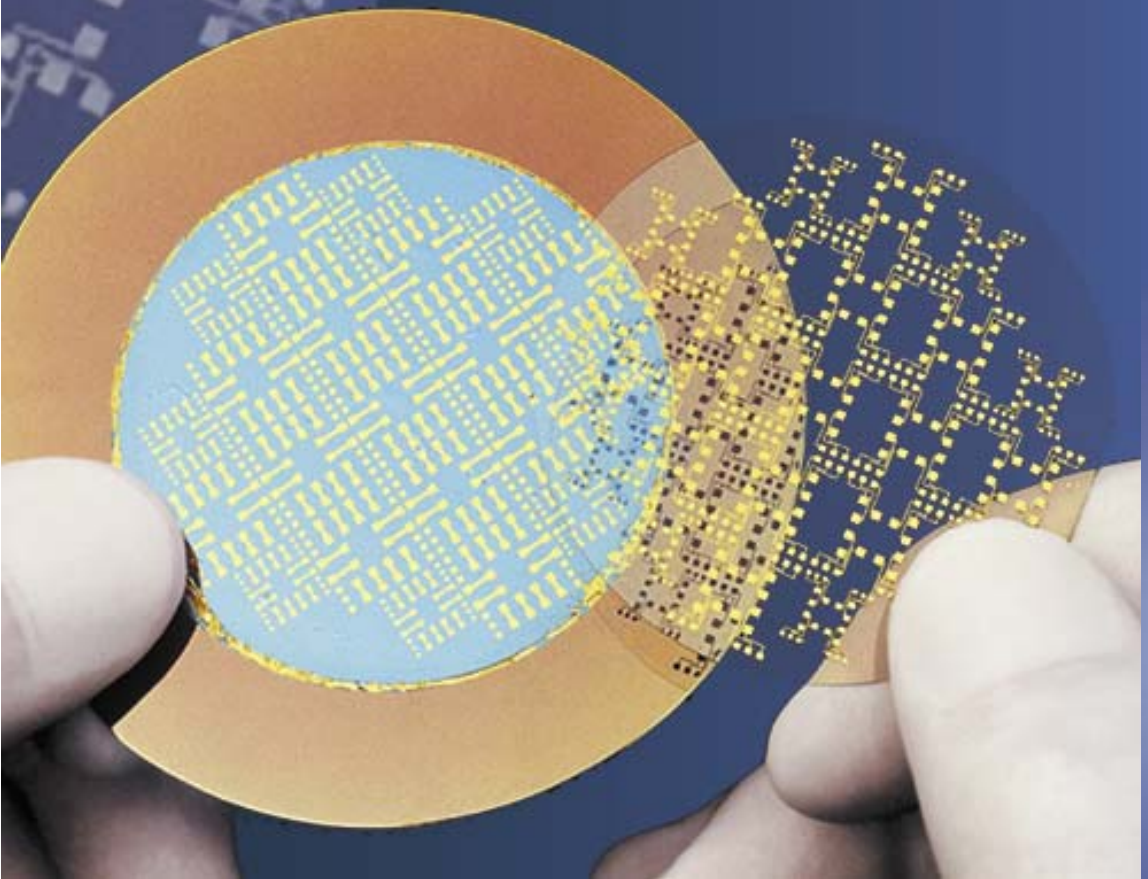
Nano-structured Thermoelectric Materials

8th Diesel Engine Emissions Reduction Conference

Loews Coronado Bay Resort

San Diego, CA

August 25, 2002



Rama Venkatasubramanian

RTI INTERNATIONAL

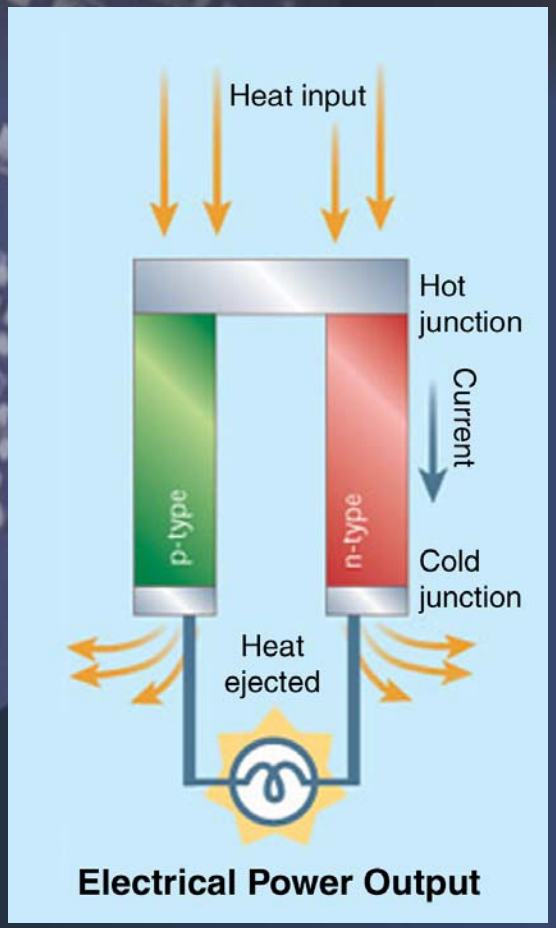
Outline

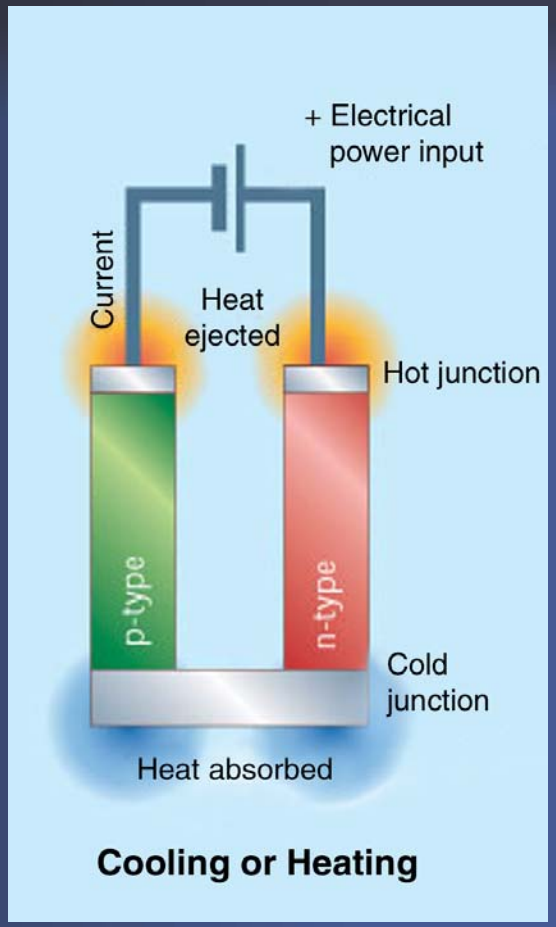
- Introduction – Relevance to CFC-free Air-conditioning in Automobiles, Energy Conservation and Emissions Reduction
- Advantages of Technology and Thin-film Cooling Examples
- Thin-film Power Conversion Examples
- Major Outstanding Issues for Research
- Emerging Thin-film TE Technology Applications

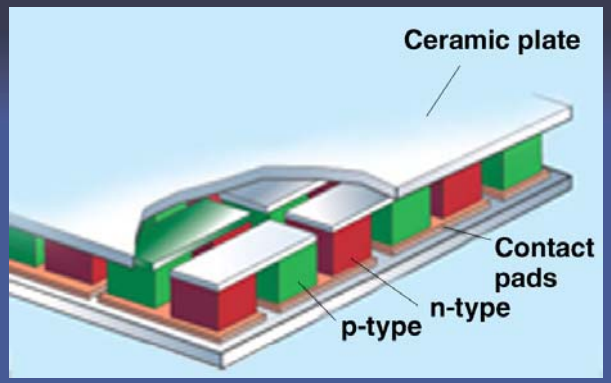
Why Thermoelectrics?

- Converts electrical and thermal energy using a solid state device with minimal moving parts
- **Chip-scale functionality** with thin-film materials using standard microelectronic processing
  - Computer Chip, Photonic Chip, Lab-on-a-Chip
- Green Technology – CFC-free refrigeration to waste-heat recovery for fuel efficiency

Thermoelectric Effect



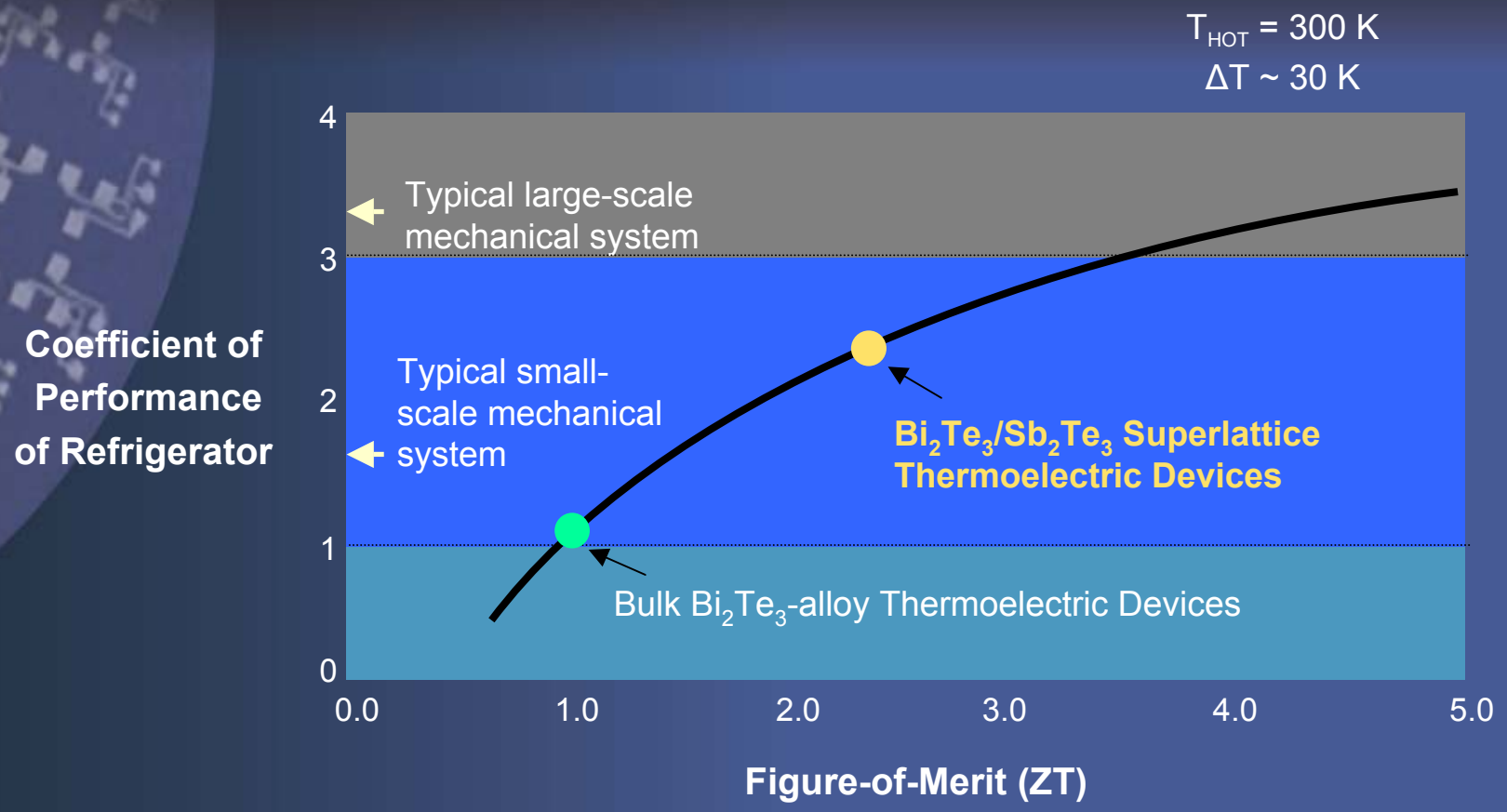




- Cooling or Power Conversion Efficiency critically dependent on the material Figure of Merit (ZT)
- $ZT = (\alpha^2\sigma/K)T$
- Minimize thermal conductivity and maximize electrical conductivity

Ref : Nature, 413, 577 (2001)

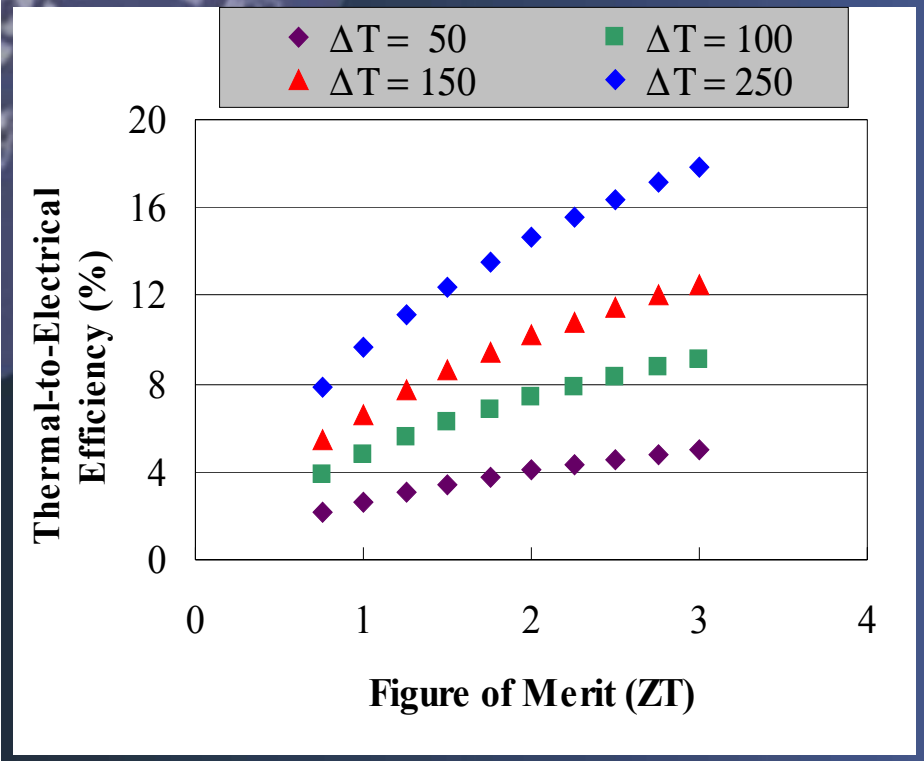
ZT and COP of Refrigerator or Air-Conditioner

