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"Workshop on Ion Beam Studies of Nanomaterials: Synthesis, Modification and Characterization"

26 June - 1 July 2006

Nanostructures by Ion Beams

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Outline

- 1. Introduction
- 2. Ion beam processing:
 - Ion Implantation (IIM)
 - Ion Beam Synthesis (IBS)
 - Ion Irradiation (IIR) of interfaces
- 3. IBS of nanostructures
- 4. IIR induced self-organization
- 5. Applications
- 6. Outlook



1. Introduction

Why ion beams?

lon beams in industry:

 widely used in microelectronic technology – doping of semiconductors (ion implantation into silicon)

lon beams in R&D:

- ➡ Ion implantation for advanced CMOS technologies < 0.15 µm technologies (low energy ion implantation for shallow junction doping, individual and cluster ion doping, doping profile tailoring, defect annealing etc. in Si)
- Ion beam synthesis and processing of advanced materials:
 - Fundamentals & defect kinetics development of simulation tools
 - Materials with noval electrical, optical and magnetic properties
 - Ion beam induced slicing & Focused Ion Beam applications
 - Surface modification hardness, texture, corrosion
 - Metastable phases plastic flow and patterning of surfaces
 - Synthesis of nanostructures and thin layers



Reasons for current effort in ion beam processing of advanced materials:

Highly developed level of ion implantation technique:

- Concentration of implanted ions (impurities) is precisely controlled (electrical current measurement in the fluence range 10¹⁰-10¹⁷ ions/cm²)
- \rightarrow Penetration depth of ions in the range 1 nm 100 µm can be precisely adjusted by choosing the ion energy in the range of $10^{-1} - 10^{5}$ keV
- Isotope clean impurity implantation (ion mass seperation)
- Wide variability between ion species and substrates to be implanted

Physical understanding of ion-solid interactions:

- Existing physical models describe ion range and straggling of implanted ions, recoil cascades and sputtering of target atoms, defects & phase separation
- \Rightarrow Existing simulation tools: TRIM; CrystalTRIM*; TRIDYN* \rightarrow depth profiles
 - 3DKLMC*
 - classical MD
 - ab initio calc.
 - *) devoloped at FZR

- \rightarrow phase separation
- \rightarrow defects, annealing
- \rightarrow atomistic structure

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What are nanostructures?



Typical Properties:

- d < mean-free-path of electrons
- d < Bohr's exiton radius

- → Metals: < 50 nm (Ag)...10 nm (Li)
- → Semiconductors: <20 nm (Ge), <10 nm (Si)

Confinement:

Electrons are spatially localized within a potential well.





Quantum dot:

(Nanodot, Nanocrystal, Nanocluster, NC)

- Number of atoms: 10...10.000
- Surface/volume-ratio ↑
- Band gap $E_g = f(d_{NC}) \rightarrow d_{NC} \downarrow = E_g \uparrow$ Indirect semiconductor silicon: at $d_{NC} < 10 \text{ nm}$
- - \rightarrow direct semiconductor







Heinig, Schmidt, Müller, 104th Annual Meeting of The American Ceramic Society, St. Louis, April 2002, invited talk

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2. Ion Beam Processing

Ion beams create disorder \rightarrow

radiation damage due to collisions of penetrating ions with atoms of the solid state target (recoil atoms, collisional cascades)

Recovery of order \rightarrow

thermal treatment of the irradiated sample for annealing of radiation damage and defined atomic arrangement of introduced ions in in the host matrix (e.g. on crystal lattice places)

 \rightarrow self-organization



IIM: Ion implantation in microelectronics



CMOS devices:

- Source/drain doping
- Channel threshold voltage adjust
- p/n-well doping
- poly-Si gate (n⁺) doping
-

Concentration of implanted ions usually below the solubility limit of impurities in Si





Phase separation: SiO₂ precipitation, Ostwald ripening, coalesence



IBS: Ion Beam Synthesis of new phases Phase Separation in Supersaturated Solid Solutions



