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

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Nanoclusters and -tubes for Swift Heavy Ion Track Electronics (SITE)

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Nanoclusters and -tubes for Swift-Heavy Ion Track Electronics (SITE)

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Contents

Basic SITE concept

Latent and etched tracks / etched track filling /applications

Nanoclusters

Ouantum electronic devices / Sterilizing foils / NCs for tailored conductivity / NC architecture

TEAMS & TEMPOS

Cuurent-Voltage characteristics / theory / sensors

Negative differential resistances

electronic devices / Sterilizing foils / NCs for tailored conductivity / NC architecture

Nanotubes

CNTs in TEMPOS structures / PCVD and thermal CVD / field emission / 3D nanoelectronics

The basic concept of SITE:



irradiate insulator with swift heavy ions (carrier-free or on semiconductor substrate)







Etch the latent tracks, fill them with (semi)conductors, contact both sides





Why Swift Ion Track Electronics (SITE) ?

There are at least 4 competing techniques in nanoelectronics:

- a) self organizing nanostructures
- b) nanomanipulations
- c) nanolithography
- d) molecular electronics

all these 4 techniques are excellent, but – a,d) restricted to relatively few systems b.c,d) very difficult, time consuming and expensive

For contrast, SITE has a number of advantages which make this technique interesting:

- Simple fast
- precise light-weight

cheap (10^{-9...10} €/track (for 10^{6...7} cm⁻²)) large area devices (> 1 m x 100 m) environmentally friendly

- mechanically flexibile
- ... and has an extremely high variability in its parameters



SITE: Great variability in material's properties

- Host material for tracks..insulators, semiconductors
 - polym., SiO₂, SiON, organomet., C₆₀, SnO₂,...
- **Substrate.....** Self-supporting, Si, glass, metal
- **Track type**.....latent $\leftarrow \rightarrow$ etched tracks
- **Track shape.....**conical, cylindrical, funnel-like,...
- Inner track material......metals, semicond., electrolytes
 - Ag, Au, Pd, Ni, C₆₀, CNTs, Phthcy, SnO₂, TiO₂, CdS, organometals, cond. Polymers, nanocomposites,.....
- Inner track structure......wires, fibrilles, nanotubules, nanoclusters, gel, liquid; axially or radially structured
- Track density.....individual or overlapping tracks
- Applications......Passive, active electronic elements

resistors, capacitors, inductors, sensors, transformers, diodes, transistors

- Peculiarity:.....hybrides with Si electronics possible
- Novel track-specific applications: TEAMS & TEMPOS





					P	
						C
	J	Stched	ion trac	ks in P	ET	
EHT = 20.00 kV Probe = 200 pA	MAG = 4.72 K X 10µm	WD = 8 mm	Detector = SE1 Stage at T = 0.0 Deg	Date :16 Jan 2002 g Time :11:58	hmi	HMI- Berlin Solarenergie





On the way to devices: axially and radially modified structures









Why nanoclusters for SITE?

Microscopic:

Quantum effects can be exploited

Macroscopic:

- Higher overall surface of NCs
- Conductivity can be tailored: well-defined order of magnitude, voltage and temperature dependence
- NCs store a considerable amount of charge
- NCs can be used as "building bricks" for construction of refined structures

conducting nanowires,...

Quantum confinement: single electron transistor

From:

D.K.Ferry, ,M,Goodnick, Transport in nanostructures, 1977



Fig. 4.10. A quantum dot coupled to two leads connected to an external circuit.





Quantum confinement of narrow wires



possible realization with ion irradiation:

FET or SET formation by combined –

High energy irradiation

•Etching

Deposition

Low energy irradiation

•contacting

•FETs: homogeneous filling

•SETs: nanocluster filling -

Patent DE10361934.8-33 (2002)



Quantum electronic ion track device, first result:



Higher overall surface of NCs:

Active areas of different pore/NC designs

estimations are based on the assumptions of 1 cm^2 large and $10 \mu \text{m}$ thick foils each, with 5×10^7 pores/cm² of cylindrical shape with 1 μm diameter, and with a close packing of TiO₂ nanoparticles with 50 nm diameter on the whole foil surface.

Membrane	Massive TiO ₂	TiO ₂ fibrilles on a	TiO ₂ nanoparticles
Arrangement	membrane	supporting foil	adsorbed to sufaces
			of microporous foil
Overall photoactive	2	15.4	40.6
TiO ₂ area [cm ²]			

Gas & Water purification by photocatalysis

Destruction of - virusses, bacteriae, fungi, algae - ethylene gas (= aging hormone)



Holes diffuse to surface, react with adsorbed H_2O , form there OH^- and H_2O_2 radicals --> atomic OAs $E_{pot}(radicals) > E_{bond}(organics)$ --> destruction

