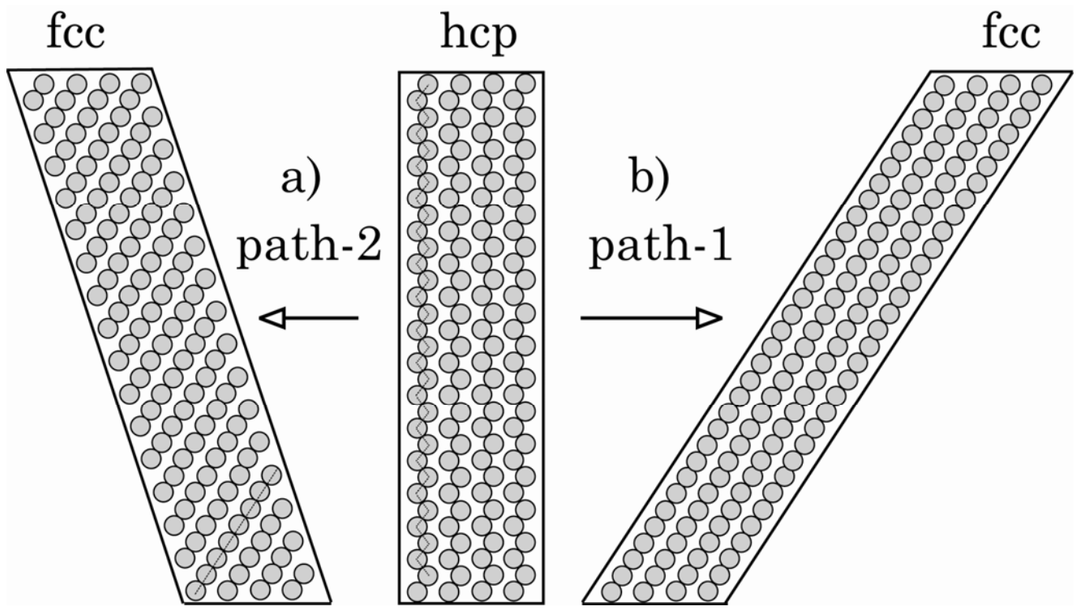
hcp-fcc path-3 and hcp-dhcp path — no change in shape of the domains

The transformation from hcp to fcc via hcp → fcc path-3 and the proposed hcp → dhcp path do not require change of the rectangular domains of hcp Pd structure in the Pd film. However, hcp → fcc path-3 requires a very high transition temperature of 1470 K (hcp → dhcp requires about 170 K)



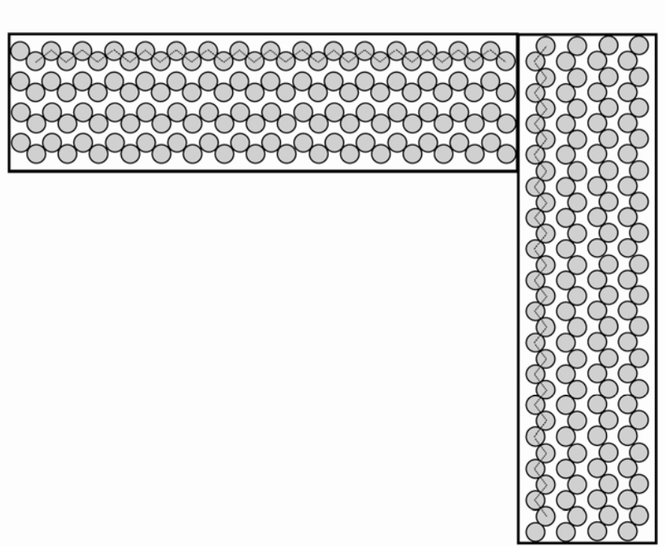
hcp-fcc paths 1 and 2 — change of shape of the domains is needed

The transformations hcp → fcc via path-1 or path-2 require a change of shape of every individual (initially rectangular) domain of hcp Pd regions. Although a "free" hcp → fcc path-2 would require a transition temperature of only ~260 K, the transformation is blocked by the necessity of long-distance movement of atoms.

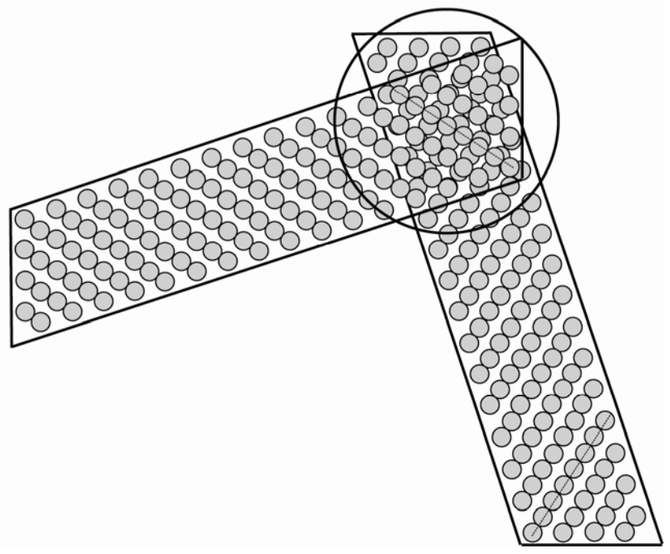


The hcp → fcc transformation via path-2 would break the orthogonal domain arrangement *(right)*

a) two orthogonal hcp Pd domains



b) these domains after Path-2



Conclusions

Ab initio calculations allow us to understand the stability of hcp Pd structure in thin films on cubic substrates [W(001), also Nb(001)]. Unlike the hcp → dhcp transformation, the studied hcp → fcc transformations are not observed experimentally because:

(i) transformations via hcp →fcc path-1 and path-3 exhibit too high energy barriers (4160 K, 1470 K)

(ii) transformation via hcp →fcc path-2 exhibits a low energy barrier (~260 K), but it is blocked by the arrangement of mutually orthogonal rectangular domains of hcp Pd. =>

The domain topology acts as an external agent stabilizing the hcp Pd structure in films on cubic substrates.

References

[1] T. J. Rupert, D. S. Gianola, Y. Gan, and K. J. Hemker, Science **326**, 1686 (2009)
[2] J. Huang, Y. Wu, and H. Ye, Acta Mater. **44**, 1201 (1996)
[3] T. Waitz, T. Antretter, F. Fischer, N. Simha, and H. Karnthaler, J. Mech. Phys. Solids **55**, 419 (2007)
[4] H. Wormeester, E. Hüger, and E. Bauer, Phys. Rev. Lett. **77**, 1540 (1996)
[5] H. Wormeester, E. Hüger, and E. Bauer, Phys. Rev. B 54, 17108 (1996)

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