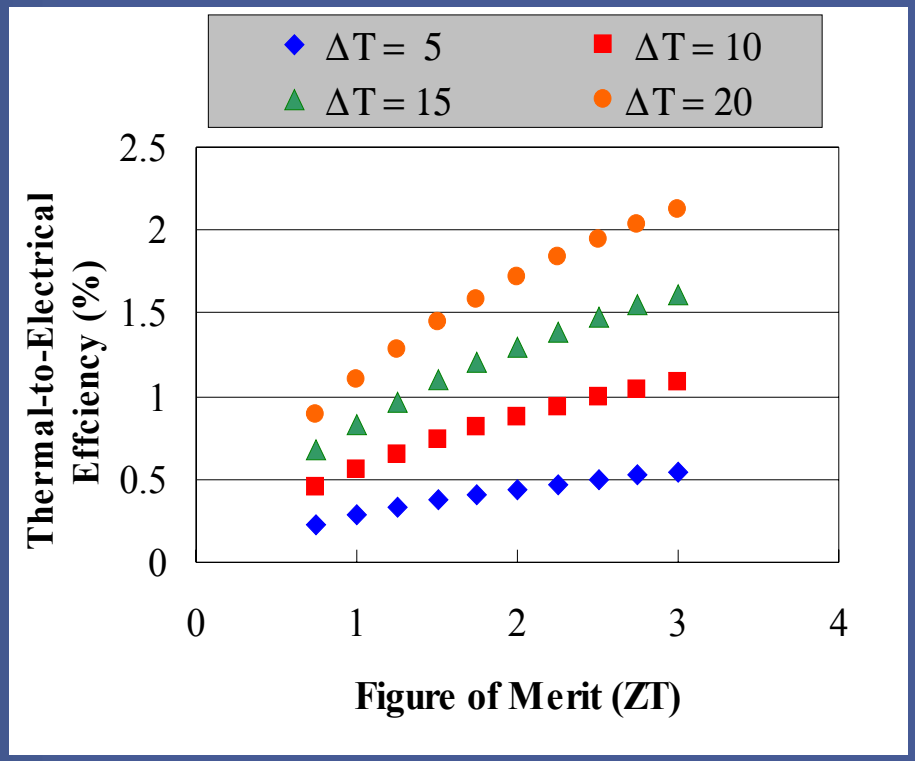


Higher ZT – Incentives for New Approaches to Implementing Higher COP Concepts

Implications for Power

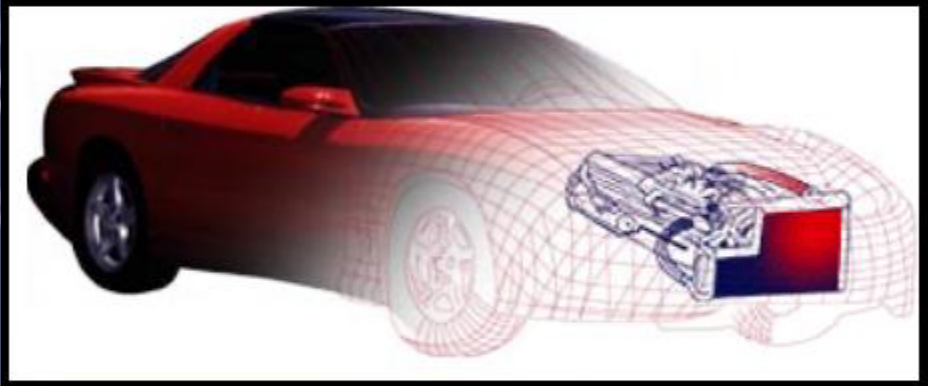
- High-density, light-weight
- Higher efficiency
- Replace Batteries



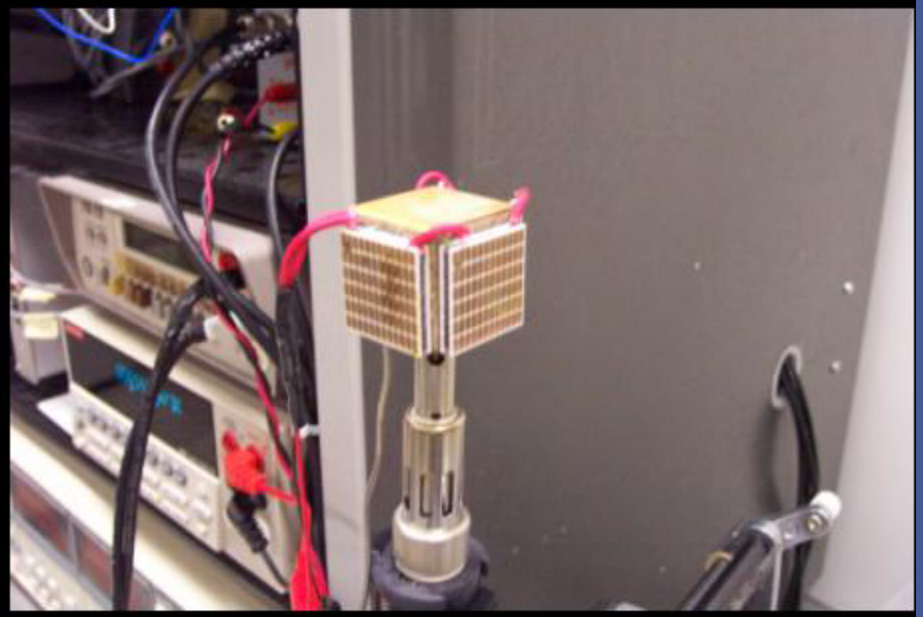


Automotive Power

Waste-heat recovery for electrical power

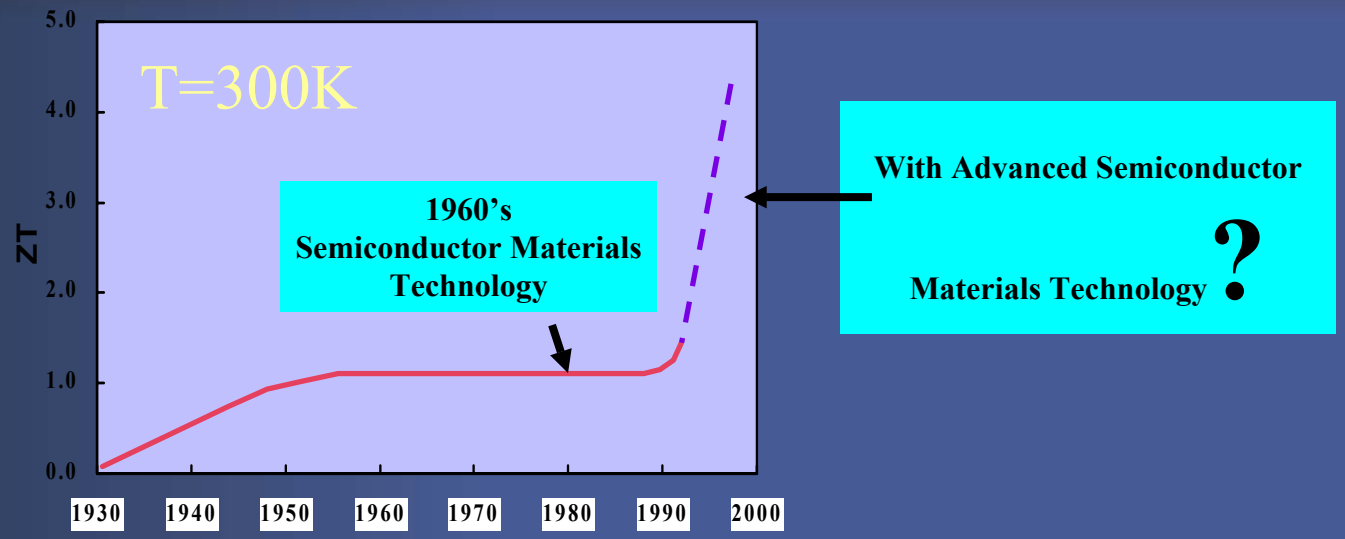


Portable power



Thermal scavenging for remote power

THERMOELECTRIC TECHNOLOGIES in 1992
Fort Belvoir Workshop Organized by Dr. Stuart Horn



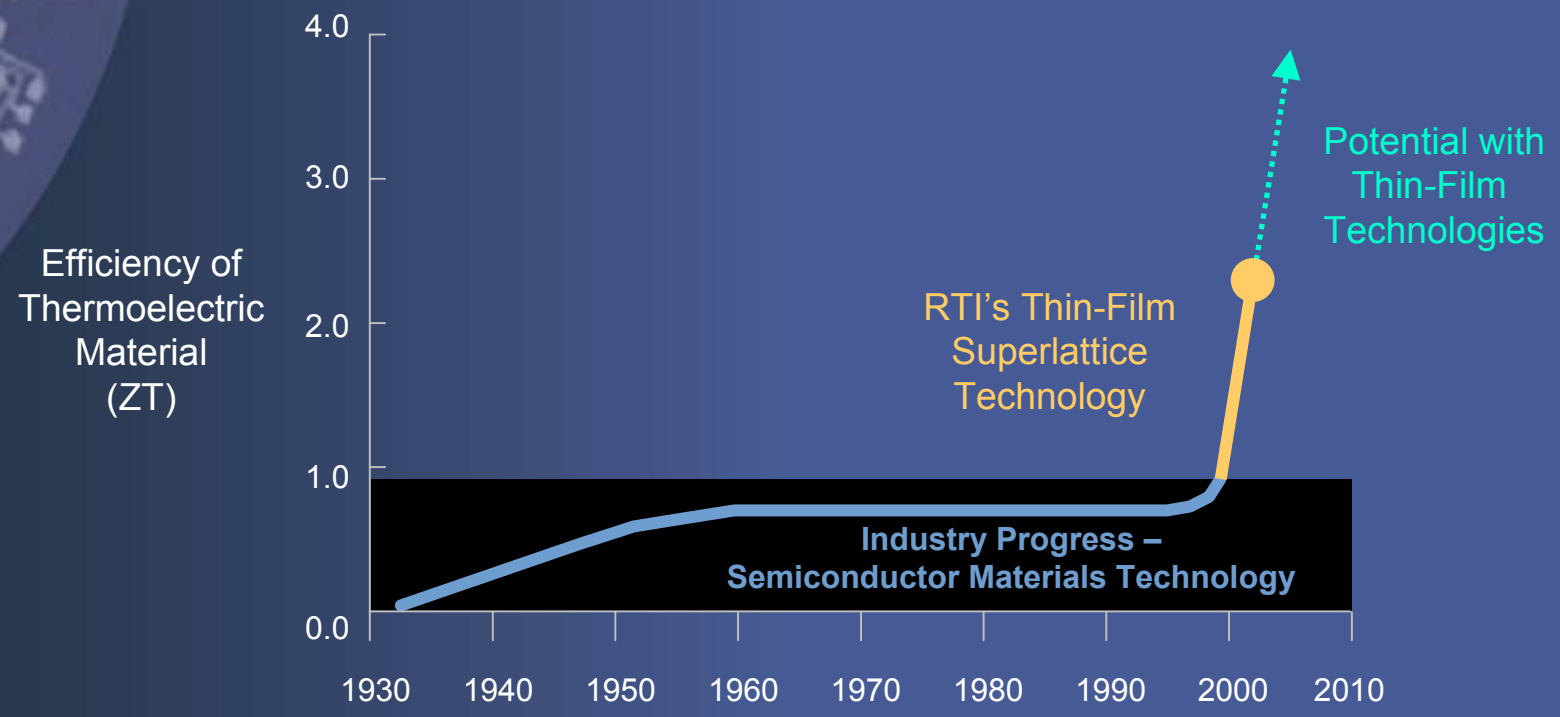
- ZT - figure of merit - has been stagnant at about 0.8 to 1 for the last 40 years - cooling and power conversion efficiencies low - useful only in applications where you <u>really need</u> it
- ZT need to improve over 1.5 at 300K for a major impact in electronics and around 2 to 2.5 for a revolutionary impact in air-conditioning, and power from waste-heat

Some of the Bulk Material and Thin-film Developments

- Cs Bi_4Te_6 (Michigan State University)
  - Bulk Materials with a ZT~ 0.8 at 225K but less than 0.8 at 300K (*Science* **287**, 1024-1027, 2000)
- Filled Skuterrudites (JPL)
  - Bulk materials with a ZT ~1.35 at 900K (Proc. Of 15th International Conf. On Thermoelectrics, 1996)
- PbTe/PbTeSe Quantum-dots (MIT Lincoln Labs.)
  - ZT~2 at 550K and ZT~0.8 at 300K based on estimated thermal conductivity values (J. Electronic Materials, 29, L1 , 2000)
- Bi_2Te_3/Sb_2Te_3 Superlattices (RTI)
  - ZT~2.4 at 300K in devices with all properties measured at the same place, same time, with current flowing and verified by two independent techniques (*Nature*, 597-602, 2001)

Thermoelectrics Research → Breakthrough Nanotechnology → Multiple Applications

RTI's 40-Year Breakthrough



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Cool new film

Metal sandwiches can pump heat rapidly to or from chips.

11 October 2001

PHILIP BALL

New composite could shrink thermoelectric coolers like this one to the size of a chip.
© Coolworks Inc.

A new composite could cool computer chips or warm scaled-down industrial chemical processing. It can pump heat rapidly to or from miniature devices.

