

Программа Фонда Дмитрия Зимина «Династия» "Краткосрочные визиты иностранных ученых в Россию"



Novel Discovery of Silicon



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"Semiconductor Nanostructures" Group at Leibniz IPHT e. V. Jena

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Department Facilities

<u>Chemical Vapor Deposition</u>: 2D a-Si:H; 2D mc-Si; 1D Si; 1D Ge; 1D SnO₂; 1D VO_x; 1D Fe₃O₄; Au, Ag

Atomic Layer Deposition: ZnO, Al₂O₃; Al:ZnO; TiO₂; SiO₂; HfO2; ZrO2

Physical Vapor Deposition: a-Si, mc-Si, Ti, AI, Au, Ag, Pd, Cr

Wet @Dry Etching and Surface Modification@Functionalization: RIE

Focused Electron Beam Technology: FEI Helios; Tescan Lyra

Surface Structuring: Photolithography, EB Lithography, PS

<u>Characterization</u>: SEM, AFM, PL, CL, μ-PL, XRD, Ellipsometry, EBSD, EBIC, I-V, C-V, Raman, CARS SER(S)S, μ-Raman

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Material Facilities



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Application







- 1. Top-down Technology
- 2. Bottom-up Technology
- 3. Top-down vs Bottom-up
- 4. NWs a Key for Novel Devices



Why Semiconductor Nanowires?



Applications of Nanowires



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How to grow SiNWs?



"Bottom-up"@, Top-down" Technologies







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Lithography, Reactive Ion Etching

SLS, VLS

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Oxidized Silicon Wafer





Lithography



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Wet Chemical Etching



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Reactive Ion Etching



Si

SiO₂

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Thermal Treatment



Si

SiO₂

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Wet Chemical Etching



Si

 SiO_2

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After RIE

1 x Oxidation

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Disadvantages of Top-Down Process:

- (i) Many steps process
- (ii) Expensive
- (iii) Min NWs diameter only ca. 70 nm
- (iv) Non-ideal geometry and high roughness of NWs

sidewalls

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Bottom-up: CVD



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Bottom-up: CVD



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Bottom-up: Gold Catalyst



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Bottom-up: Aluminum Catalyst



Wang, Y., V. Schmidt, S. Senz, and U. Gösele, Nature Nanotechnology 1 (3), p 186 (2006) Allon I. Hochbaum, Rong Fan, Rongrui He, and Peidong Yang, Nano Lett., 5(3), 457(2005) V. Sivakov, IPHT/Jena 06.03.2014 24

Problematic: Gold Contamination



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Direct Au implantation



Bottom-up: Au Implantation

ROMEO 400 keV Implanter

Energy: Temperature: Fluence: 30 keV RT and 350°C 1 x 10¹⁵ ... 5 x 10¹⁶ cm⁻²

The <u>S</u>topping and <u>R</u>ange of <u>I</u>ons in



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Bottom-up: Au Implantation



Th. Stelzner et al., Nanotechnology 17, 2895 (2006)

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Bottom-up: Au Implantation

SiNWs CVD growth from implanted Au catalyst

Si(111)



SEM micrographs

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EBE

80mA 475°C Si(111) Au-1.2nm 1h

 $\rightarrow \text{ EBE NWs} \\ \text{II < 111>}$

V. Sivakov et al. PSSa 203(15), 3692 (2006) V. Sivakov et al., J. Cryst. Growth *300*, 288(2007)

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v. siva Schubentert al. APL 84, 4968 (2004) 2014









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Substrate:p-Si(111)Au thickness:0.6-2.4 nm T_s : $450-550 \ ^{\circ}C$ I_E :30-80 mAV:1-100 nm/mint:5-240 min

V. Sivakov, IPHV/JeSivakov et al., Phys. Status. 504. A, 203(15), 3692 (2006). 35

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Bottom-up: PVD




- <u>Si Nanowires (NWs) Growth Kinetic</u>
- -NWs diameter as a function of catalyst thickness
- -NWs length as a function of emission current
- -NWs length and diameter as a function of process temperature
- -NWs length as a function of NWs diameter
- -Ostwald ripening





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V. Sivakov et al., J. Cryst. Growth 300, 288(2007).

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Bottom-up: PVD



V. Sivakov, IPHT/Jeva. Sivakov et al., J. Cryst. Officiath, 300, 288(2007). 39





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Bottom-up: PVD



For the CVD growth by the VLS mechanism whiskers with larger diameter grow faster those with a smaller diameter due to the Gibbs-Thomson effect discussed by Givargizov.







