Ge Charge-Coupled Device Development

LBNL LDRD project (3rd year)

Steve Holland, David Schlegel, Co Tran
Lawrence Berkeley National Laboratory

January 16th, 2019

LBNL Ge R&D (LDRD)

- This is an LDRD-funded effort to develop scientific CCDs on Germanium substrates
  - The next logical step in terms of increasing the long-wavelength response of scientific CCDs

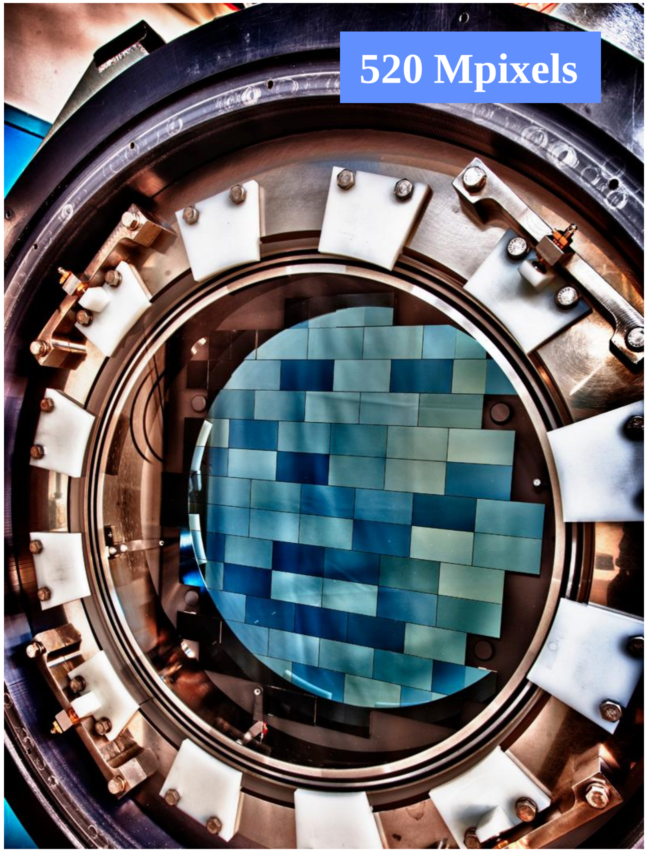
~ 10 - 20 um thick CCDs perform to λ ~ 700 nm

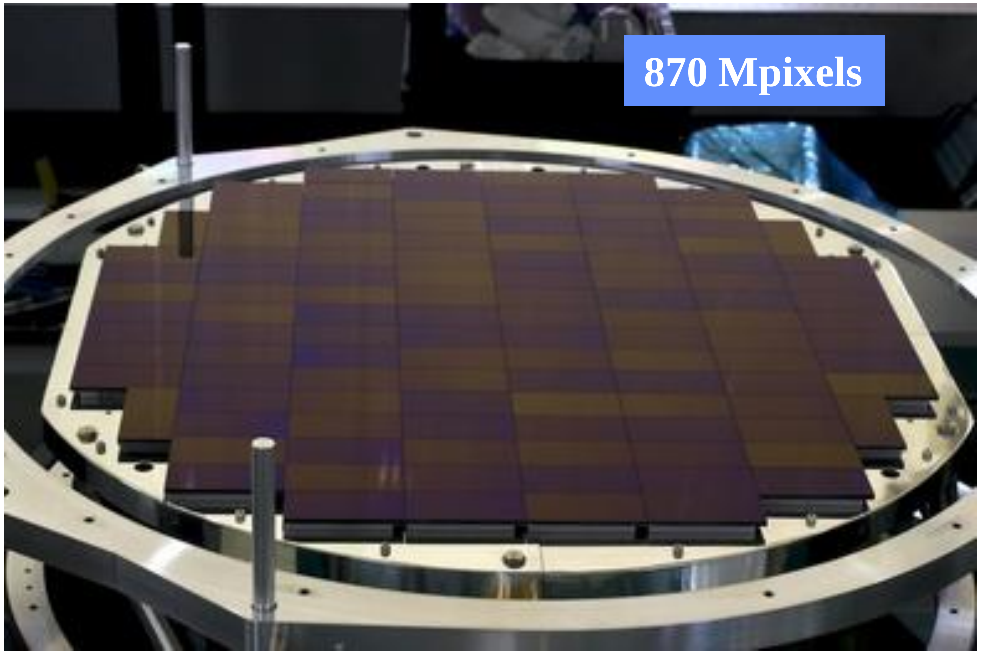
250 um thick fully depleted CCDs λ ~ 1 um

Ge CCDs could work out to λ ~ 1.4 um

  - Direct application to the study of high red-shift objects of interest in Dark Energy studies

Examples of astronomical CCD cameras





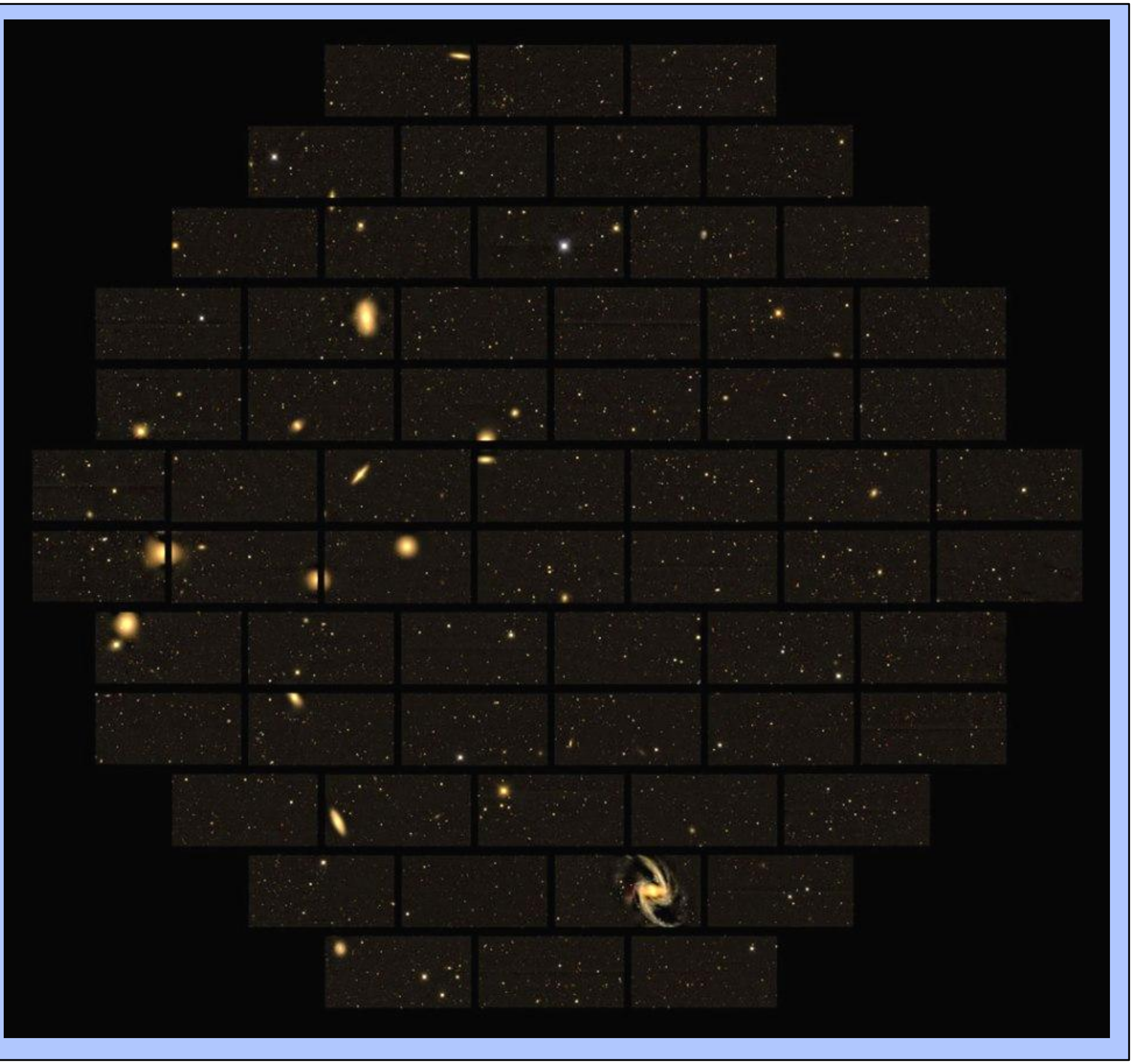
HyperSuprimeCam – 116 2k x 4k, (15 µm)^2-pixel CCDs
CCDs from Hamamatsu Corporation
Licensed CCD technology from LBNL
Subaru 8-m Telescope

FermiLab Dark Energy Survey Camera (DECam)
62 2k x 4k, (15 µm)^2-pixel CCDs
CCDs from DALSA Semiconductor / LBNL
NOAO Cerro Tololo Blanco 4-m Telescope

Both use fully depleted CCDs (200 – 250 um thick)
Operational since 2012

Astronomical cameras with fully depleted CCDs

Full moon
for scale

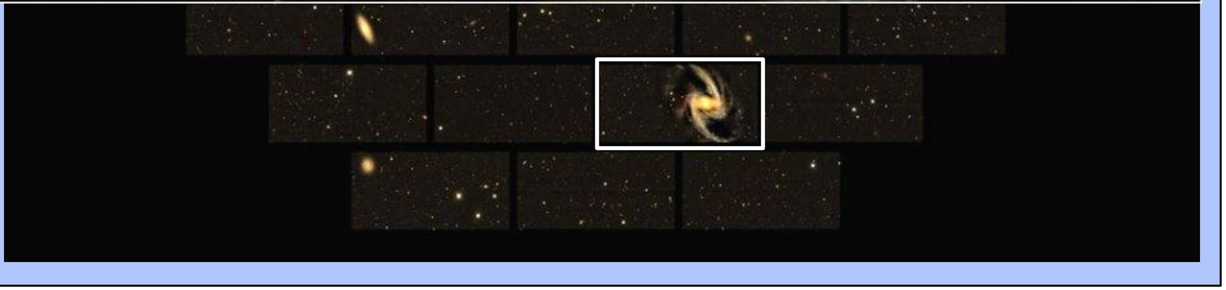


FermiLab Dark Energy Survey Camera (DECam)
62 2k x 4k, (15 µm)^2-pixel CCDs (520 Mpixels)
CCDs from DALSA Semiconductor / LBNL

Astronomical cameras with fully depleted CCDs

Roughly 50k galaxies per image

6 year DES survey complete as of last week / DECam remains



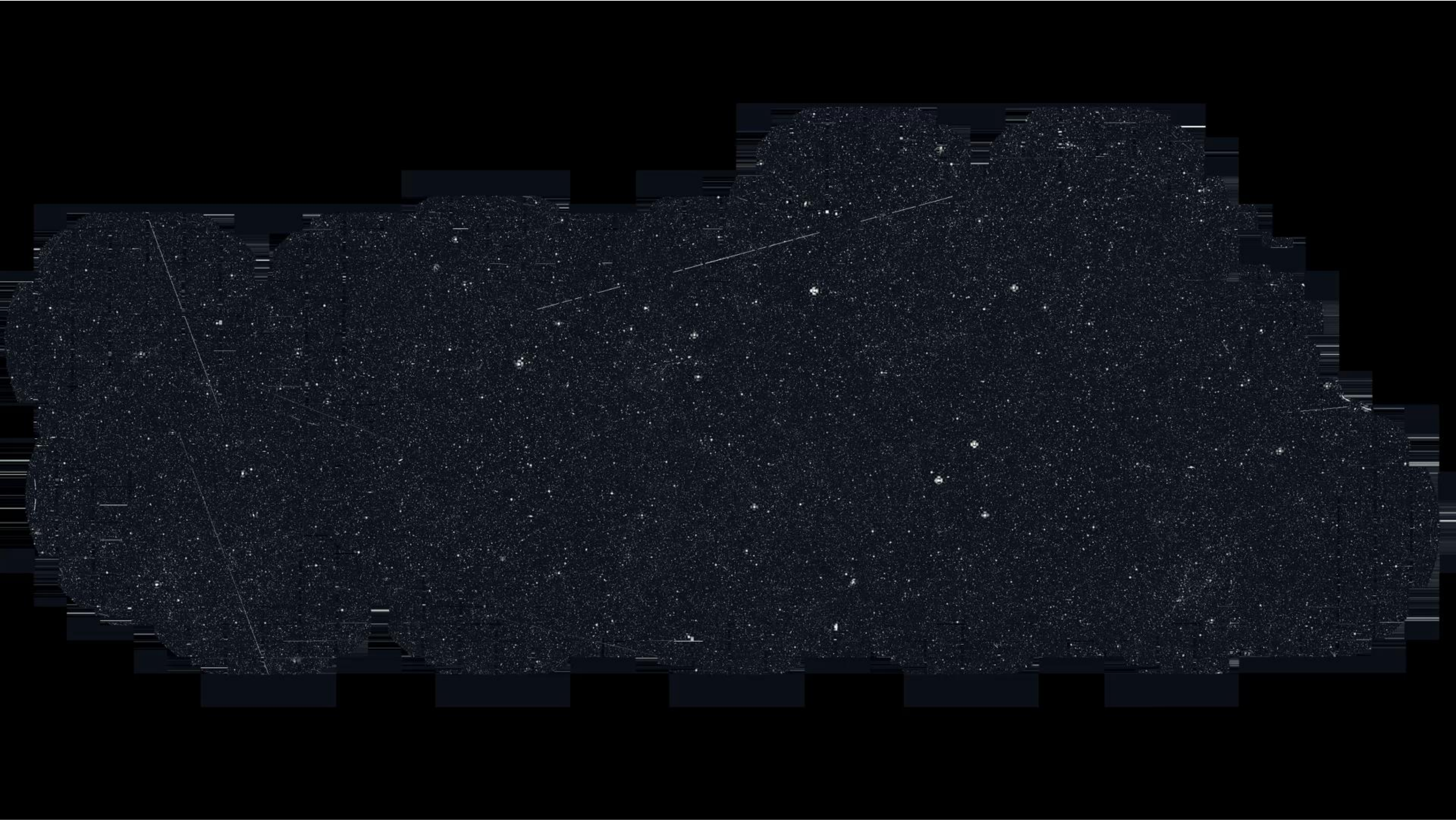
FermiLab Dark Energy Survey Camera (DECam)
62 2k x 4k, (15 µm)^2-pixel CCDs (520 Mpixels)
CCDs from DALSA Semiconductor / LBNL

M1/Crab Nebula in z band: “First and Last”

MOSAIC 3 Camera / 500 μm thick LBNL CCDs

David Schlegel, Chris Bebek, Armin Karcher, Sufia Haque

Astronomical cameras with fully depleted CCDs



HyperSuprimeCam – *8 degrees x 3 degrees field of view*

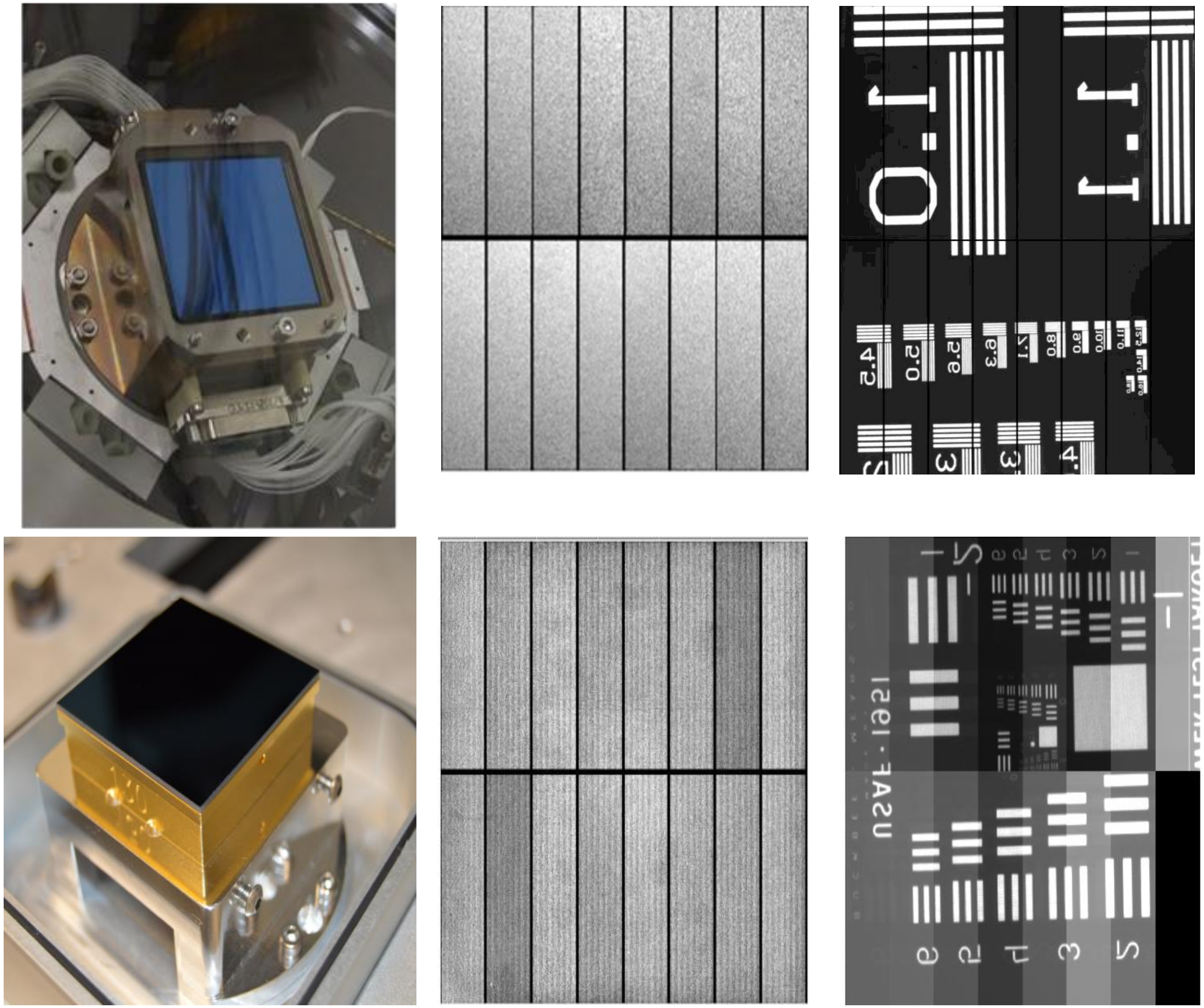
Video courtesy of Satoshi Miyazaki / Subaru Telescope

LSST CCDs (in production)

CCD in test fixture | Uniform illumination | Test target image

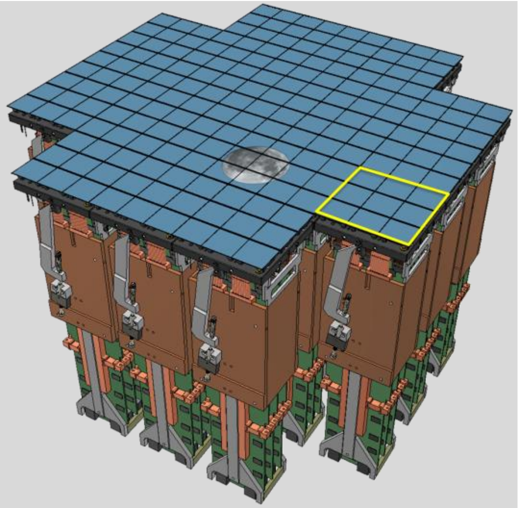
T-E2v CCD250

T-DALSA/ITL STA3800C



- ☐ 100 μm thick
- ☐ Fully depleted
- ☐ 4k x 4k
- ☐ 10 μm pixels
- ☐ 16 amplifiers

- ☐ 189 CCDs
- ☐ 3.2 Gpixels



Courtesy of Paul O’Connor of Brookhaven National Laboratory

LBNL Ge R&D (LDRD)

- In the following we compare material properties of silicon and germanium, and discuss how these material properties affect the electrical and optical performance

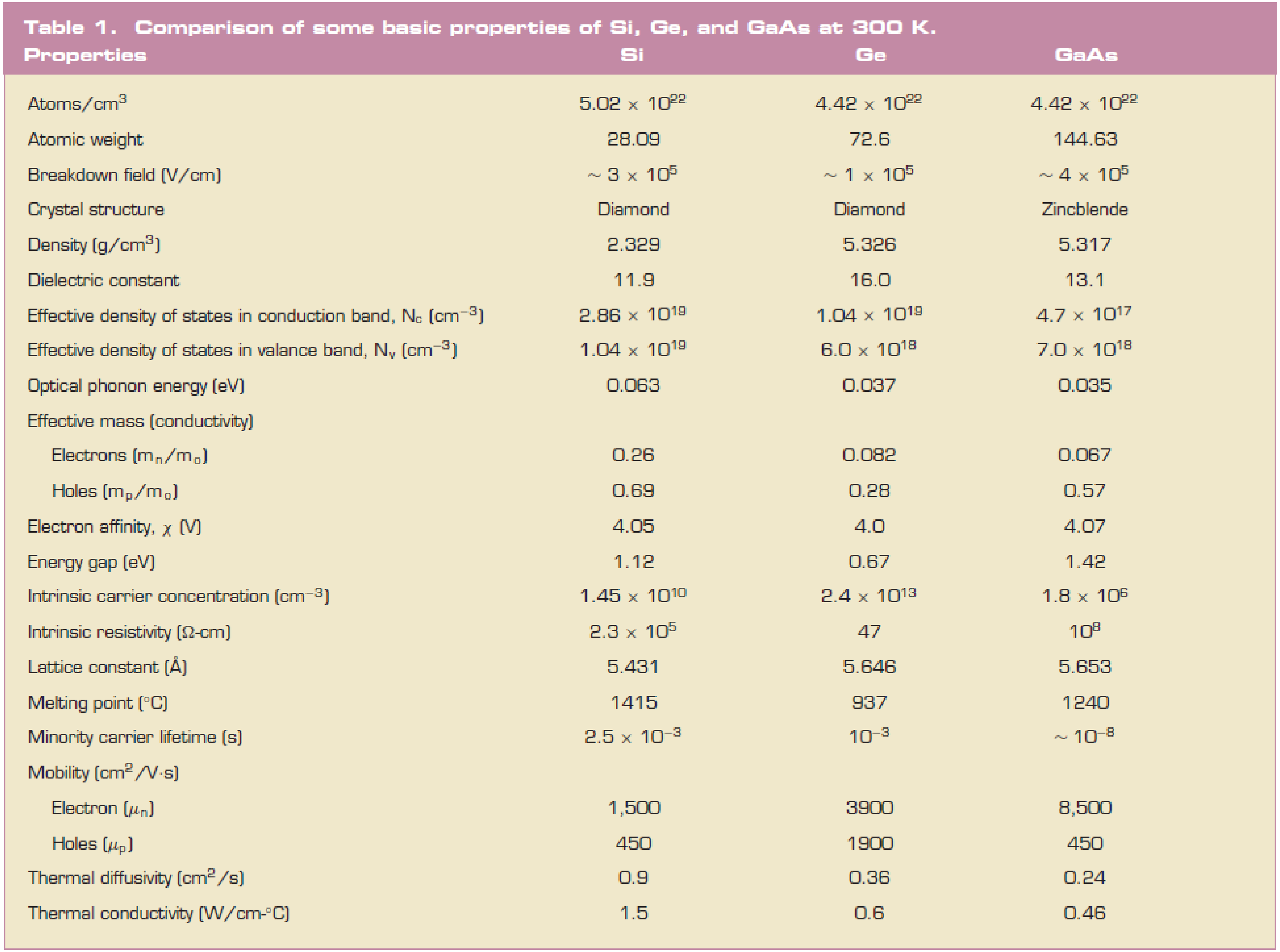
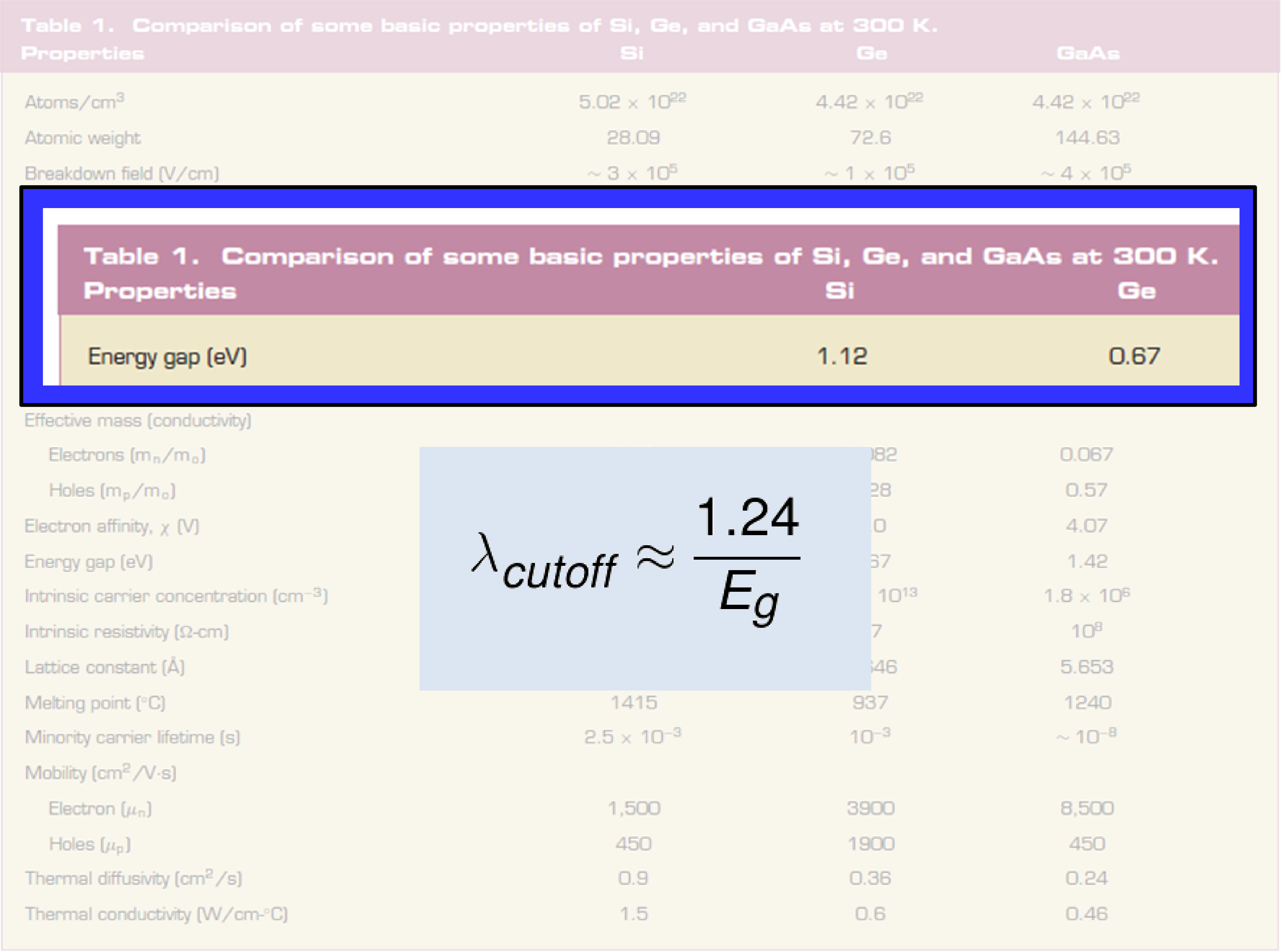


Table 1. Comparison of some basic properties of Si, Ge, and GaAs at 300 K.