The material, devised by Rama Venkatasubramanian and colleagues at the Research Triangle Institute in North Carolina[1], relies on both aspects of the thermoelectric effect. The first aspect is that current is generated in two electrically conducting materials in contact when one is hotter than the other. The

relatedstories

- **Holes plug leaky circuits** *24 July 2001*
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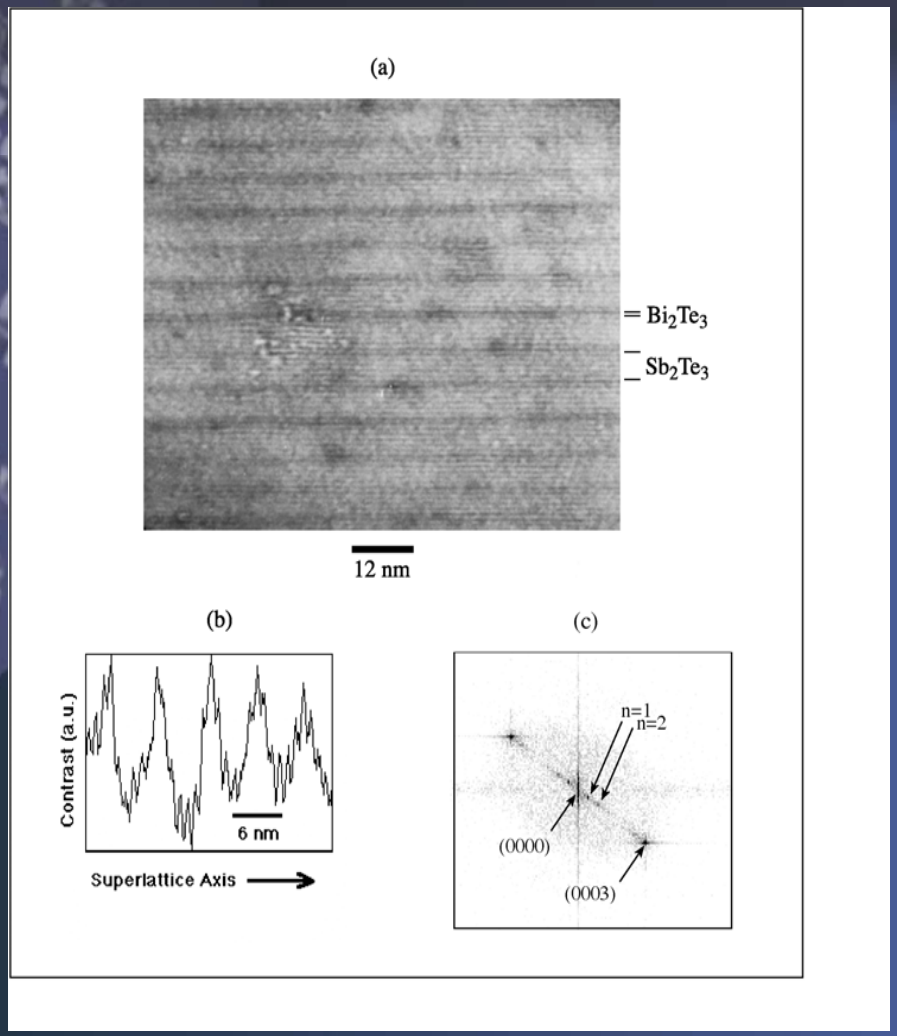
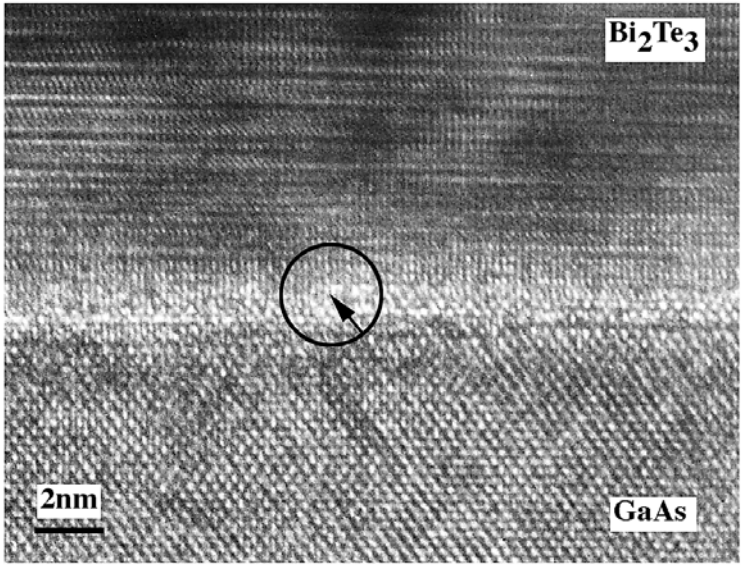
RTI's Nano-structured Superlattice Material



- 10Å/50Å Bi_2Te_3/Sb_2Te_3 Structure
- Optimized for disrupting heat transport while enhancing electron transport perpendicular to the superlattice interfaces

Applied Physics Letters, 75, 1104 (1999)

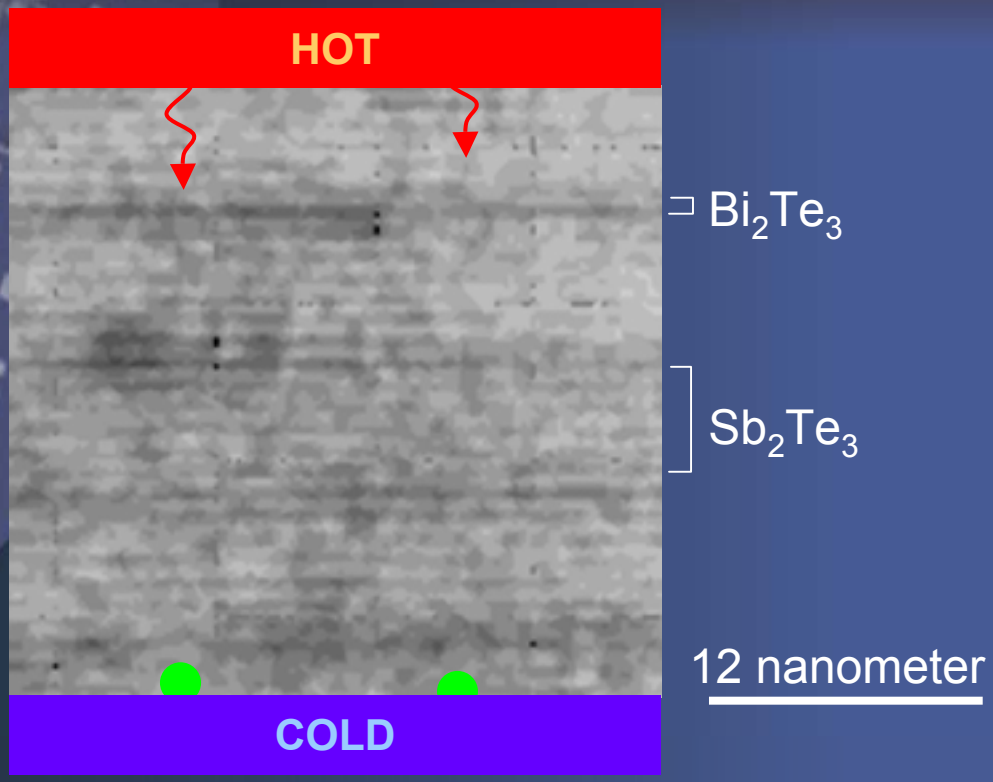
MOCVD Growth of Superlattices



<110> GaAs zone axis

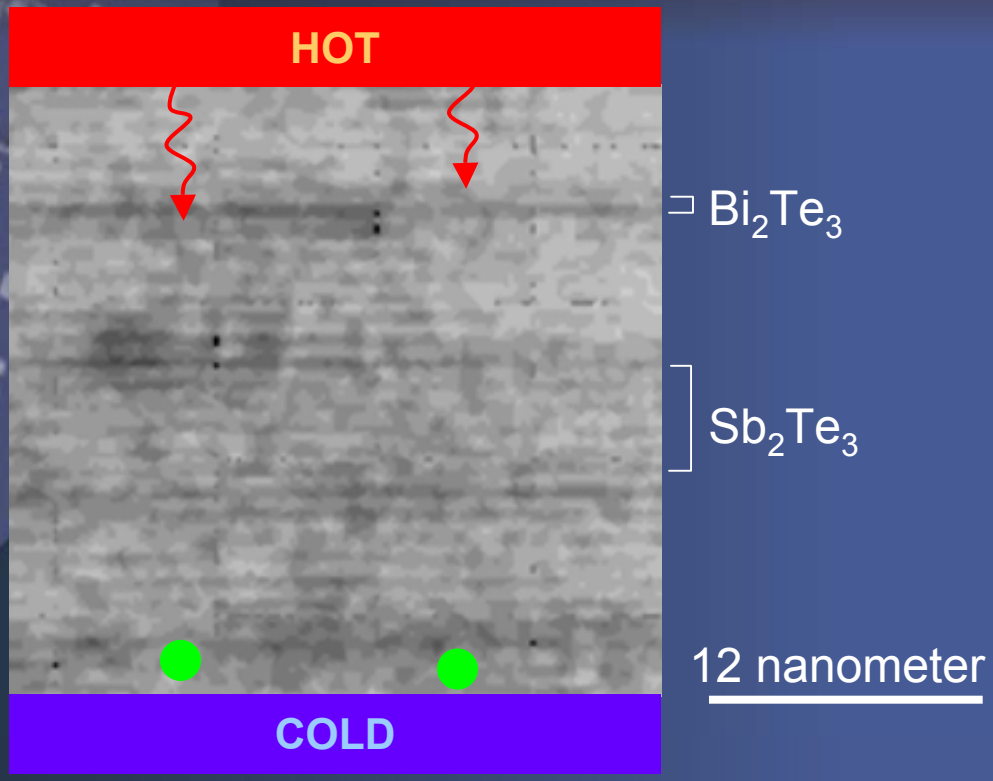
- Low-temperature technology and scaleable for large areas
- In-situ ellipsometry for nanometer-scale control of deposition

RTI's Superlattice Material



The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

RTI's Superlattice Material



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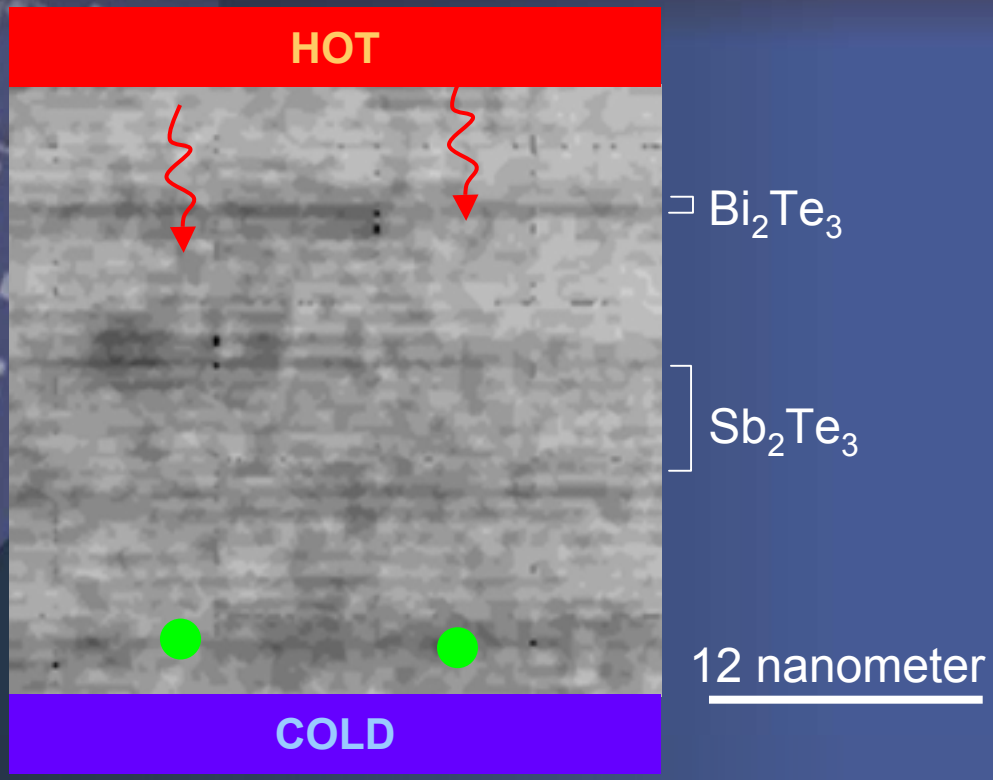

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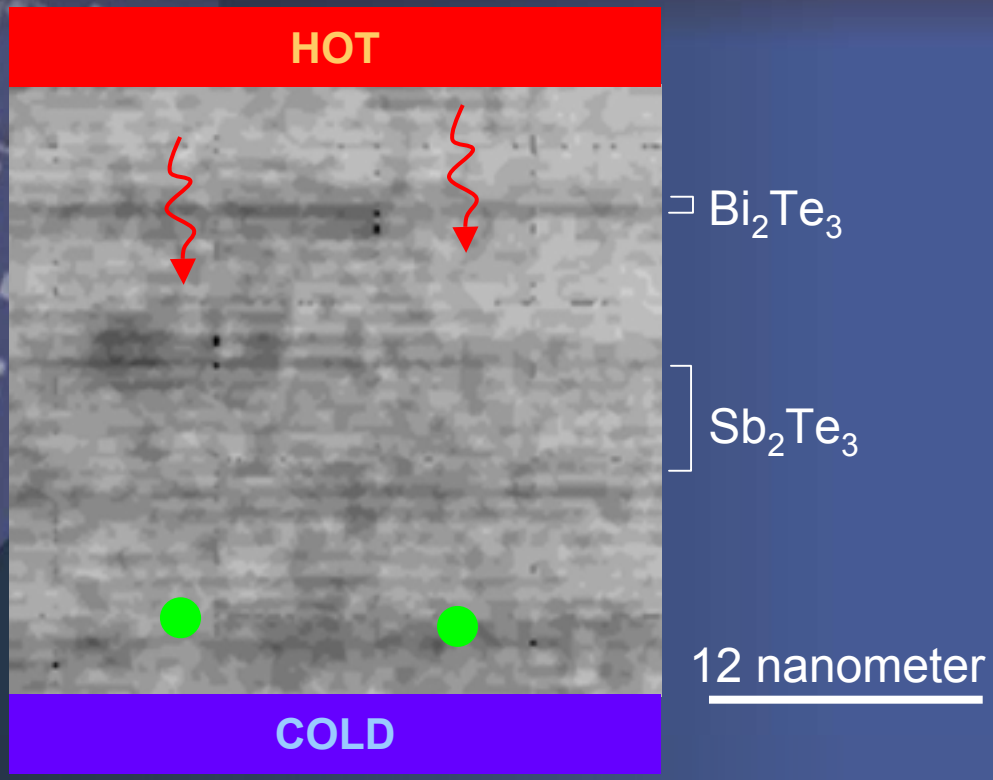

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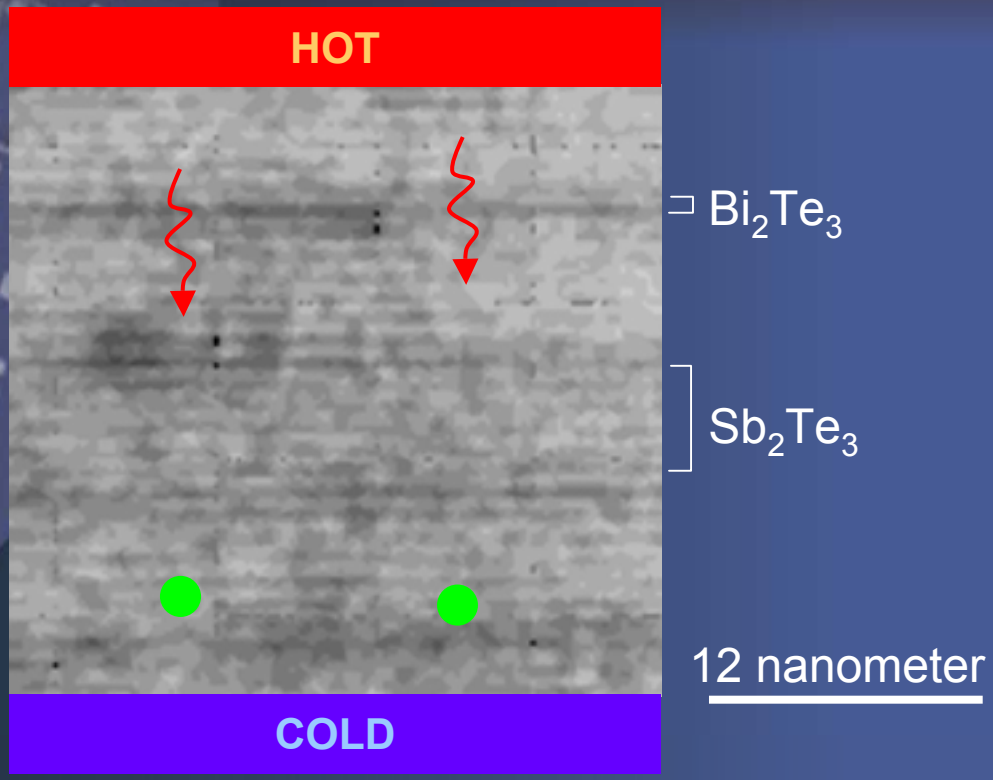