 TiO_2 ZnO, SnO_2 , CaTiO₃, Fe₂O₃ MoO_2 MoS₂, NbO₅, CdS, KNbO₃, SrTiO₃, CdSe, CdS, WO₃, $Ti_{x}Zr_{1-x}O_{2}$, SiC

candidates



Food sterilization with TiO₂-track-foil



Bionik-Systeme Bremen Dr.-Ing. Udo Küppers 8.2004

Intelligent solar water purification system

Anatase sensor records the photocatalytical activity of anatase



Nanocluster architecture:

nanowire formation by SHI irradiation

Biswas et al. 2002/2003: 120 MeV Au → Au/Teflon AF





alignment of Au clusters along the ion tracks

Macroscopic properties of dispersed conducting nanoclusters: tailoring of conductivity

Bulk metal

touching clusters

small distance

larger distances

larger distances







contaminants, moisture

metallic conductivity (Ohmic)
percolation (grain boundaries)
tunneling (quantum physics)
Schottky emission (thermal)
field emission (high fields)

ionic conductivity

From: S.M.Sze, Physics of semiconductor devices. John Wiley & Sons, 1981

Basic conduction mechanism in insulators

for a supposed MIS (metal-insulator-semiconductor) arrangement.

Process Name	Description
Schottky emission	Thermionic emission
Frenkel-Poole emission	Field-enhanced thermal excitation of trapped electrons into the conduction band
Tunnel or field emission	Field ionization of trapped electrons into the conduction band, or by electron tunneling from the metal Fermi energy into the insulator conduction band
Space-charge limited current	carrier injection into the insulator, where no compensating charge is present
Poole-Frenkel, Gill	Current is carried by thermally excited electrons hopping from one isolated state to the next
Ohmic conduction	Migration of electrons
Ionic conduction	Diffusion of ionic charge carriers

From: S.M.Sze, Physics of semiconductor devices. John Wiley & Sons, 1981

Quantitative relations for various conduction mechanisms

Voltage and temperature dependence

Process

Schottky emission Frenkel-Poole emission Tunnel or field emission	~ $T^2 \exp(c_1 \sqrt{V/T} - c_2/T)$ ~ $V \exp(2c_1 \sqrt{V/T} - c_2/T)$ ~ $V^2 \exp(-c_2/V)$: temperature indep
Space-charge limited current Poole Frenkel Gill	$\sim V^2$; temperature indep $\sim V^2$; temperature indep
Ohmic conduction	$\sim \exp(\sqrt{T})$ $\sim V \exp(c_4/T)$
Ionic conduction	$\sim V \exp(c_4/\Gamma)$

The c_i are coefficients containing information about the barrier height, insulator dynamic permittivity, effective charge carrier mass, insulator thickness, and/or the activation energy of the charge carriers, respectively.

From: S.M.Sze, Physics of semiconductor devices. John Wiley & Sons, 1981

Tailoring of nanowire properties by aligning (semi)conducting nanoclusters along latent or etched tracks

A possible recipe:

Bring nanoparticles into solution as colloides by attaching to them hydrophile ligands, let the solution dry within the tracks Other recipe:

let a solid precipitate from solution at preferred nucleation centers; interrupt the precipitation process in a very early stage

Examples verified by us:

LiNbO₃, SiO₂, TiO₂, Cu, Ag, Au, Ni, Pd, CdS, PbS, ...







Current/voltage relations



The current/voltage characteristics of Ni-filled micropo- rous PET foils, as compared with se-veral conduction theories. Conductivity values mea-sured along the ion track directions (i.e. through the foils).

10 s: Schottky emission \geq 30 s: Ohmic conduction

Porous SiO₂ on Si es filled with Ag nanoclusters

 Mag = 131 30 K X
 Pixel Size = 2.00 nm
 WD = 2 mm
 Detector = InLens
 Date .17 May 2002
 HMI- Berlin

 EHT = 7.50 kV
 200nm
 File Name = SiO2-Ag_03 tif
 Time 1124
 File Name = SiO2-Ag_03 tif
 Time 1124
 File Name = SiO2-Ag_03 tif
 File Name = SiO2-Ag_03 tif








Tuneable Electronically Anisotropical Material on Silicon (TEAMS)

Tunable Electronic Material with Pores in Oxide on Silicon (TEMPOS)



Example of an in-situ measurement: Polysilane-TEAMS (350 MeV ¹⁹⁷Au²⁶⁺ at ISL,HMI Berlin)



The creation of SiC nanorods along the ion tracks changes the I/V characteristics



Result:

GATING VOLTAGE DEPENDENCE OF POYLSILANE-TEAMS

PECULIARITIES:

Transistor-like gating in 1st quadrant,

diode dependence in 3rd quadrant,

hysteresis near the origin











FernUniversität Hagen

Lehrgebiet Bauelemente



Transistor properties at some operating points

M easurement	А	В	С	D	Е
point	$V_{vw} = -4 V$	$V_{vw} = -6 V$	$V_{vw} = -2 V$	$V_{vw} = 0.5 V$	$V_{vw} = -1 V$
	$I_v = -0.2 \text{ m A}$	$I_v = -1.0 \text{ m A}$	$I_v = -0.6 \text{ m A}$	$I_v = -0.5 \text{ m A}$	$I_v = -1.1 \text{ m A}$
M _P					
Common					
em itter	0.18	1.17	0.64	0.054	0.053
common					
base	0.4	0.12	0.04	0.64	1.12
common					
collector	0.05	24	0.034	0.017	0.074



Theoretical approach to TEMPOS





TEAMS & TEMPOS sensors

There are some intrinsic physical properties which enable the TEAMS & TEMPOS structures to act as a sensor.