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T. Müller, K.H. Heinig, W. Möller, Appl. Phys. Lett. 81 (2002) 3049

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IIR: Ion Irradiation through Interfaces – computer simulation

Separation of non-stoechiometric phases at SiO₂/Si interfaces: Precipitation, Ostwald-ripening, NC formation



A.E. White et al., Appl.Phys.Lett. 50 (1987) 95; M.Strobel, S.Reiss, K.H.Heinig, Nucl. Instr. Meth. B120 (1996) 216

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4. IIR induced self-organization

Despite the absence of Ge⁺ ions at the SiO_2/Si -interface, O and Si recoils cause ion beam mixing there of a few dpa's

Kin. MC simulation of SiO₂ dissociation & Si and O diffusion

Unbonded O and Si migrate and recombine to SiO_2 , but the interface can act as a sink for O and therfore $C_{Si} > C_O$ at the interface Kin. MC simulation of ion beam mixing and diffusion

O and Si recoils cause ion-induced detachment of Si atoms into the SiO₂, higher steady state Si-concentration in SiO₂ can lead to nucleation of tiny Si-NC's

S.Reiss, K.H.Heinig, Nucl. Instr.&Meth. **B84** (1994) 229, ibid. **B112** (1996) 223 V.Borodin, K.H.Heinig, S.Reiss, Phys. Rev. **B56** (1997) 5332

IIR: Ion Irradiation through Interfaces

K.H. Heinig, B. Schmidt, M. Strobel, H. Bernas, MRS2000 Fall Meeting, Boston, 2000, inv. talk

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- Si precipitates next to the interface <u>must</u> exist to which Ge atoms attach
 - \rightarrow formation of NCs during annealing
- Ge decoration improves mass contrast in TEM
- a denuded zone (~3nm) exists in-between NC layer and substrate

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PREDICTIONS for Si NCs in buried SiO₂ layers after ion irradiation

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Si NCs near irradiated interfaces – "just" predictions or real?

Loss Spectroscopy (EELS)

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low contrast

 $(\underline{\cdot})$

Energy Filtered Transmission Electron Microscopy

(EFTEM by M. Klimenkov, Research Center Jülich)

clusters faintly visible

NC diameter below 3 nm !

L. Röntzsch, et al., phys. Stat. Sol (a) 2002 (2005) R170

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no clusters visible

50 nm poly-Si/14,5 nm SiO₂ Si⁺, E = 50 keV D = 7.0×10^{15} cm⁻² T_A = 1100°C, 160 s

IIR: Ion Irradiation through <u>curved interfaces</u> -Inverse Ostwald ripening of NCs

NCs have curved interfaces – how do they respond to ion irradiation?

Narrow size distributions are required for many applications !

- It is desirable to control
- the size
- the size distribution
- of ion beam synthesized nanocluster ensembles.

Examples:

- size dependent optical absorption and luminescence
- size dependent Coulomb blockade effect

A new method for re-ensembling of NC size distributions using irradiation induced Inverse Ostwald Ripening (IOR) was predicted, which should allow even the formation of monodispersive NC size distribution !

> K.H. Heinig, B. Schmidt, M. Strobel, H. Bernas, Mat. Res. Soc. Proc. **650** (2001) R9.6.1 K.H. Heinig, T.Müller, B.Schmidt, M.Strobel, W.Möller, Appl. Phys. **A 77** (2003) 17

IIR: Ion Irradiation through <u>curved interfaces</u> -Inverse Ostwald ripening of NCs

Ion beam processing far-from-equilibrium for controlled tailoring of ion beam synthesized Au NC ensembles in SiO₂:

B.Schmidt, K.H.Heinig, A.Mücklich, Mat. Res. Soc. Proc. 647 (2001) O11.20.1

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IIR: Ion Irradiation through <u>curved interfaces</u> -Inverse Ostwald ripening of NCs

lon beam processing far-from-equilibrium allowes controlled tailoring of ion beam synthesized NC ensembles in SiO₂.