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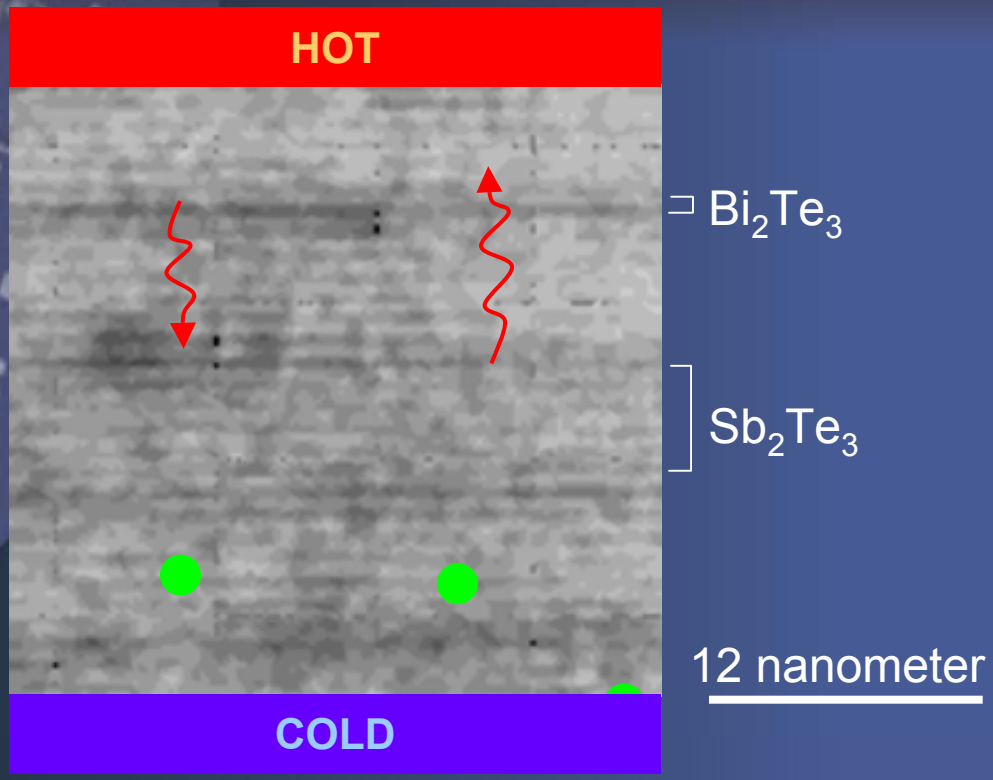

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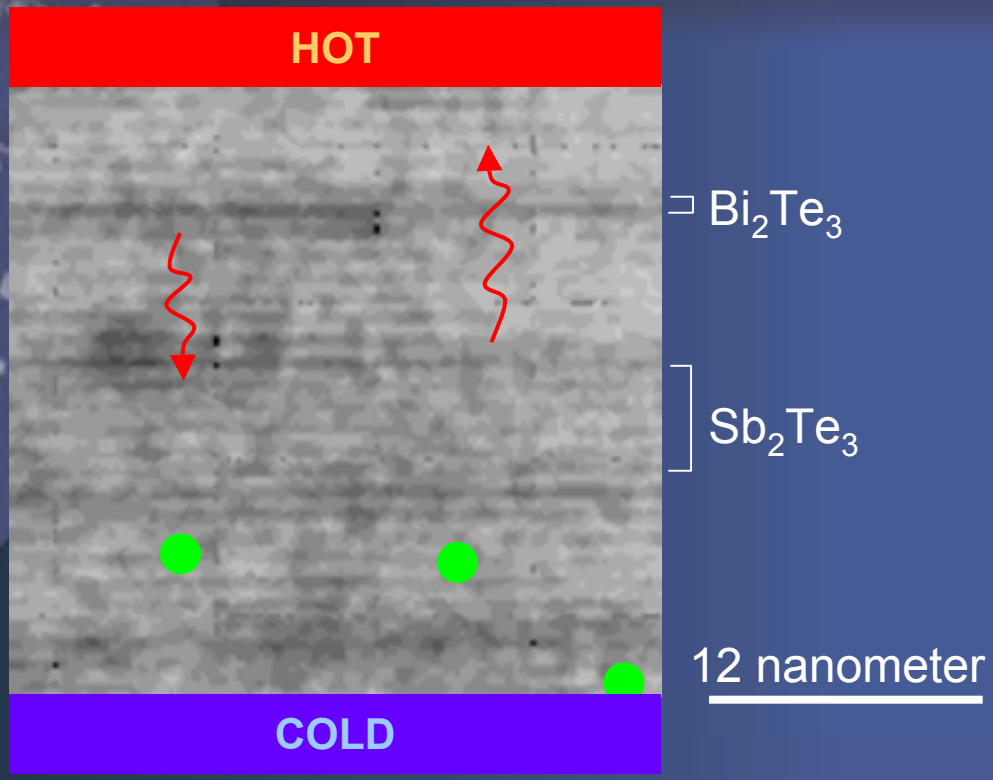

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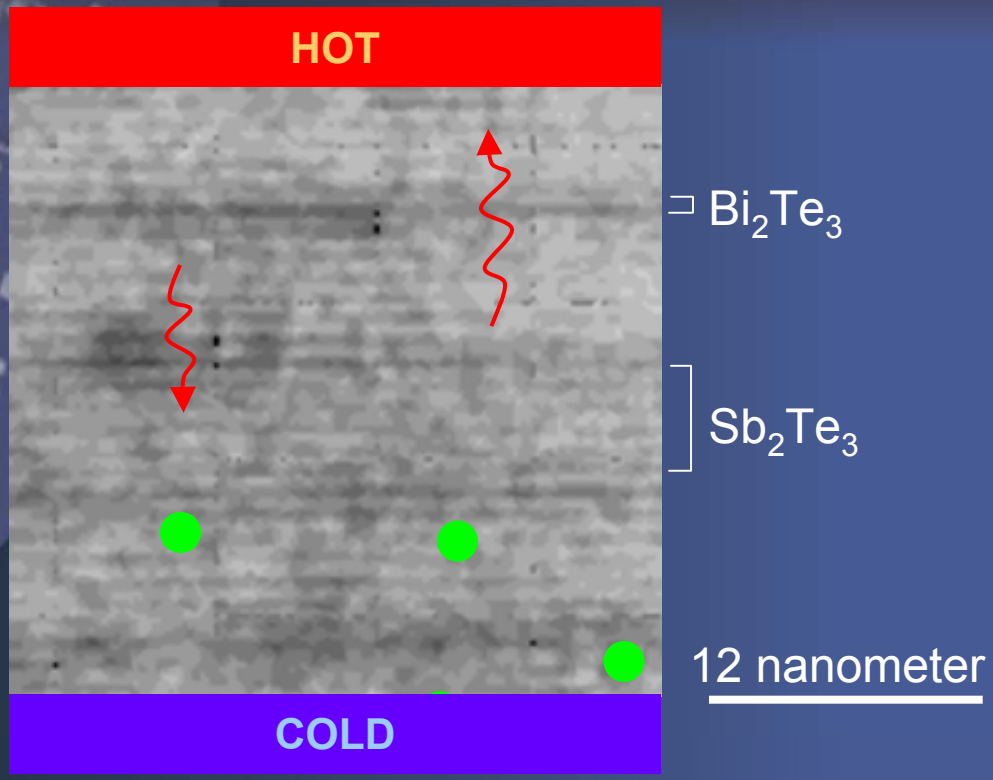

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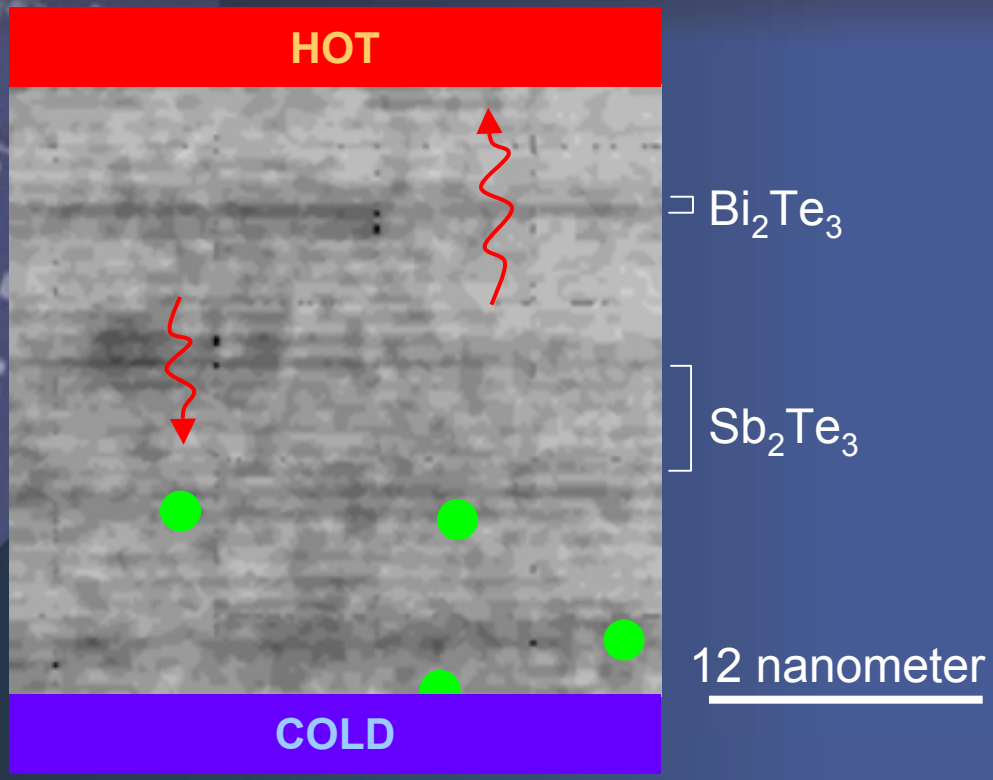

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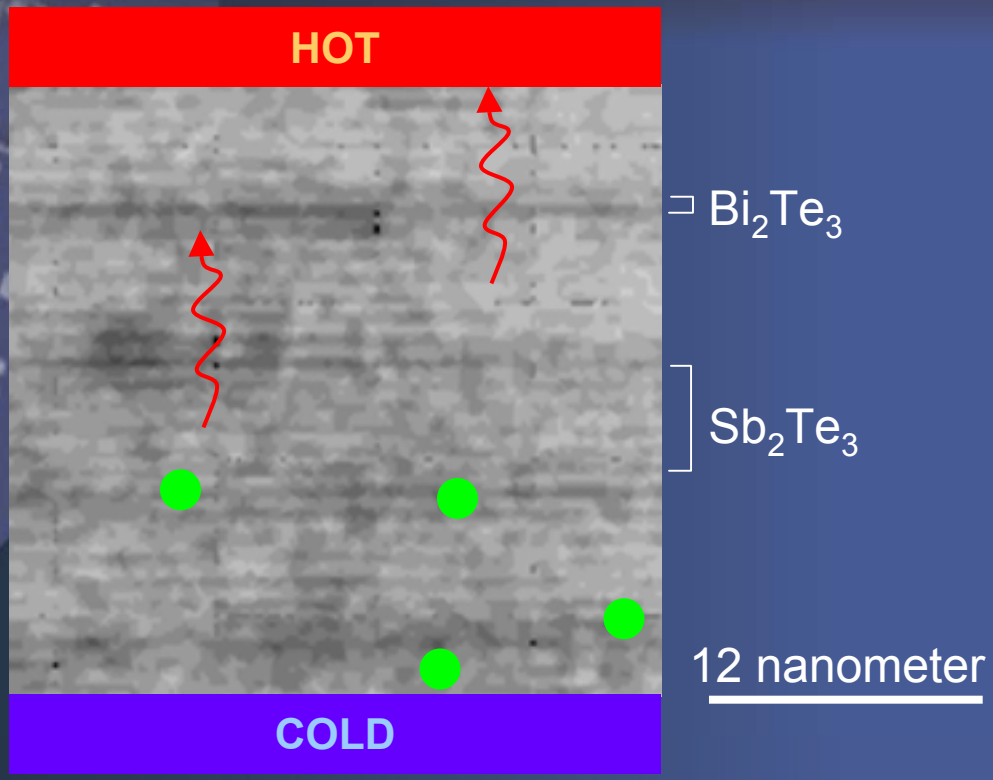

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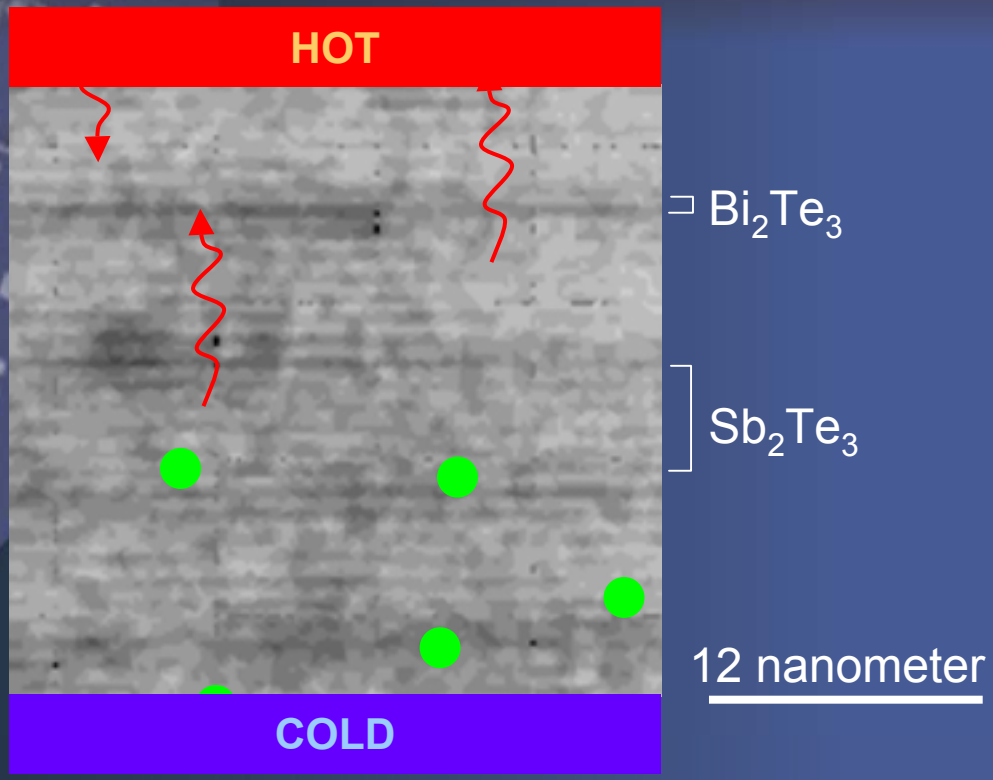