Properties	Si	Ge	GaAs
Atoms/cm^3	5.02×10^{22}	4.42×10^{22}	4.42×10^{22}
Atomic weight	28.09	72.6	144.63
Breakdown field (V/cm)	$\sim 3 \times 10^5$	$\sim 1 \times 10^5$	$\sim 4 \times 10^5$
Crystal structure	Diamond	Diamond	Zincblende
Density (g/cm^3)	2.329	5.326	5.317
Dielectric constant	11.9	16.0	13.1
Effective density of states in conduction band, N_c (cm^{-3})	2.86×10^{19}	1.04×10^{19}	4.7×10^{17}
Effective density of states in valance band, N_v (cm^{-3})	1.04×10^{19}	6.0×10^{18}	7.0×10^{18}
Optical phonon energy (eV)	0.063	0.037	0.035
Effective mass (conductivity)			
Electrons (m_n/m_o)	0.26	0.082	0.067
Holes (m_p/m_o)	0.69	0.28	0.57
Electron affinity, χ (V)	4.05	4.0	4.07
Energy gap (eV)	1.12	0.67	1.42
Intrinsic carrier concentration (cm^{-3})	1.45×10^{10}	2.4×10^{13}	1.8×10^6
Intrinsic resistivity (Ω-cm)	2.3×10^5	47	10^8
Lattice constant (Å)	5.431	5.646	5.653
Melting point (°C)	1415	937	1240
Minority carrier lifetime (s)	2.5×10^{-3}	10^{-3}	$\sim 10^{-8}$
Mobility (cm^2/V·s)			
Electron (μ_n)	1,500	3900	8,500
Holes (μ_p)	450	1900	450
Thermal diffusivity (cm^2/s)	0.9	0.36	0.24
Thermal conductivity (W/cm-°C)	1.5	0.6	0.46

Properties of the semiconductors Si, Ge, and GaAs



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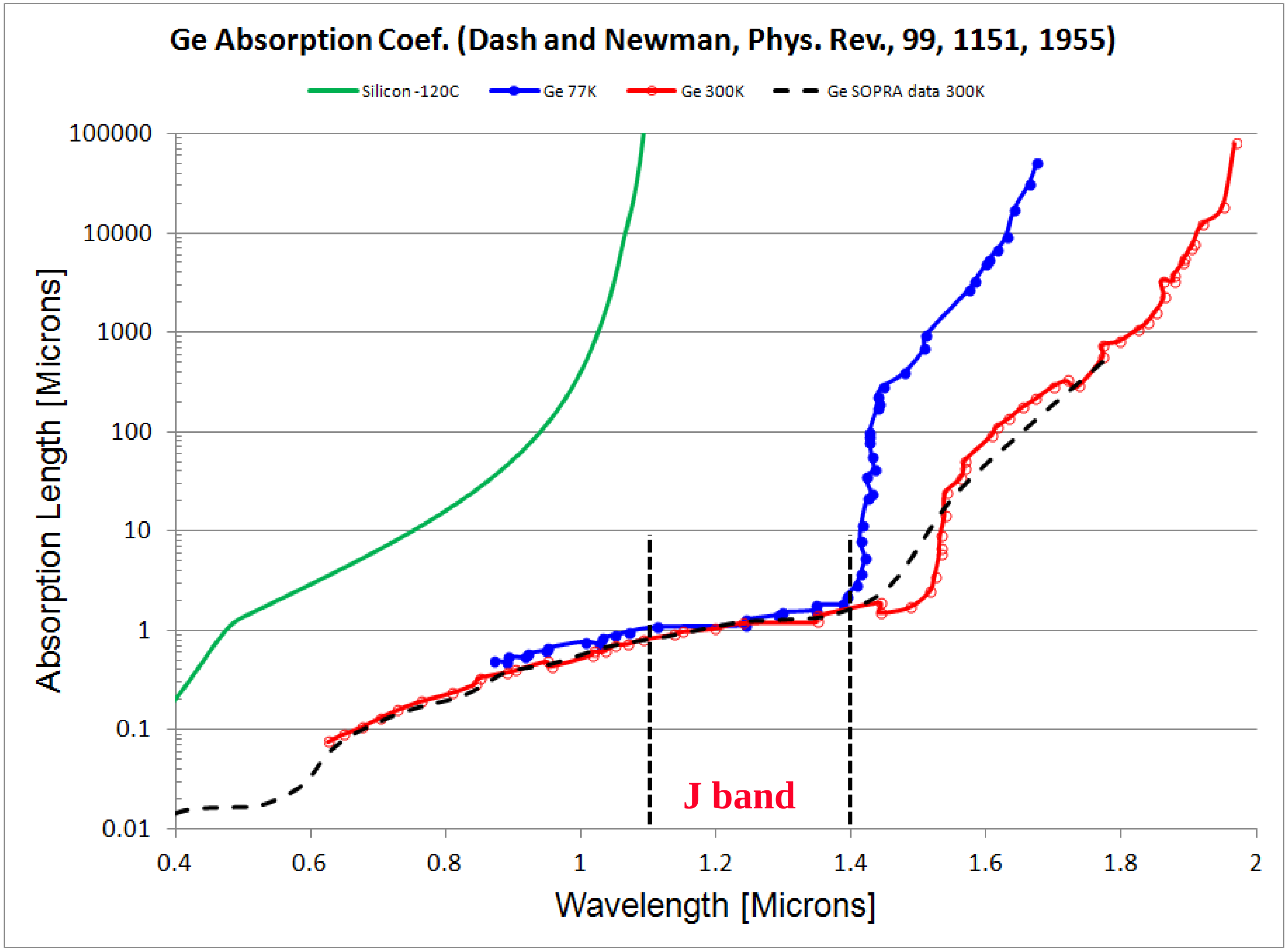
Properties	Si	Ge
Energy gap (eV)	1.12	0.67

$$\lambda_{cutoff} \approx \frac{1.24}{E_g}$$

Germanium vs Silicon



- Higher redshifts, e.g. z = 1.6 to 2.6 for DESI [O II] (Si to Ge)
  - 2x volume reach for future DESI with Ge CCDs

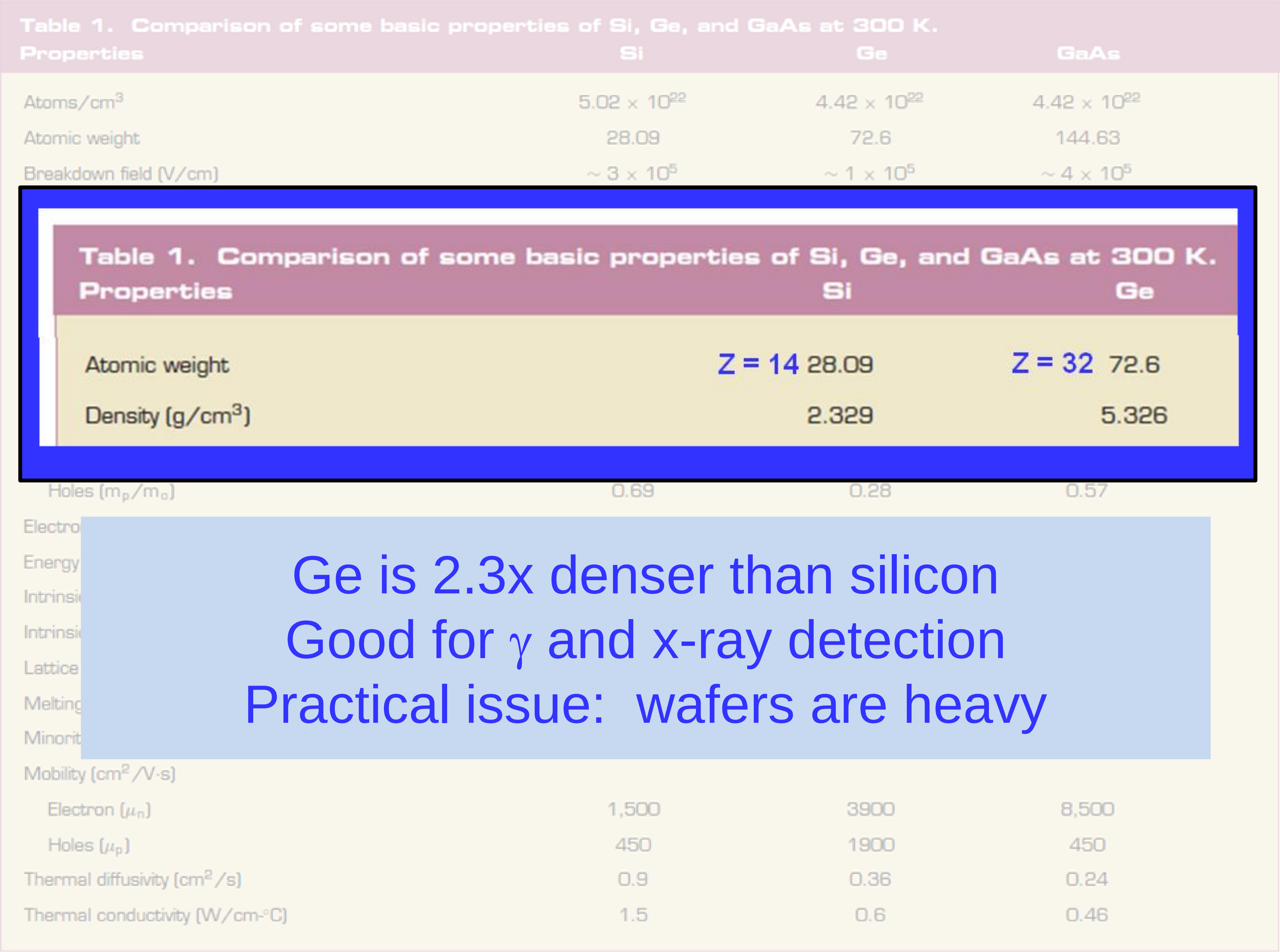


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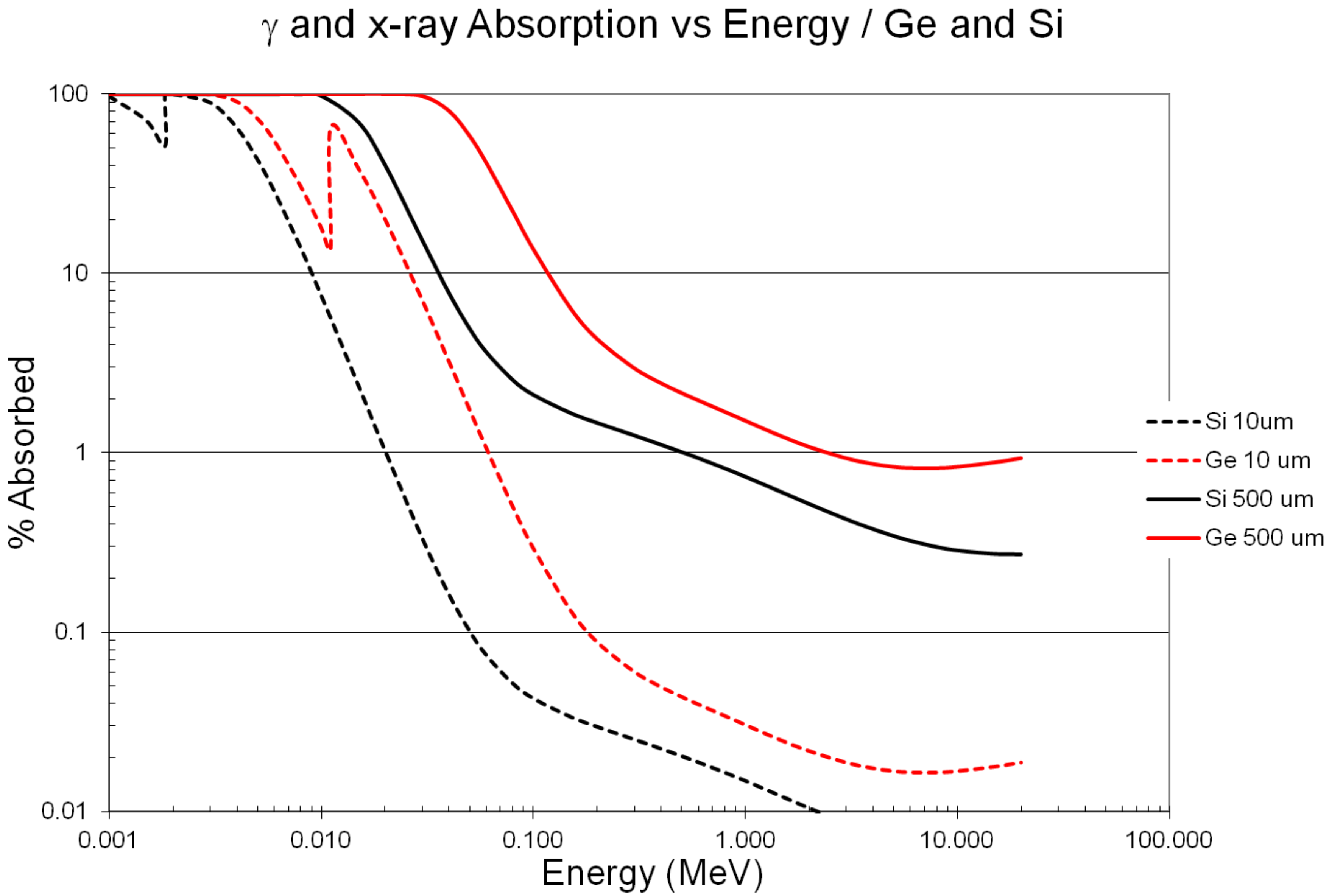
Table 1. Comparison of some basic properties of Si, Ge, and GaAs at 300 K.

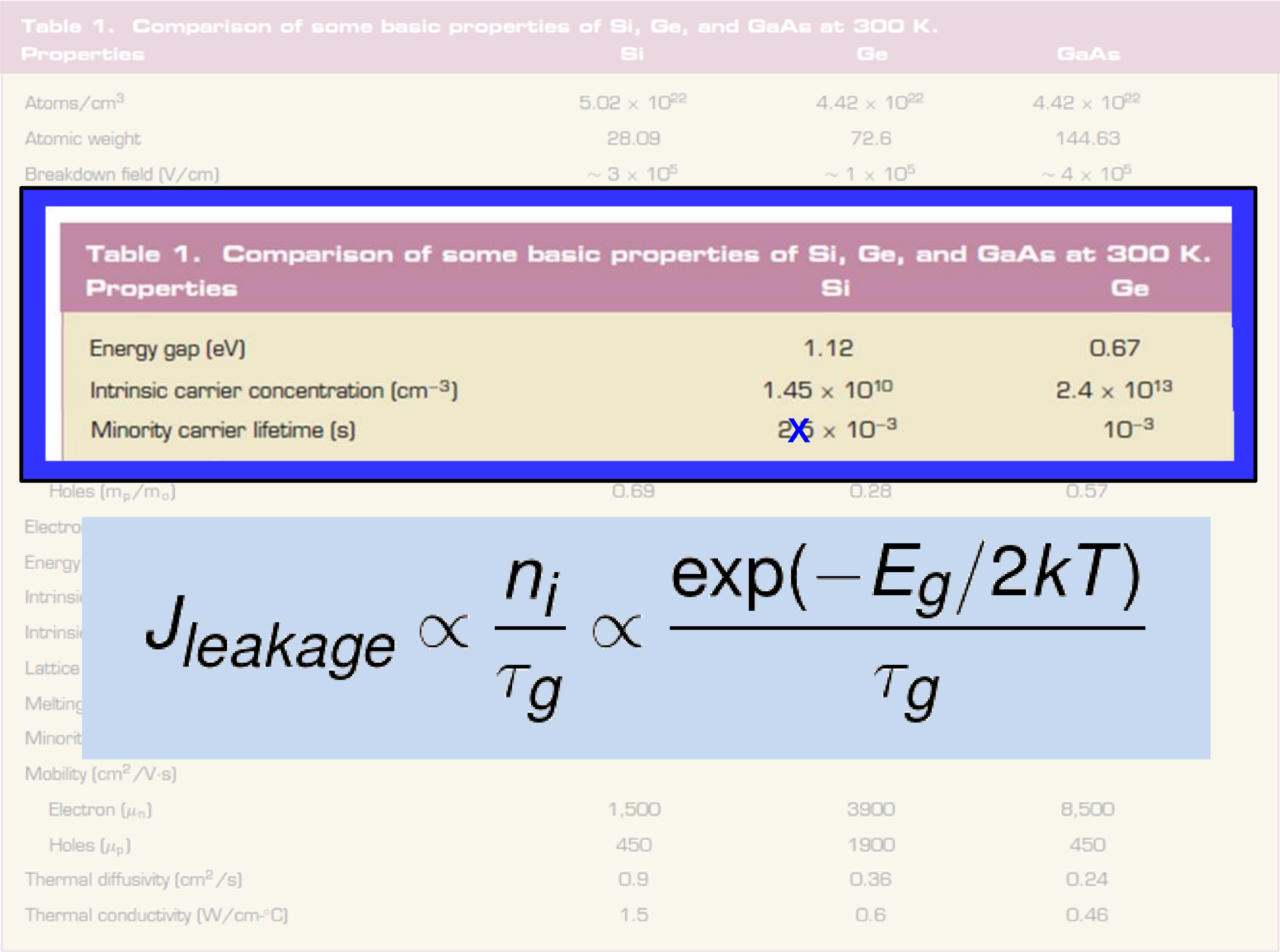
Properties	Si	Ge
Atomic weight	Z = 14 28.09	Z = 32 72.6
Density (g/cm^3)	2.329	5.326

Ge is 2.3x denser than silicon

Good for γ and x-ray detection

Practical issue: wafers are heavy


γ and x-ray Absorption vs Energy / Ge and Si
% Absorbed
100
10
1
0.1
0.01
0.001
0.010
0.100
1.000
10.000
100.000
Energy (MeV)
Si 10um
Ge 10 um
Si 500 um
Ge 500 um



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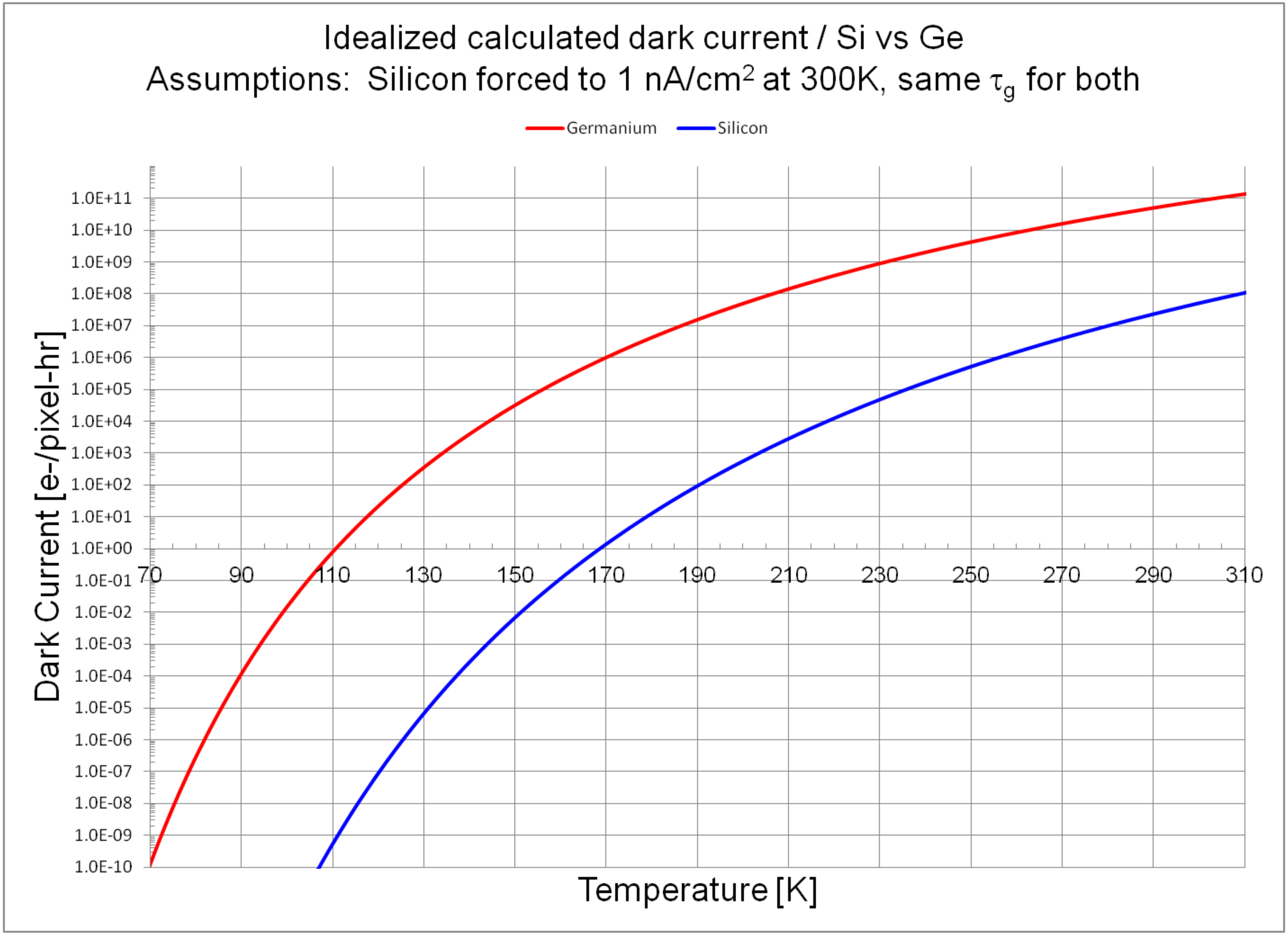
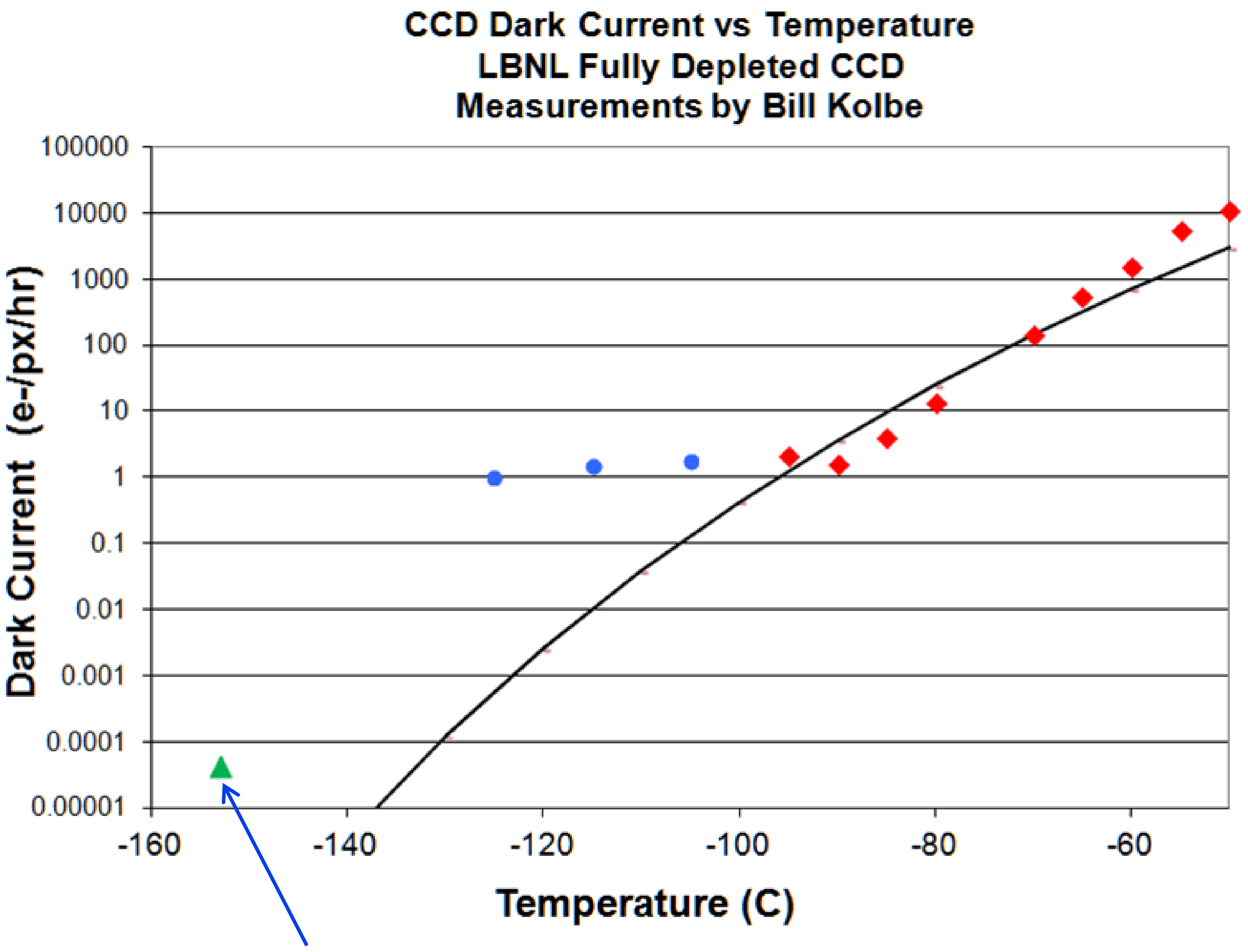
Intrinsic carrier concentration (cm^{-3})	1.45×10^{10}	2.4×10^{13}
Minority carrier lifetime (s)	2X5 × 10^{-3}	10^{-3}

$$J_{leakage} \propto \frac{n_i}{\tau_g} \propto \frac{\exp(-E_g/2kT)}{\tau_g}$$



Idealized calculated dark current / Si vs Ge
Assumptions: Silicon forced to 1 nA/cm^2 at 300K, same τ_g for both

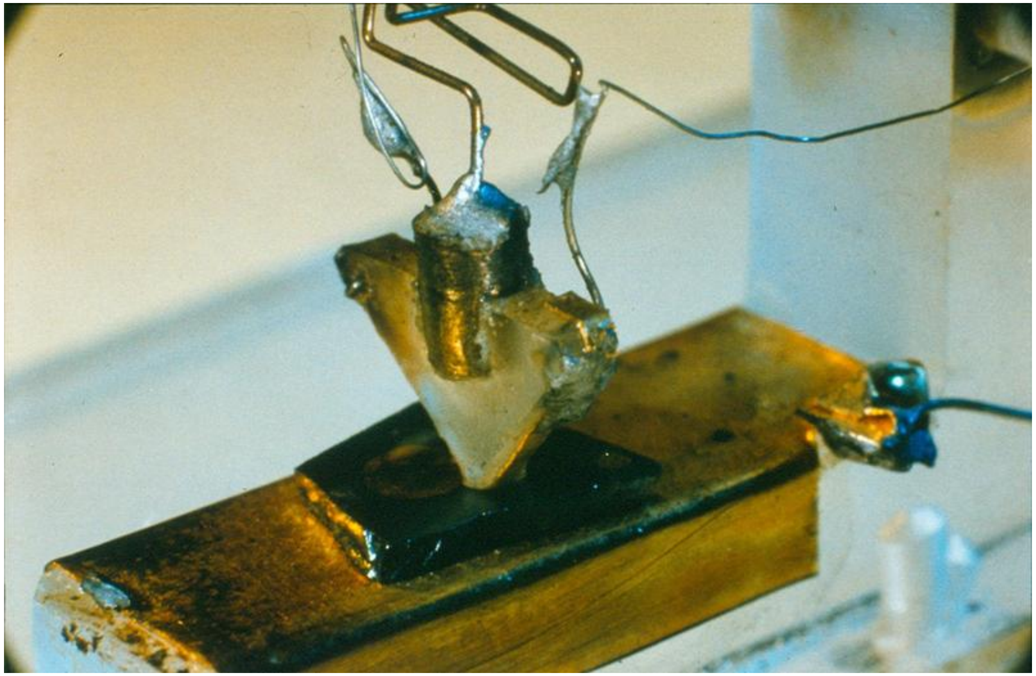
LBNL CCD Dark Current



DAMIC roughly here with their cooled Cu box enclosure
0.001 e- / pixel-day at 120K (4 x 10^{-5} e- / pixel-hr)

Very brief transistor history

- The first transistor was realized in Ge (Dec. 1947)
  - — Bardeen and Brattain, then Shockley's junction transistor

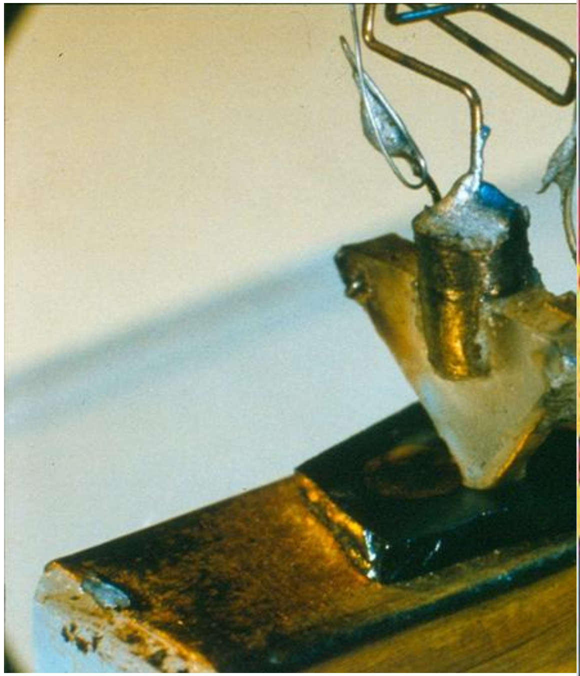


- 1st Ge transistor
  - Point contact
- Ge because the purification process was more advanced than that for silicon due to the lower melting point of Ge
  - 937°C vs 1415°C (Si)

- At a 1954 IRE conference Texas Instruments demonstrates the silicon grown junction transistor
  - — Ge and Si transistors in an audio amplifier dunked in hot oil

