Formation of helical multishell gold nanowire

Experiment :

Y. Kondo and K. Takayanagi, Science 289, 606 (2000)

Theory :

Y. Iguchi, T. Hoshi and T. Fujiwara, PRL 99, 125507 (2007)
T. Hoshi and T. Fujiwara, JPCM21, 272201 (2009).
T. Hoshi, Y. Iguchi, and T. Fujiwara, *Handbook of NanoPhysics 4*, Ed. D. Sattler, CRC Press, pp.36.1-18, (2010)(*)

ex. '11-4'-type nanowire with L = 12 nm



(*) Preprint:

http://www.damp.tottori-u.ac.jp/~hoshi/info/2010_Hoshi_AuNW_HNP_preprint.pdf

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ex. '11-4'-type nanowire with L = 12 nm

ex. TEM image of 11-4 structure



Specific shell configurations with "magic number"

: 7-1, 11-4, 13-6, 14-7-1, 15-8-1 structures



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H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar	$\overset{27}{\text{Co}}_{_{3d^7}4s^2}$	Ni 3d ⁸ 4s ²	$\mathop{Cu}\limits_{^{3d^{10}}4s^1}^{^{29}}$
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe Fr Pa La Hf Ta W/ Pa Or Ir Dt Au Hg Tl Pb Pi Pa At Pr	${\mathop{\mathrm{Rh}}\limits^{45}}_{{}^{4d^8}5\mathrm{s}^1}$	${\mathop{\rm Pd}}_{{}^{46}}$	$\mathop{Ag}\limits_{^{4d^{10}}5s^1}^{^{47}}$
	$\operatorname{Ir}_{^{5d^9}}^{^{77}}$	$\mathop{Pt}\limits_{5d^96s^1}^{78}$	$\mathop{Au}\limits_{^{5d^{10}}6s^1}^{^{79}}$

FCC metals, except Co (HCP)



Geometrical theory for helical multishell gold nanowires

→ "Magic number" for specific multishell configuration



Iguchi, Hoshi, Fujiwara, Phys. Rev. Lett. 99, 125507 (2007)

Two-stage formation model for helical structure

- (1) Dissociation of the outermost shell from the inner shells
- (2) Slip deformation at the outermost shell
 - : from (001)-like (square) str. into (111)-like (hexagonal) str.
- ex. 11-4 structure



Two-stage formation model for helical multishell gold nanowires in various (experimentally observed) multishell configurations

- \rightarrow confirmed by simulation (thermal relaxation)
- (a) 7-1 (section view)













Two-stage formation model for helical multishell gold nanowires

(1) Dissociation of the surface (outermost) shell from the inner shells

(2) Shear-like deformation at the surface shell

(001)-like (square) lattice ---> (111)-like (hexagonal) lattice

(Physical origin: wide 5d band)



Two-stage formation model for helical multishell gold nanowires

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Defect-induced helicity by atom movement from inner shell

(11-4) type, (length) = 12 nm

 Multiple helical domains with different twisting directions
 A posible thinning process (?)





Relaxation simulation with longer nanowire (L=12 nm)

'Green' atom pairs are moved from the inner shell --> Helical domain boundary Shear-like deformation on 'red' atoms : square --> hexagonal



Relaxation simulation with longer nanowire (L=12 nm)

'Green' atom pairs are moved from the inner shell --> Helical domain boundary

Initial

Final

Red atoms: initially on the (001)-type (square-lattice) surface area Green atoms: initially in the inner shell

Technical details (Iguchi, Hoshi, Fujiwara, PRL99, 125507 (2007)) Relaxation with thermal motion (T = 600K, dt = 1fs) Tight-binding Hamiltonian in the NRL form Kirchhoff, et al. PRB63, 195101 (2001) da Silva et al. PRL 87, 256102 (2001). Amorim and da Silva PRL 101, 125502 (2008)



Analysis : Why gold forms helical nanowire ?

'Nanoscale competition' beween

- (a) Energy gain of helical transfomation on surface ('red' atoms)
- (b) Energy loss of at domain boundary ('green' atoms)
- \rightarrow surface stabilization mechanism
- \rightarrow simple energy scaling theory with domain length L

(a) ΔE~**O(L)** (b) ΔE~**O(1)**

Physical origin : wide 5d band of gold (unlike 3d, 4d metals)

 \rightarrow consistent to the features in reconstruction on equllibrium surfaces





Change of the atom energy during the relaxation simulaiton

- P, Q: Atoms with energy gain (in surface reconstruction)
- R, S: Atoms with energy loss (atom pair movement from inner shell)



A simple energy-scaling theory with respect to domain length

Competitive feature of

- (a) Energy gain of surface reconstruction ('red' atoms)
 - (shear-like deformation : square --> hexagonal)
- (b) Energy loss of defect fomation at domain boundary ('green' atoms)

(atom movement into wire surface)

$$\Delta E_{\rm a} = -1.2 \text{ eV per unit layer} \longrightarrow O(L_{\rm dom})$$

$$\Delta E_{\rm b} = +2.4 \text{ eV at domain bounary} \longrightarrow O(1)$$

 $\rightarrow L_{dom} > 2$ unit layers

consistent to resultant domain length



Conclusion: Helical domain formation on multishell gold nanowire

Surface stabilization mechanism with $L_{dom} > 2$ unit layers

(a) Energy gain of surface reconstruction

(shear-like deformation : square --> hexagonal)

(b) Energy loss of defect fomation at domain boundary

(atom pair supply into wire surface)

Possible physical origin : wide 5d band



The same explanation holds on the equillibrium surfaces : Reconstruction into (111)-like (hexagonal) strucutre on the Au(110) surface

'Missing row' structure in FCC(110) surface

\rightarrow (111)-type surface regions as successive nanofacets



Experiment: thinning process of gold multishell nanowire

in situ TEM images

Y. Oshima, Y. Kondo, K. Takayanagi, J. Elec. Microsc. 52, 49-55 (2003)