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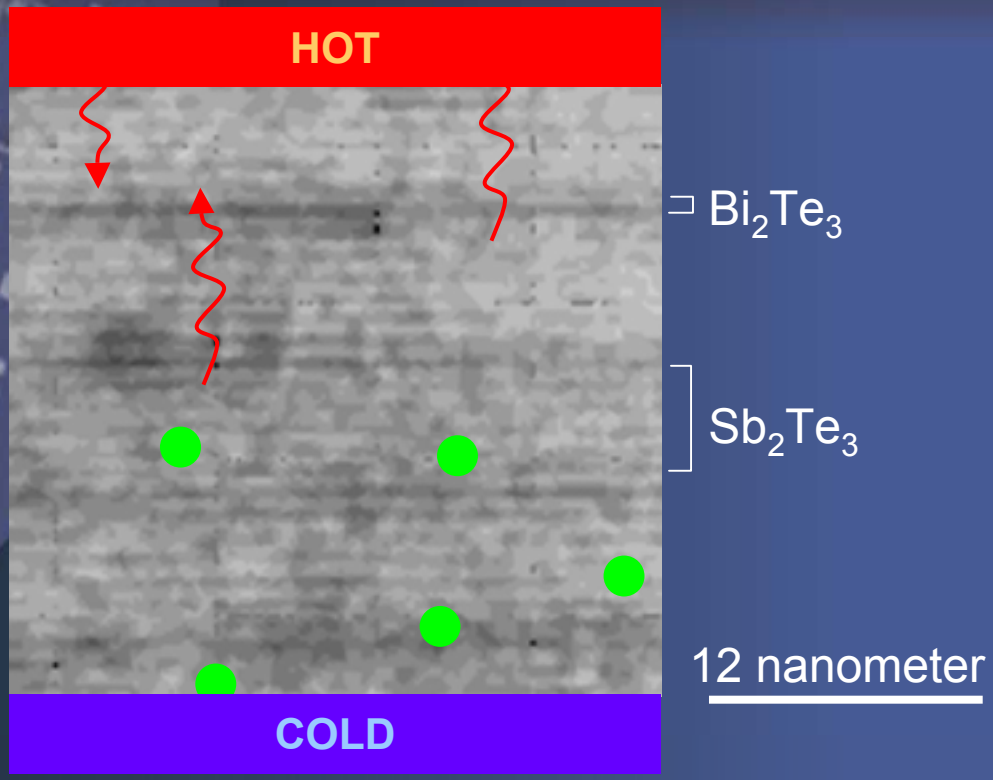

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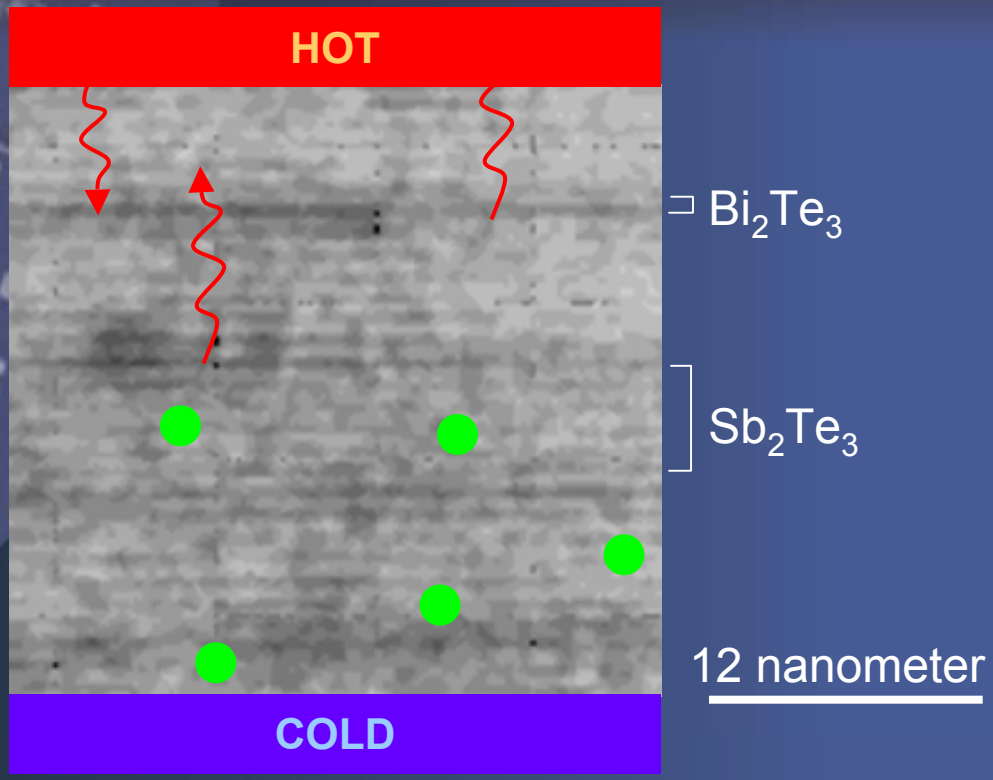

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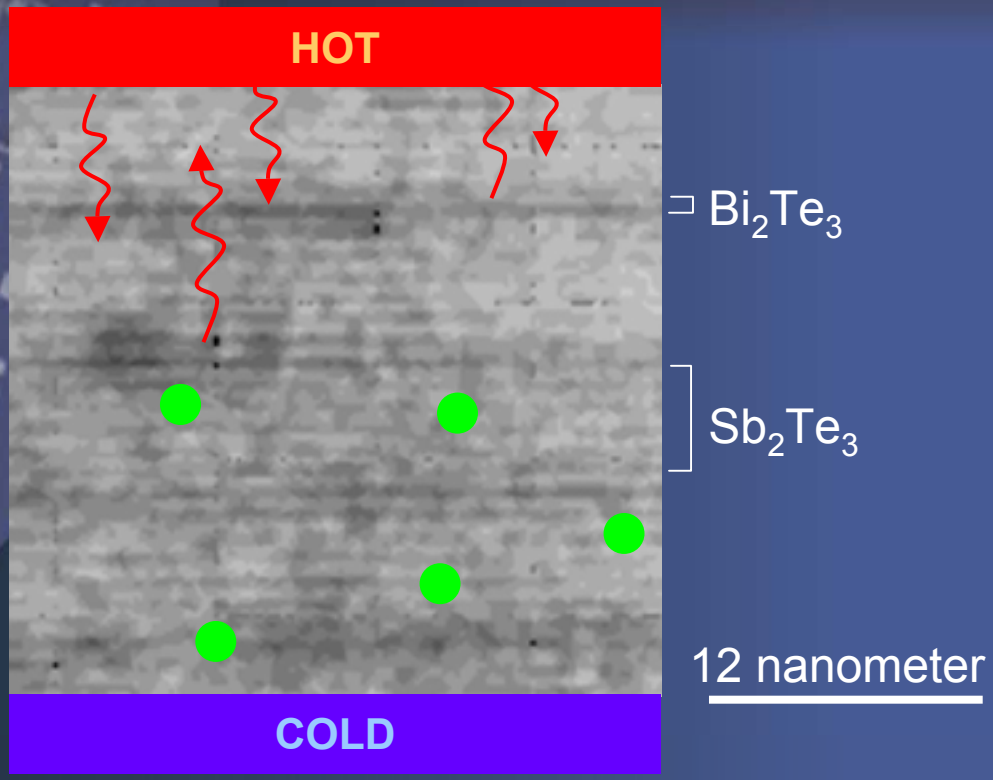

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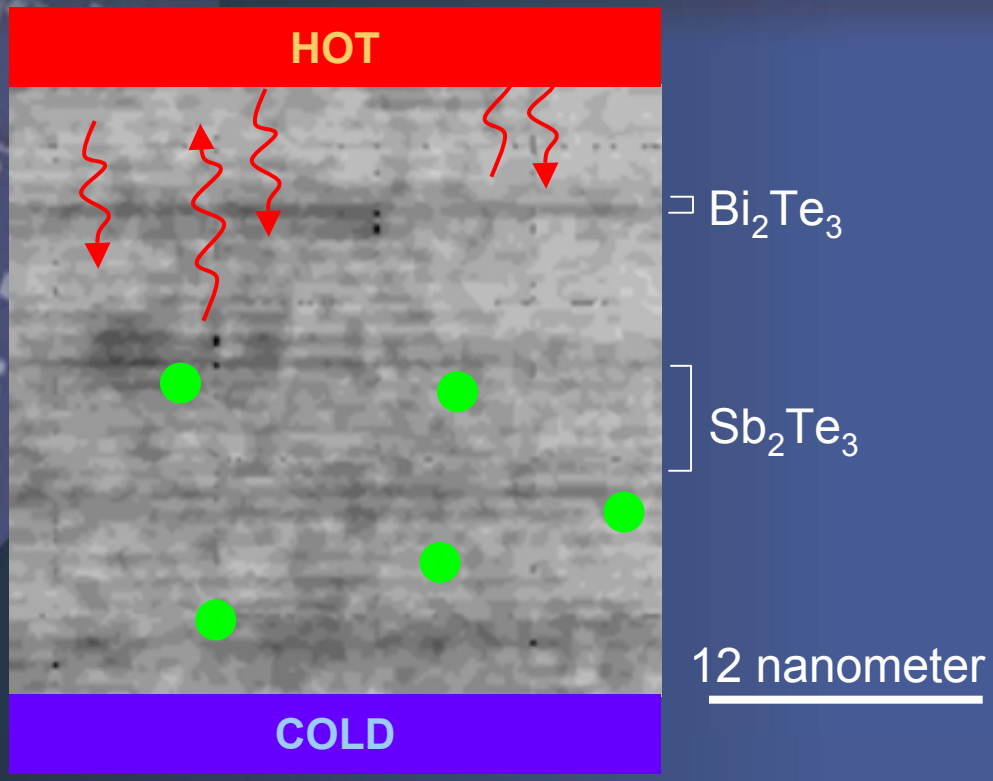

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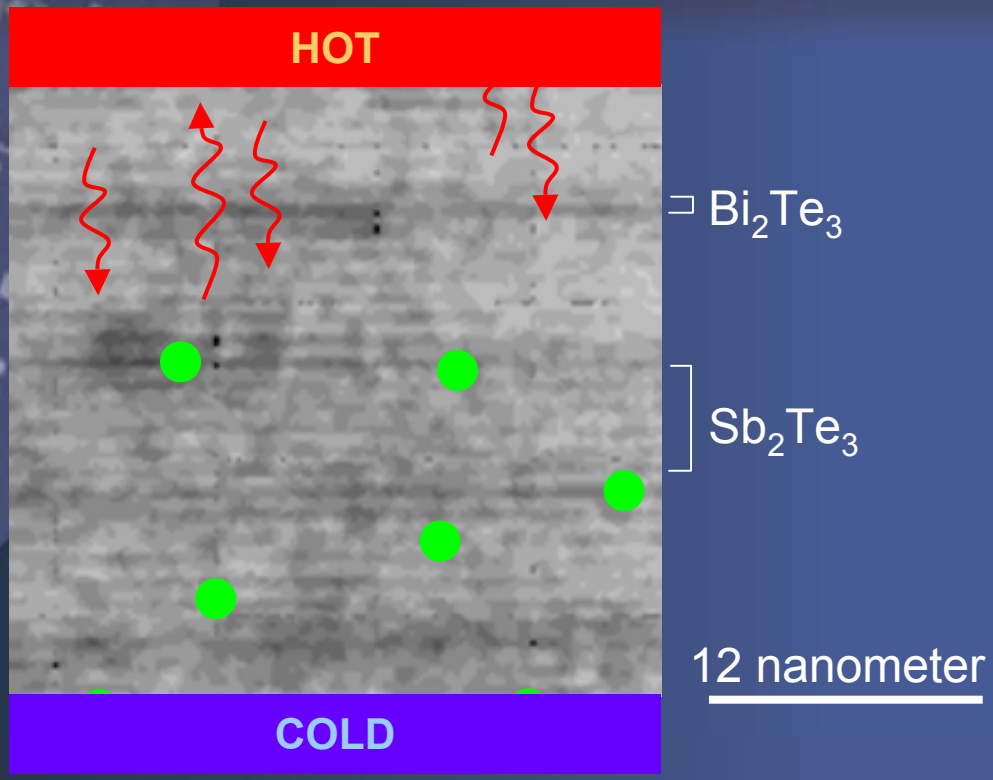

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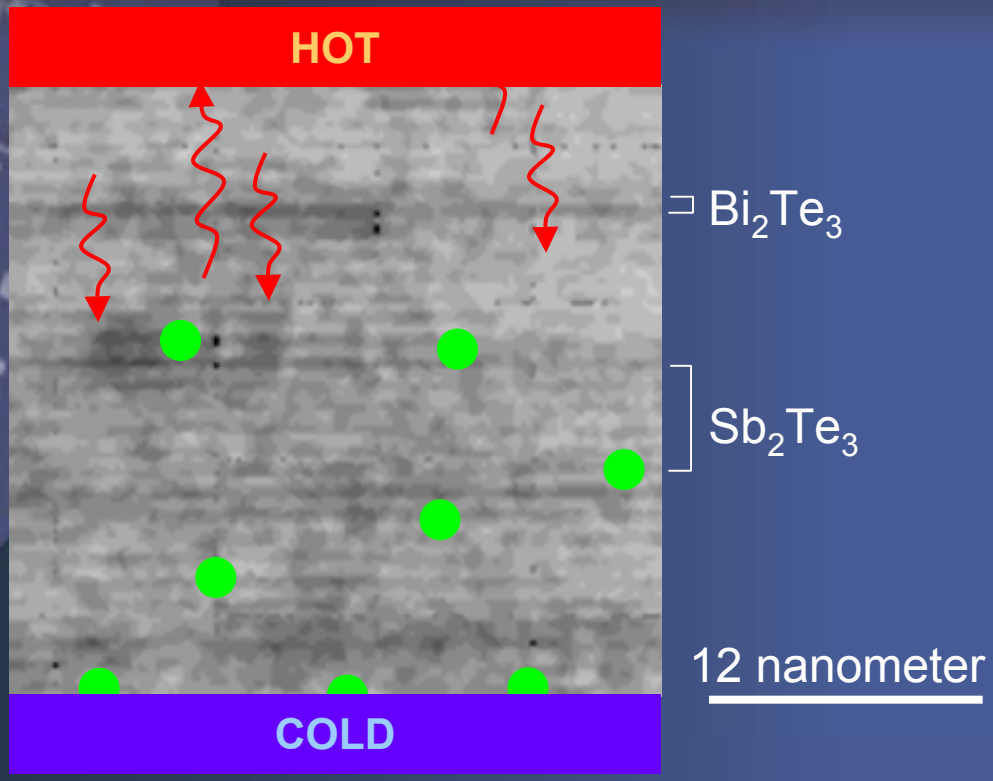