Very brief transistor history

- The first transis
  (Dec. 1947)
  - Bardeen and B
    nction transistor



transistor

nt contact

cause the

ation process was

advanced than that

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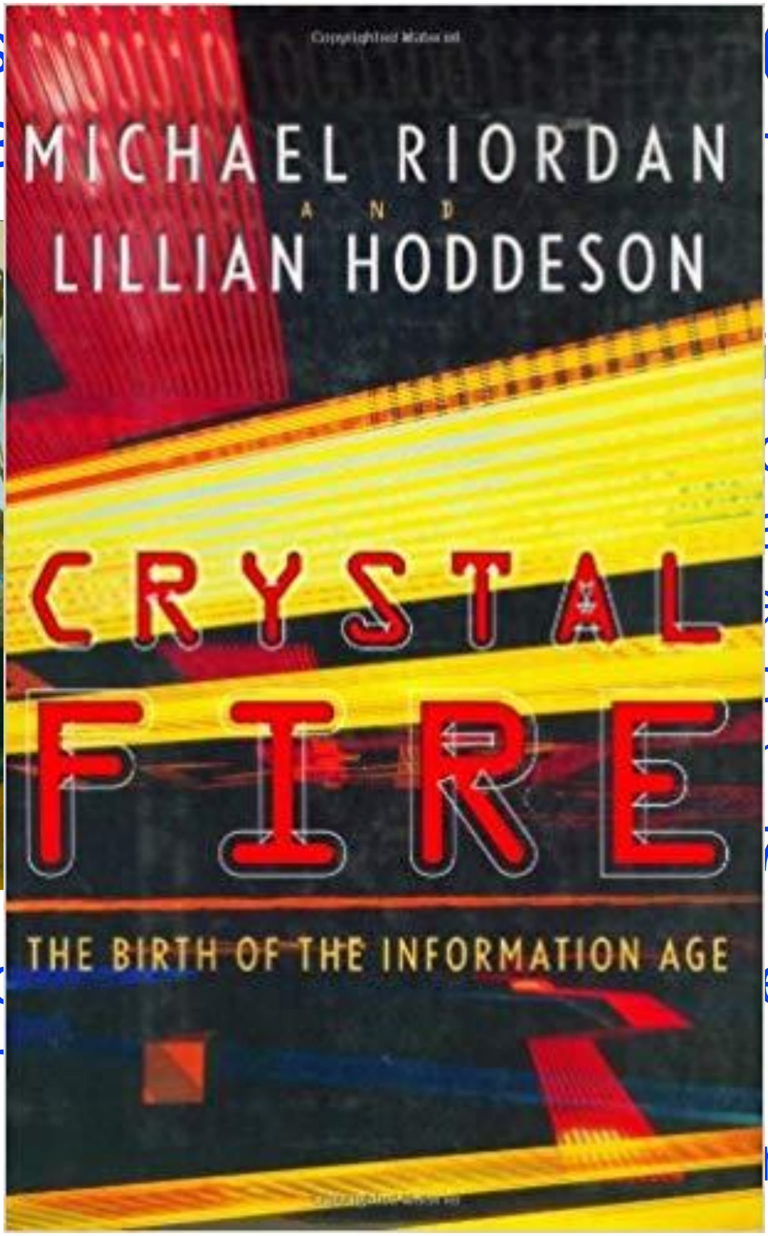
melting point of Ge

7°C vs 1415°C (Si)



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CRYSTAL FIRE

THE BIRTH OF THE INFORMATION AGE

- At a 1954 IRE co
  ents demonstrates
  the silicon grown
  - Ge and Si tran
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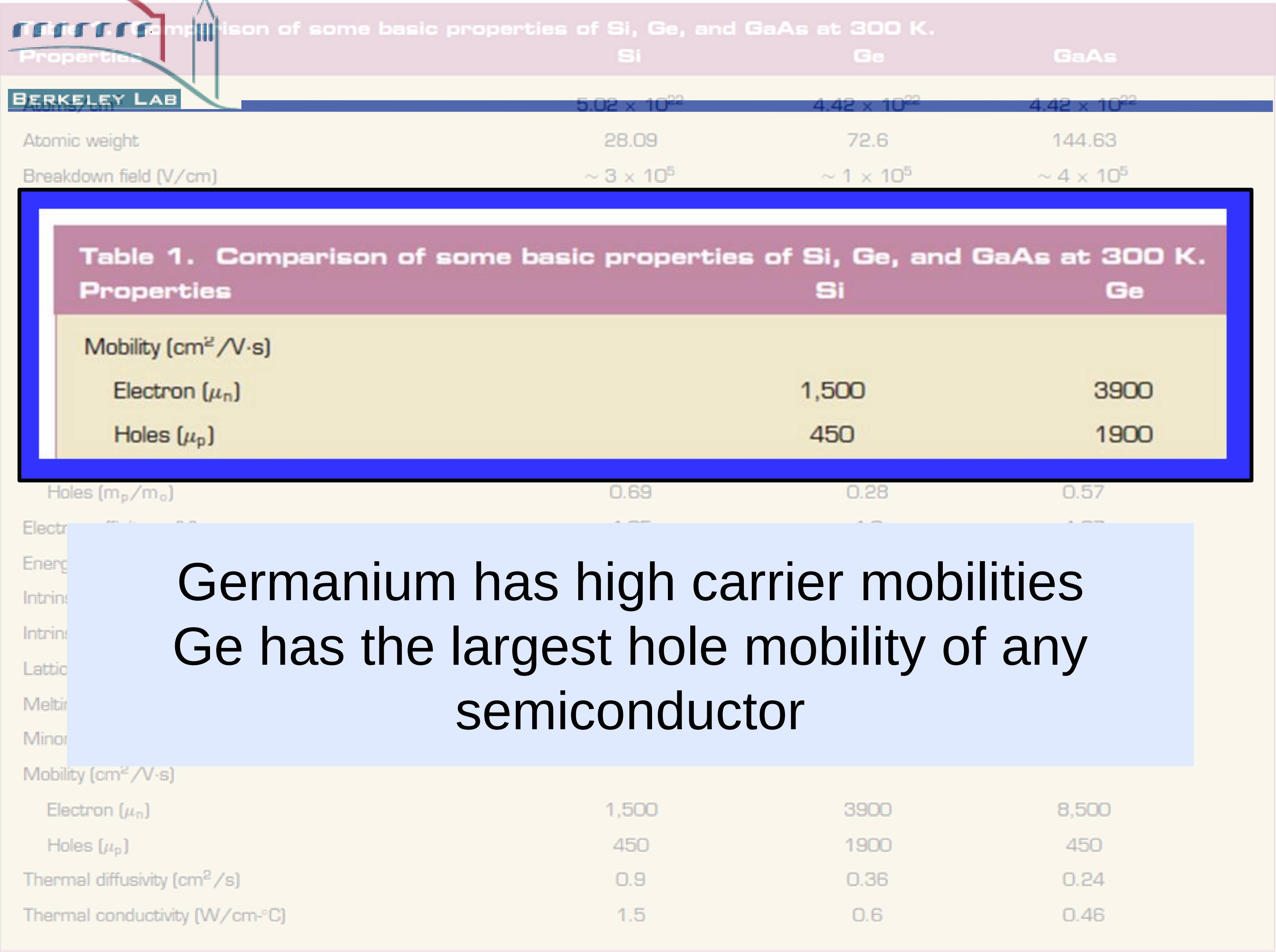

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Properties	Si	Ge
Mobility (cm^2/V·s)		
Electron (μ_n)	1,500	3900
Holes (μ_p)	450	1900

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Melti			
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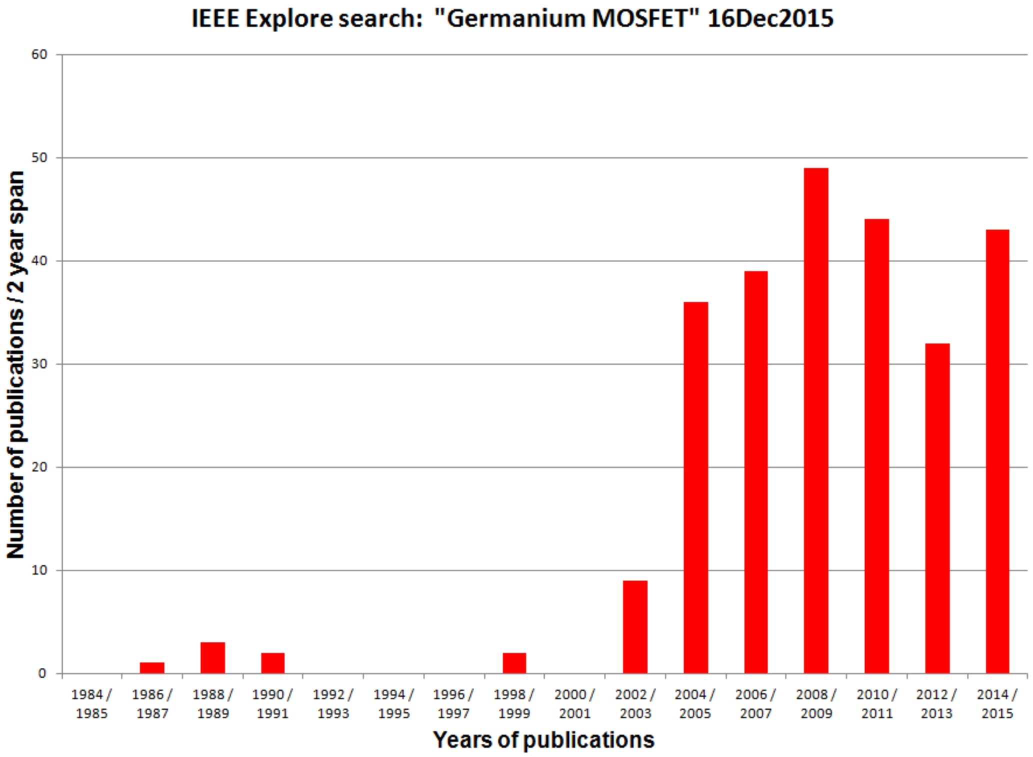
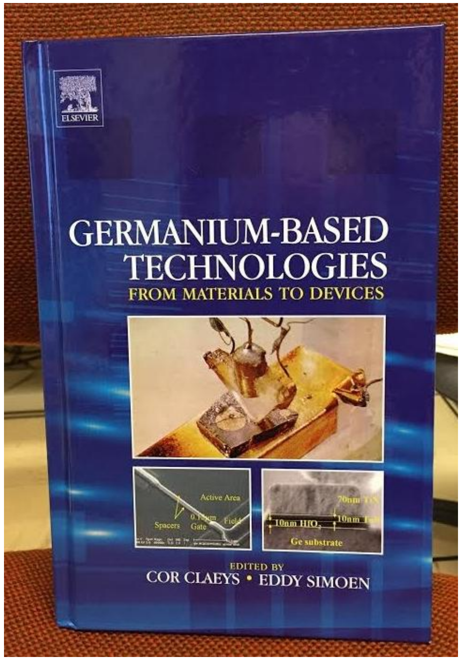
Thermal diffusivity (cm^2/s)	0.9	0.36	0.24
Thermal conductivity (W/cm-°C)	1.5	0.6	0.46

Germanium has high carrier mobilities
Ge has the largest hole mobility of any semiconductor

Opportune time for Ge R&D

— Renewed interest in Ge due to high mobilities

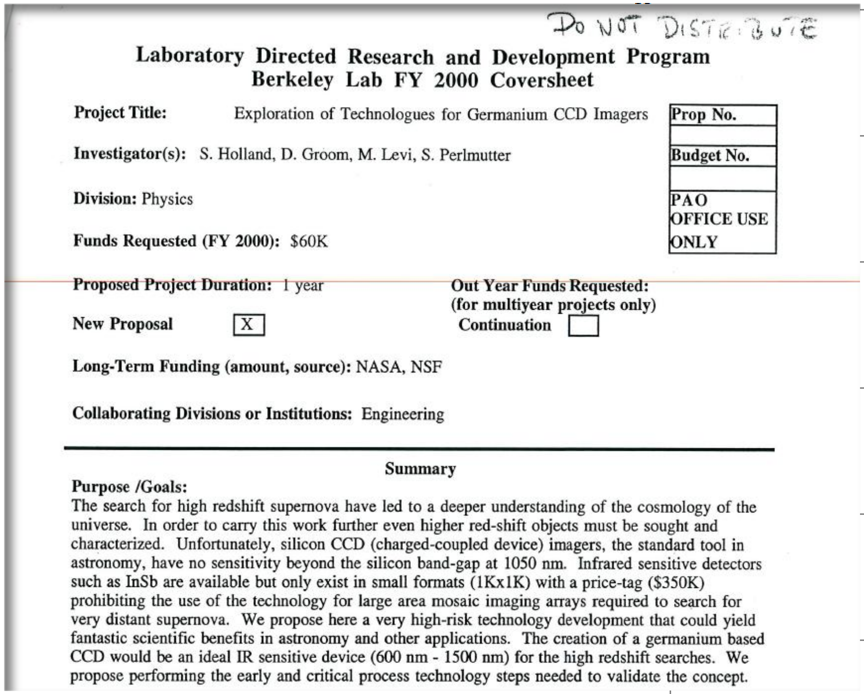




— Umicore produces 150 and 200 mm Ge wafers (low resistivity) for mostly photovoltaic applications

— Ge CCD effort at M.I.T. Lincoln Laboratories

Opportune time for Ge R&D



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Laboratory Directed Research and Development Program
Berkeley Lab FY 2000 Coversheet

Project Title: Exploration of Technologues for Germanium CCD Imagers

Investigator(s): S. Holland, D. Groom, M. Levi, S. Perlmutter

Division: Physics

Funds Requested (FY 2000): $60K

Prop No.	
Budget No.	
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Proposed Project Duration: 1 year

Out Year Funds Requested:
(for multiyear projects only)

New Proposal ☒

Continuation ☐

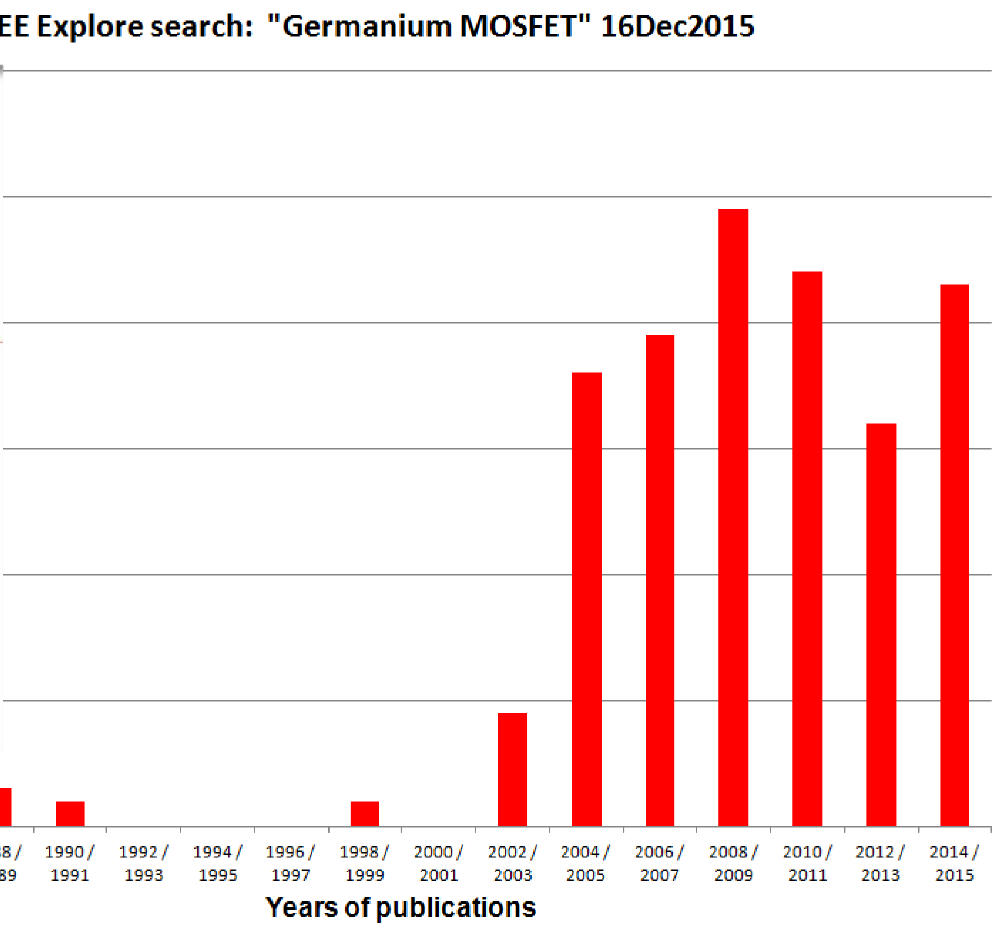
Long-Term Funding (amount, source): NASA, NSF

Collaborating Divisions or Institutions: Engineering

Summary

Purpose /Goals:
The search for high redshift supernova have led to a deeper understanding of the cosmology of the universe. In order to carry this work further even higher red-shift objects must be sought and characterized. Unfortunately, silicon CCD (charged-coupled device) imagers, the standard tool in astronomy, have no sensitivity beyond the silicon band-gap at 1050 nm. Infrared sensitive detectors such as InSb are available but only exist in small formats (1Kx1K) with a price-tag ($350K) prohibiting the use of the technology for large area mosaic imaging arrays required to search for very distant supernova. We propose here a very high-risk technology development that could yield fantastic scientific benefits in astronomy and other applications. The creation of a germanium based CCD would be an ideal IR sensitive device (600 nm - 1500 nm) for the high redshift searches. We propose performing the early and critical process technology steps needed to validate the concept.

IEEE Explore search: "Germanium MOSFET" 16Dec2015

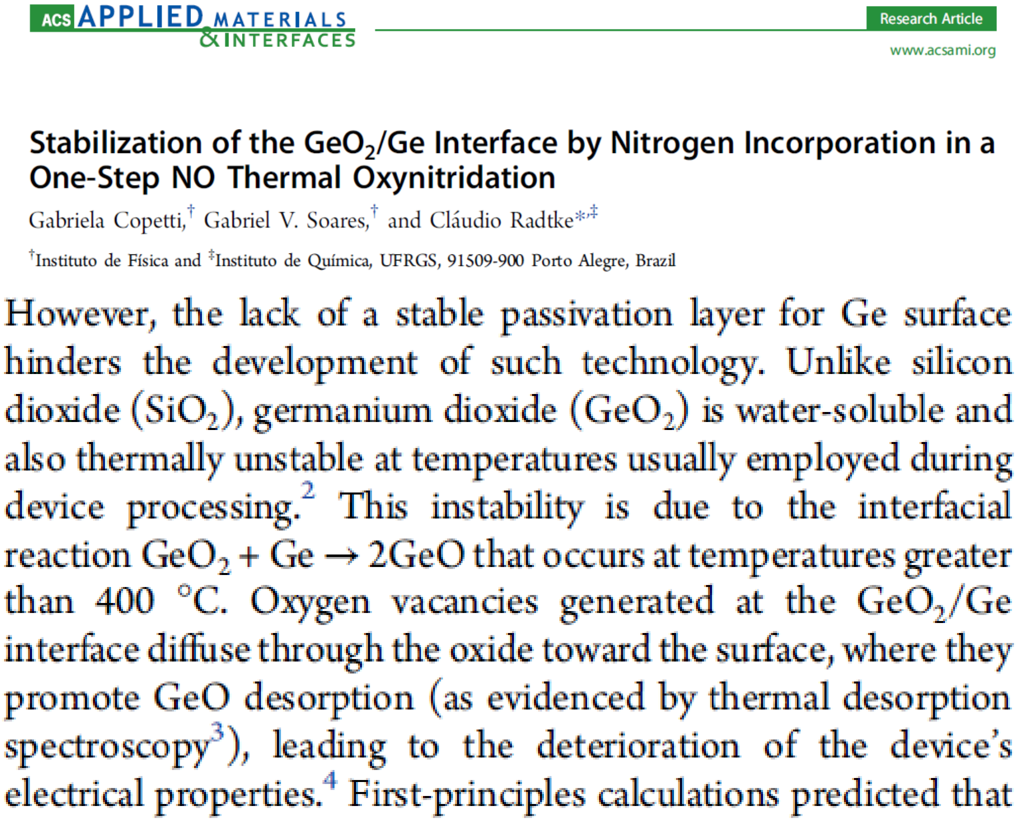


We applied for a Ge CCD LDRD in 2000

Luckily it was not approved

Ge issues

- Numerous technical challenges with Ge
  - — Water soluble GeO_2 insulator that degrades starting at 400°C due to GeO_2 decomposition (more on this later)



ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

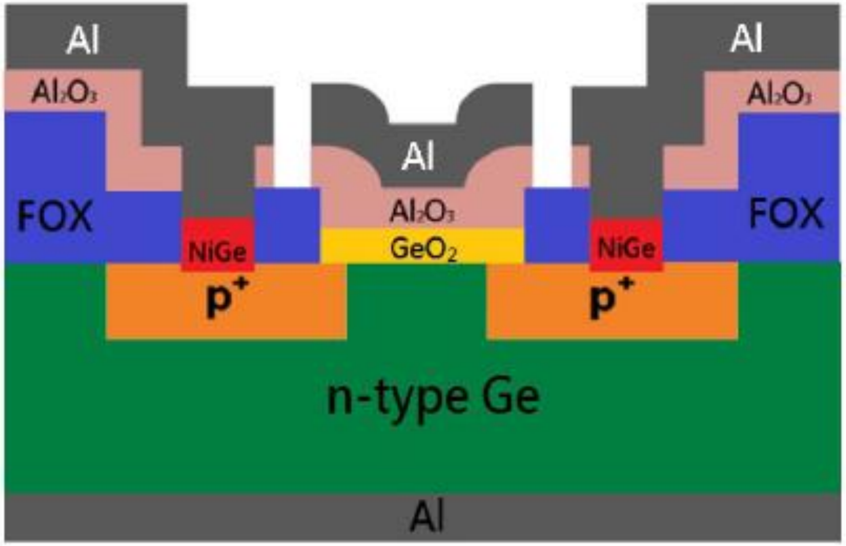
Stabilization of the GeO_2/Ge Interface by Nitrogen Incorporation in a One-Step NO Thermal Oxynitridation

Gabriela Copetti,[†] Gabriel V. Soares,[†] and Cláudio Radtke[*,‡]

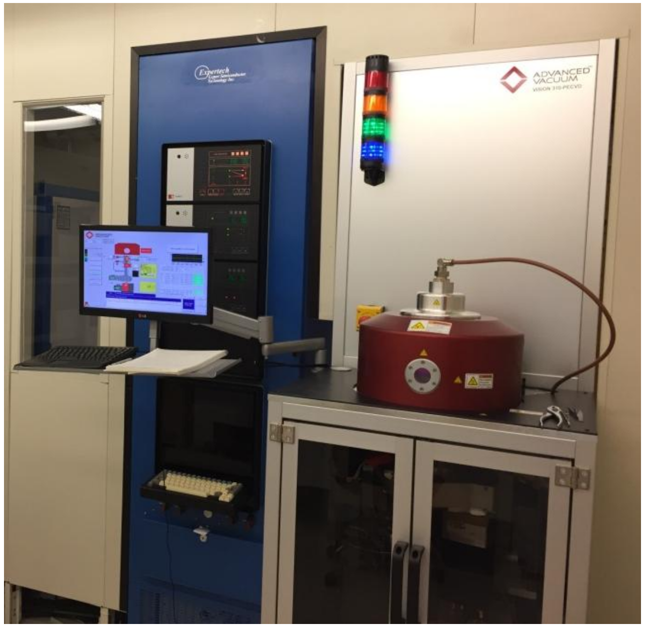
[†]Instituto de Física and [‡]Instituto de Química, UFRGS, 91509-900 Porto Alegre, Brazil

However, the lack of a stable passivation layer for Ge surface hinders the development of such technology. Unlike silicon dioxide (SiO_2), germanium dioxide (GeO_2) is water-soluble and also thermally unstable at temperatures usually employed during device processing.[2] This instability is due to the interfacial reaction $GeO_2 + Ge \rightarrow 2GeO$ that occurs at temperatures greater than 400 °C. Oxygen vacancies generated at the GeO_2/Ge interface diffuse through the oxide toward the surface, where they promote GeO desorption (as evidenced by thermal desorption spectroscopy[3]), leading to the deterioration of the device's electrical properties.[4] First-principles calculations predicted that

❑ Nonetheless, GeO_2/Ge interface is better than the alternatives, so cap with another insulator



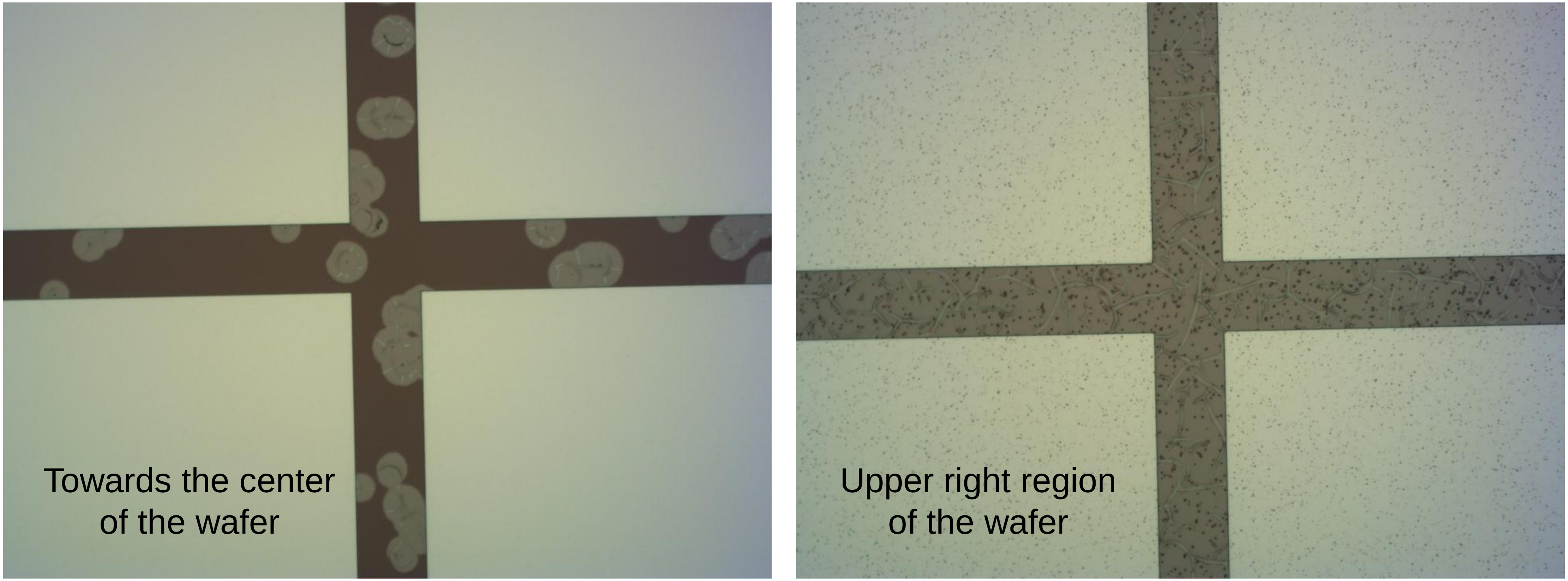
LBNL MicroSystems Laboratory



- Class 10 clean room
  - —150 mm wafer processing
  - — DECam / DESI CCDs with DALSA
  - — Ge CCD R&D

LBNL Ge R&D (LDRD)

- 1st attempt at GeO_2-SiO_2 gate insulator
  - — Low temperature (300°C) SiO_2 deposition over GeO_2
    - Pinholes in the deposited SiO_2 result in etching of the water-soluble GeO_2 when exposed to e.g. H_2O

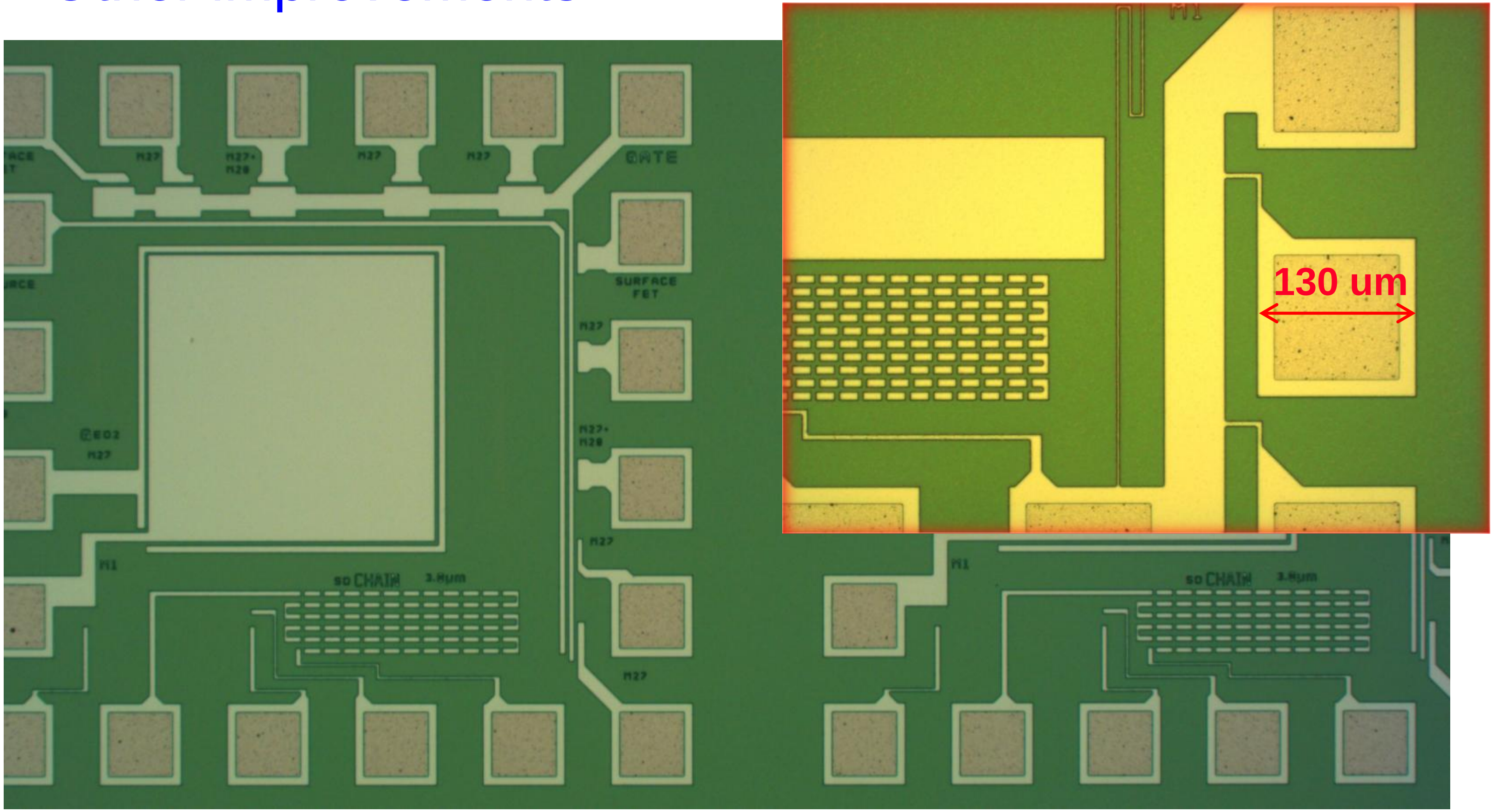

Towards the center of the wafer

Upper right region of the wafer

Capacitor-only wafer: Aluminum over SiO_2 over GeO_2

LBNL Ge R&D (LDRD)