Small NC's grow at the expense of larger ones, and, consequently, the NC size distribution becomes narrower.

K.H. Heinig, B. Schmidt, M. Strobel, H. Bernas, Mat. Res. Soc. Proc. **650** (2001) R9.6.1 K.H. Heinig, T.Müller, B.Schmidt, M.Strobel, W.Möller, Appl. Phys. **A 77** (2003) 17

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K.H. Heinig, B. Schmidt, M. Strobel, H. Bernas, Mat. Res. Soc. Proc. **650** (2001) R9.6.1 K.H. Heinig, T.Müller, B.Schmidt, M.Strobel, W.Möller, Appl. Phys. **A 77** (2003) 17

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5. Applications

Synthesis of Si NC- δ -layers in SiO₂ a few nm above the SiO₂-Si interface:

- A) Si ion implantation phase separation (IBS) Low energy ion implantation, E < 10 keV
- B) Self-organization by Si ion irradiation (IIR) Medium energy ion irradiation, E > 10 keV

for non-volatile Nano-Crystal Memory devices (nv-NCM)

Can we fabricate and control δ -layers of Si NC by lon Beam Processing?

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nMOSFET characteristics (low thermal budget) :

Endurance

- superior endurance (very limited degradation up to 10⁷ cycles)
- limited data retention only (pre-cycling of 10⁷)
- improved RT retention for reduced pre-cycling

data retention (after pre-cycling)

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Ion Beam Synthesis – Direct Implantation vs. Ion Beam Mixing

conventional: lon implantation

Unprotected gate oxide → serious impact of the ambient during processing

Low Energy, High dose implantation → strong sputtering & swelling of SiO₂

NC location due to implantation → difficulty to place NCs close to channel

lons and recoils come to rest in the interface region \rightarrow degradation of the channel

here: Ion beam mixing

Gate oxide potected during processing by poly-Si → no contamination by impurities and/or humidity*

Irradiation with low fluences \rightarrow no sputtering & no swelling of SiO₂

NCs due to ion beam mixing → Self-alignment of NC layer close to the channel (ion energy is **not** critical)

lons come to rest deep within Si → defects do not deteriorate the channel

* B. Schmidt et al., NIM B **191**, (2002) 482

→ ion beam mixing delivers the more stable process of Si NC synthesis

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Focused ion beam synthesis of nanostructures time of FIB implantation time of annealing Beam spot **Diameter:** < 50 nm Ion implantation by FIB: Phase separation & coarsening (wire growth): lon energy E Annealing temperature T_A Ion fluence ϕ Annealing time $\mathbf{t}_{\mathbf{A}}$ Substrate temperature T_{S} Orientation of FIB trace relative to crystal orientations Pixel dwell & relax. time t_{d.r}

Prediction: Narrowing during phase separation and coarsening by a factor ~ 5 !!!

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Promising fabrication of nanostructures by FIB

FIB-IBS: Phase separation of CoSi₂ from Si **FIB-IBS:** Phase separation of Ge, Au,... from SiO₂ FIB-assisted MOCVD:FIB-assistedDeposition of Au, W,...(sputtering):onto SiO2Wettening &

FIB-assisted templating (sputtering): Wettening & nucleation seeds

Kinetic 3D Lattice Monte-Carlo Simulation of phase separation of Ge from SiO₂

Cylindrical Gaussian profile as initial distribution of implanted impurities with a peak concentration of 31% and diameter of 16 nm (95% of the atoms lay within this range)

A continuous Ge nanowire forms under thermal treatment (diameter 5nm) !

