# Tritium: <u>A MicroPower Source for On-Chip Applications</u>

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# Outline

- Tritium: Basics
- Tritium: A MicroPower Source
  - Beta-Voltaics
  - Beta-Powered MEMS
  - Beta-Luminescence
  - Cold Electron Source
- Tritium: A Characterization/Diagnostic Tool
  - Tritium Tracer Studies
  - Tritium Effusion Studies
  - Defect Dynamics
  - Particle Sensor Applications
- Summary

#### Tritium

- Isotope of Hydrogen
- <sup>3</sup>H  $\rightarrow$  <sup>3</sup>He<sup>+</sup> +  $\beta^-$  +  $\overline{\nu}_e$  + 18.6 keV
- Nuclear Half-life:  $t_{\frac{1}{2}} = 2$

t  $_{\frac{1}{2}}$  = 12.32 years  $\lambda$  = 1.78 x 10<sup>-9</sup> s<sup>-1</sup>

- Activities: 1 Ci = 3.7 x 10<sup>10</sup> Bq 1 Ci = 0.39 std cc 1 Ci = 33.7 μW
- Biological: Half-life: 10 days ALI\*: 80 mCi

\*Annual Limit on Intake

- Chemically: Identical to <sup>1</sup>H Mass effect (~3amu) Beta catalysis
- Range (max): 4.5 6 mm in air
   5 7 micron in water





### Producers & Users

- Producers of Tritium
  - Ontario Power Generation (OPG)
    - ~1 kg/year
  - Korean Electric Power Company (KEPCO)
  - USA
    - 225 kg produced since 1955
    - 12-75 kg stockpiled
  - Russia
  - India, Pakistan

Tritium Producing Burnable Absorber Rods (TPBARs) (Lithium Rods in a Light Water Reactor)

> Tritium Lighting

- Users of Tritium
  - Pharmaceutical Research (~100g)
  - Tritium Lighting Industry (~30g)
  - Fusion Studies
    - Magnetic Confinement (ITER ~40g)
    - Inertial Confinement
  - Other



Tritium in Natural Waterways



D(n. 2)

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### **BetaVoltaics**

- 1951, Ehrenberg, Lang, & West:
   <u>– Electron-voltaic effect</u> (on a Se device)
- 1956, Rappaport
  - First direct conversion betavoltaic device (planar configuration, 0.4% efficiency)
- 1968, Klein
  - Band-gap dependence of electron-hole pair (ehp) generation by ionizing radiation
- 1974, Olsen
  - Theoretical treatment of betavoltaic conversion efficiencies for a variety of semiconductor materials
- 1970s, D W Douglas Laboratories
  - Planar silicon betavoltaics fueled with <sup>147</sup>Pm
  - Efficiencies ranged in 0.7 to 2%







### **Renewed Interest in Radioisotope Batteries**

- Continual miniaturization of electronic and electromechanical systems
  - Decreased power consumption
- Integrated Power Sources (SoC)
- High energy densities compared to chemical batteries
- Operation in extreme environments

   For example, temperatures of -100 to +150 °C

# **MicroPower** Applications

# Sensor/Memory Chips Power requirement: 1-10 $\mu$ W

#### SoC Microsystem Power requirement: 1-10 mW



#### Non-volatile Memory







Electrostatic actuation of MEMS/NEMS









Micro-gas

Analyzer

Chip-scale Navigation system

# Market

• All Batteries:

\$50 billion

#### Target markets for betavoltaic batteries

- Oil, gas, and environmental
- Military
- Medical
- Space
- Emerging MEMS/NEMS
- Market for betavoltaics

\$1 billion +

### **Electron/Beta Voltaics**



#### *ehp*: electron-hole pair

# Choice of Radioisotope

Isotope	Eavg	Emax	Ρ	Work	<b>T</b> 1/2
	(keV)	(keV)	(W/g)	(kWh/ 4y/g)	(yrs)
H-3	5.7	18.6	0.34	10.3	12.3
Ni-63	21	66	0.07	2.5	92
Sr-90	540	900	0.75	25	28
Pm-147	62	230	0.34	7.3	2.6