- 2^{nd} attempt at SiO_2-GeO_2 using improved methods
  - — Two step SiO_2 deposition / pinholes not likely coincident
  - — Other improvements



Capacitor-only wafer: Entire region is SiO_2 over GeO_2

LBNL Ge R&D (LDRD)

- Next step: Fabricate Ge buried-channel MOSFETs
  - Basic building block of CCDs

—Short-loop study to debug the basic Ge process

- Metal gate transistors now, future polyGe gate

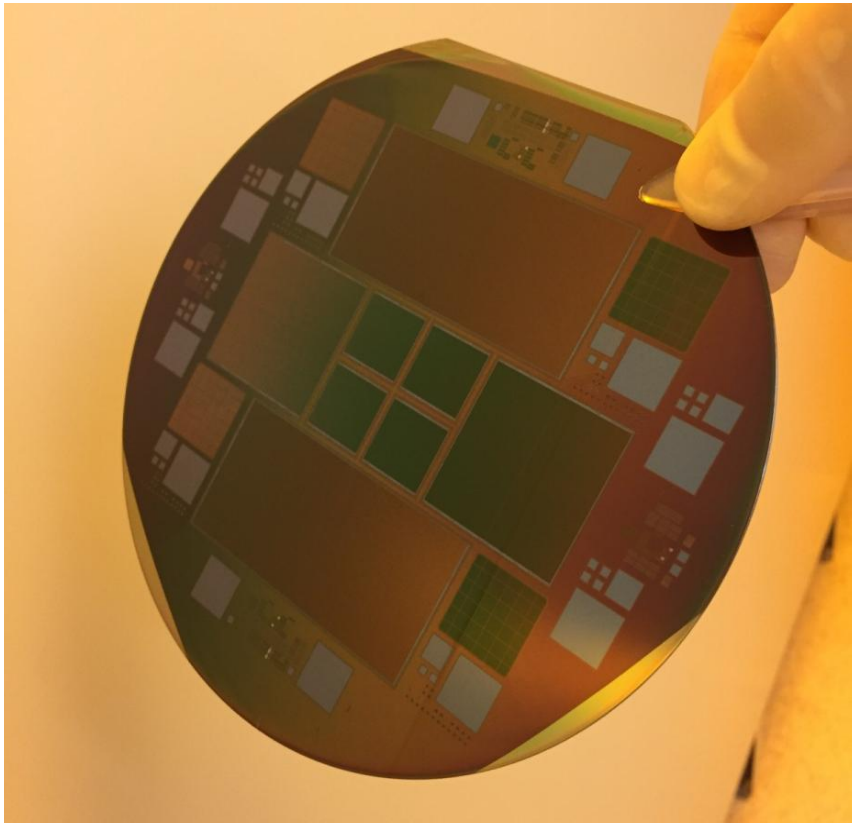
—Required two ion implantation steps

- Work with implant vendor Innovion regarding their concerns with heavy / fragile Ge substrates

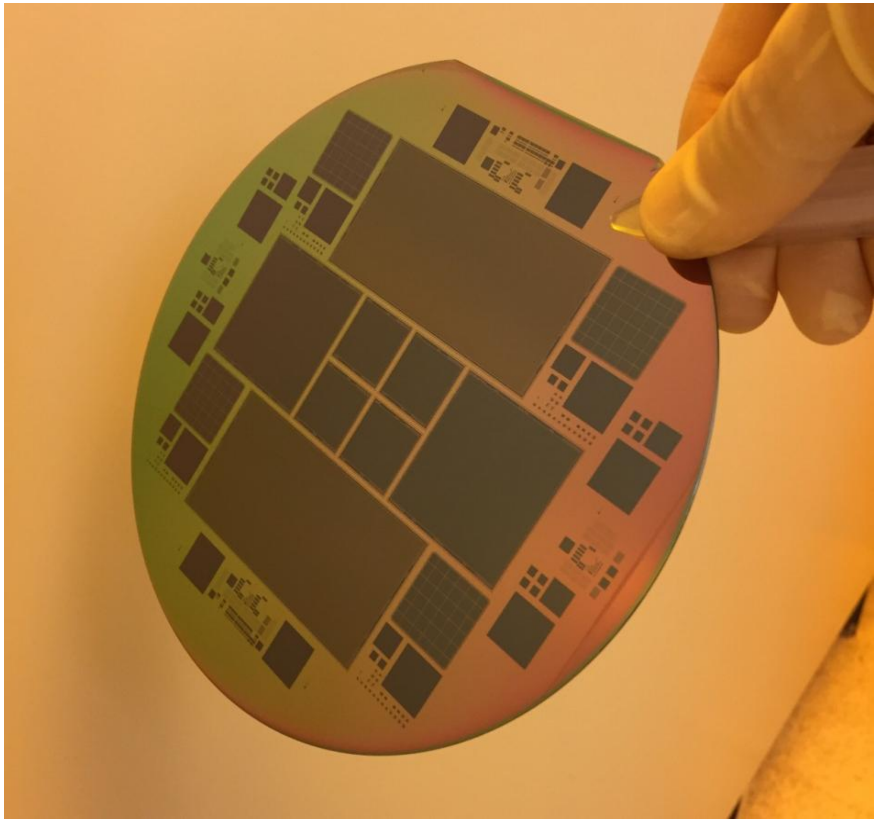
—Required MSL equipment upgrade for photoresist removal after high-dose implants

- H_2SO_4-H_2O_2 often used in silicon not compatible with Ge (as is the case with most silicon cleans)

LBNL Ge R&D (LDRD)



Post high-dose implant with resist mask



After plasma resist strip (previously unused “asher” outfitted with special wafer handler)

LBNL Ge R&D (LDRD)

- Buried channel MOSFETs for CCDs

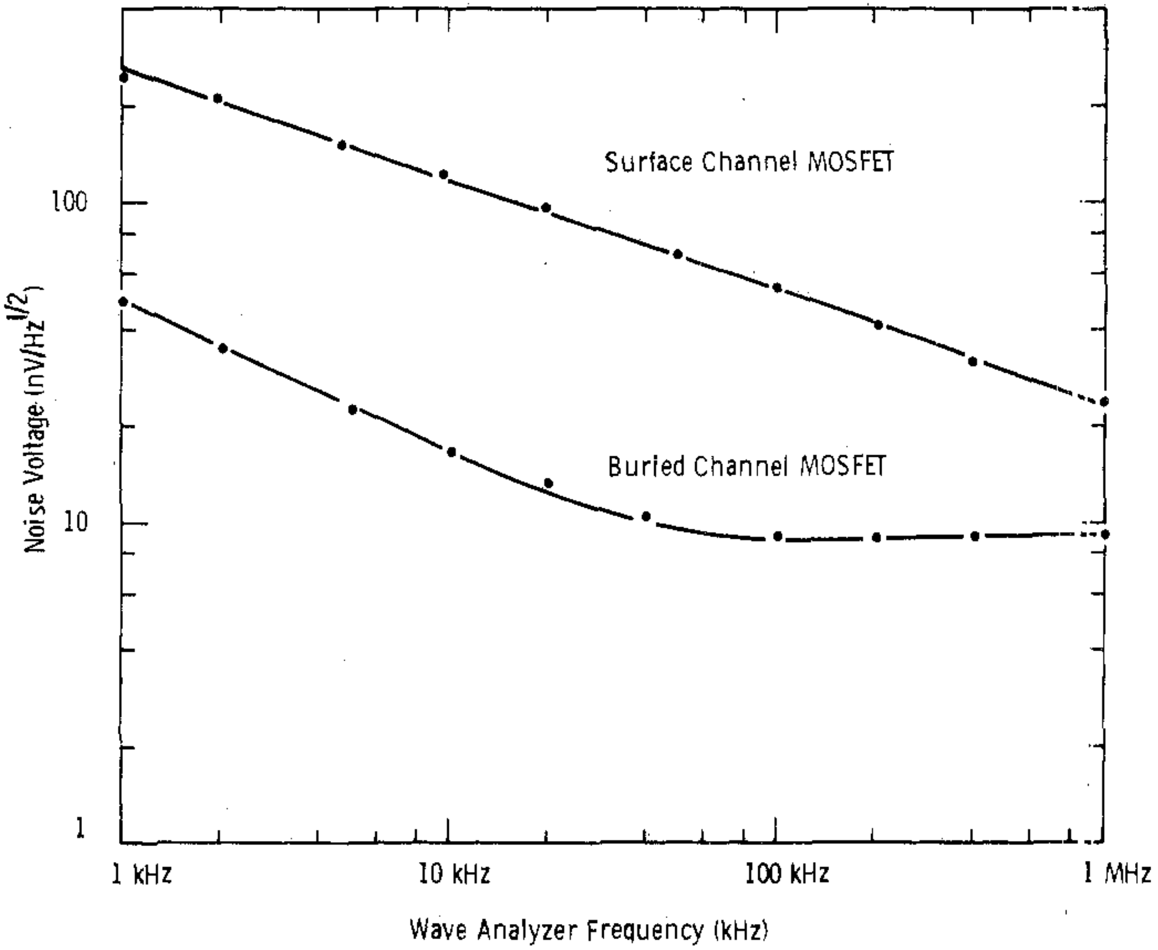


Fig. 4. Comparison of noise voltage for buried and surface channel MOSFET's.

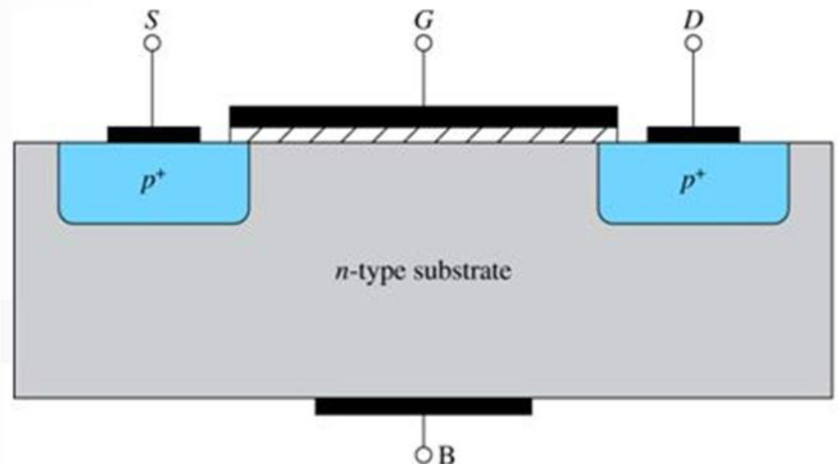
IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. ED-23, NO. 2, FEBRUARY 1976 215

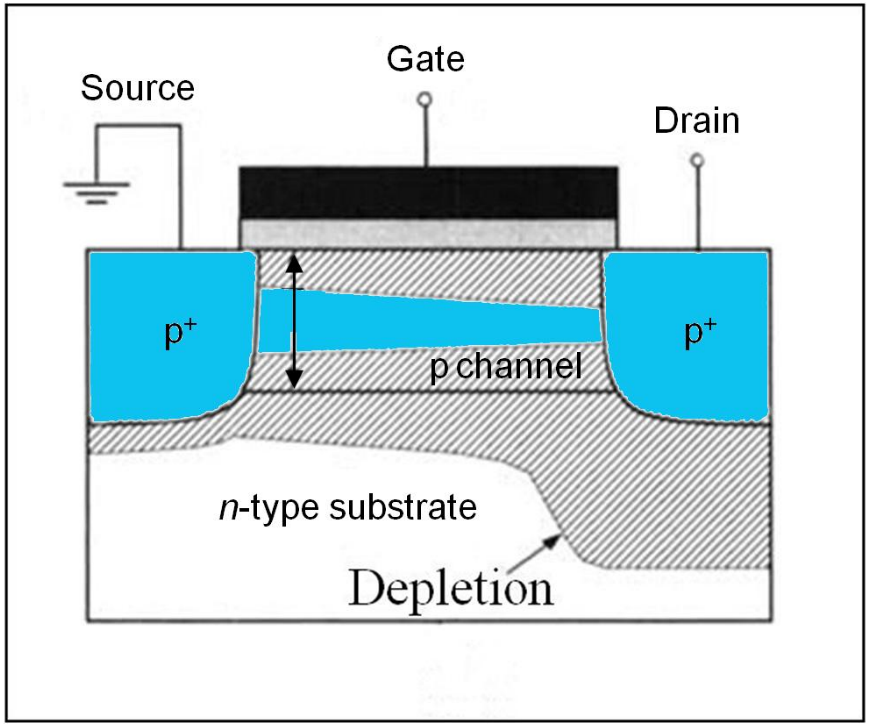
Noise in Buried Channel Charge-Coupled Devices

ROBERT W. BRODERSEN AND STEPHEN P. EMMONS, MEMBER, IEEE

LBNL Ge R&D (LDRD)

- Surface versus buried channel MOSFETs



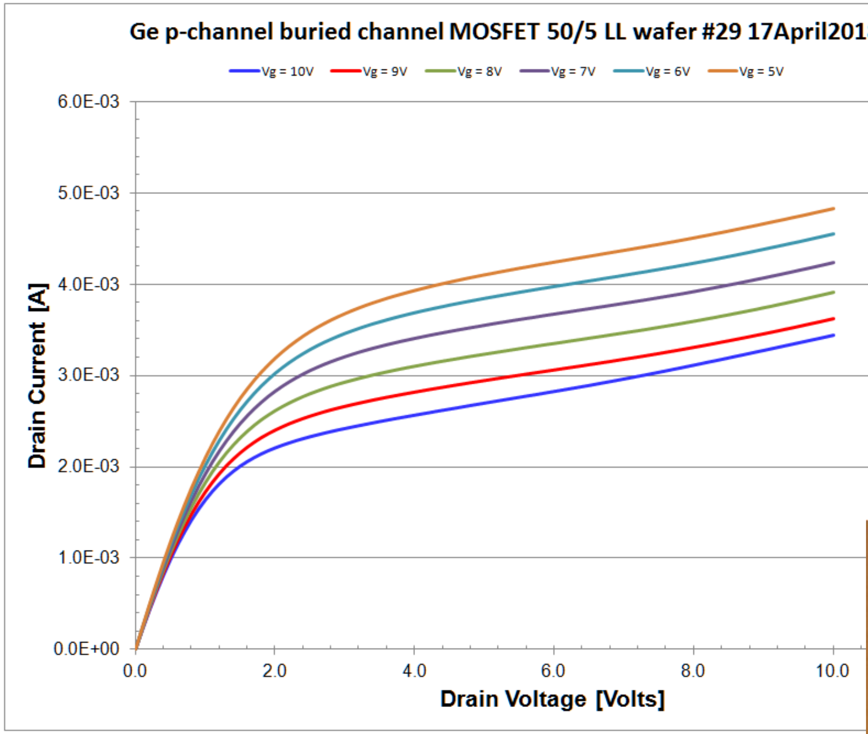


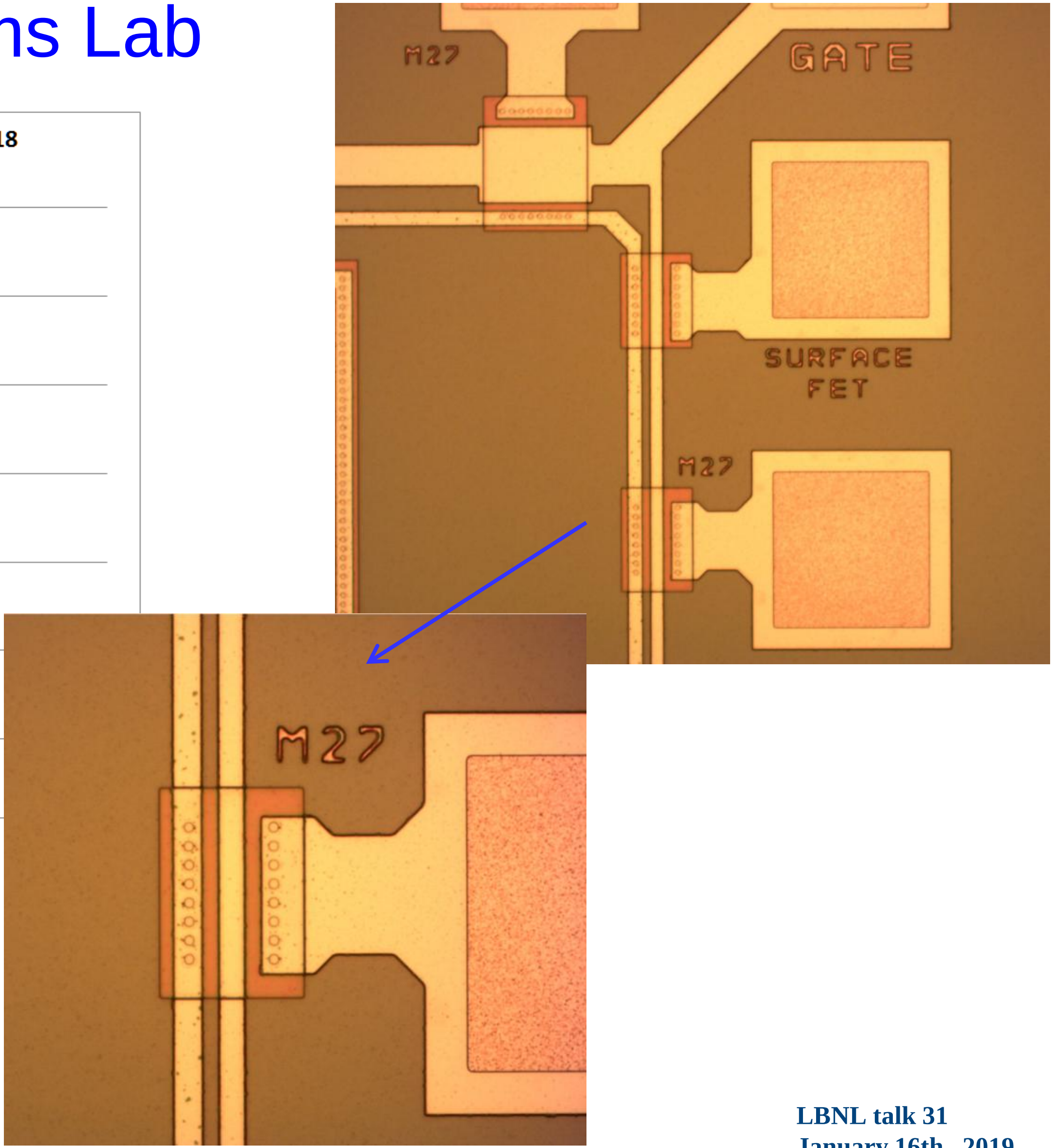
- Surface channel MOSFET
- Conduction in a narrow inversion layer along the surface next to the gate insulator
- Interface-states trap charge and increase the 1/f noise

- Buried channel MOSFET
- Conduction below the surface (blue region)
- Less sensitive to interface states

LBNL Ge R&D (LDRD)

- Germanium buried-channel MOSFET fabricated at the LBNL MicroSystems Lab



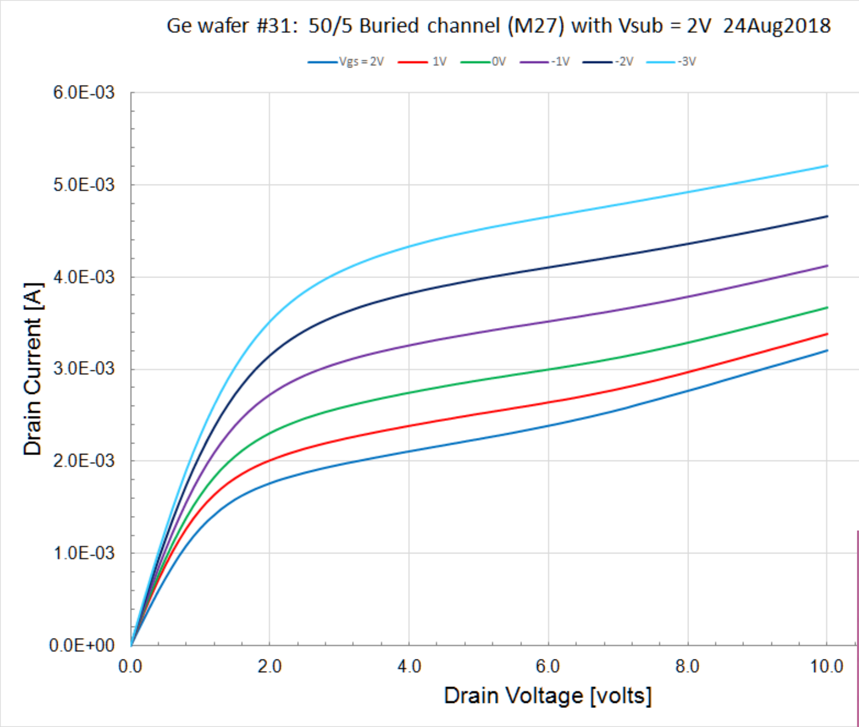


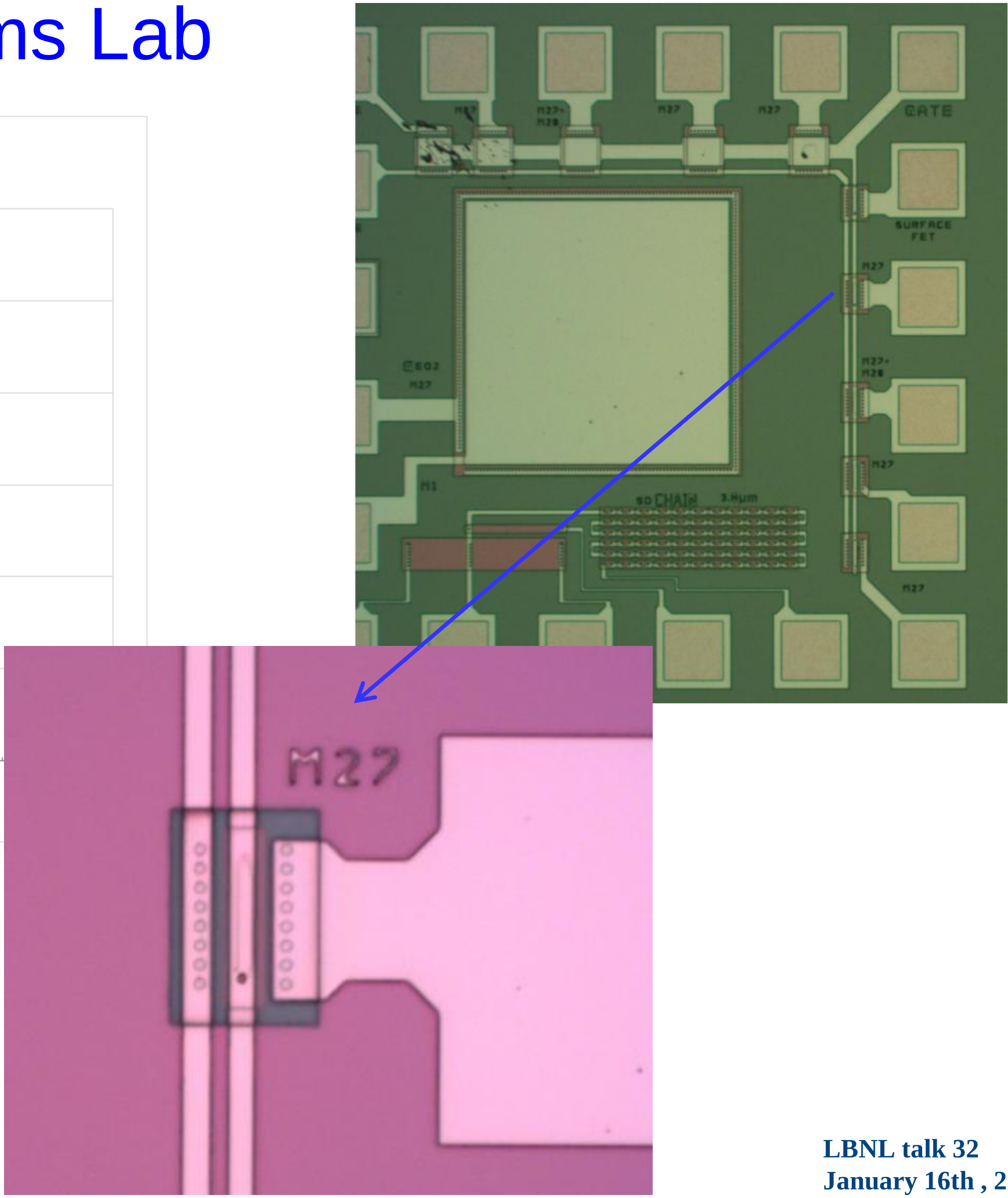
PECVD[†] SiO_2 gate dielectric
Metal-gate transistor

[†] Plasma-enhanced chemical vapor deposition

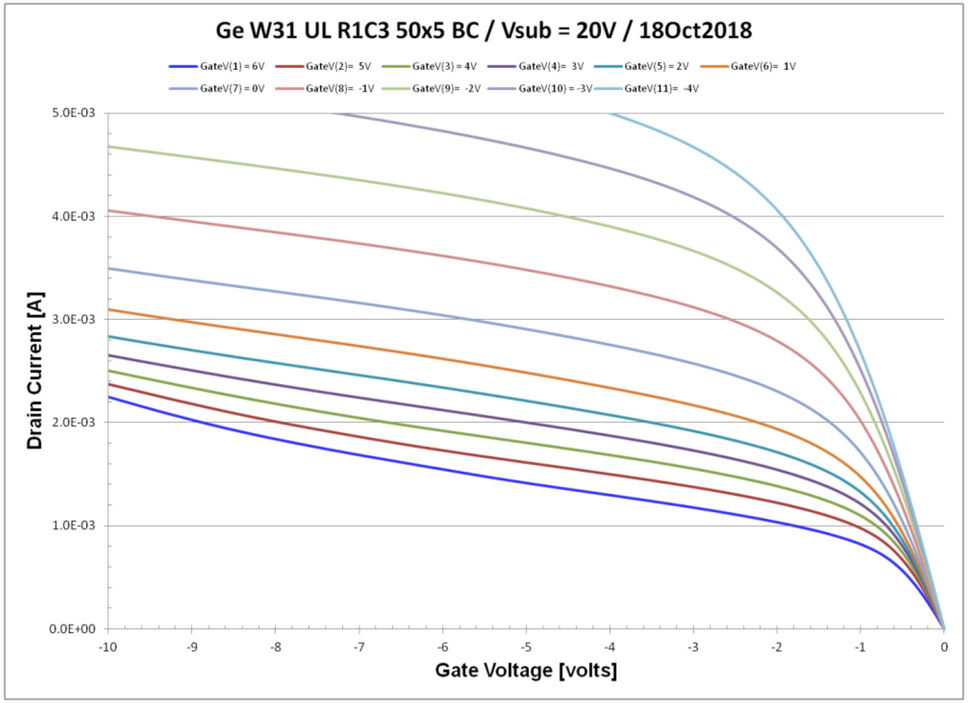
LBNL Ge R&D (LDRD)

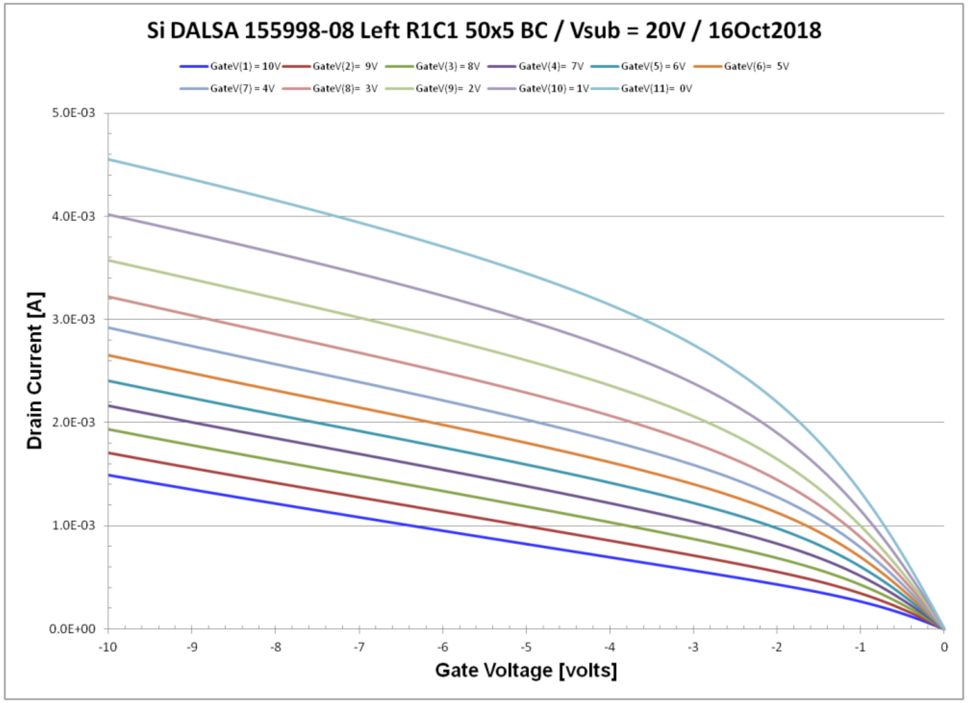
- Germanium buried-channel MOSFET fabricated at the LBNL MicroSystems Lab