Example: light sensitivity.

Application of a light source shifts the characteristic from a low conductive state to a high conductive one due to increase in carrier concentration in space charge region





Humidity sensing with TEMPOS:



Sensitive humidity recording

by frequency measurement



Comparison of transistor electronics and SITE



A common feature for SITE: Negative differential resistances (NDR)

NDRs can have two origins:

- Instabilities in individual entities (traps, tracks)
- Collective track-track interactions

In spite of different mechanisms, both effects lead to similar effects

First hints for NDRs in pores from biology ~ 1970

Current-Voltage relationship of the electrogenic pump in Acetabularia mediterranea. by: D.Gradmann, W.Klemke in: Membrane Transport in Plants, U.Zimmermann and J.Dainty eds., Springer 1974, p.131-138

Also frequent pore effects: Pulsating current in latent tracks in PET (Correlation with NDRs?)







At 20°C, when the pump is operating, additional current passes through the pump channels. The most striking feature of the steady state I-V curve at 20°C is its N-shape under depolarisation; it finally merges with the high conductance potassium branch. This is certainly a rather complex phenomenon, since voltage- and space-dependent events in different pathways seem to be involved. At the moment this question will not be pursued turtner.

NDR of individual entities (shown here for the example of deep traps)

Suppose -

- deep traps are produced by irradiation of a material, e.g. SnO₂ in a TEAMS structure
- these traps are filled by charge carriers
- the sample is subject to a strong field gradient
- \rightarrow Then a slight trigger may release all charges simultaneously

Ētrap

- Strong "stimulated emission" current
- Breakdown of applied voltage
- Negative differential resistance

Permanent repitition of this game \rightarrow pulsation









Negative resistance of TEMPOS example: electronic noise at high currents



Negative resistance of TEMPOS example: local differential negative resistance





Negative resistance of TEMPOS example: extended negative resistance



The amount of amplification can be controlled by the intensity of impinging light.

Above threshold light intensity: amplification breaks down.

TEMPOS acts like Esaki or tunnel diode



Switching behaviour of TEMPOS structures

simplifications:

take SiON as dielectric layer
 → cylindrical tracks
 restriction to only one track each below the surface contacts.
 restriction to p-Si only (simplest case: no inversion layers)
 --> equivalent circuit





... in other words, TEMPOS structures behave similarly as Esaki diodes or double-base diodes = unijunction transistors = filamentary transistors

Vow

D

p-Si

Ro

v

О

NDRs, Conclusions \rightarrow Applications:

- Many SITE structures (e.g. TEAMS + TEMPOS) show instabilites (due to individual or collective jumps between two working states)
 → flip-flop construction → digital electronics...
- Instabilities have often negative differential resistances
- Can be explained by collective interaction of neighboring diodes
 - \rightarrow application for amplifiers, oscillators

Flip-Flops with TEMPOS



One can exploit the Esaki diode-like negative characteristics to produce flip-flops, with A_1 and A_2 being the working points.

This means, one can produce transistor-less computers!







Tandem Oscillators with TEMPOS

As only one surface contact is used for amplification or oscillation, one can build tandem devices.

Attention: capacitative coupling might influence the circuits.





Conclusions and Outlook for TEAMS&TEMPOS:

- TEAMS/TEMPOS: in principle now well-established and understood
 Future:
- Study TEAMS/TEMPOS with
 - + metal-polymer nanocomposites
 - + biological systems
 - + diamond / EG /CNTs
- CNT-TEMPOS for 3D structuring
- direction-dependent TEMPOS sensors
- 2D position sensitive TEMPOS sensors
- intelligent TEAMS/TEMPOS systems
- GHz TEMPOS modulators & transducers



Growth of carbon nanotubes in etched tracks.

1st step:

deposit Ni or Fe nanocluster catalysts in tracks by electrochemical routes

(~ 4 sec, 4V)

→ Growth of carbon nanotubes with base diameter equal to the inner diameter of the etched tracks


PCVD Growth of CNTs in etched tracks







For comparison: Thermal CVD grown CNTs in tracks







examples:





Conclusion and Outlook:

- Nanoclusters and nanotubes are valuable building blocks for nanoelectronics, specifically to SITE
- As well "classical" as novel electronic devices can be constructed with the help of NCs and NTs
- Especially promising are
 - * NCs for sensors
 - * NCs for TEMPOS structures
 - * CNTs for 3D nanoelectronics

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