T.Müller, K.H.Heinig, B. Schmidt, Mat. Sci. Eng. C19 (2002) 209

Long lasting thermal treatment (atomistic simulation): Decay of a semi-infinite wire under surface diffusion

(FZR, MC simulation, T. Müller, K.H. Heinig, L. Röntzsch)

Wire diameter: 6.2 nm

Mean droplet diameter: 11.9 nm

Droplet diameter prediction from lin. stability analysis: 11.7 nm (Rayleigh-Instabilität)

$$d_{cluster} = \sqrt[3]{6\lambda_m R_0} = 1.89d_{wire}$$

T.Müller, K.H.Heinig, B. Schmidt, Mat.Sci.Eng. C19 (2002) 209

Kinetic Monte-Carlo Simulation of phase separation in quasi-2D structures

(FZR, MC simulation, T. Müller, K.H. Heinig)

Phase separation through:

- spinodal decompositition,
- wire formation at prolonged boundaries
- droplet formation

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Experiments of FIB-IBS

Mat. Sci. Engn. C26 (2006), 818

Microelectronics Engineering 83 (2006), 800

Experiments – CoSi₂- Nanowires

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Results: CoSi₂- nanowire growth & decay

Results: CoSi₂- nanowire growth & decay

- (a) wire growth in dependence on the implanted cobalt dose (FIB trace along <110> direction !)
- (b) small misalignment of about 1° leads to the decay of the nanowire
- (c) at a misalignment of about 15° the nanowire transforms into a chain of crystalline nanoparticles. (sample temperature during implantation 450°C)

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Results: CoSi₂- nanowire growth & decay

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Vision: nanowires as well as NC chains & single quantum dots for optics and electronics

1st example: Single Electron Transistor (SET)

structure

Prediction of SET fabrication using FIB-IBS (atomistic simulation):

2nd example: Plasmonics - highly integrated optical devices

Plasmon waveguides for electromagnetic energy below the diffraction limit using ordered arrays of metal nanoparticles:

Atwater, Brongersma et al., California Institute of Technology, Pasadena, CA

How to synthesize?

Possibly by FIB–IBS through:

Line-shape implantation: Au into SiO₂, Co into c-Si

Point-like implantation: Au into SiO₂ Co into c-Si

Subsequent annealing to form: Au-nanowires and chains of Au-NC's CoSi₂-nanowires and chains of CoSi₂-NC's

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Finally a look to the "Nanoelectronics Roadmap":

Some fabrication problems of the "System-on-a chip" can be solved by emerging technologies like ion beam induced self-assembling of nanostructures:

- Nonvolatile memories (nvRAMs)
- Single Electron Transistors (SETs)
- Optical (plasmon) waveguide
- Optical pumped light amplification

•

"System-on-a-chip" for the future

In the last decades ion implantation has been established itselfs as an basic technology in microelectronics.

This lecture showed you that ion beam assisted processing has the potential as a basic technology for nanoelectronics & nanooptics !

IBS of Nanocrystals

Project support

SMWK-Project (1998-2002)

DFG-Project (2000-2003)

BMBF-Project "Konsul"+"Isotop" (2001-2003)

EU-Project "Neon" (2001-2004)

Collaboration

Cinfineon Lechnologies

IBS by FIB

Project support

DFG-Project I (2004-2006) DFG-Project II (2004-2006) (Theory)

FIB patterning

Project support

EU-Project TUD (2004-2006)

Collaboration

Collaboration

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Implantation	J. Schneider I. Winkler G. Winkler	S. Buschbeck KH. Stegemann HJ. Thees ¹⁾ E. Votintseva M. Wittmack ¹⁾ now with Infineon
Theory	Dr. KH. Heinig L. Röntzsch (PhD) T. Müller (PhD, now at INFINEON)	
Analytics	Dr. A. Mücklich (TEM) Dr. R. Grötzschel (RBS) E. Christalle (REM)	
FIB	Dr. L.Bischoff Dr.C. Akhmadaliev	
Clean room	H. Felsmann C. Neisser B. Scheumann G. Schnabel	

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FIB – ART: FZR-Logo in the eye of a fly

IMSA-Orsay Physics FIB (FZR, L. Bischoff, C. Akhmadaliev, 2003)

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