SiO_2-GeO_2 gate dielectric
Metal-gate transistor

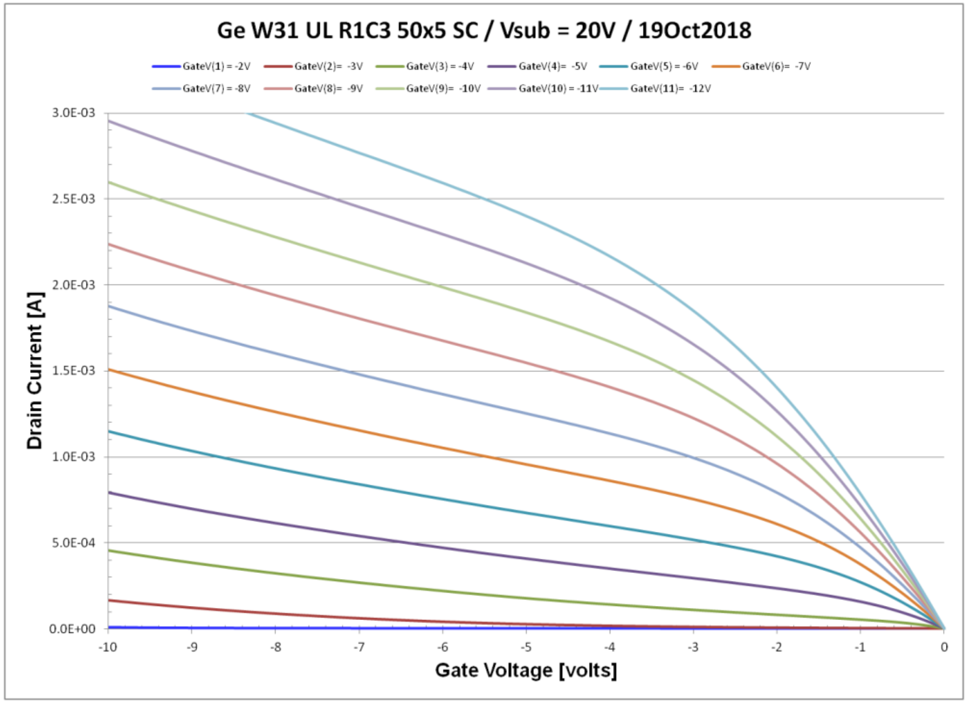


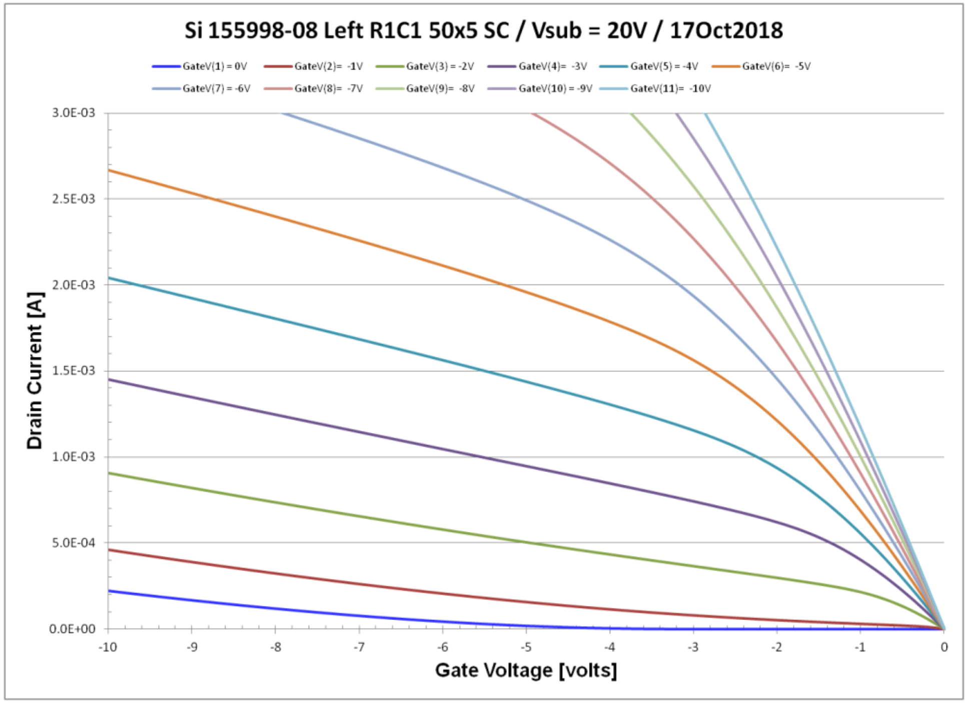


- ○ Ge buried channel MOSFET
- ○ W/L: 50 um / 5 um
- ○ Metal gate

- ○ Si buried channel MOSFET
- ○ W/L: 50 um / 5 um
- ○ Polysilicon gate

Detailed comparisons difficult, but encouraging that the Ge MOSFET has similar performance to the Si device





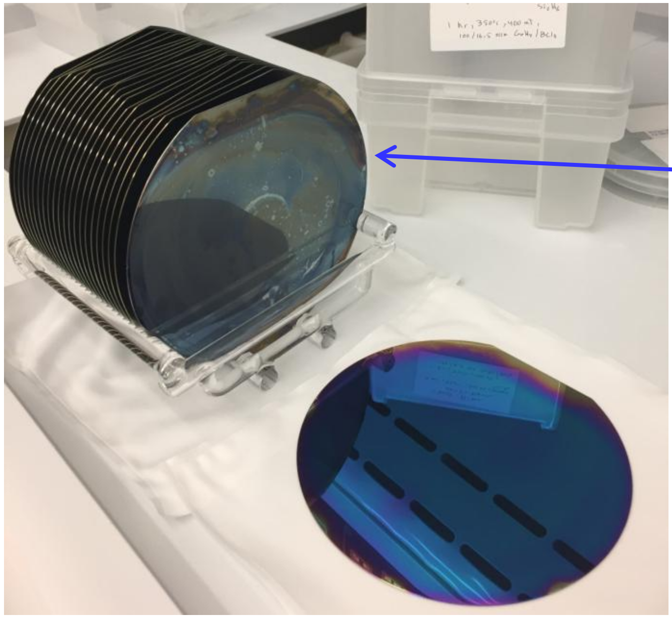
- Ge surface channel MOSFET
- W/L 50 um / 5 um
- Metal gate

- Si surface channel MOSFET
- W/L 50 um / 5 um
- Polysilicon gate

Ge surface channel MOSFET appears to be inferior
GeO_2/Ge versus SiO_2/Si interface

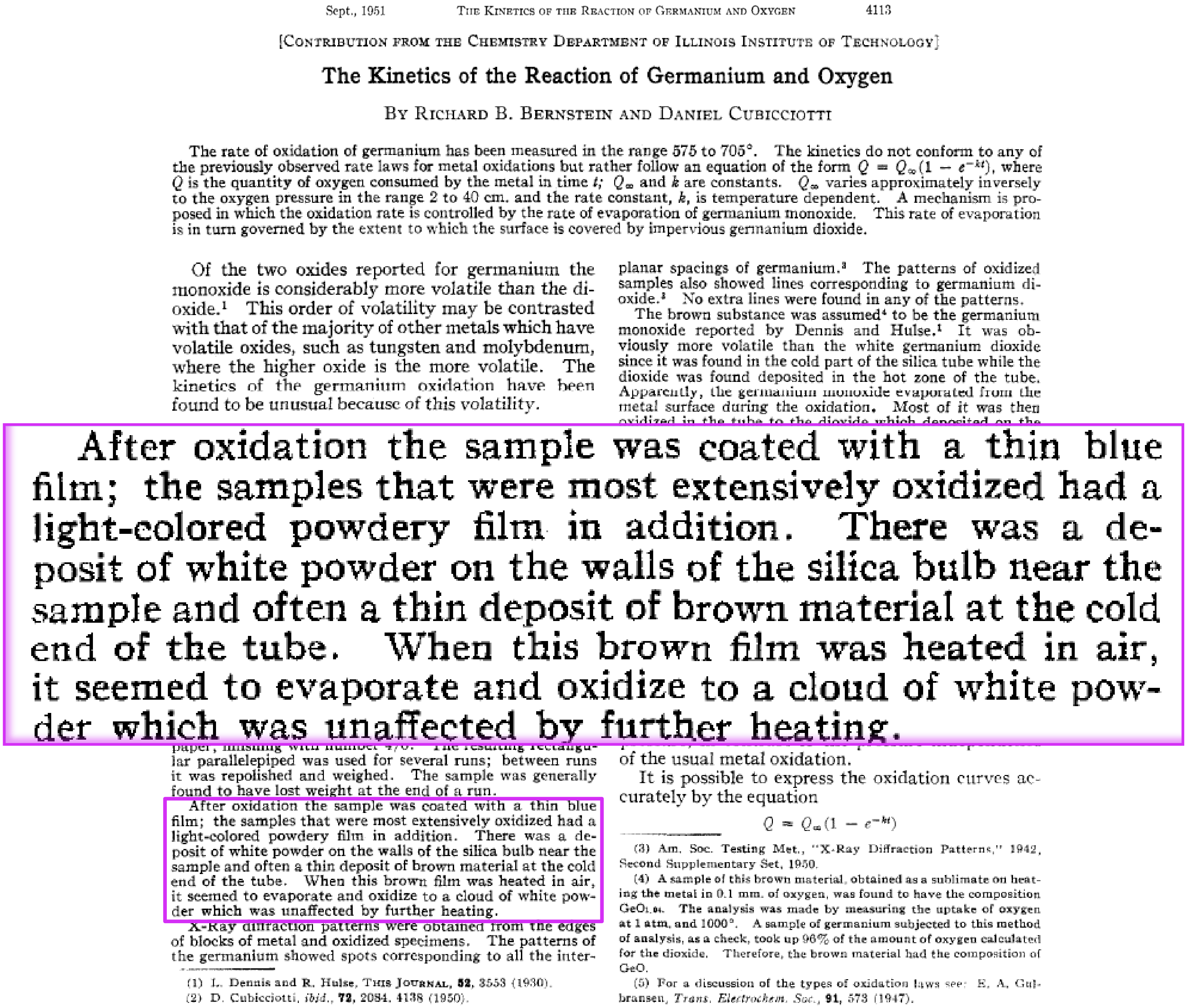
LBNL Ge R&D (LDRD)

- Non-ideal effects noted in the first transistor fabrication, the worst shown below
  - 600°C oxidation step on a Ge wafer with no coating on the backside of the wafer
  - Adjacent silicon wafer had blue film deposited that was water soluble (likely GeO_2)



Back side of a Ge wafer after 1 hour, 600°C in O_2

Water soluble film deposited on adjacent, oxidized silicon wafer



[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Kinetics of the Reaction of Germanium and Oxygen

BY RICHARD B. BERNSTEIN AND DANIEL CUBICCIOTTI

The rate of oxidation of germanium has been measured in the range 575 to 705°. The kinetics do not conform to any of the previously observed rate laws for metal oxidations but rather follow an equation of the form $Q = Q_\infty(1 - e^{-kt})$, where Q is the quantity of oxygen consumed by the metal in time t; Q_∞ and k are constants. Q_∞ varies approximately inversely to the oxygen pressure in the range 2 to 40 cm. and the rate constant, k, is temperature dependent. A mechanism is proposed in which the oxidation rate is controlled by the rate of evaporation of germanium monoxide. This rate of evaporation is in turn governed by the extent to which the surface is covered by impervious germanium dioxide.

Of the two oxides reported for germanium the monoxide is considerably more volatile than the dioxide.[1] This order of volatility may be contrasted with that of the majority of other metals which have volatile oxides, such as tungsten and molybdenum, where the higher oxide is the more volatile. The kinetics of the germanium oxidation have been found to be unusual because of this volatility.

lar parallelepiped was used for several runs; between runs it was repolished and weighed. The sample was generally found to have lost weight at the end of a run.

After oxidation the sample was coated with a thin blue film; the samples that were most extensively oxidized had a light-colored powdery film in addition. There was a deposit of white powder on the walls of the silica bulb near the sample and often a thin deposit of brown material at the cold end of the tube. When this brown film was heated in air, it seemed to evaporate and oxidize to a cloud of white powder which was unaffected by further heating.

X-Ray diffraction patterns were obtained from the edges of blocks of metal and oxidized specimens. The patterns of the germanium showed spots corresponding to all the interplanar spacings of germanium.[3] The patterns of oxidized samples also showed lines corresponding to germanium dioxide.[3] No extra lines were found in any of the patterns.

The brown substance was assumed[4] to be the germanium monoxide reported by Dennis and Hulse.[1] It was obviously more volatile than the white germanium dioxide since it was found in the cold part of the silica tube while the dioxide was found deposited in the hot zone of the tube. Apparently, the germanium monoxide evaporated from the metal surface during the oxidation. Most of it was then

of the usual metal oxidation.

It is possible to express the oxidation curves accurately by the equation

$$Q = Q_\infty(1 - e^{-kt})$$

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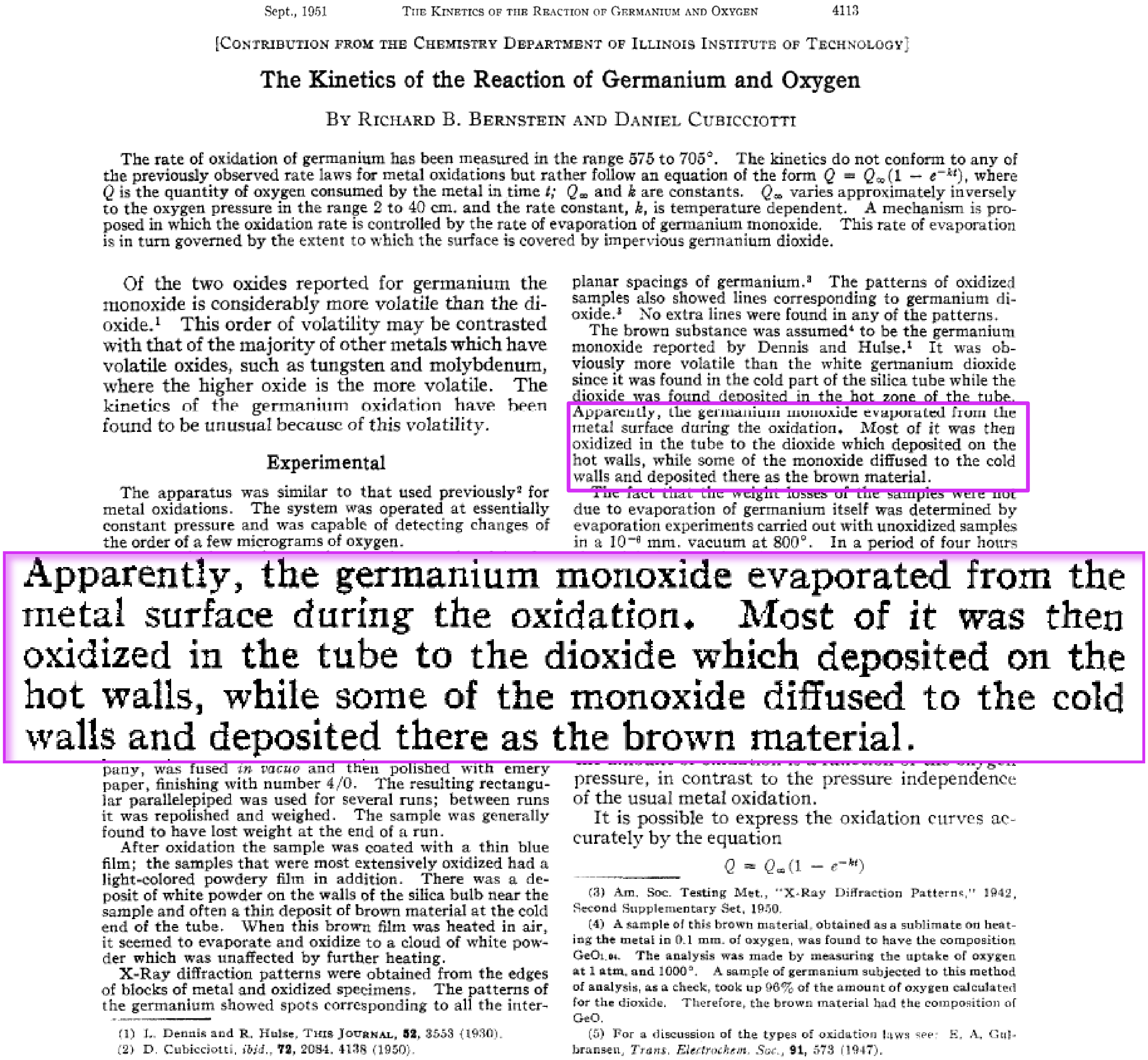
(1) L. Dennis and R. Hulse, THIS JOURNAL, **52**, 3553 (1930).

(2) D. Cubicciotti, *ibid.*, **72**, 2084, 4138 (1950).

(3) Am. Soc. Testing Met., "X-Ray Diffraction Patterns," 1942, Second Supplementary Set, 1950.

(4) A sample of this brown material, obtained as a sublimate on heating the metal in 0.1 mm. of oxygen, was found to have the composition $GeO_{1.04}$. The analysis was made by measuring the uptake of oxygen at 1 atm. and 1000°. A sample of germanium subjected to this method of analysis, as a check, took up 96% of the amount of oxygen calculated for the dioxide. Therefore, the brown material had the composition of GeO.

(5) For a discussion of the types of oxidation laws see: E. A. Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).



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Experimental

The apparatus was similar to that used previously[2] for metal oxidations. The system was operated at essentially constant pressure and was capable of detecting changes of the order of a few micrograms of oxygen.

pany, was fused *in vacuo* and then polished with emery paper, finishing with number 4/0. The resulting rectangular parallelepiped was used for several runs; between runs it was repolished and weighed. The sample was generally found to have lost weight at the end of a run.

After oxidation the sample was coated with a thin blue film; the samples that were most extensively oxidized had a light-colored powdery film in addition. There was a deposit of white powder on the walls of the silica bulb near the sample and often a thin deposit of brown material at the cold end of the tube. When this brown film was heated in air, it seemed to evaporate and oxidize to a cloud of white powder which was unaffected by further heating.

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The fact that the weight losses of the samples were not due to evaporation of germanium itself was determined by evaporation experiments carried out with unoxidized samples in a 10^{-6} mm. vacuum at 800°. In a period of four hours

Apparently, the germanium monoxide evaporated from the metal surface during the oxidation. Most of it was then oxidized in the tube to the dioxide which deposited on the hot walls, while some of the monoxide diffused to the cold walls and deposited there as the brown material.

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LBNL Ge R&D (LDRD)

- We now coat the backsides of the Ge wafers with SiO_2 to inhibit the oxidation and the consequent GeO / GeO_2 issues

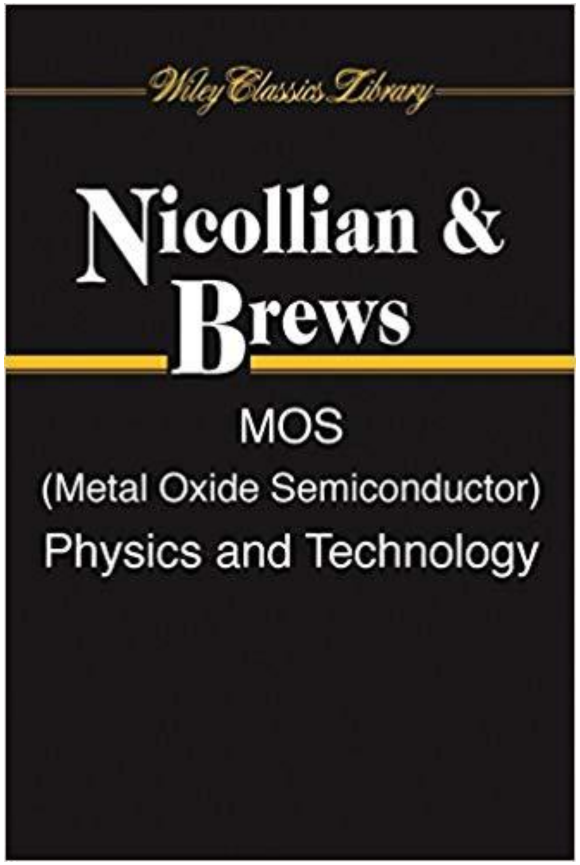
- We next fabricated capacitor-only wafers to see if the Ge-GeO_2 interface could be improved via process changes and address some of the issues seen in the first attempt
  - Simple 2 mask process
  - No ion implantation steps

LBNL Ge R&D (LDRD)

- MOS capacitors used to study the quality of the gate insulator and the semiconductor-insulator interface

- C-V curves yield much information about the quality of the insulator

- After much R&D in the 1970’s, the Si-SiO$_2$ interface typically has defect levels in the low 10^{10} cm^{-2}, or about 1 defect per every 10^5 Si atoms
  - Ge-GeO$_2$ interface is at best 10x worse



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MOS

(Metal Oxide Semiconductor)

Physics and Technology

LBNL Ge R&D (LDRD)

- For SiO_2 the two major advances (1970's) were
  - "Deal triangle"
    - Address fixed oxide charge
  - Post metallization anneal in H_2
    - Minimize interface states
    - H_2 PMA in Ge not effective
    - Implemented on CDF strip detectors in late 1980's

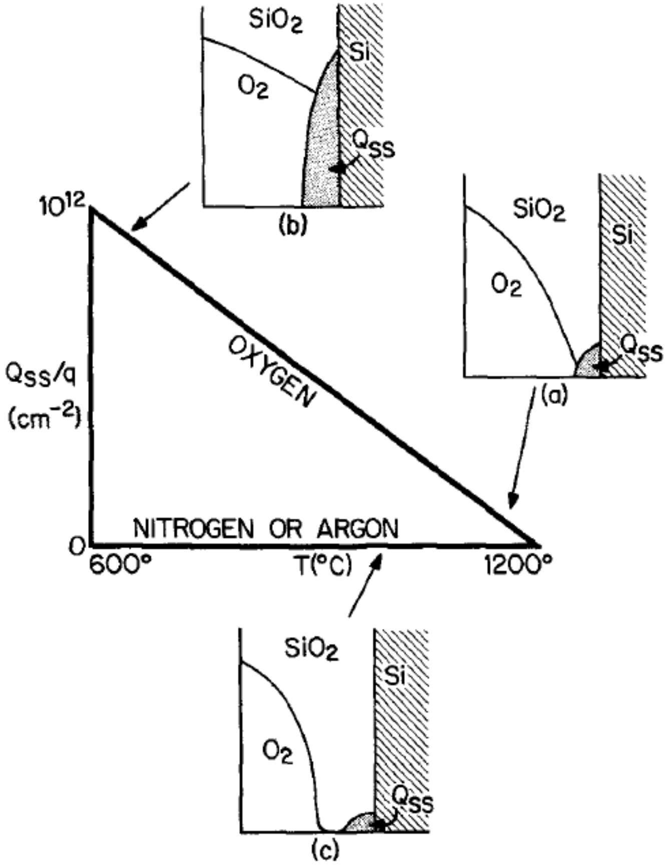


Fig. 6. The dependence of Q_{SS} on final oxidation temperature and ambient as represented by the Q_{SS}-oxygen triangle. Data are for (111) oriented silicon. Also shown are sketches of thermal oxide cross section indicating proposed relationship of Q_{SS} to oxidation conditions.

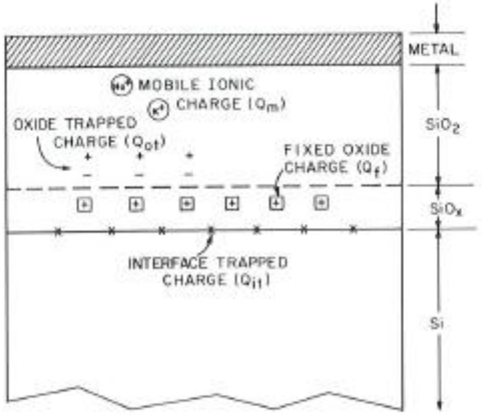
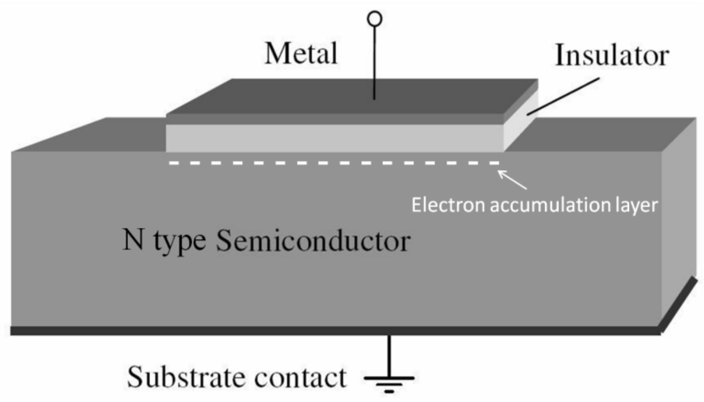
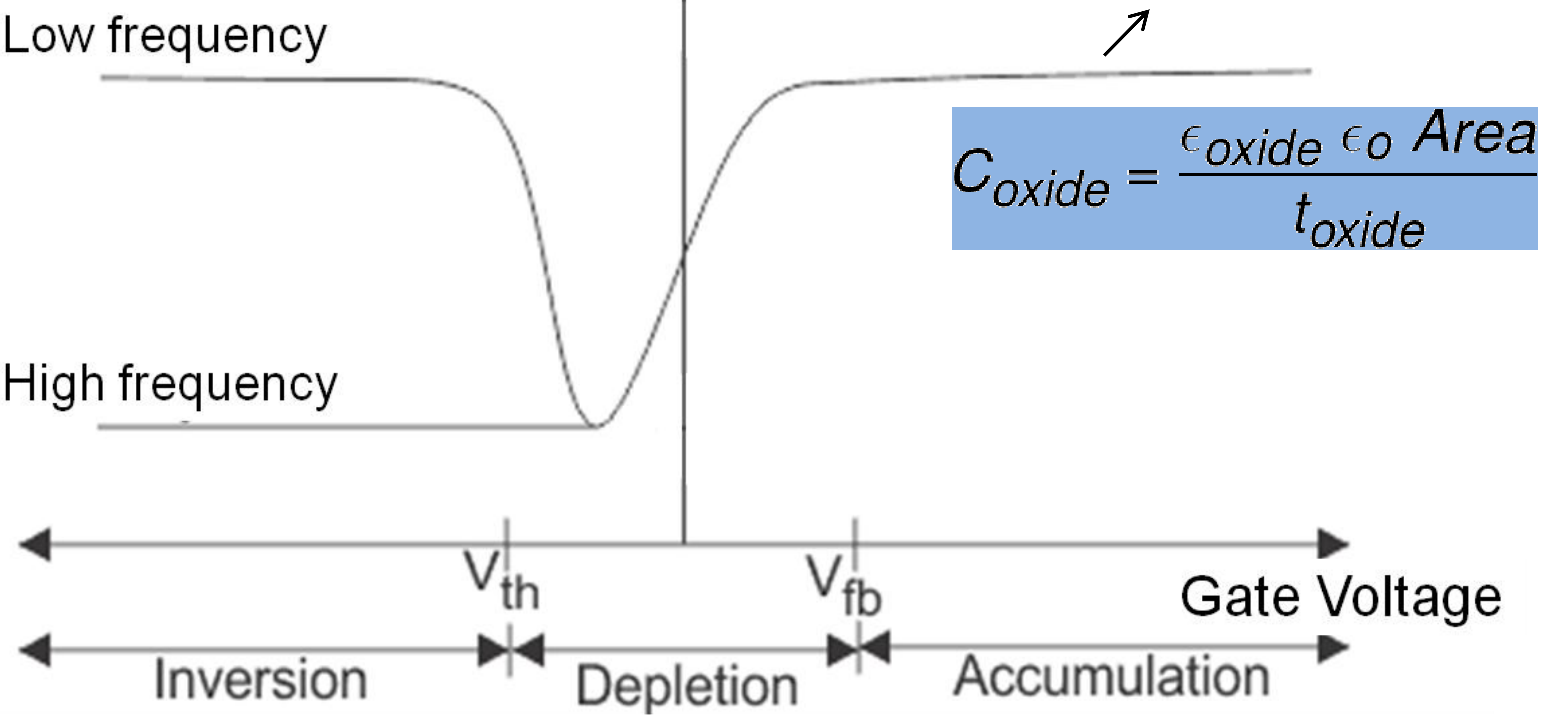
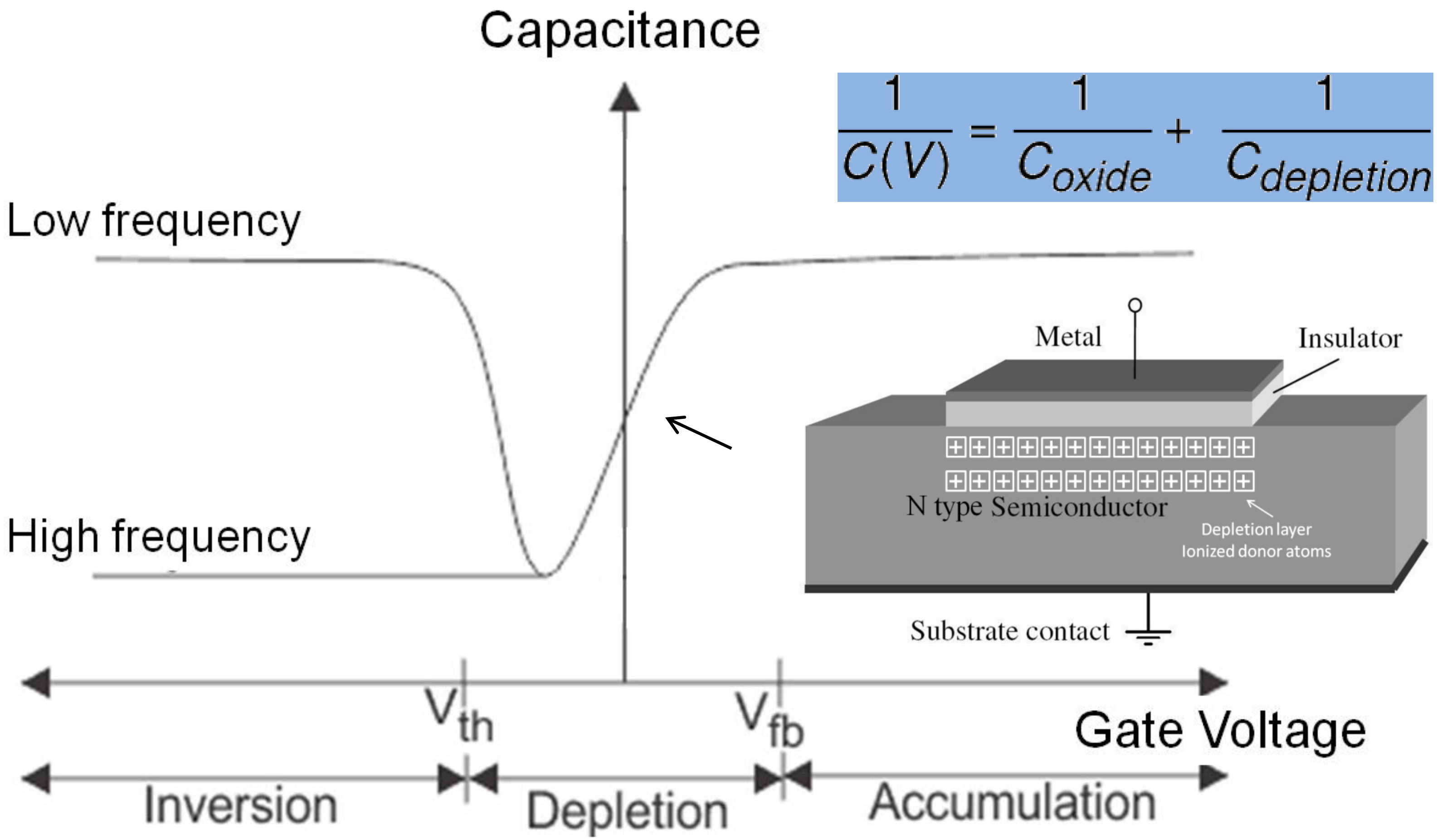


Fig. 15 Terminology for charges associated with thermally oxidized silicon. (After Deal, Ref. 19.)