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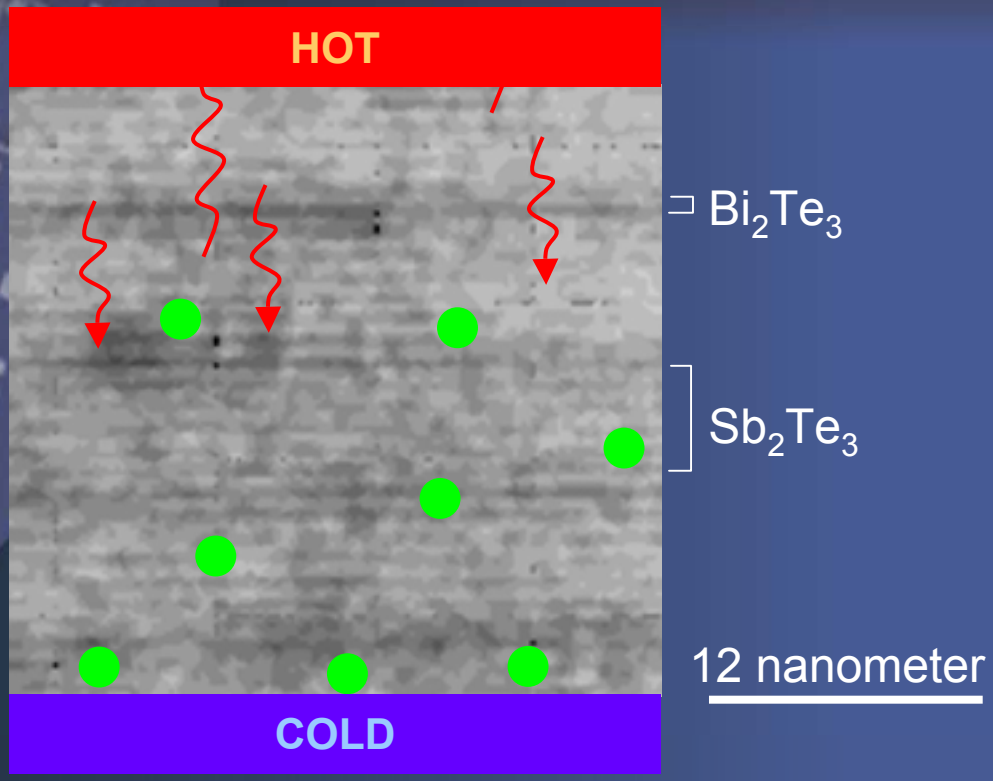

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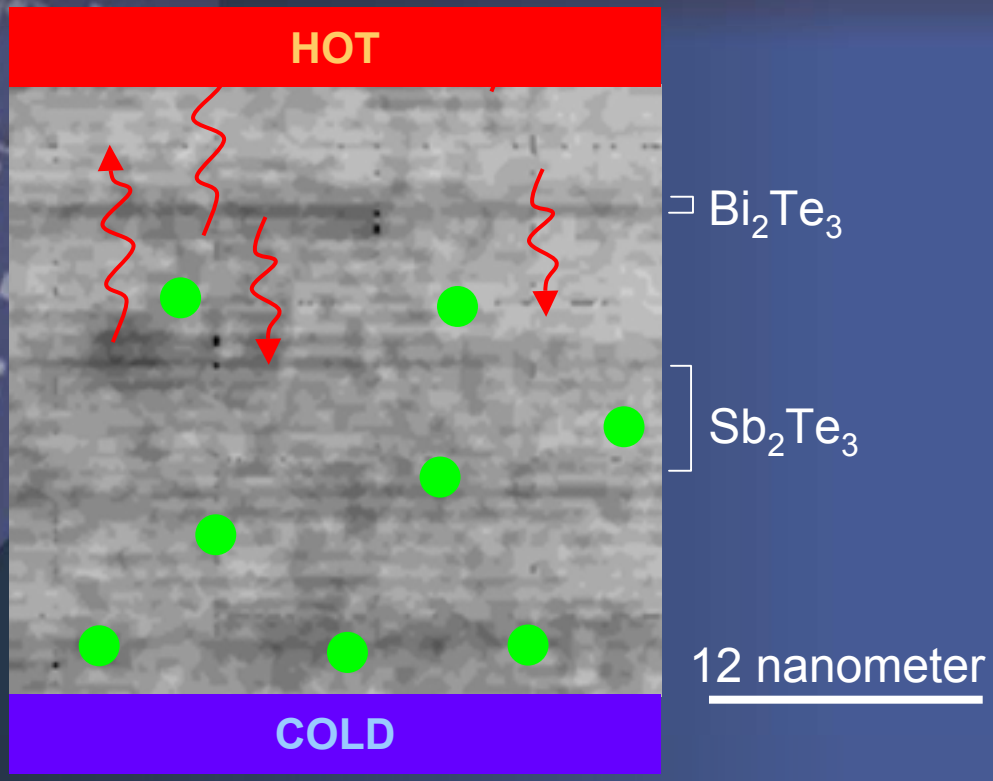

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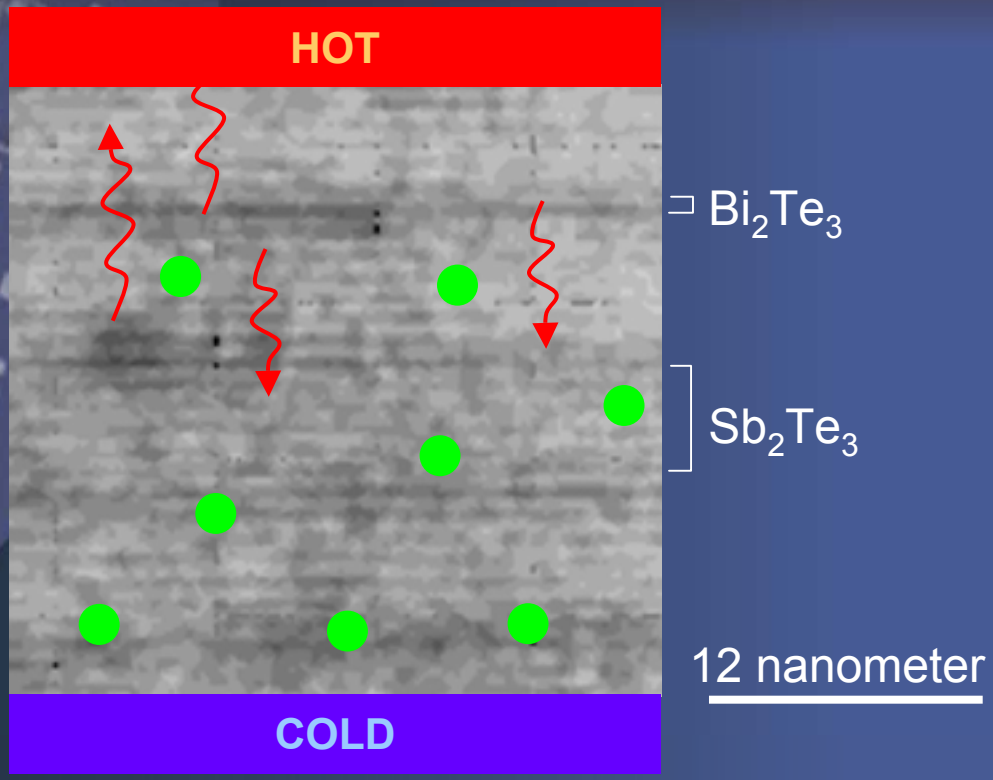

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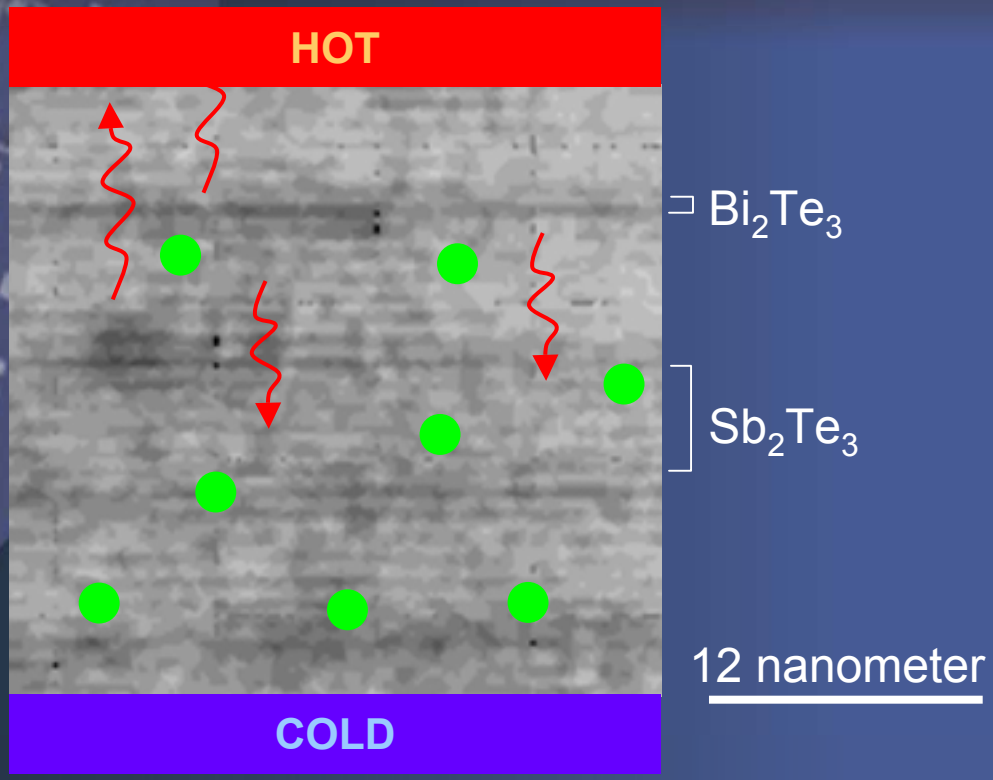

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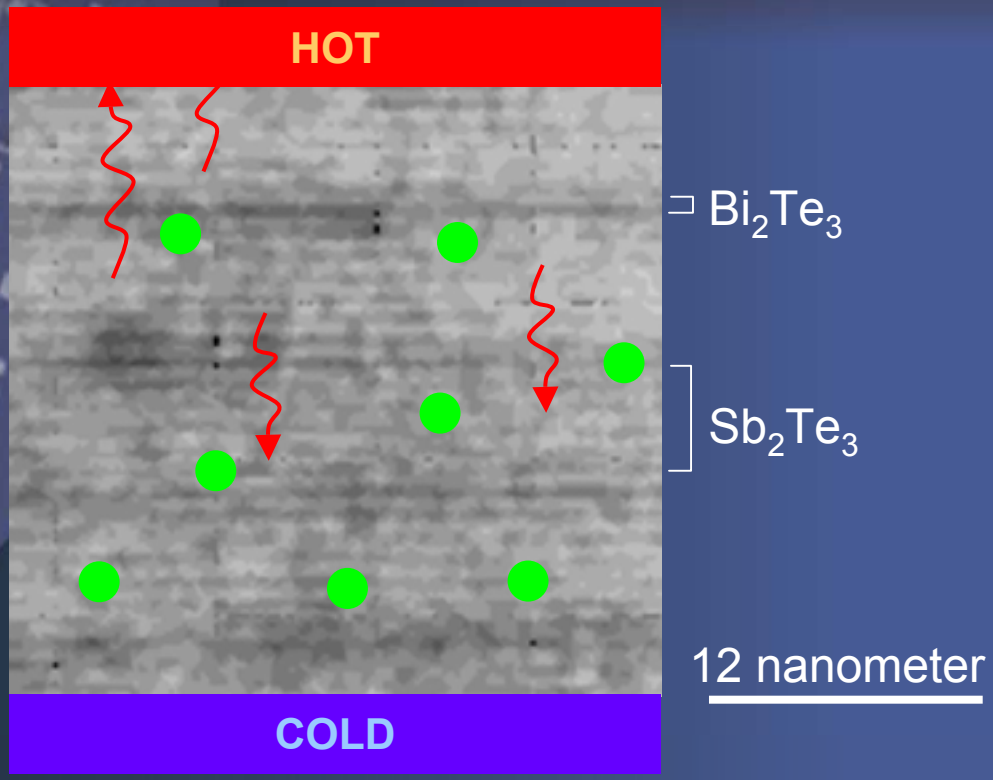

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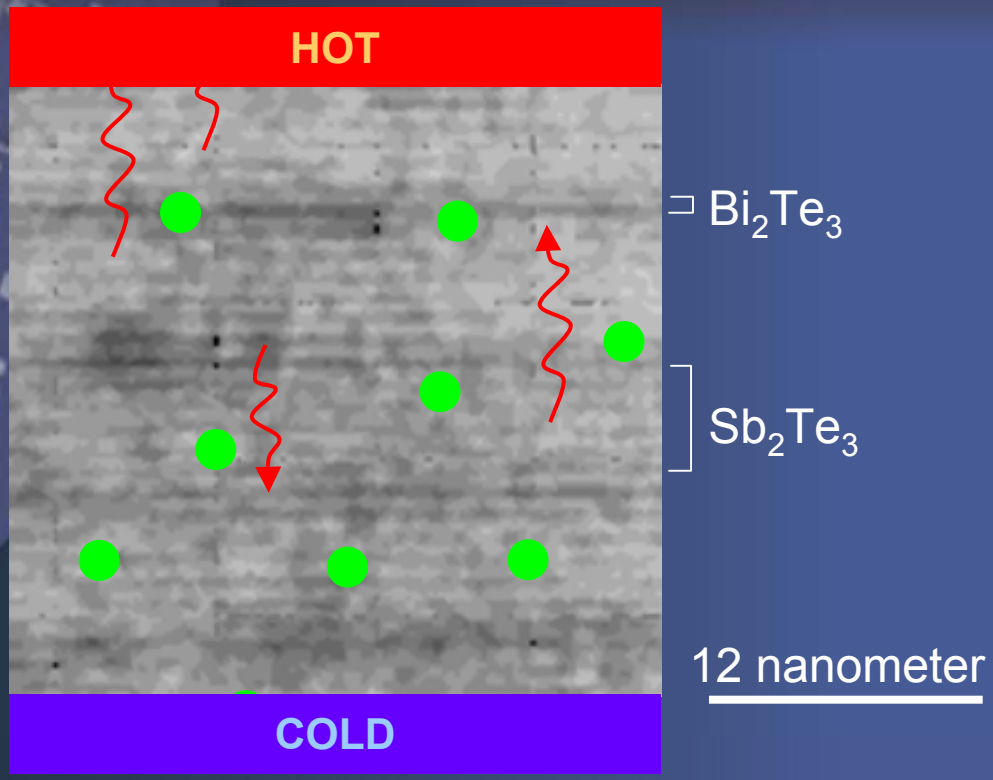