#### Tritium

- Low energy β- emitter (benign radioisotope)
- Low cost: \$2.5-\$4/Ci
- Long enough lifetime
- Can be immobilized in a solid matrix
- On-chip integration
- Mature (existing tritium lighting industry)

#### Intrinsic Tritiated Amorphous Silicon Betavoltaic Device

- Substitute tritium for hydrogen in hydrogenated amorphous silicon pin photovoltaic devices
- Tritium within the energy conversion layer
  - In contrast to betas originating from a source external to the device
- Volume source battery
  - Attained through stacking of many cells
  - In contrast to a planar surface source battery



#### a-Si:T Betavoltaic Device

<u>At t ~ 10 days</u>

 $I_{sc} < 0.1 \text{ nA}$ 

 $\frac{At t \sim 0}{I_{sc} = 0.98 \text{ nA}}$  $V_{oc} = 21 \text{ mV}$  $\eta = 0.1\%$ 



Kosteski, Kherani, Stradins, Gaspari, Shmayda, Sidhu, Zukotynski, *IEE Proc. Circuits Devices Syst.* **150**, *No.4*, (2003) 27-281.



### a-SiH Betavoltaic Cell Powered by T<sub>2</sub> Gas

#### a-SiH Betavoltaics with ultrathin contact



#### *At t* ~ 46 *days* $\eta < 0.1\%$



pressure: 678 torr



### **Porous Silicon 3D Betavoltaics**

- Introduce micropores in silicon through electrochemical anodization
- Create *pn* junction in the pores through diffusion of n-type dopant
- Introduce an appropriate radionuclide in the pores
- A Volume Source Battery



Gadeken, Sun, Kherani, Fauchet, Hirschman, US Patent 7250323 (2007).

### **3D Versus 2D Betavoltaics**



Sun, Kherani, Hirschman, Gadeken, Fauchet, *Adv Mater* **17** (2005) 1230-1233.







### **III-V Betavoltaics**

#### AlGaAs/GaAs Heterojunction Betavoltaics

p <sup>+</sup> GaA	\s				
ρ Al <sub>0.85</sub> Ga <sub>0,15</sub> As	0.01-0.03 μm				
ρ Al <sub>x</sub> Ga <sub>1-x</sub> As	0.3-0.7 µm				
n Al <sub>x</sub> Ga <sub>1-x</sub> As	2-4 μm				
n GaAs buffe	rlayer 10 µm				
ļ.					
n GaAs subst	rate 450 μm				
	contact				

Source of betas	Generate d current density µA/cm <sup>2</sup>	Open circuit Voltage, V	Output Power, μW/cm <sup>2</sup>	Efficiency (%)
Tritium- titanium	0.04	0.75	0.024	5.6
Tritium gas	0.76	0.91	0.55	5.8
Tritium green lamp	0.12	0.78	0.074	

Andreev, Kavetsky, Kalinovsky, Larionov, Rumyantsev, Shvarts, Yakimova, Ustinov, 28<sup>th</sup> PVSEC, 2000.

### **Silicon Carbide Betavoltaics**

#### 4H SiC BV Cell

1 mCi, <sup>63</sup>Ni Source (66keV)  $I_{sc} = 16.8 \text{ nA/cm}^2$   $V_{oc} = 0.72 \text{ V}$  $\eta = 6\%$ 



#### 4H SiC pin BV Cell

8.5 GBq, <sup>33</sup>P Source (249 keV)  $I_{sc} = 2.1 \ \mu A/cm^2$   $V_{oc} = 2.04 \ V$  $\eta = 4.5\%$ 



Eiting, Krishnamoorthy, Rodgers, George, Robertson, Brockman, *Appl. Phys. Lett.*, *88* (2006) 064101.