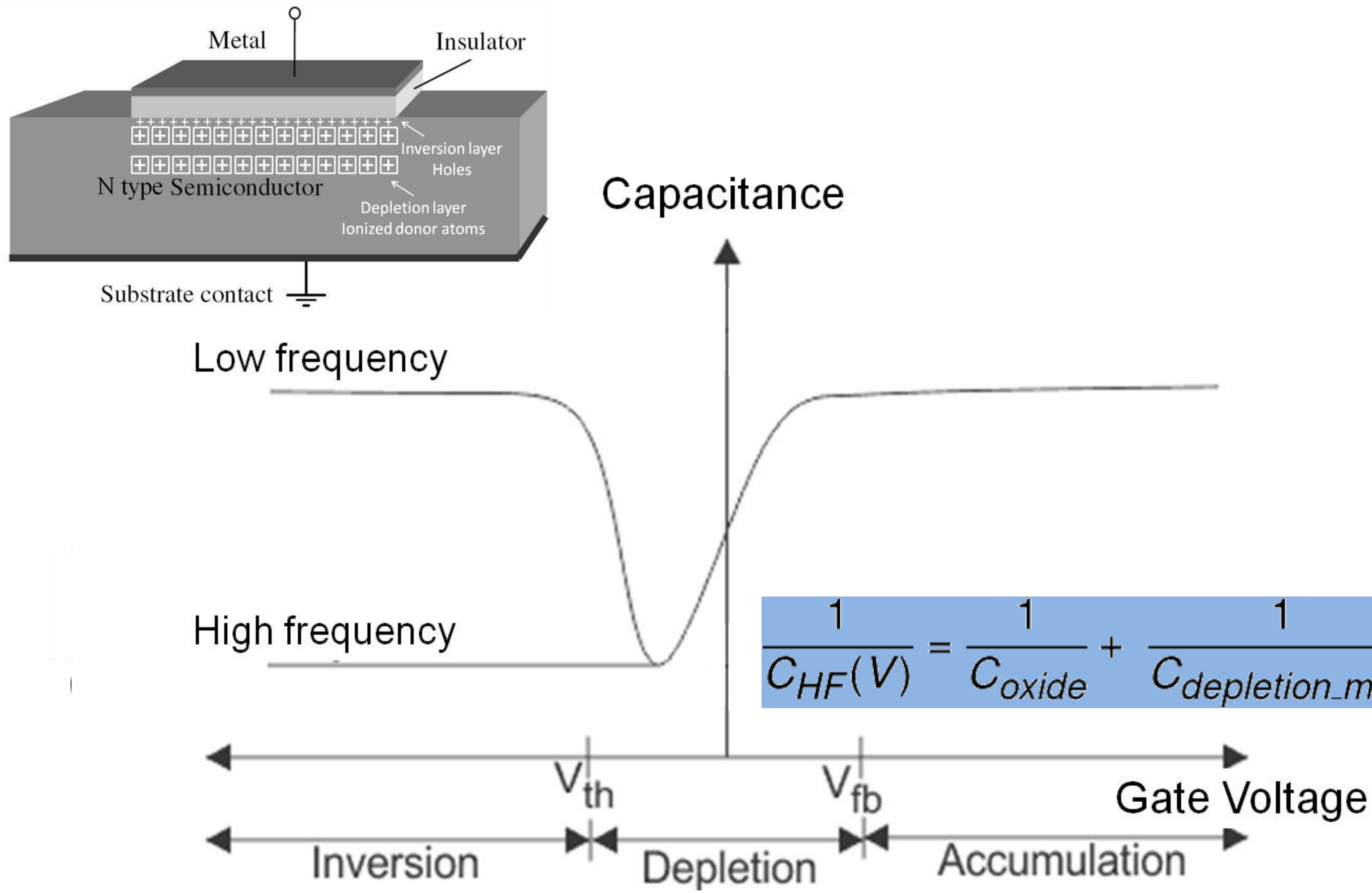




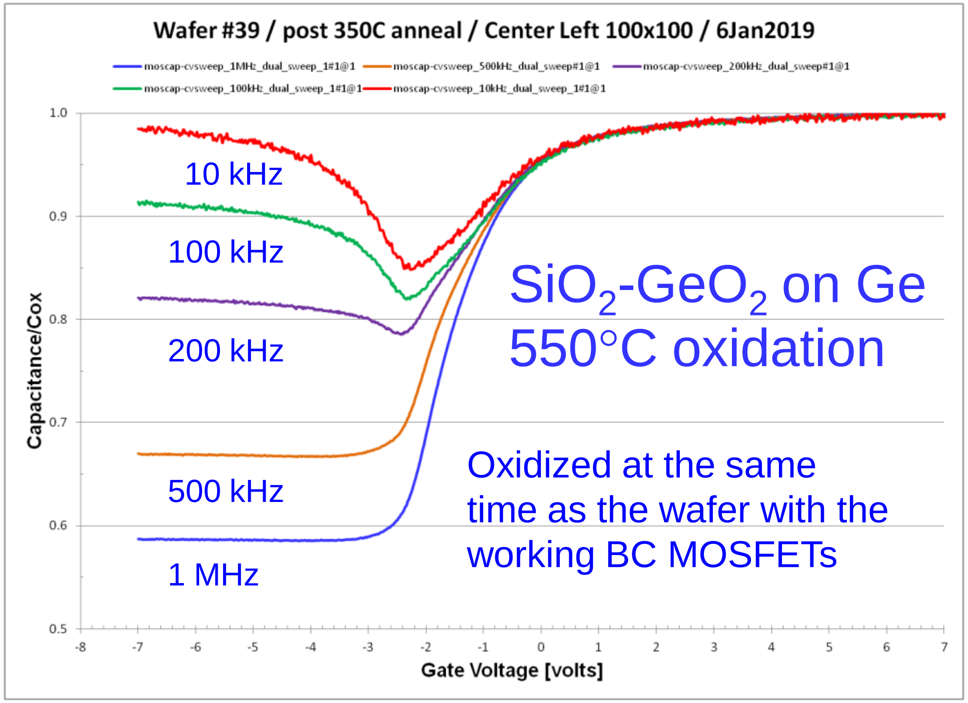
$$C_{oxide} = \frac{\epsilon_{oxide}\,\epsilon_o\,Area}{t_{oxide}}$$



$$\frac{1}{C(V)} = \frac{1}{C_{oxide}} + \frac{1}{C_{depletion}}$$

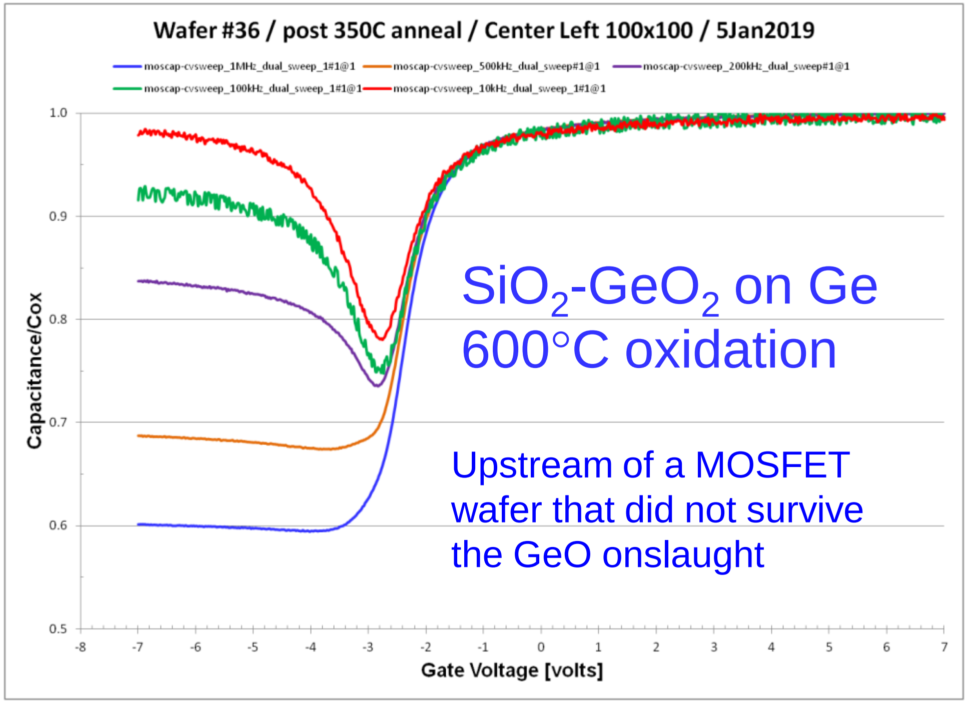


$$\frac{1}{C_{HF}(V)} = \frac{1}{C_{oxide}} + \frac{1}{C_{depletion\_max}}$$


Wafer #39 / post 350C anneal / Center Left 100x100 / 6Jan2019

SiO_2-GeO_2 on Ge
550°C oxidation

Oxidized at the same time as the wafer with the working BC MOSFETs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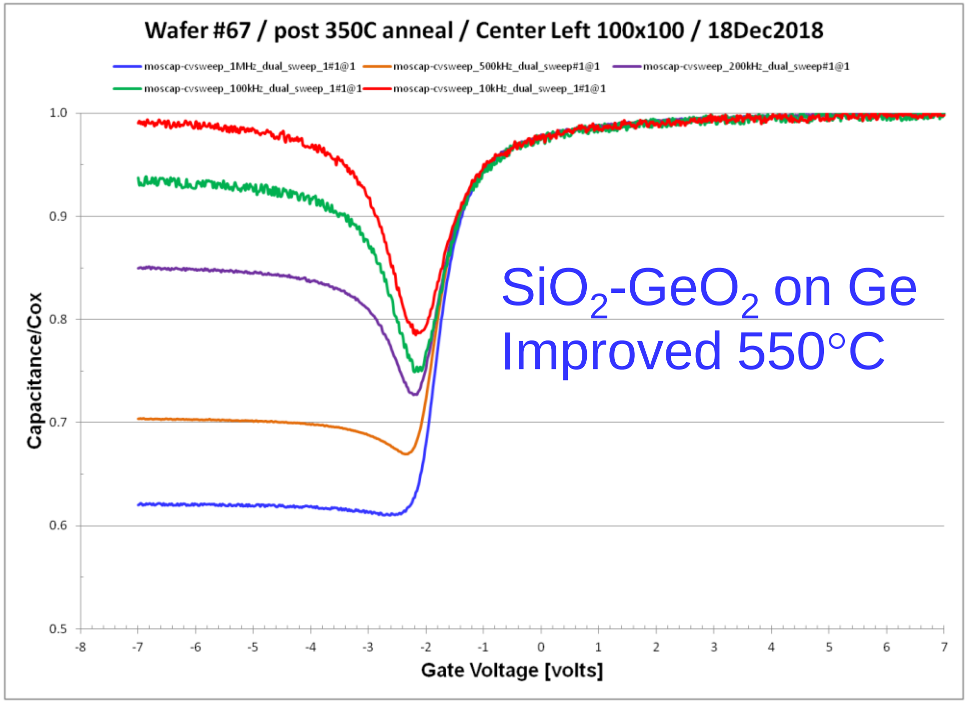
SiO_2-GeO_2 on Ge
600°C oxidation

Upstream of a MOSFET wafer that did not survive the GeO onslaught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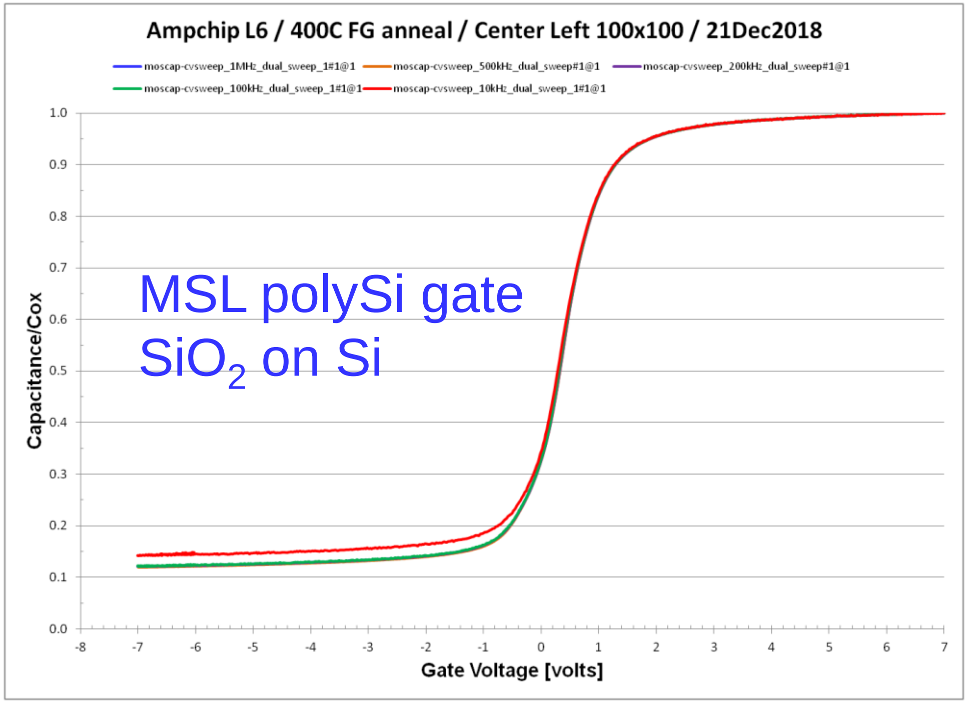
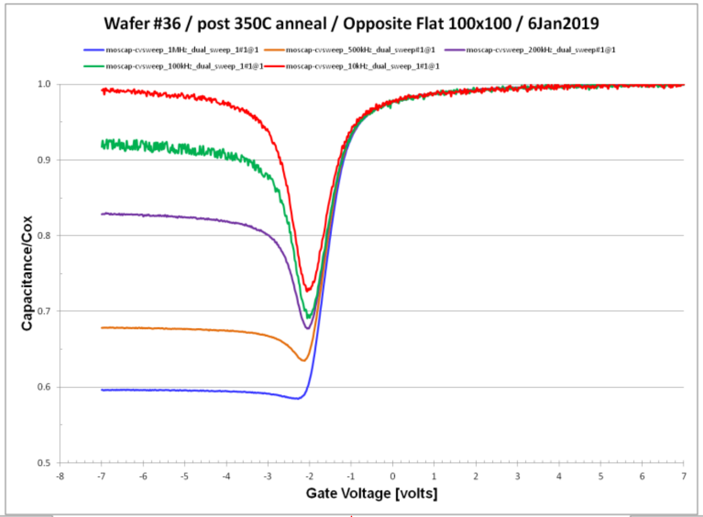
SiO_2-GeO_2 on Ge
Improved 550°C


Ampchip L6 / 400C FG anneal / Center Left 100x100 / 21Dec2018

MSL polySi gate
SiO_2 on Si

Best so far

SiO$_2$-GeO$_2$ on Ge
600°C oxidation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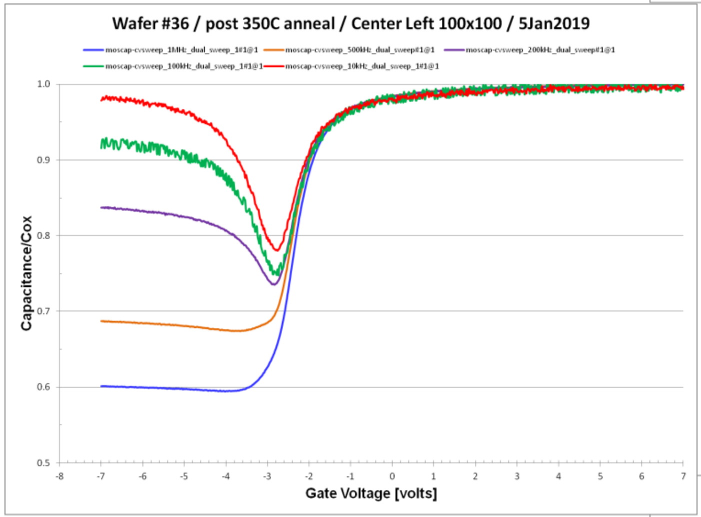
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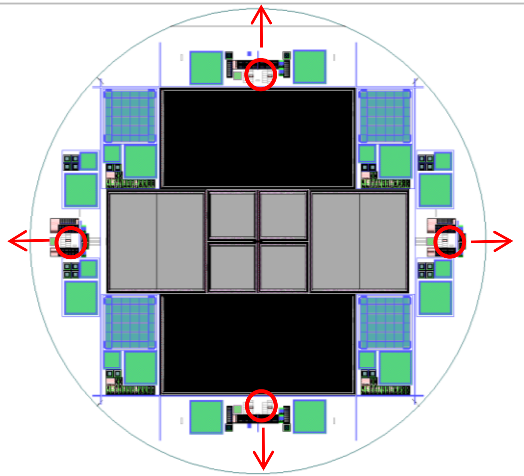
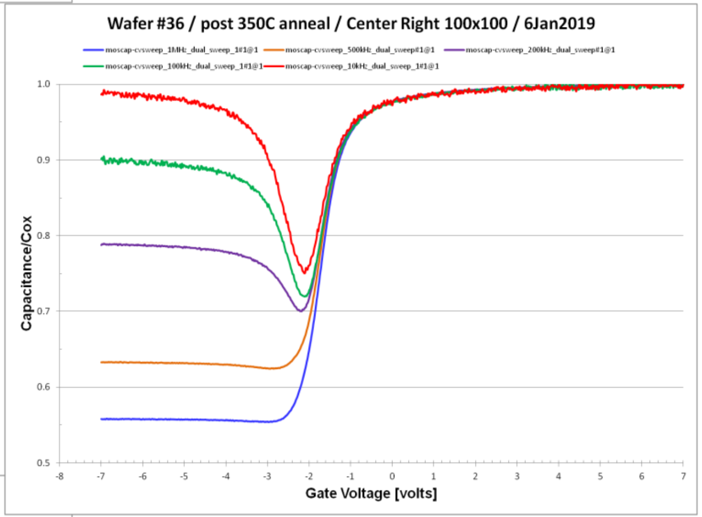
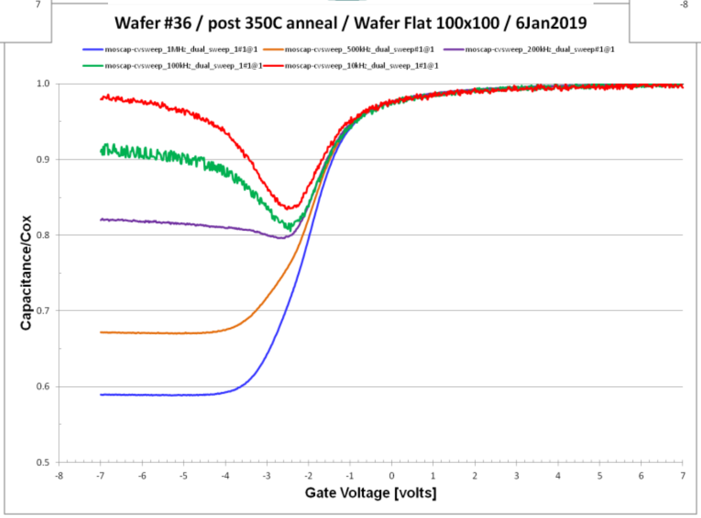
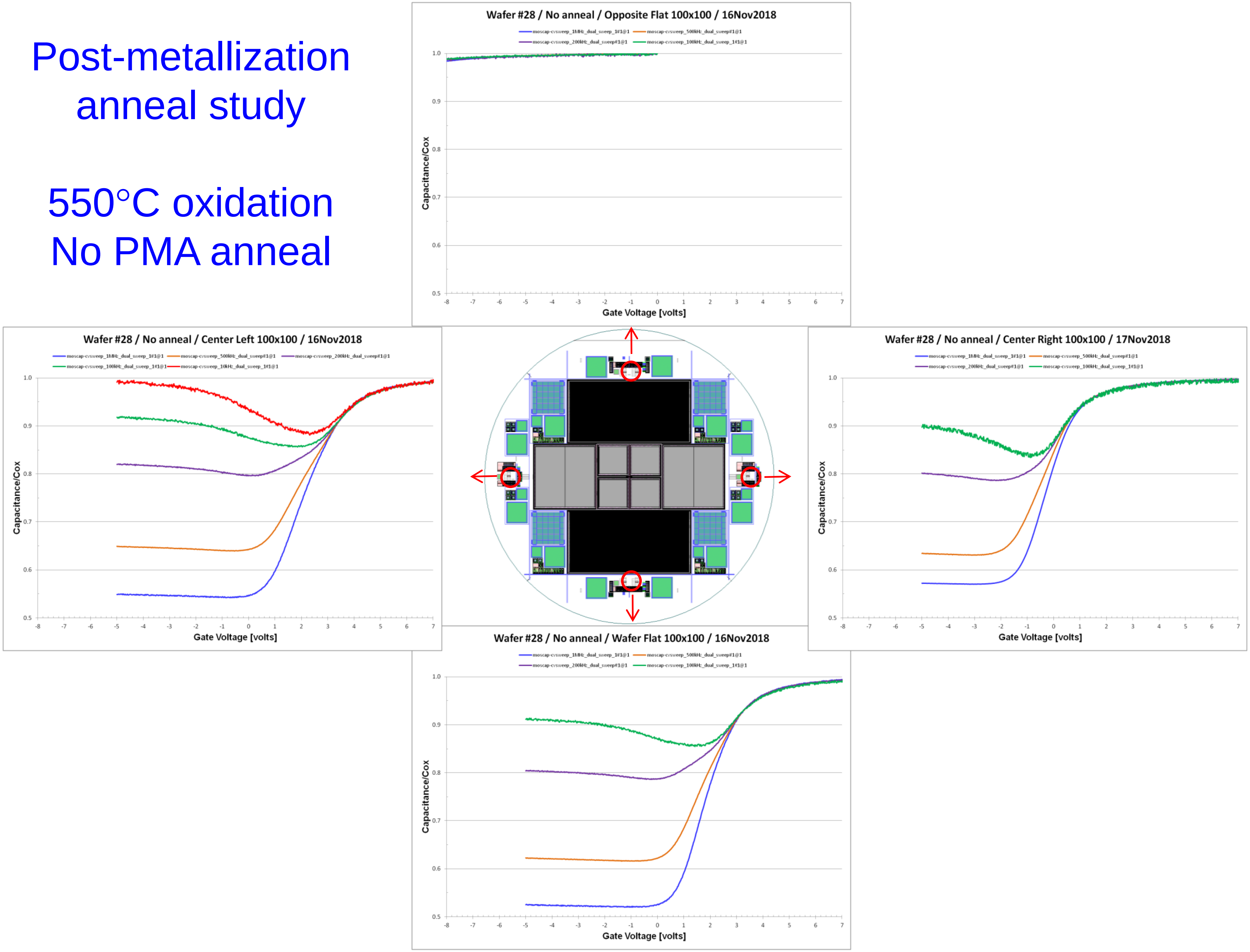