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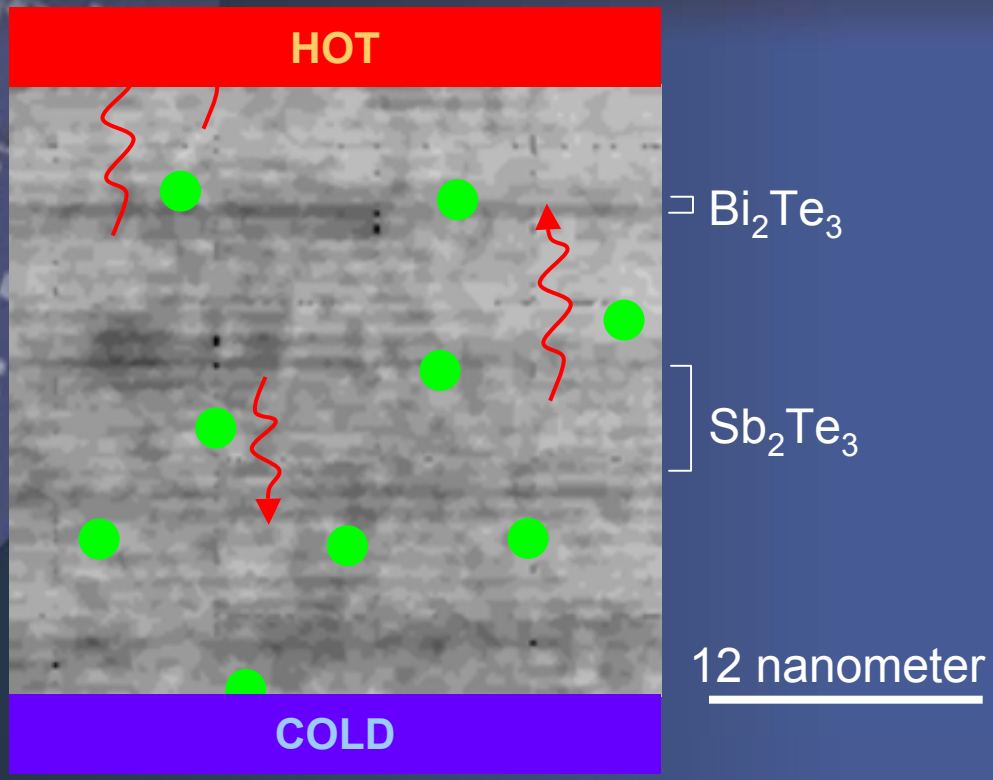

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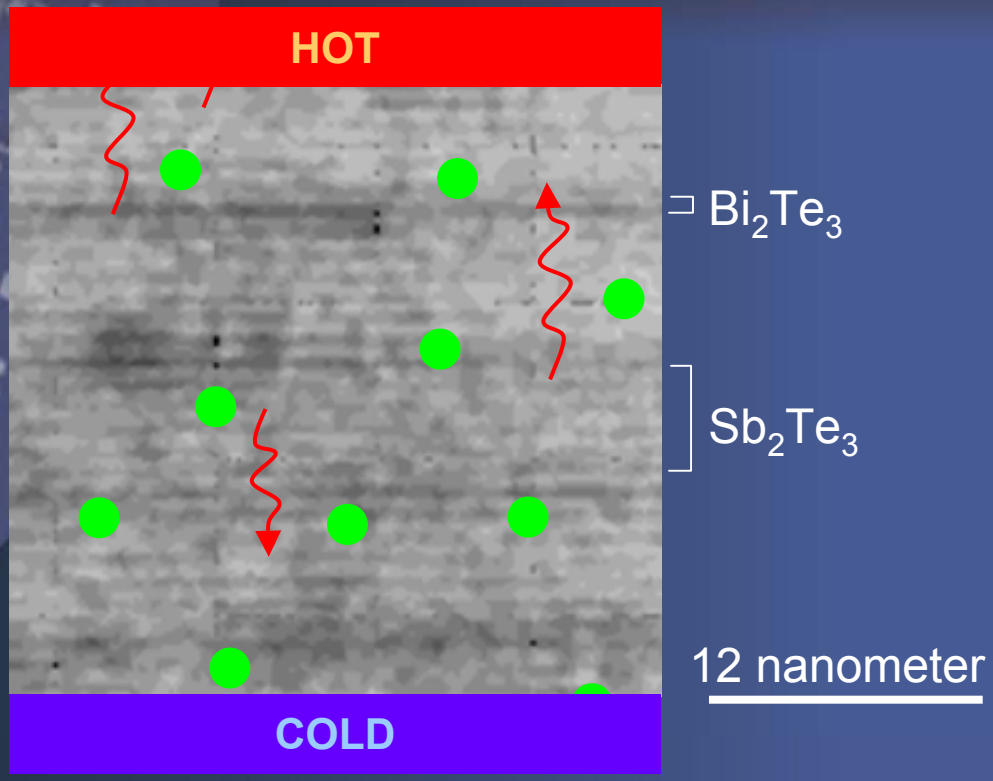

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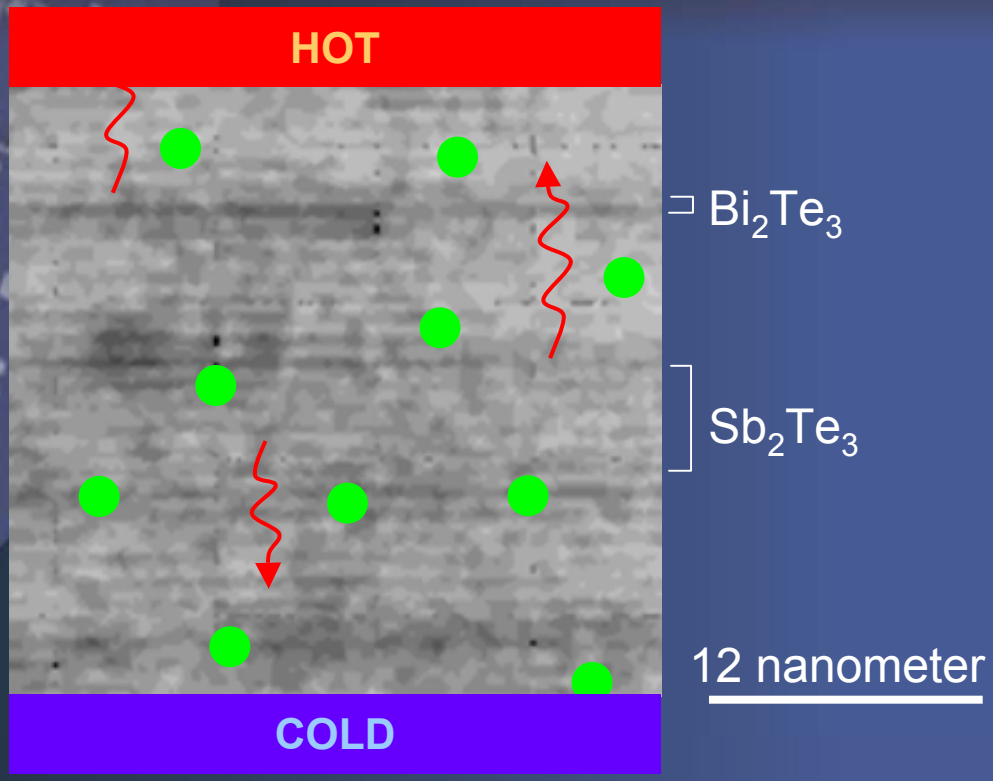

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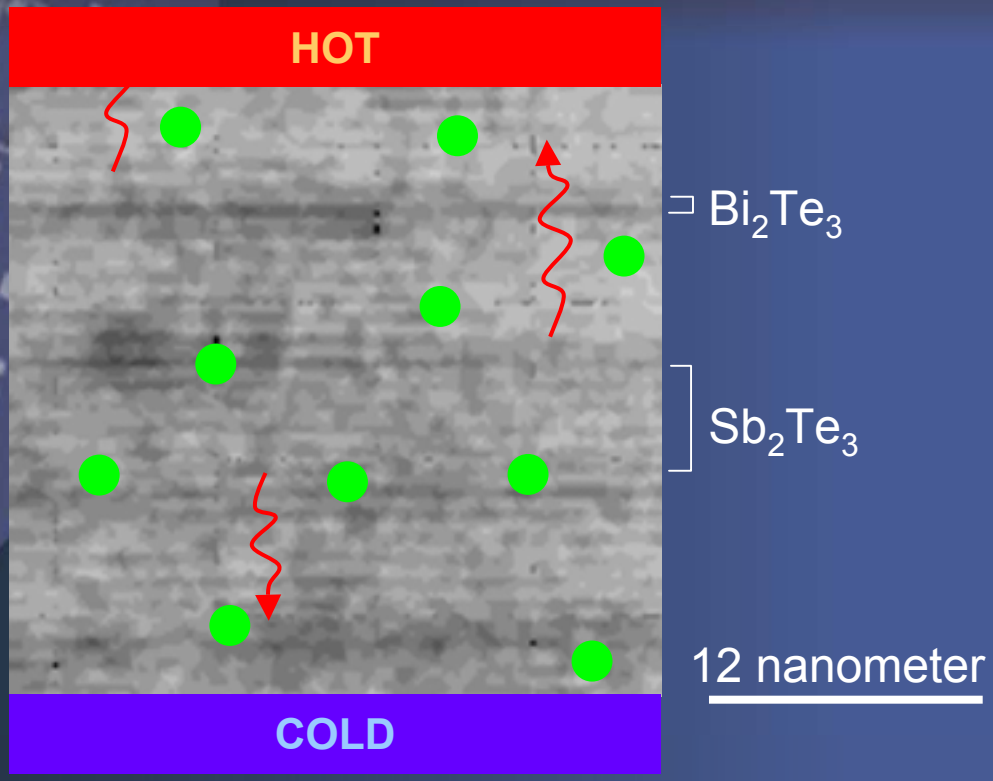

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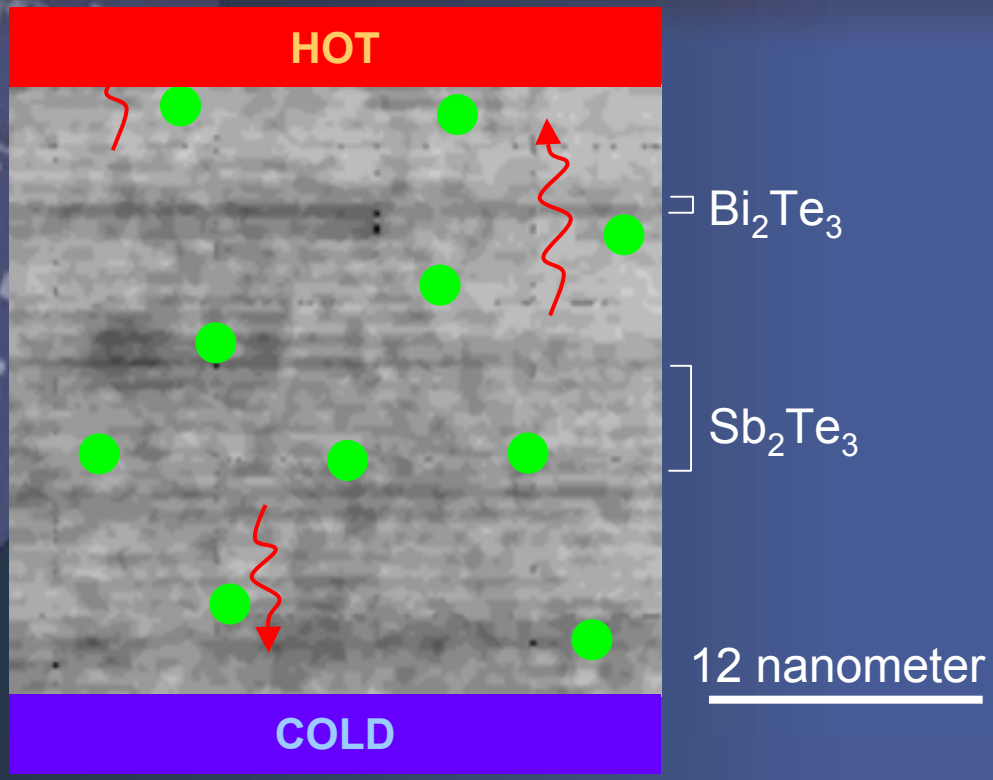

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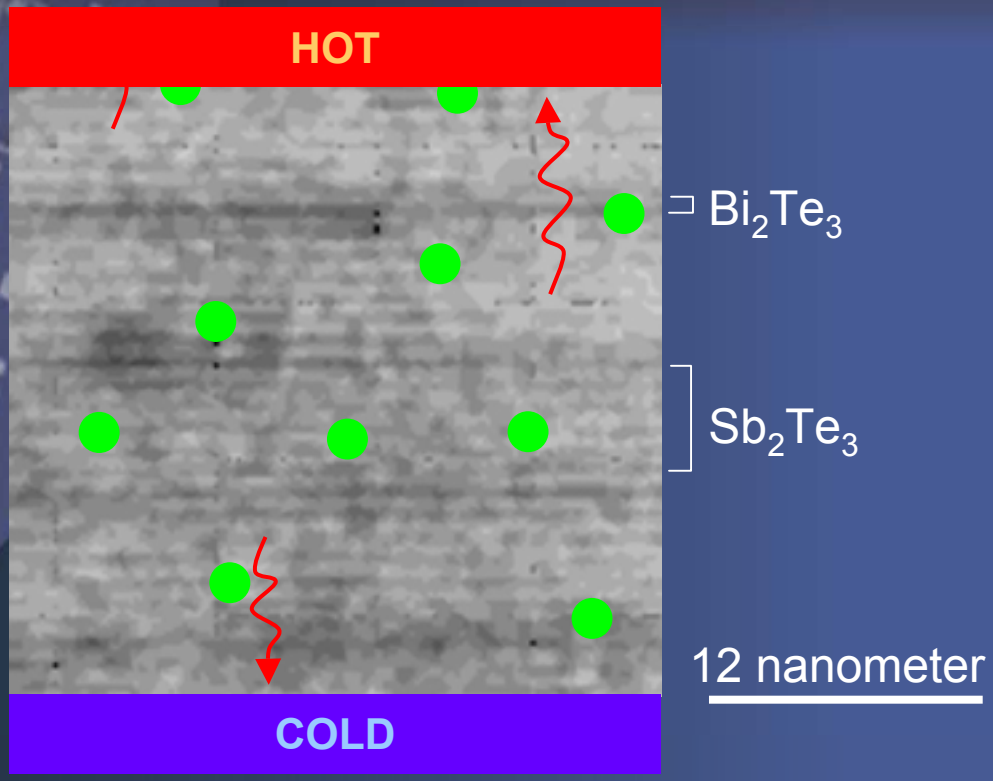