### **Contact Potential Difference Betavoltaics**

Air-medium CPD BV  $I_{sc} = 2.7 \ nA/cm^2$  $V_{oc} = 0.5 \ V$ 



Solid CPD BV  $I_{sc} = 5.3 nA/cm^2$  $V_{oc} = 0.16 V$ 



Liu, Chen, Kherani, Zukotynski, Antoniazzi, *Appl. Phys. Lett.*, **92** (2008).

#### **MEMS:** Radioisotope-Powered Piezoelectric Generator

- Self-reciprocating direct-charging cantilever
- Direct conversion of collectedcharge-to-motion energy into electrical
  - Radioisotope kinetic energy stored in the cantilever
  - Piezoelectric generator converts stored mechanical energy into electrical energy
- Overall efficiency 2.78%



Lal, Duggirala, Li, IEEE Pervasive Computing, 4, (2005), pp. 53-61.

# **BetaLuminescence**

- 1898, Becquerel
  - Radioluminescence
  - Phosphorescence material: potassium uranyl sulphate
- 1920s, Elster, Geitel, and Cookers
  - Alpha radiation induced scintillations in ZnS.
- 1967, International Atomic Energy Agency (IAEA)
  - Standards for the use of common RL sources.
  - Most common: tritium beta-luminescence

#### Present

- Tritium gas lighting
- Radium ZnS:Cu paint
- Novel materials & technologies in Betaluminescence
  - Organic
    - all-organic formulation: polystyrene and fluorescent dye
    - organic system with inorganic phosphor
  - Inorganic
    - semiconductor pn junctions
    - incorporation of tritium in solid matrix: amorphous materials, hydrides, carbon nanotubes, zeolites









# **Cold Electron Source**

#### Tritium immobilized in a solid

Materials

- Tritiated metal tritides
- Tritiated amorphous silicon
  - Plasma enhanced chemical vapour deposition: entire film
  - Tritiation post film deposition: ~50 nm
- Tritiated silica on Si-chip
  - High pressure tritium loading
  - Laser irradiated locked tritium
- Tritiated silicon
  - High pressure tritium loading
  - Surface region: ~ 10 nm
- Tritiated carbon nanotubes

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### **Tritium Tracer Technique**



- Tritium as a tracer in
  measurement of hydrogen
  permeation in polymer for
  selection of new material in
  hydrogen fuel cell.
- Two diagnostics to trace permeating HT: an ionization chamber tritium detector and an HTO water trap/copper oxide furnace/HTO water trap system
- Tritium radiotracer method: simple, effective, reliable.

Stodilka, Kherani, Shmayda, Thorpe, Intl. J. Hydrogen Energy 25 (2000) 1129-1136

### Tritium Tracer Technique (cont'd)



Materials Tested: EPDM, Teflon, Viton, Santoprene and Noryl

Permeation Parameters in reasonable agreement with referenced values of H, D, T

Characteristic permeation curve for Noryl at 60 °C

Arrhenius plot of tritium permeation for the five polymers

Stodilka, Kherani, Shmayda, Thorpe, Intl. J. Hydrogen Energy 25 (2000) 1129-1136

Polymer	Temperature (°C)	$P_0^{\mathbf{b}}$	$E_{\mathbf{P}}^{\mathbf{c}}$	$D_0^{\mathbf{b}}$	$E_{d}^{c}$
Viton	63-129	$1.72  imes 10^{-4}$	47.7	$2.22 \times 10^{-5}$	29.1
Teflon	74-150	$8.38 \times 10^{-9}$	16.7	$1.39 \times 10^{-7}$	14.9
EPDM	44-76	$2.74 \times 10^{-7}$	24.4	$3.50 \times 10^{-5}$	27.9
Santoprene	20-60	$1.21 \times 10^{-6}$	25.1	$1.36 \times 10^{-5}$	21.2
Noryl	18-70	$2.11 \times 10^{-9}$	12.3	$4.05  imes 10^{-7}$	16.9