J. B. Hannon, S. Kodambaka, F. M. Ross, and R. M. Tromp, *Nature*, DOI: 10.1038/nature04574 (2006) U. Gösele, *Nature*, DOI: 10.1038/nature04609 (2006) V. Sivakov, IPHT/Jena 06.03.2014







Silicon NWs Facetting





HRSEM micrographs of Si NWs grown by EBE on Si(111) at 550°C for 1h at emission current 80 mA and Au thickness of 1.2 nm. The faceting along three sides of Si NWs is clearly visible in (a) and (b). The growth direction is <111>.

v. Sivekov stal., MRS Fall Meeting, 11027,20142.01. 2006, Boston USA.

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Bottom-up: PVD





HRTEM

EBE

T = 550°C 60 min Si(111) 80mA



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V. Sivakov et al., MRS Fall Meeting 2006, Boston USA. V. Sivakov et al., Nanotechnology, 20, 405607 (2009).

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<u>Gold Migration@Oxidation of Si NWs</u>

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CVD on EBE

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Electron microscopy micrographs of the Si NWs grown by EBE on Si(111) at 700°C for 1h at emission current 80 mA and Au thickness of 1.2 nm: (a) scanning electron microscopy (SEM) image; (b) transmission electron microscopy (TEM) image.

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Electron microscopy micrographs of the Si NWs annealed in air at 800 °C for 1h: (a) TEM image; (b) SEM image.

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Electron energy loss spectrosc. (EELS) & Energy-filtered TEM

Elemental distributions in the region of Si nanowires on Si(111) in cross-section (Growth by EBE)

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EBE

T = 550°C 60 min Si(111) 80mA



T_{ox} = 800°C 60 min







SEM cross section micrographs of the silicon nanowires heat treated at oxidative atmosphere for: (a) Oh, as deposited; (b) 300 °C, 3 h; (c) 500 °C, 3h; (d) 800 °C, 3h; (e) 900 °C, 3h; (f) Au EDX mapping of the sample, heat treated at 900 °C. 06.03.2014 55











It is well known [1] that when O_2 reacts with Si surfaces two processes can occur:

(i) <u>passive oxidation</u>, at low T and high O_2 partial pressures (pO₂, which results in the formation of SiO₂ through the reaction

 $Si+O_2 \rightarrow SiO_2(1)$

(ii) <u>active oxidation</u>, at high T and low pO_2 , which results in the etching of the Si surface by the formation of volatile SiO via the reaction

(iii) SiO can be released by the decomposition of the SiO₂ layer at the Si/SiO₂ interface through the reaction

 $Si+SiO_2 \rightarrow 2SiO(3)$

This reaction is also known to occur at high T and low pO₂ and generate voids in thin SiO₂ layers [2].26 The equilibrium SiO partial pressure associated with this reaction is quite high at T = 900 C (pSiO ~ 10^{-3} Torr),[1] and thus this reaction can also be a parallel source of volatile SiO.

[1]. J.J.Landers and J.Morrison, *J. Appl. Phys.* 33, 2089 (1962). [2]. R.T romp, G.W .Rublof f, P.Balk, and F.K.LeGoues, *Phys. Rev. Lett.* 55, 2332 (1985). V. Sivakov, IPH f/Jena 06.03.2014





900°C, O₂, with Au



900°C, air, with Au



900°C, air, without Au



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 $\begin{array}{cccc} \text{Si+SiO}_2 \rightarrow 2\text{SiO}???? & 2\text{SiO} \rightarrow \text{Si+SiO}_2??? \\ 900^{\circ}\text{C} & 900^{\circ}\text{C}, 10^{-3} \text{ Torr}_{60} \end{array}$



<u>SERS@TERS</u> M. Becker, V. Sivakov et al., NanoLett. 7(1), 75(2007). Electronic Devices Implantation of p- and ndopands

<u>1D Nanosensors</u>





1. Bottom-up (VLS) Technology

Application and Problematic of VLS NWs Top-down vs Bottom-up NWs a Key for Novel Devices



Disadvantages of Bottom-Up/VLS Process

- Expensive, Many Steps Process
- Contamination by Catalyst
- Difficulties by Epitaxy Realization
- Defects in Single Crystal (twins)
- Arrays Realization Difficulties



Electronic Imaging & Signal Processing DOI: 10.1117/2.2200812.0002

Black silicon is ready to revolutionize photoelectronics

Mark Crawford

The light-absorption properties of this accidentally discovered material promise sweeping advances from cameras to solar cells.

Black silicon moves out of the laboratory

OLE • December 2008 • optics.org/ole

A new photonic material could have significant advantages for detection, imaging andpowergeneration applications

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Motivation

<u>Harvard University and SiOnyx Partner to</u> <u>Commercialize Black Silicon</u>

Harvard University's Office of Technology Development (OTD) and SiOnyx, Inc. today announced that SiOnyx has exclusively licensed Harvard's portfolio of black silicon patents.