Wafer #36 / post 350C anneal / Center Right 100x100 / 6Jan2019


Wafer #36 / post 350C anneal / Wafer Flat 100x100 / 6Jan2019

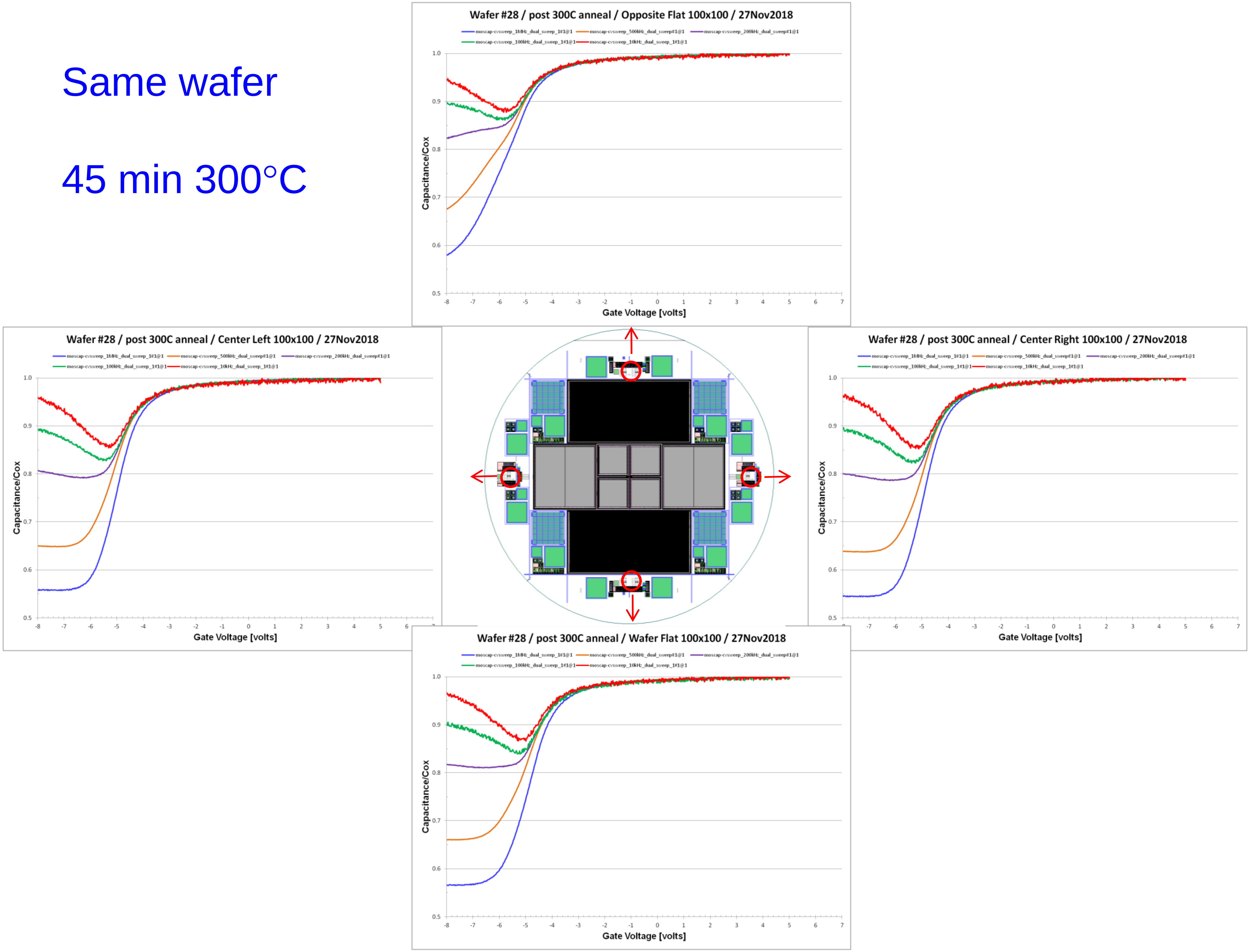
Post-metallization anneal study

550°C oxidation
No PMA anneal



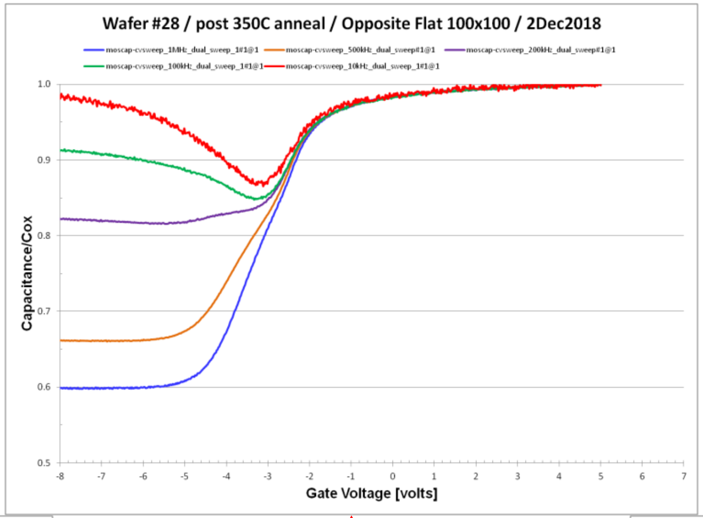
Same wafer

45 min 300°C

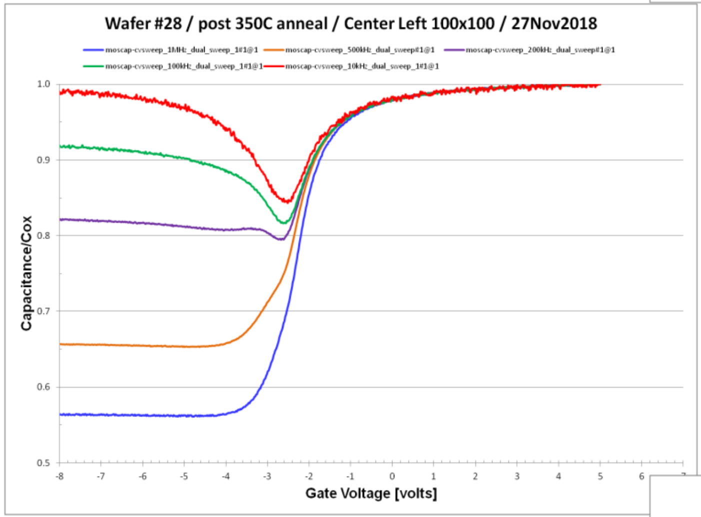


Same wafer

1 hr 350°C



Wafer #28 / post 350C anneal / Opposite Flat 100x100 / 2Dec2018



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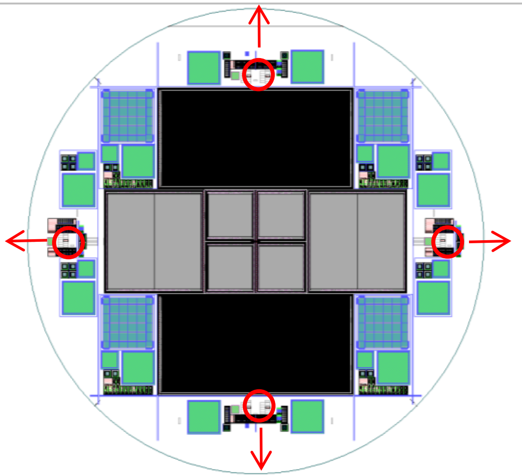

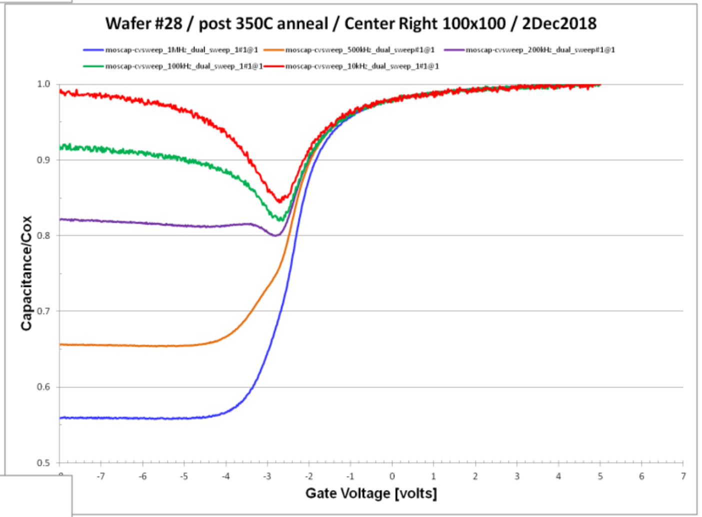

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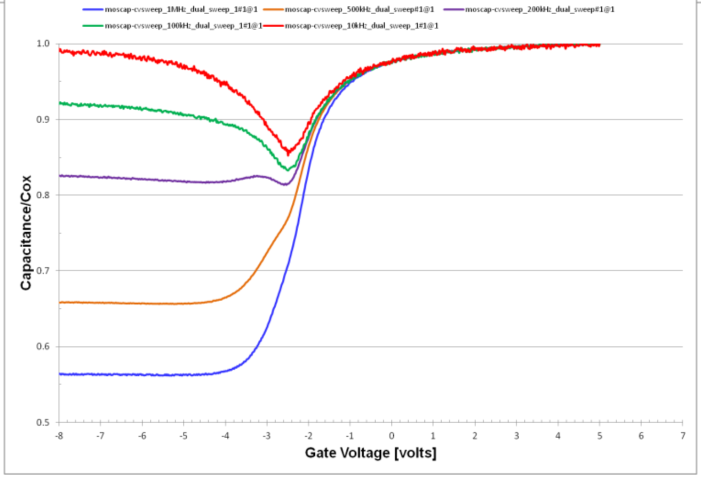
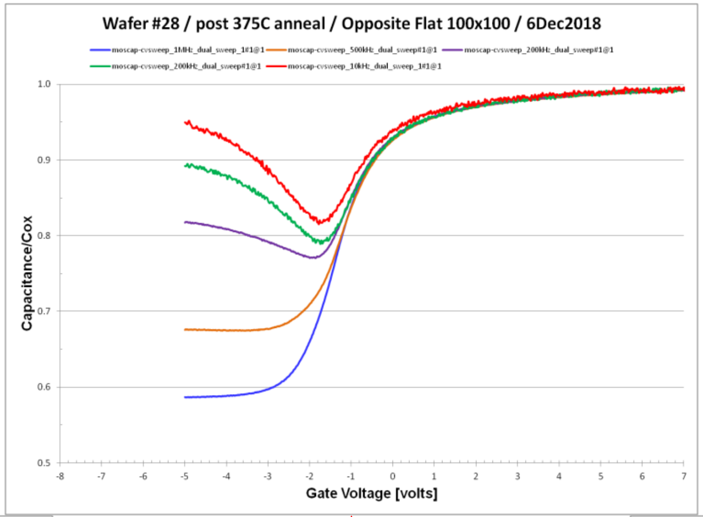


Wafer #28 / post 350C anneal / Wafer Flat 100x100 / 2Dec2018

Same wafer

1 hr 375°C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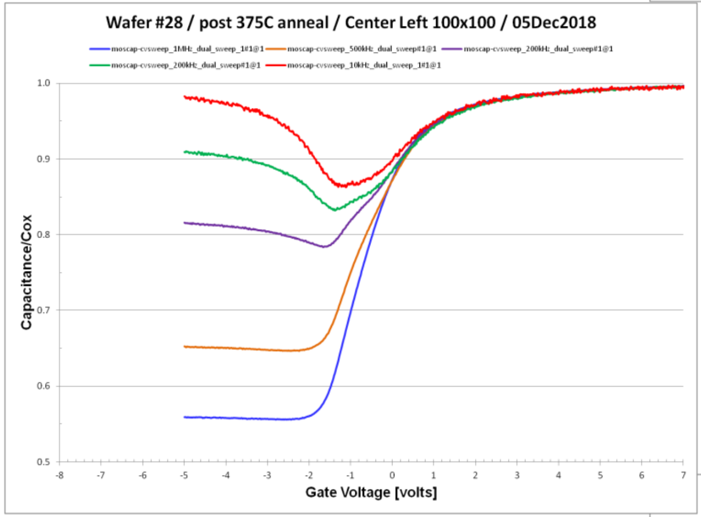
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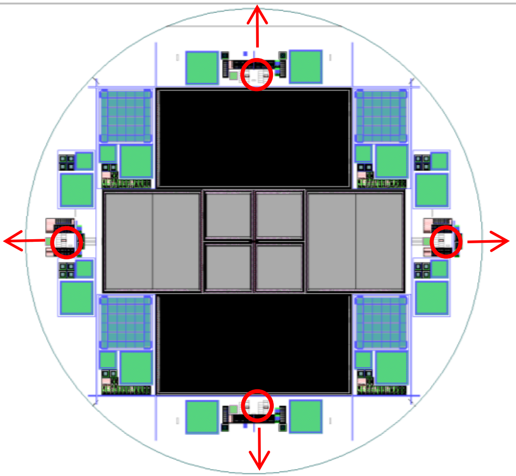
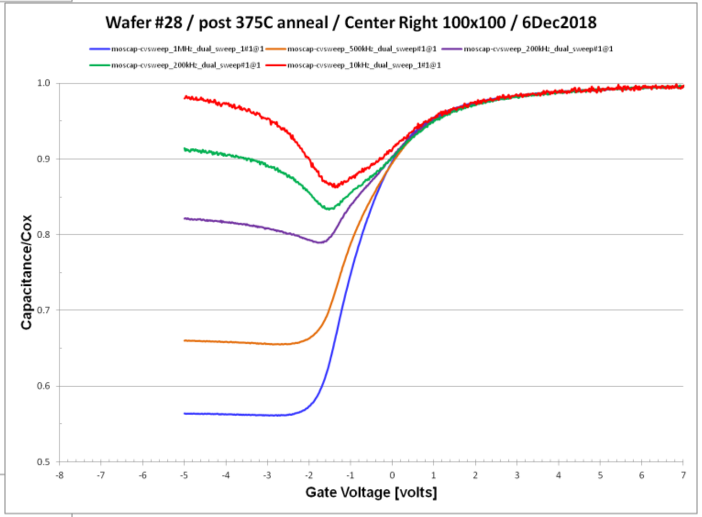
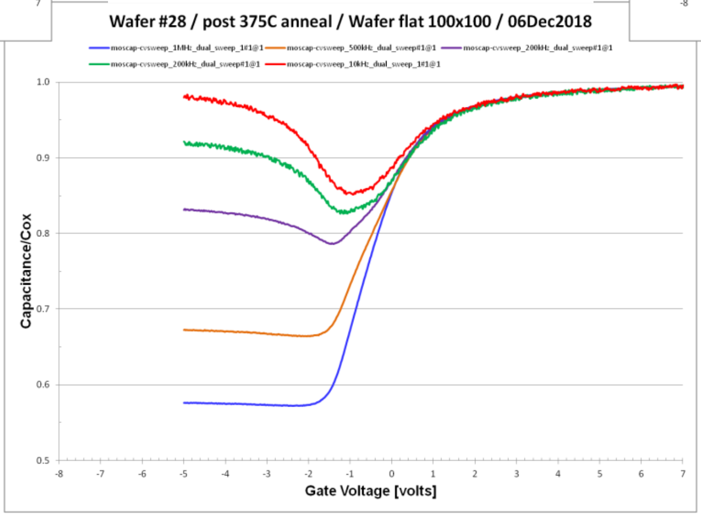



Wafer #28 / post 375C anneal / Center Right 100x100 / 6Dec2018


Wafer #28 / post 375C anneal / Wafer flat 100x100 / 06Dec2018

LBNL Ge R&D (LDRD)

- Three remaining topics
  - High purity Ge wafer production via SBIR
  - Brief overview of work at the UC-Berkeley Marvell Nanofabrication Laboratory
  - Lincoln Labs Ge CCD effort

LBNL Ge R&D (LDRD)

—The table of material properties shown earlier listed millisecond minority carrier lifetimes

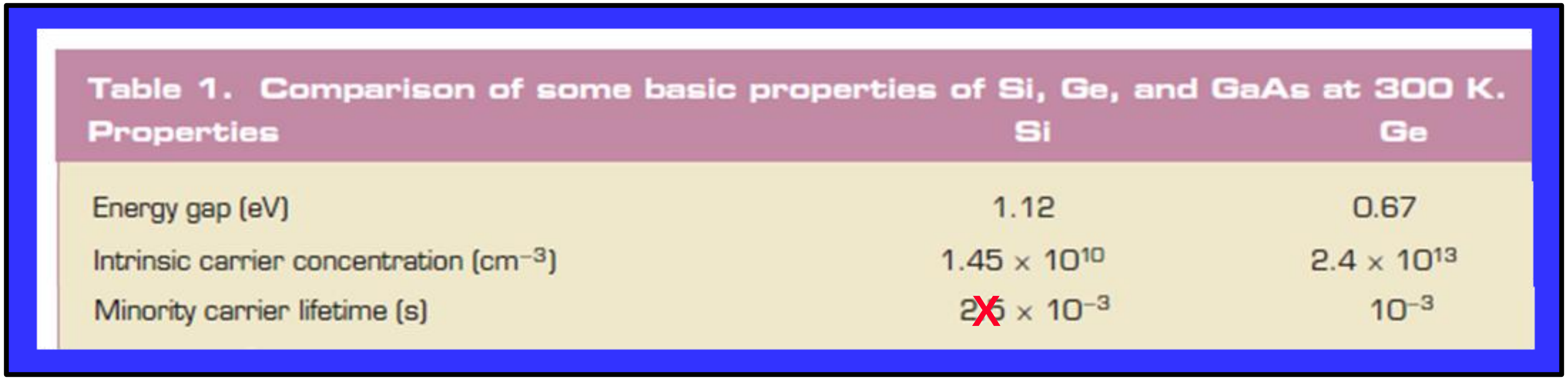


Table 1. Comparison of some basic properties of Si, Ge, and GaAs at 300 K.

Properties	Si	Ge
Energy gap (eV)	1.12	0.67
Intrinsic carrier concentration (cm^{-3})	1.45×10^{10}	2.4×10^{13}
Minority carrier lifetime (s)	2X5 × 10^{-3}	10^{-3}

$$J_{leakage} \propto \frac{n_i}{\tau_g} \propto \frac{\exp(-E_g/2kT)}{\tau_g}$$

—Only valid for detector-grade materials

- High resistivity silicon (FD CCDs), HPGe

LBNL Ge R&D (LDRD)

— Concern that we only have one viable Ge supplier with 10’s μsec lifetimes

— Explore the possibility of producing 150 mm wafers from HPGe

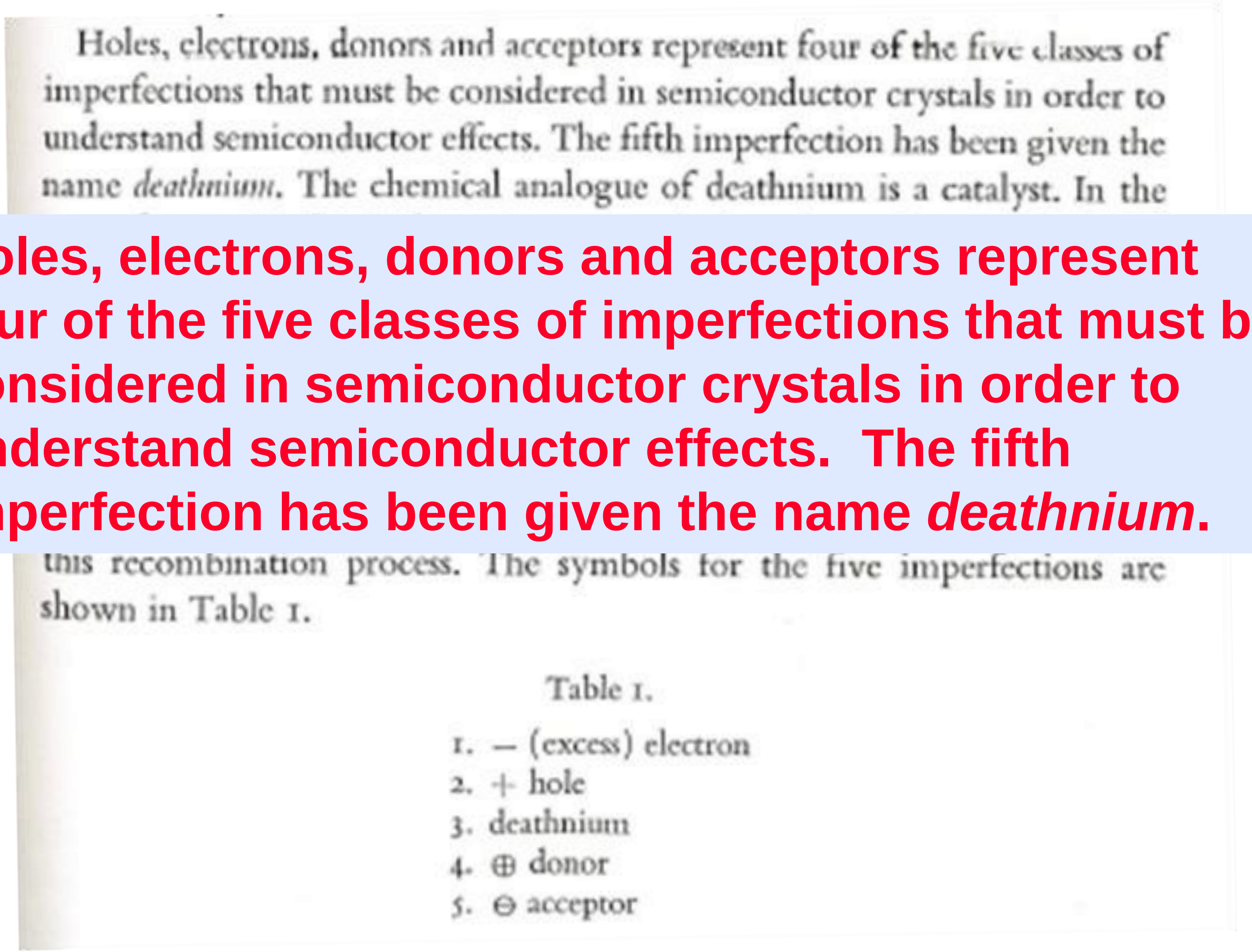
- Analogous to the high-resistivity Si effort

— CCD parameters like dark current and charge transfer efficiency depend critically on lifetime via the presence of harmful impurities

» *Deathnium* (W. Shockley)

LBNL Ge R&D (LDRD)

- From William Shockley’s 1956 NP lecture



Holes, electrons, donors and acceptors represent four of the five classes of imperfections that must be considered in semiconductor crystals in order to understand semiconductor effects. The fifth imperfection has been given the name *deathnium*. The chemical analogue of deathnium is a catalyst. In the

Holes, electrons, donors and acceptors represent four of the five classes of imperfections that must be considered in semiconductor crystals in order to understand semiconductor effects. The fifth imperfection has been given the name *deathnium*.

this recombination process. The symbols for the five imperfections are shown in Table 1.

Table 1.

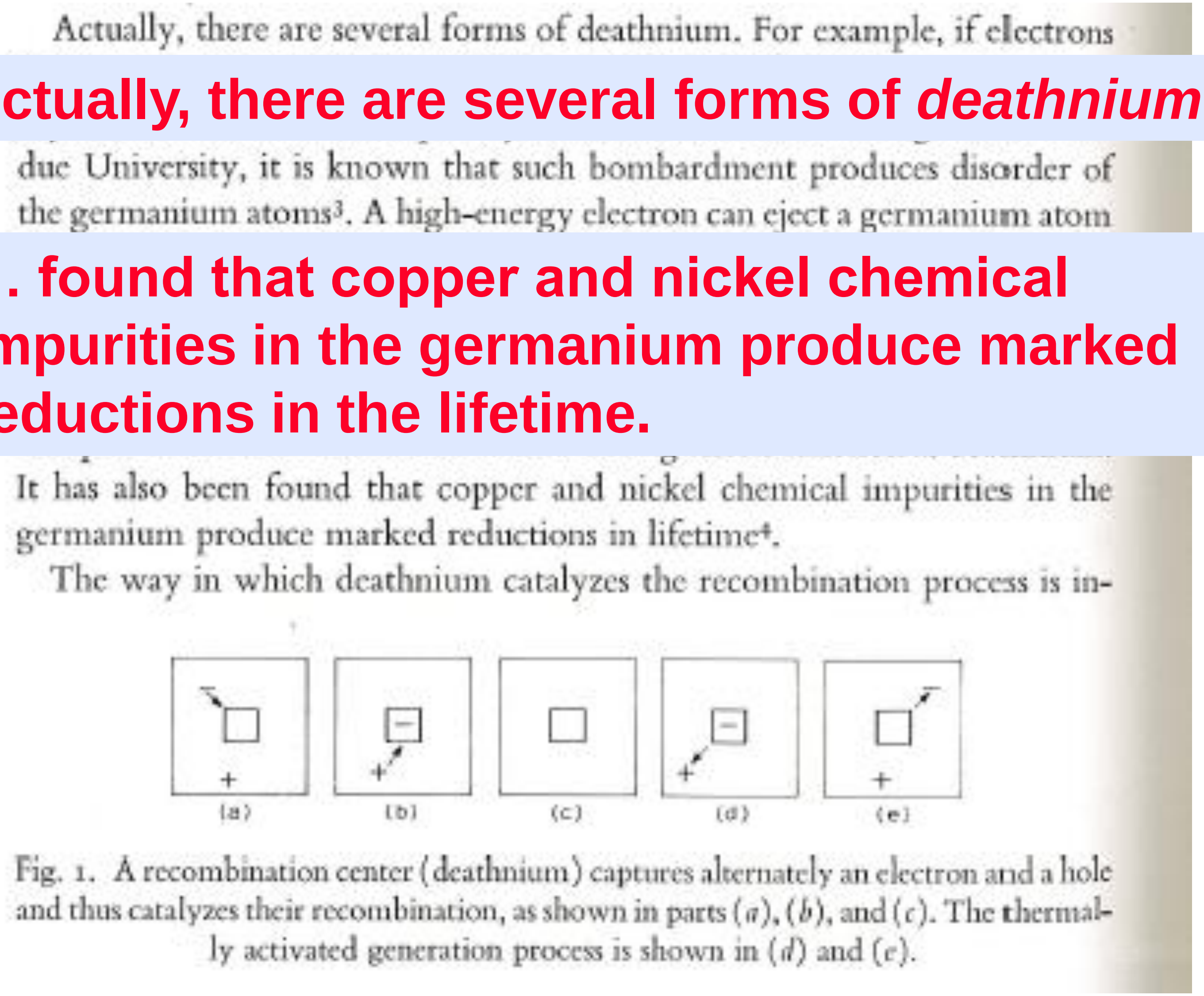
1. — (excess) electron
2. + hole
3. deathnium
4. ⊕ donor
5. ⊖ acceptor

LBNL Ge R&D (LDRD)

- From William Shockley’s 1956 NP lecture

Actually, there are several forms of *deathnium*.

… found that copper and nickel chemical impurities in the germanium produce marked reductions in the lifetime.



Actually, there are several forms of deathnium. For example, if electrons

due University, it is known that such bombardment produces disorder of the germanium atoms[3]. A high-energy electron can eject a germanium atom

It has also been found that copper and nickel chemical impurities in the germanium produce marked reductions in lifetime[4].

The way in which deathnium catalyzes the recombination process is in-

Fig. 1. A recombination center (deathnium) captures alternately an electron and a hole and thus catalyzes their recombination, as shown in parts (*a*), (*b*), and (*c*). The thermally activated generation process is shown in (*d*) and (*e*).

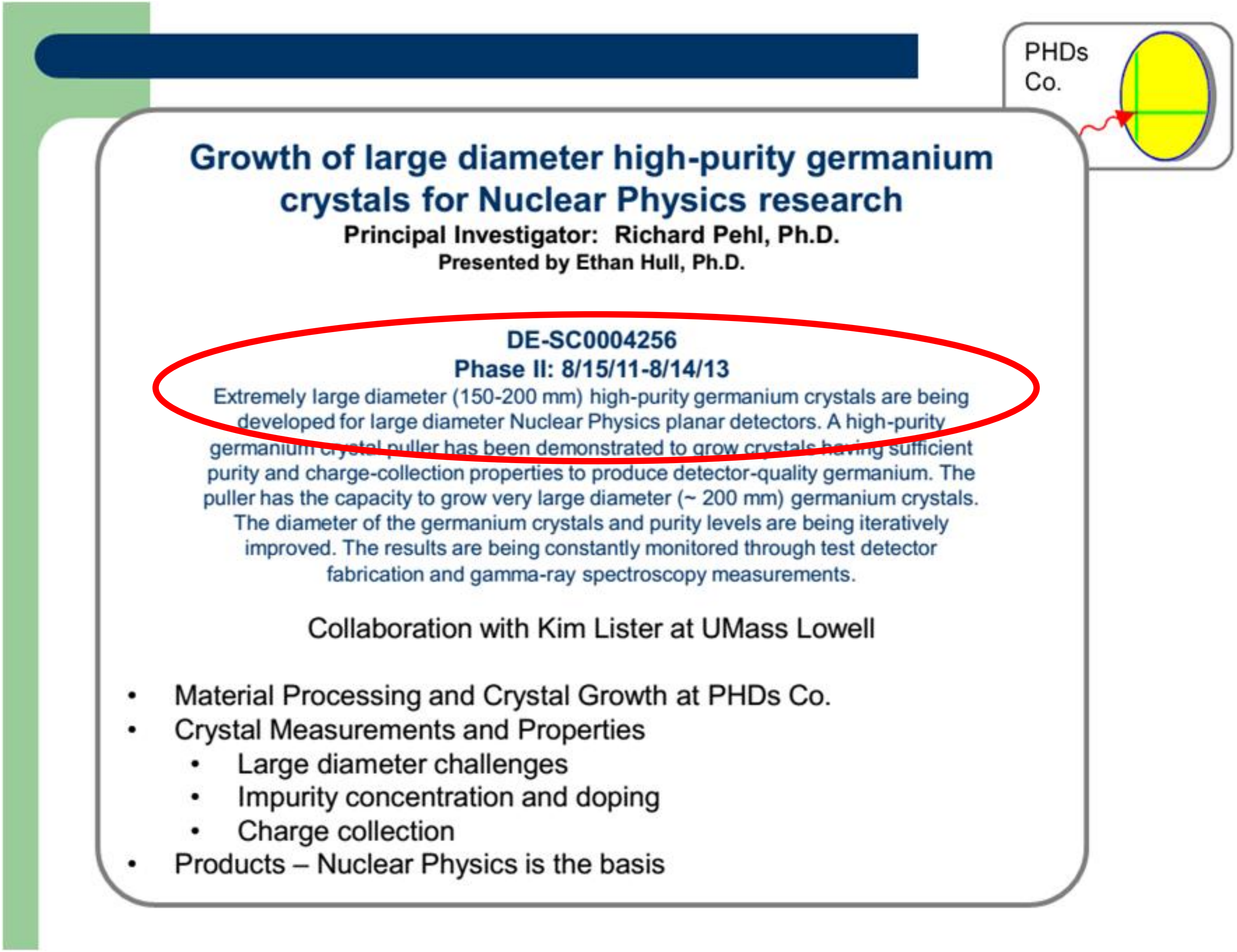
High-purity Ge

- Impressive history at LBNL of HPGe work
  - The late Eugene Haller, R. Pehl, W. Hansen, J. Beeman, Paul Luke of “Luke phonons”, M. Amman, graduate students, e.g. Nick Palaio, apologies for omissions

- With assistance from Maurice Garcia-Sciveres and Helmut Marsiske of the DOE, we placed an SBIR call for HPGe wafer production

- We targeted the company PHDS Co. given that they had received previous SBIRs and were capable of producing 150 mm diameter crystals

High-purity Ge



PHDs Co.

Growth of large diameter high-purity germanium crystals for Nuclear Physics research

Principal Investigator: Richard Pehl, Ph.D.

Presented by Ethan Hull, Ph.D.

DE-SC0004256

Phase II: 8/15/11-8/14/13

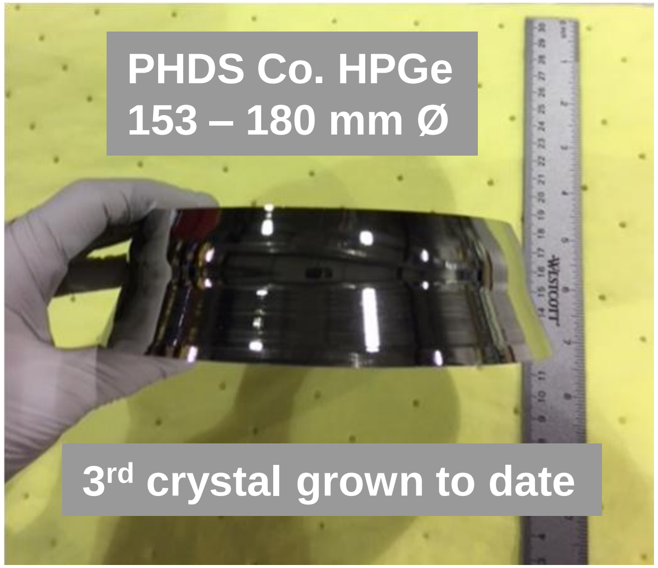
Extremely large diameter (150-200 mm) high-purity germanium crystals are being developed for large diameter Nuclear Physics planar detectors. A high-purity germanium crystal puller has been demonstrated to grow crystals having sufficient purity and charge-collection properties to produce detector-quality germanium. The puller has the capacity to grow very large diameter (~ 200 mm) germanium crystals. The diameter of the germanium crystals and purity levels are being iteratively improved. The results are being constantly monitored through test detector fabrication and gamma-ray spectroscopy measurements.