# **Tritium Outgassing Studies**

- A tool to study hydrogen stability in materials
- High sensitivity
  - Difficult-undetectable for the inactive Hisotope using conventional methods
- Dry and wet test
  - Absorption of HTO desorbed from surface of a given sample
- Tritiated amorphous silicon at room temperature
  - Atomic T concentration: 9%
  - Asymptotic evolution: 2x10<sup>8</sup>atmcm<sup>-2</sup>s<sup>-1</sup>
  - Equivalently: Void-Network H diffusion half-life of 60 years
  - This is for a low H stability material, owing to the high void fraction of the material

Kosteski, Ph.D thesis, Univ. Toronto. (2001) Kherani, Liu, Virk, Kosteski, Gaspari, Shmayda, Zuktoynski, Chen. J Appl Phys, **103**, (2008), 024906





# **Tritium Effusion Monitor**





# **Tritium Effusion**

- Tritiated amorphous silicon
  - No tritium evolution at room temperature
  - Characteristic peaks observed at temperatures above the film growth temperature
    - Lower temp peak: higher hydrides SiHx
    - Higher temp peak: mono-hydride SiH
- Tritiated carbon nanotubes
  - Tritium exposure:
    - 100 bar at 100 °C for 3 days
  - Concentration:
    - Atomic: 1.9%
    - Weight: 0.5%.
  - Gaussian deconvolution:
    - Peaks at 240 °C and 500 °C
    - High temp peak: chemisorbed T
    - Low temp peak: physisorbed T

Kherani, Liu, Virk, Kosteski, Gaspari, Shmayda, Zuktoynski, Chen. J Appl Phys, 103, (2008), 024906





- Purified Single
   Walled Carbon
   Nanotubes (SWNT)
- ~25 µm paper-like film
- Surface Area: 1500 m<sup>2</sup>/g
- Density: ~0.9 g/cm<sup>3</sup>.



### **Defect Dynamics**

- Hydrogenated amorphous silicon solar cells
  - Staebler-Wronski effect
  - Formation of Si- dangling bonds upon light exposure
  - Drop in efficiency

#### Tritiated amorphous silicon

- Defined rate of tritium decay, hence formation of Sidangling bonds
- Can study samples under defined condtions (no light exposure)

#### Dynamic defect model



S. Pisana, S. Costea, T. Kosteski, W. T. Shmayda, N. P. Kherani, S. Zukotynski, J Appl Phys 98 093705 (Nov 2005) 1-5.; Stefan Costea, Nazir P. Kherani, Stefan Zukotynski, J Mat Sci, Vol. 18, Supp. 1, 175-182. (October 2007).

### **Beta Source Particle-Smoke Detector**

- Tritium beta source instead of traditional alpha source
  - No gamma emission (as in Am-Be alpha source)
  - Provides bipolar and unipolar regions in the detector
  - Higher absolute current signal
  - Higher sensitivity
    - Several to forty fold more responsive than alpha based detectors
    - Functions like a dual detector (ionization and photoelectric detectors)
      - Smouldering fires
      - Open flame fires





Liu, Alvarez-Ossa, Kherani, Zukotynski, Chen, *IEEE Sensors J.* **7** (2007) 917.

### Summary

#### • Tritium a micro-power source

- Radio-Isotope Micropower Sources (RIMS) is an active area of R&D
- Renewed interest is motivated by continual miniaturization of electronic and electromechanical devices with concurrent reduction in power requirements
- Tritium an amenable radioisotope given its properties and availability
- Tritium a powerful diagnostic for hydrogen-material studies
  - Ease of experimentation given hydrogen is pervasive
  - Unparalled sensitivity under "non-vacuum" conditions
  - Fundamental studies

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