Black silicon, a novel laser implant technique that <u>radically alters the photonic</u> properties of semiconductor devices, was discovered by Harvard's Eric Mazur, Balkanski Professor of Physics and Applied Physics, who holds a joint appointment in the Faculty of Arts and Sciences (FAS) and the School of Engineering and Applied Sciences (SEAS). <u>A highly light-absorbent material</u>, black silicon absorbs nearly twice the visible light of regular silicon and detects infrared light that is normally invisible to silicon based devices, a capability that allows for <u>dramatic performance enhancements</u> in applications ranging from simple light detection to advanced <u>digital imaging and solar energy</u>. In consideration for licensing the patents, Harvard has received an equity position in SiOnyx and will receive downstream royalties. SiOnyx also recently raised <u>\$11 million</u> in funding from Harris & Harris, Polaris Venture Partners and RedShift Ventures.

Is it possible to realize such nanostructures by chemical methods?

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M-Si-HF Interaction M= Pt, Au, Ag

Boring Deep Cylindrical Nanoholes in Silicon Using Silver Nanoparticles as a Catalyst

Silicon shows unique electrochemical properties in solutions containing hydrofloric acid. Cylindrical holes electrochemically formed in silicon in these solutions have recently attracted much attention due to their possible applications in photonic crystals, micromachining, etc.

Etching Solution 300 nm (b) 50% HF+30%H₂O₂ (d) 600 nm 308ni 009195 20.0kV X20.0K 1.50Pm 206 BAV X (c) (d) 600 nm 100 nm 100 nm 100 20.0kV X300K 889848 Adv. Mater. 8(18), 17(2005) 809848 28.8kV X20.0K 1.50. X300K i00nm 009046 20.0kV

K. Tsujino, <u>M. Matsumura</u>

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Au-Si-HF Interaction Arrays formation procedure



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p-Si(100),C

Au-Si-HF Interaction

SEM 60° image: p-Si(100),CVD, 0.5 mbar, 650°C, 6 sccm Ar/3 sccm SiH₄, 10 min.

> SEM planar image: Si surface after electrolysis

00010188

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0.090 98 20.0k

00010193

06.03.2014

mm

500 nm



Au_{colloid}-Si-HF Interaction Arrays formation procedure: Gold Colloids



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uphtiena Au_{colloid}-Si-HF Interaction

SEM planar image:

0001002

00010027

SEM planar image: p-Si(111), 60 nm Au aq., HF@H₂O₂ CVD, 650°C 0.5 mbox 6 coom A n/2 coom Sitt 10 min

> SEM 60° image: p-Si(111), 60 nm Au aq., HF@H₂O₂ CVD, 650°C, 0.5 mbar, 6 sccm Ar/3 sccm SiH₄, 10 min.

00008939

000089

p-S

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1 µm

uphtiena Au_{colloid}-Si-HF Interaction



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Au_{colloid}-Si-HF Interaction Arrays formation procedure: Gold Colloids



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M-Si-HF Interaction M= Pt, Au, Ag

More optic investigations are required!!! May be photonic crystal properties???



VS445 total integrated reflectance





00020657



Ag-Si-HF Interaction



Preparation of silver layers by Dr. H. Schneidewind is gratefully acknowledgedV. Sivakov, IPHT/Jena06.03.201474



Ag-Si-HF Interaction

SEM image: 25 nmAg//Si(111) treatment for 0.5h in HF/H₂O₂



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$AgNO_3$ -Si-HF Interaction

Growth Mechanism of SiNW Arrays



 $4Ag^{+}(aq.) + Si^{0}(s) + 6F^{-}(aq) \rightarrow 4Ag^{0}(s) + SiF^{2-}_{6}(aq.)$

K. Peng et.al., Adv. Funct. Mater., 13(2), 127(2003)

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$AgNO_3$ -Si-HF Interaction

Arrays formation procedure: Silver Nitrate



RCA@HF treatment HNO₃ conc. treatment



Si(100)/(111)

AgNO₃/HF treatment





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$AgNO_3$ -Si-HF Interaction

TEM@HRTEM: SiNWs





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20nm



V. Sivakov et al., Intech "Nanowires - Fundamental Research", ISBN 978-953-307-327-9, p45 (2011) V. Sivakov, IPHT/Jena 06.03.2014 80

ıpht <mark>jena</mark> **Top-down: Wet-Chemical Etching** Si(100) Etched area 100 <100 <100> 100 C.-Y. Chen, et al. Adv. Mater. 2008, 20, 3811 00021365 5 µm