Collaboration with Kim Lister at UMass Lowell

- Material Processing and Crystal Growth at PHDs Co.
- Crystal Measurements and Properties
    - Large diameter challenges
    - Impurity concentration and doping
    - Charge collection
- Products – Nuclear Physics is the basis

SBIR efforts PHDS Co.

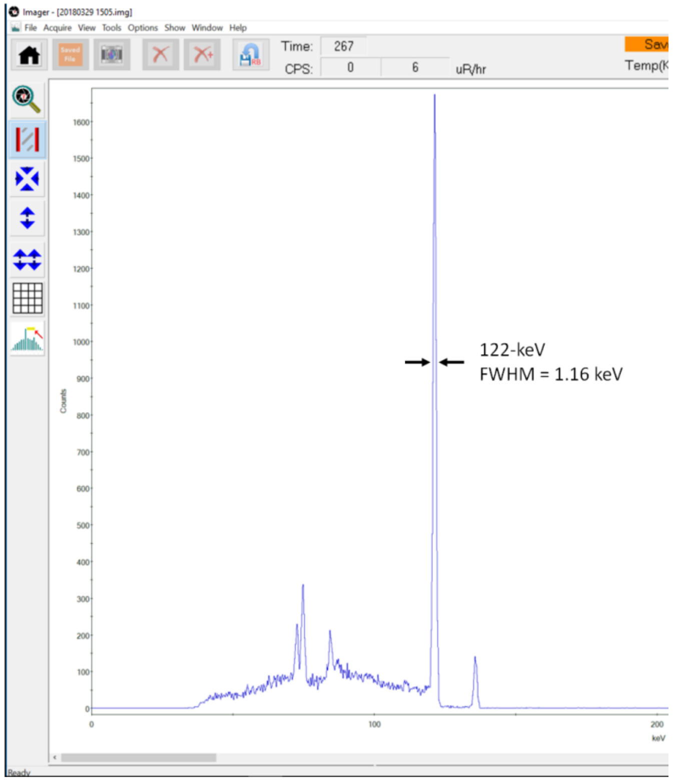
- High purity Ge wafer production (SBIR Phase I)



PHDS Co. HPGe
153 – 180 mm Ø

3rd crystal grown to date

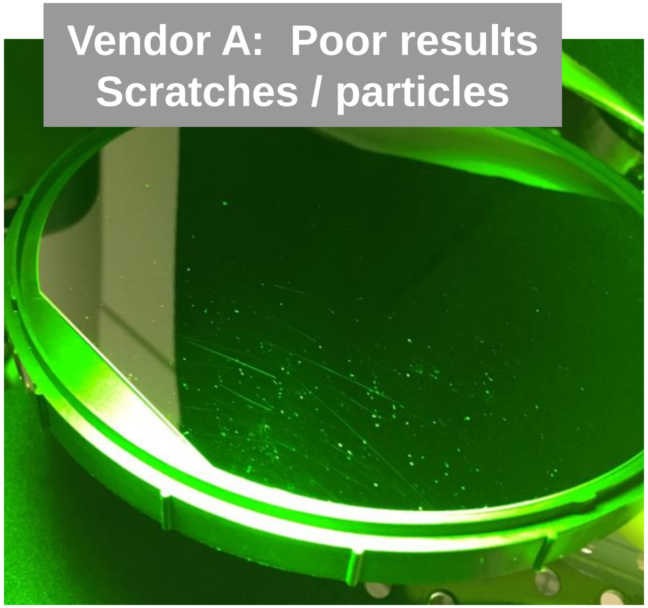
Umicore slicing
and polishing
yielded 41 wafers
(48 mm thick)



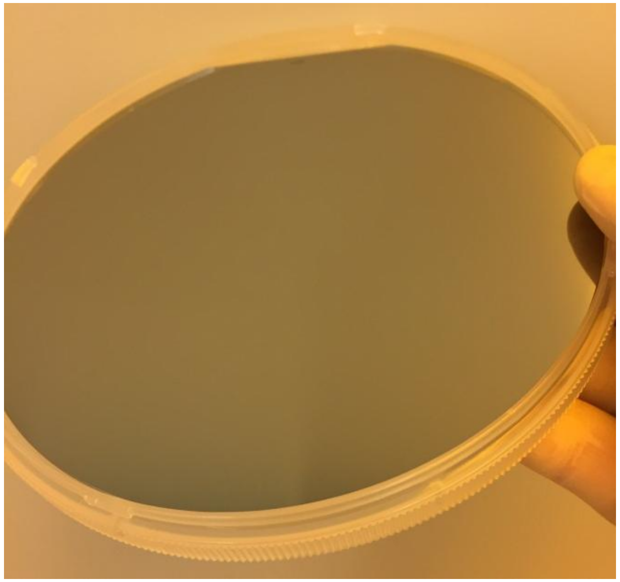
Time: 267

CPS: 0 6 uR/hr

122-keV
FWHM = 1.16 keV



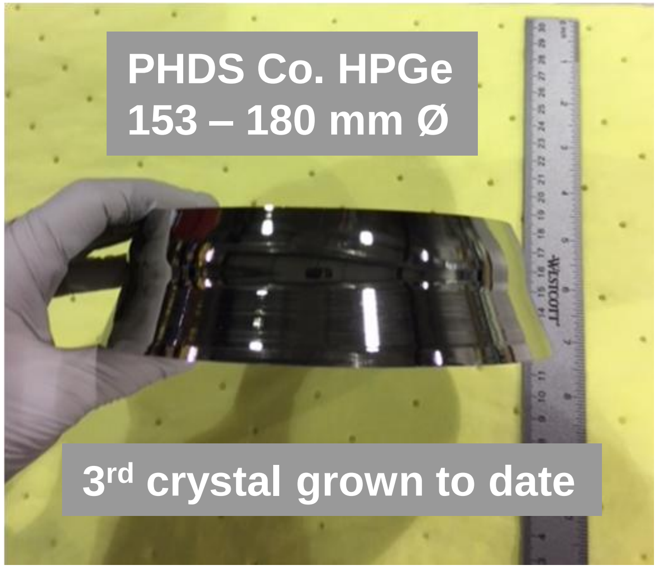
Vendor A: Poor results
Scratches / particles



γ-ray spectra from a
scrap piece of the Ge
crystal processed at
Umicore
(courtesy PHDS Co.)

SBIR efforts (Phase II awarded to PHDS Co.)

- High purity Ge wafer production (SBIR Phase I)



PHDS Co. HPGe
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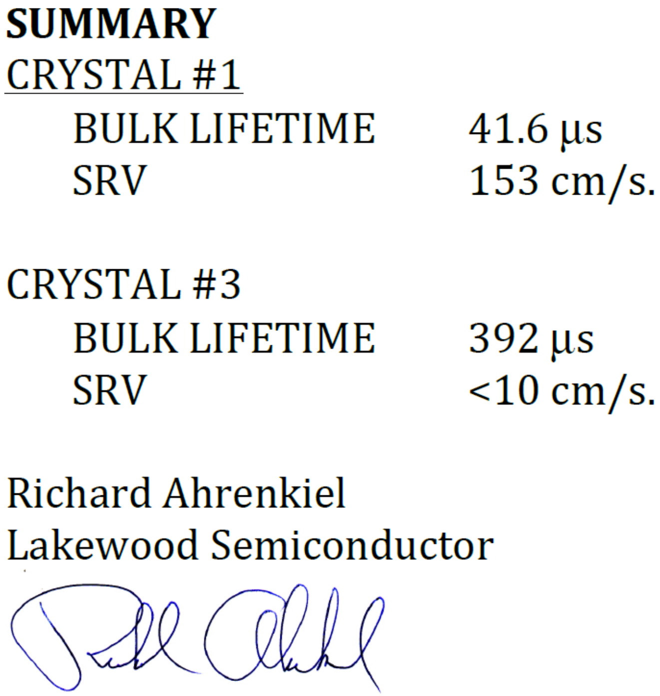


SUMMARY

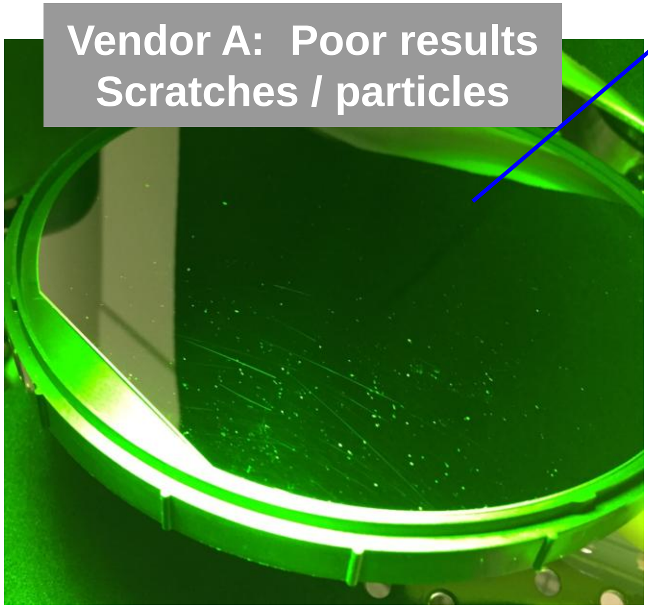
CRYSTAL #1

BULK LIFETIME	41.6 µs
SRV	153 cm/s.

CRYSTAL #3

BULK LIFETIME	392 µs
SRV	<10 cm/s.

Richard Ahrenkiel
Lakewood Semiconductor



Vendor A: Poor results
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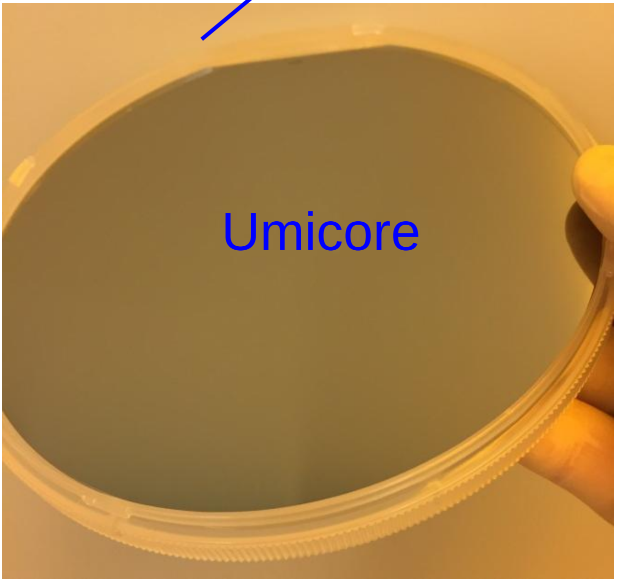
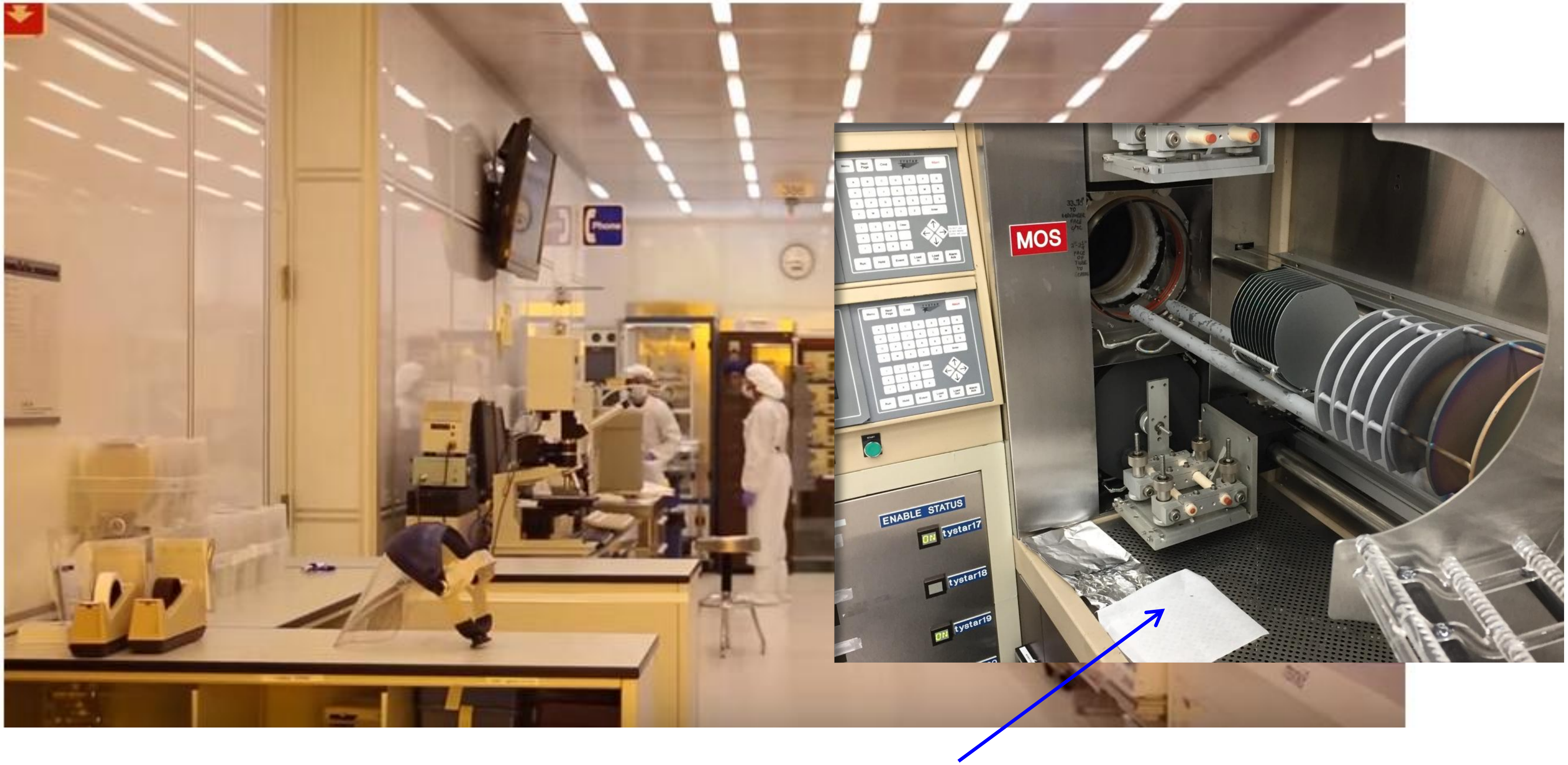


Umicore

Photoconductive decay lifetime measurements

LNBL processing in progress

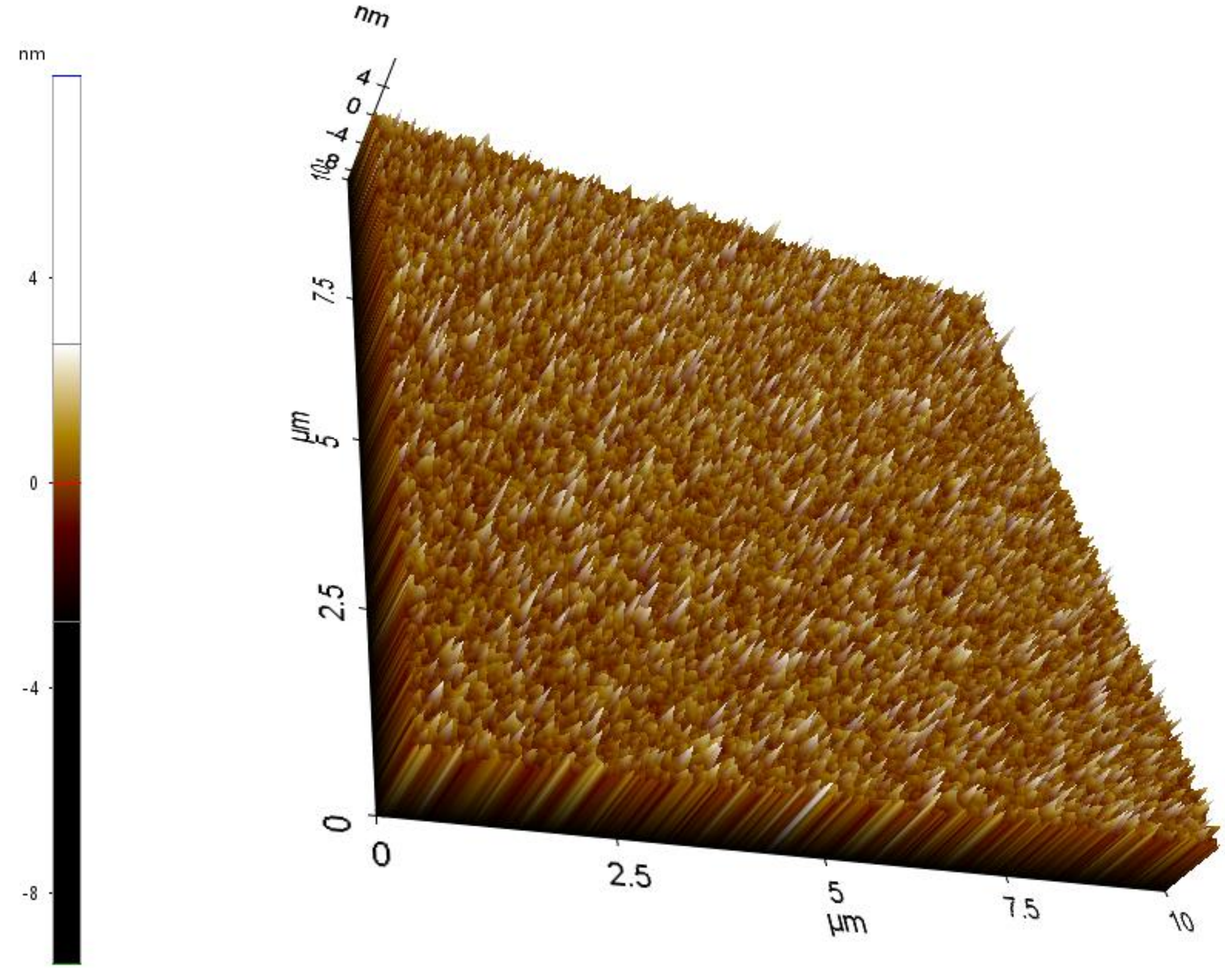
UCB Nanofabrication Laboratory



- Polycrystalline Ge (in-situ doped) capabilities
- Advanced characterization tools for the Ge technology development
  - — Spectroscopic Ellipsometer and Atomic Force Microscopy
- Deep UV wafer stepper (250 nm lines / spaces) and TCP polysilicon etcher
- Atomic layer deposition

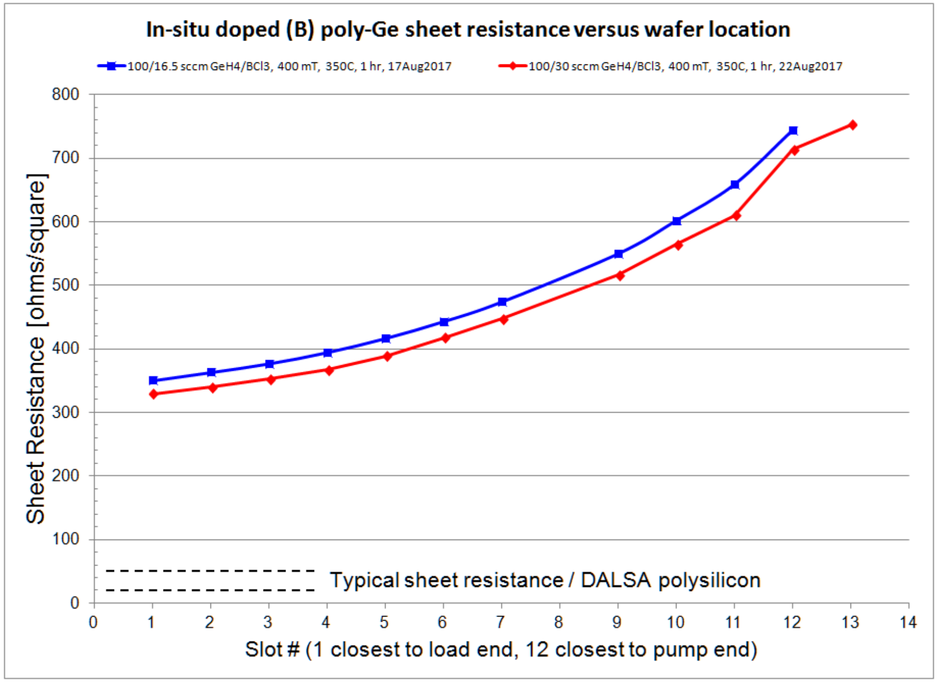
UCB Nanofabrication Laboratory

- Atomic Force Microscopy study
  - —SiO_2-GeO_2-Ge gate stack fabricated in the MSL



LPCVD Ge investigations

- Interest in an in-situ doped poly-Ge film that could be deposited at ~ 350°C / possible gate electrode
- Sheet resistance high and variable across the chamber despite numerous attempts varying the BCl_3 to GeH_4 ratio



LPCVD Ge investigations

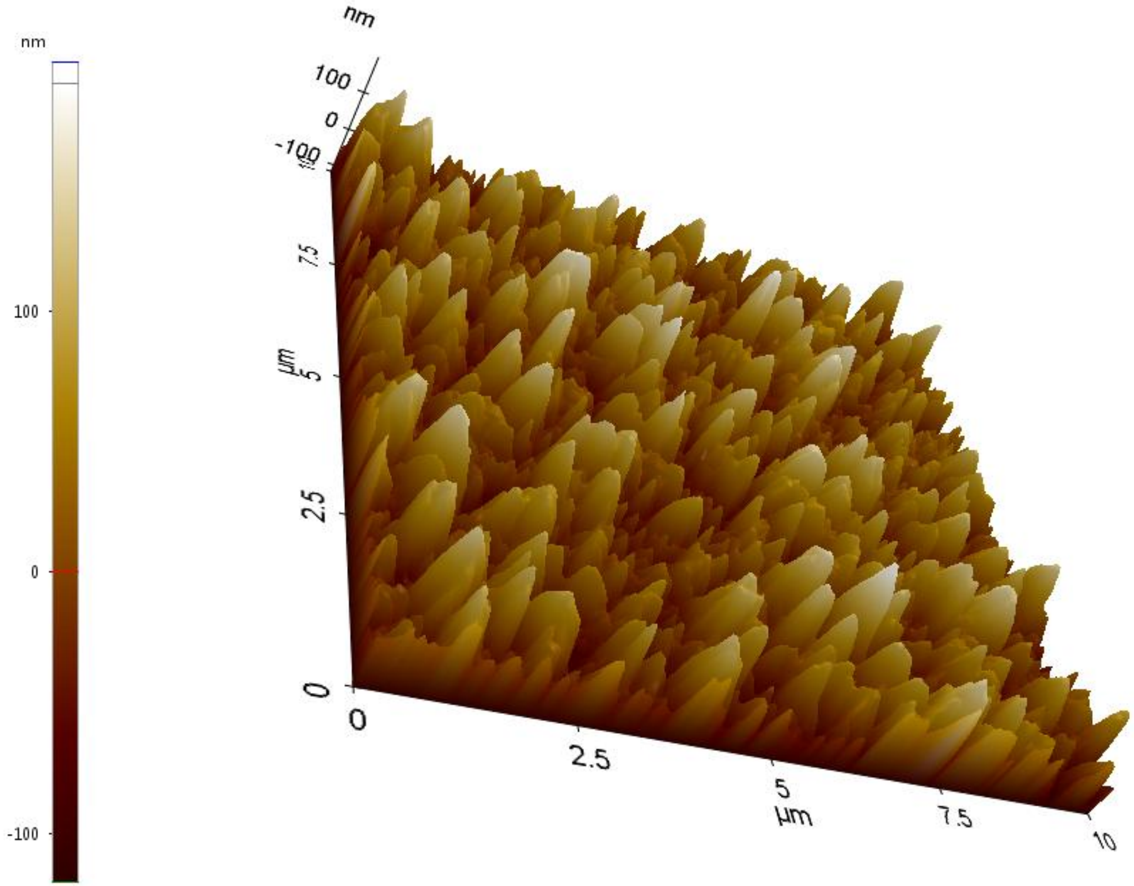
- Table below shows some results from Boron implantation and post-implant annealing

Sheet resistance in ohms/square	1 hr 350C	1 hr 375C	1 hr 400C	1 hr 425C
Process #1	2038K ± 9.5%	76.9 ± 219%	17.6 ± 2.2%	17.5 ± 1.1%
Process #2	1431 ± 33.9%	19.2 ± 131%	17.0 ± 0.83%	16.7 ± 0.85% 👍
Process #3	3500K ± 6.2%	1919K ± 7.0%	13.9 ± 3.5%	12.7 ± 1.2%
Process #4	10.0M ± 5.8%	5281K ± 7.4%	28.7 ± 9.5%	16.6 ± 0.55%
Process #5	95.4 ± 12.5%	22.7 ± 3.6%	20.9 ± 1.3%	👍

- Permission has been granted by the Nanolab staff to deposit polyGe films on Ge transistor wafers
- Plan to add this deposition capability to the MSL

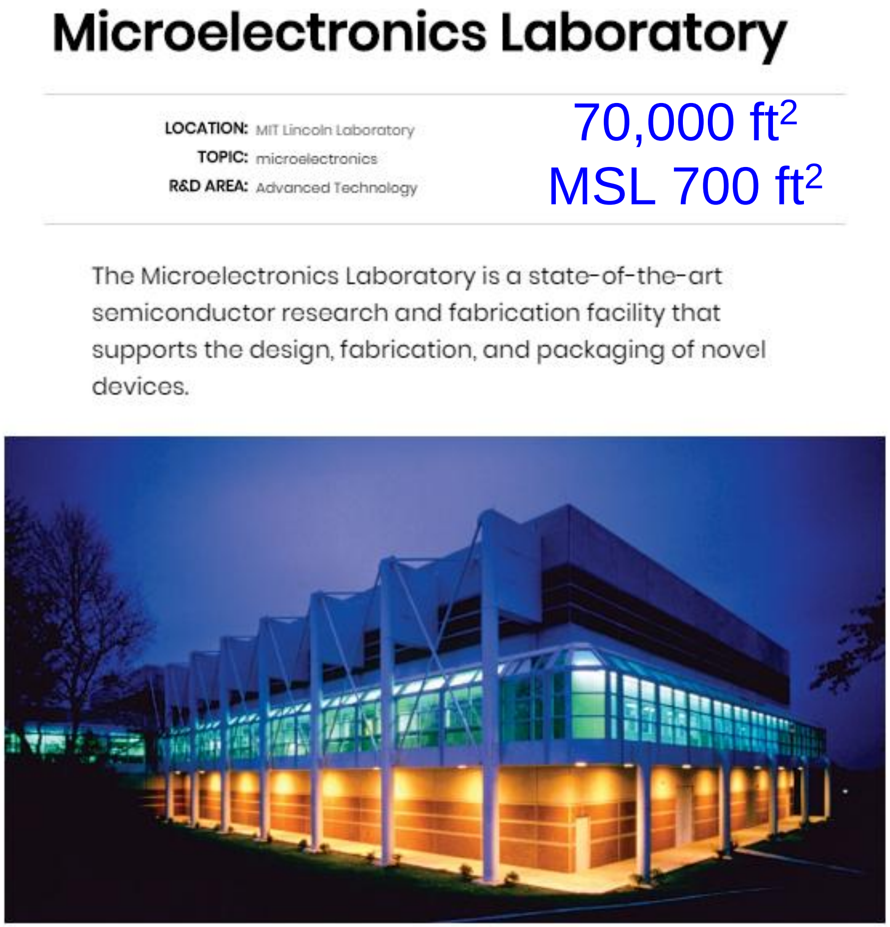
LPCVD Ge investigations

- LPCVD polyGe films:
  - More effort needed in terms of film flatness



Lincoln Labs Ge CCD effort

- MIT Lincoln Laboratory has a long history of CCD production (Keck DEIMOS, PAN-STARRS, new TESS exoplanet satellite, latter two fully depleted CCDs)
  - Initial Ge CCD report published Sept. 2015
  - Advanced technologies (193 nm litho, high-k dielectrics, 200nm gaps)
    - Very open about the Ge issues they have observed
  - Our approach is geared to possible tech transfer (DALSA)
    - Must demonstrate results



Microelectronics Laboratory

LOCATION: MIT Lincoln Laboratory
TOPIC: microelectronics
R&D AREA: Advanced Technology

The Microelectronics Laboratory is a state-of-the-art semiconductor research and fabrication facility that supports the design, fabrication, and packaging of novel devices.

70,000 ft^2
MSL 700 ft^2

Summary

- Making progress with transistor fabrication with SiO_2-GeO_2 gate insulators
  - Quite exciting to see the prior R&D efforts progressing from a hopeless water soluble film to that same film showing encouraging properties
- High-purity Ge effort well underway
- Looking forward to polyGe devices
- Prototype CCD layouts are included on the mask design / more technology development
- Implement cryogenic studies of test structures

Special thanks to Co Tran / Expert on MSL processing and equipment