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Ag-Si-HF Interaction



 K. Peng, M. Zhang, A. Lu, R. Zhang and S.-T. Leea, Appl. Phys. Lett., 90, 163123 (2007).

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 06.03.2014
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Substrate : n or p-type Si (100) wafers

PS spheres

Formation of hexagonal array of PS spheres: Ø $0.2\mu m$ to 4 mm

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Au, Ag, Pt, Pd/Au

Reduction of the size and fixation of PS spheres: RIE (O2 plasma) + Heat treatment

Deposition of metal catalyst:

Etching of Si nanowire arrays

Removal of PS spheres and metal

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0 min, RIE



5 min, RIE



8 min, RIE









V. Sivakov et al., Nano Lett. 9, 1549 (2009). V. A. Sivakov et al., J. Phys. Chem. C, *114*, 3798–3803 (2010)

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ipht jena **Top-down: Wet-Chemical Etching**





V. A. Sivakov et al. Phys. Rev. B 82, 125446(2010) 06.03.2014 87



F. Voigt, V. A. Sivakov et al. Proceedings EMRS Spring Meeting 2010, Strasbourg, France, 7-11.06.2010.

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V. A. Sivakov et al. Phys. Rev. B 82, 125446 (2010); F. Voigt , V. Sivakov et al., PSSa, 208(4), 893 (2011)

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ıpht <mark>jena</mark> **Top-down: Wet-Chemical Etching**







6. 7. Position of the PL maximum as a function of the size of nanoclusters determined by TOFMS. For the data of the t work we have used filled symbols (squares for the first and nds for the second series) whereas the results of an earlier PL (Ref. 17) are plotted as open circles. The dashed curve reps the theoretical results of Delerue, Allan, and Lannoo (Ref. 37), whereas the dotted curve includes the correction due to the lattice variation according to Eq. (4).

Ledoux, G., et al., V. Phys. Rev. B 62, 15942 (2000) V. Sivakov, IPHT/Jena







WCE vs VLS

-0,

Cheap Formation
 Catalyst Free
 High Absorption
 Room PL (E_g=1.5 eV)
 Low Reflection

Photonic, Optoelectronic, PV, Sensoric

V. Sivakov et al. Intech . Nanowires / Book 1, p45-80 (2011)

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SELF-CLEANING

Wetting of Silicon Nanograss: From Superhydrophilic to Superhydrophobic Surfaces

By Christian Dorrer und Jürgen Rühe*

Self-Cleaning Properties



Figure 1. Drops on nanograss surfaces with different polymer coatings. a) Composite wetting on a poly (heptadecafluorodecylacrylate)-coated surface, b) Wenzel wetting on a polystyrene-coated surface, and c) superwetting on a poly (dimethylacrylamide)-coated surface.

Adv. Mater, 20, 159 (2008)

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ENERGY

Silicon nanowires as efficient thermoelectric materials





Enhanced thermoelectric performance of rough silicon nanowires Vol 451 10 January 2008 doi:10.1038/nature06381

Allon I. Hochbaum¹*, Renkun Chen²*, Raul Diaz Delgado¹, Wenjie Liang¹, Erik C. Garnett¹, Mark Najarian³, Arun Majumdar^{2,3,4} & Peidong Yang^{1,3,4}



ZT (blue squares) using the measured k of the 52 nm nanowire in Fig. 2c. By

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 $F_g = G \frac{m_1 m_2}{\nu^2}$

Newton's Law of Gravity



The Proverbial Apple The famous story that Newton came up with the idea for the law of gravity by having an apple fall on his head is not true, although he did begin thinking about the issue on his mother's farm when he saw an apple fall from a tree.



Friedrich August Kekulé said that he had <u>discovered</u> the ring shape of the benzene molecule <u>after having a reverie or day-</u> <u>dream</u> of a snake seizing its own tail (this is a common symbol in many ancient cultures known as the <u>Ouroboros</u>). This vision, he said, came to him <u>after years of</u> <u>studying the nature</u> of carbon-carbon bonds.

Observation of <u>NATURE</u> V. Sivakov, IPHT/Jena

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Prof. Ulrich Gösele Dr. Peter Werner Prof. Jürgen Popp **Prof. Alois Lungstein Dr. Thomas Stelzner Dr. Johannes Michler Prof. Steffen Teichert** Dr. Silke Christiansen **Dr. Fritz Falk Dr. Bela Pecz** Dr. György Radnoczi **Dr. Felix Voigt....**



Dipl. Ing. Alexander Schleusener Dipl. Phys. Johannes Mühlenstädt Dipl. Phys. Florian Talkenberg Dipl. Phys. Arne Bochmann.....





Bundesministerium für Bildung und Forschung



Thanks for your attention!

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Спасибо за внимание!

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