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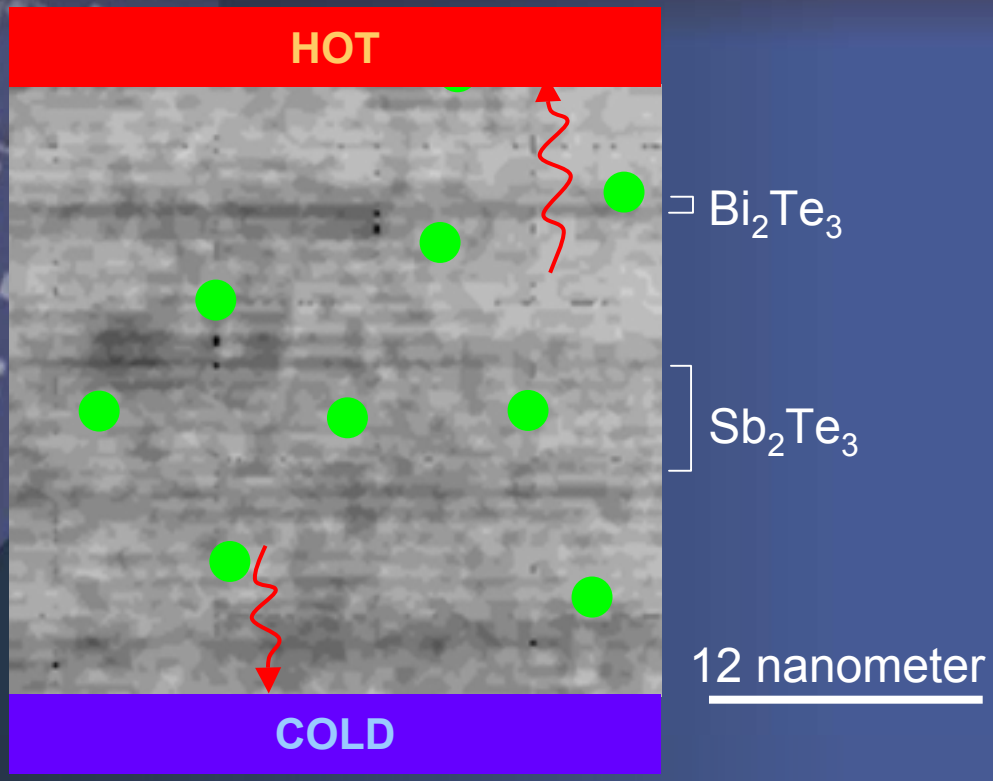

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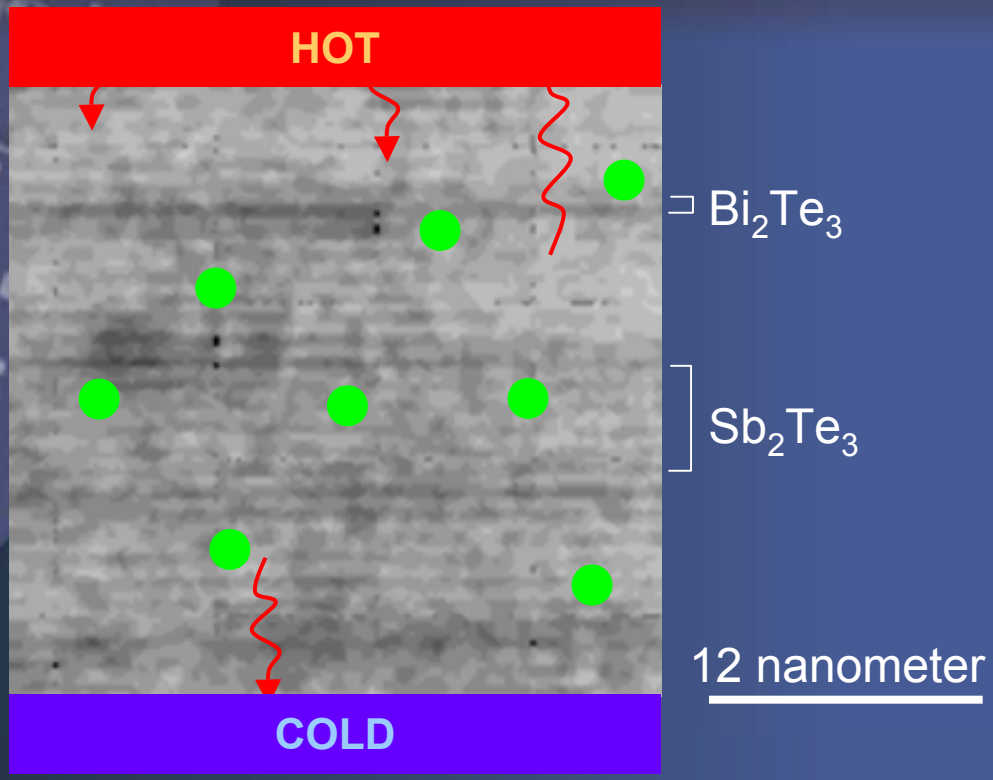

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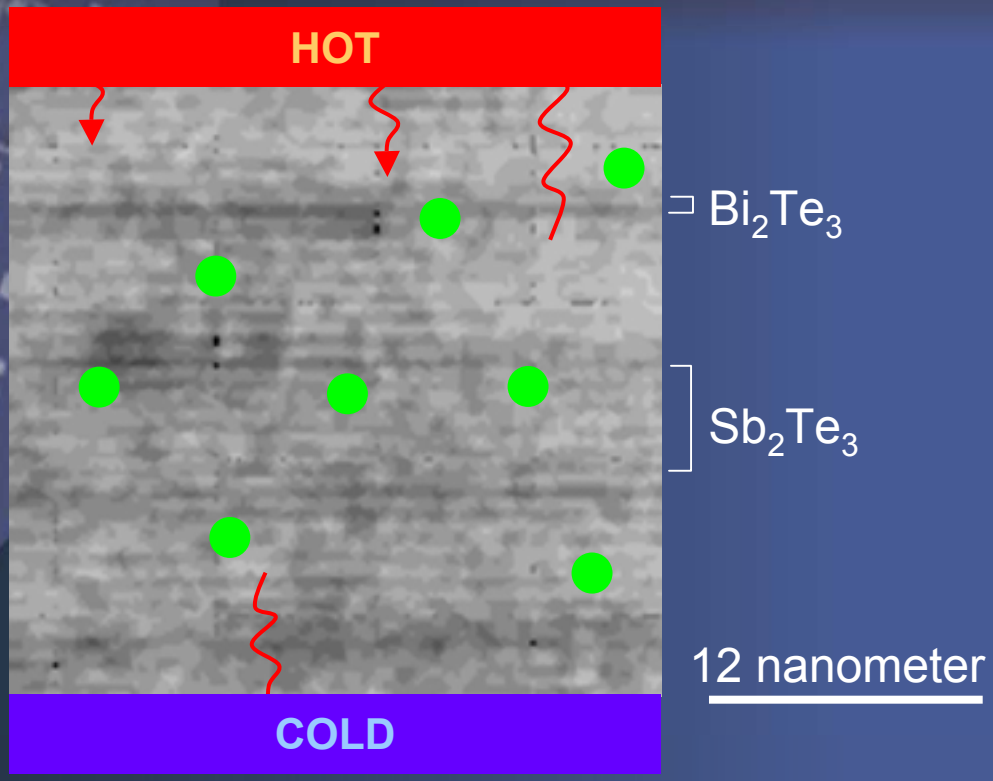

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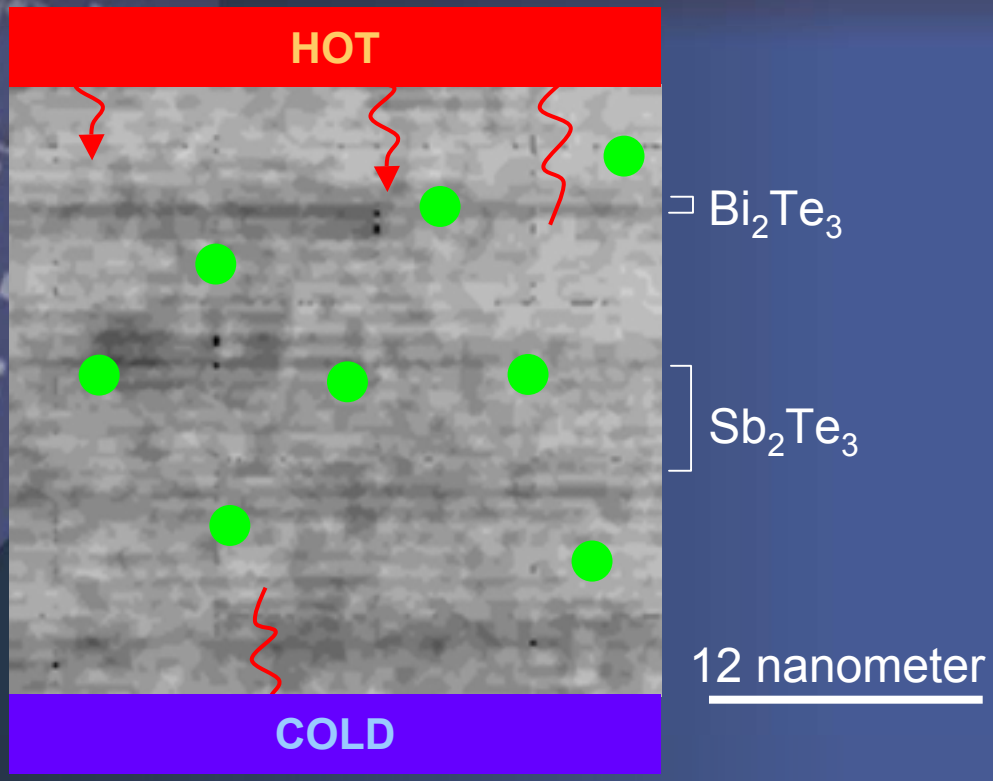

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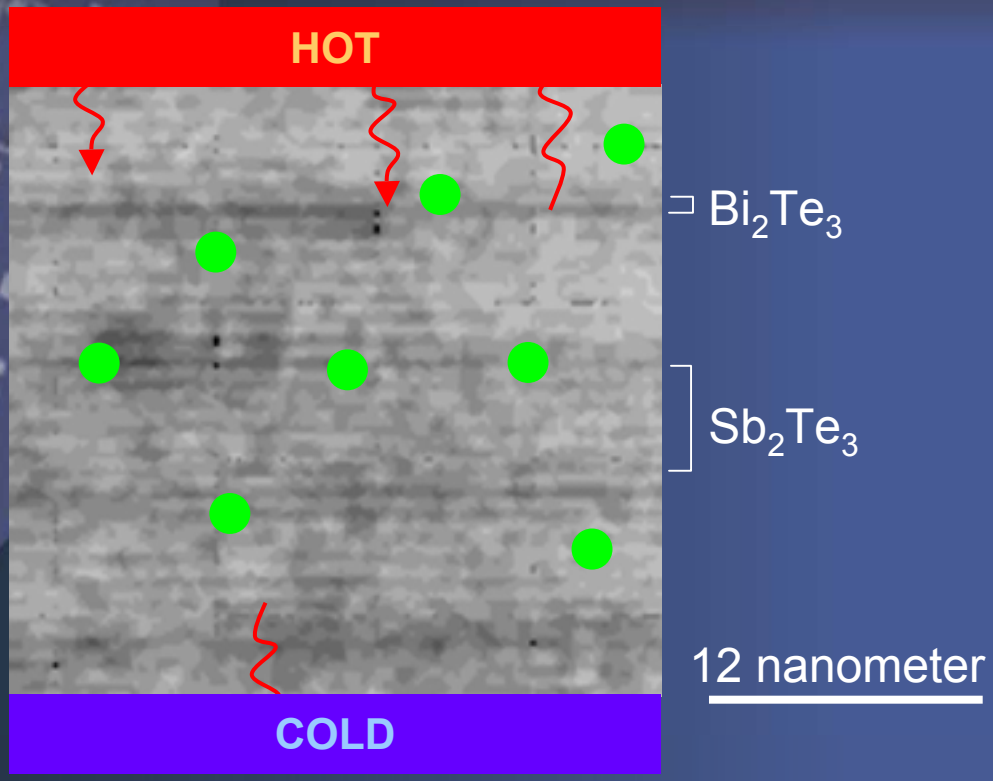

The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

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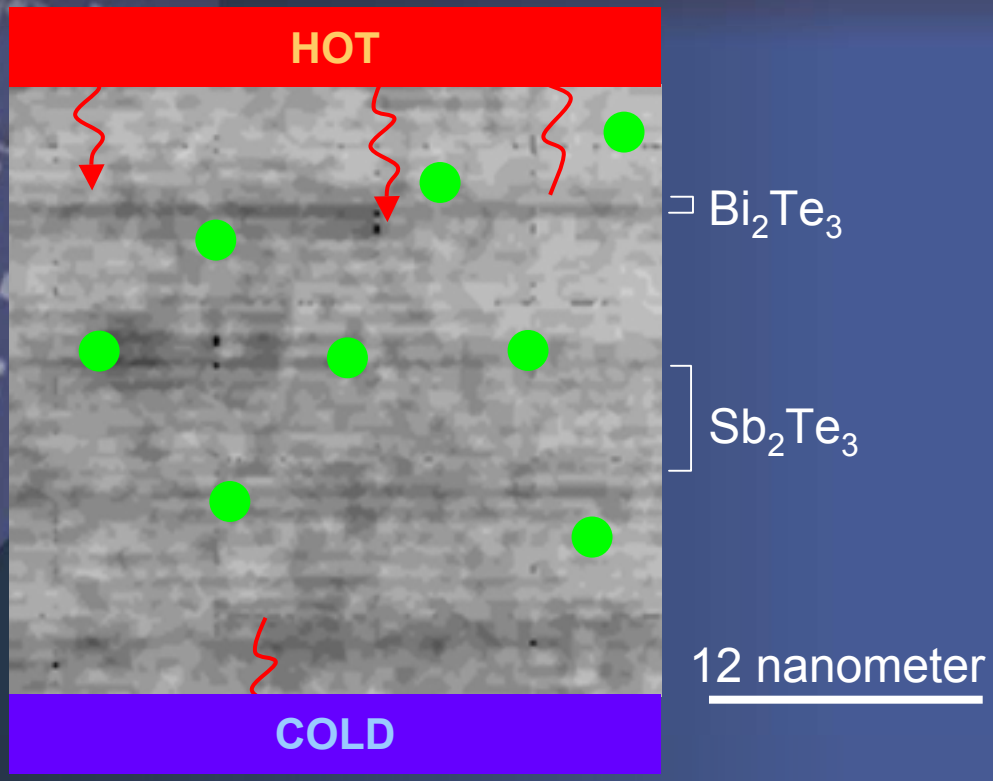

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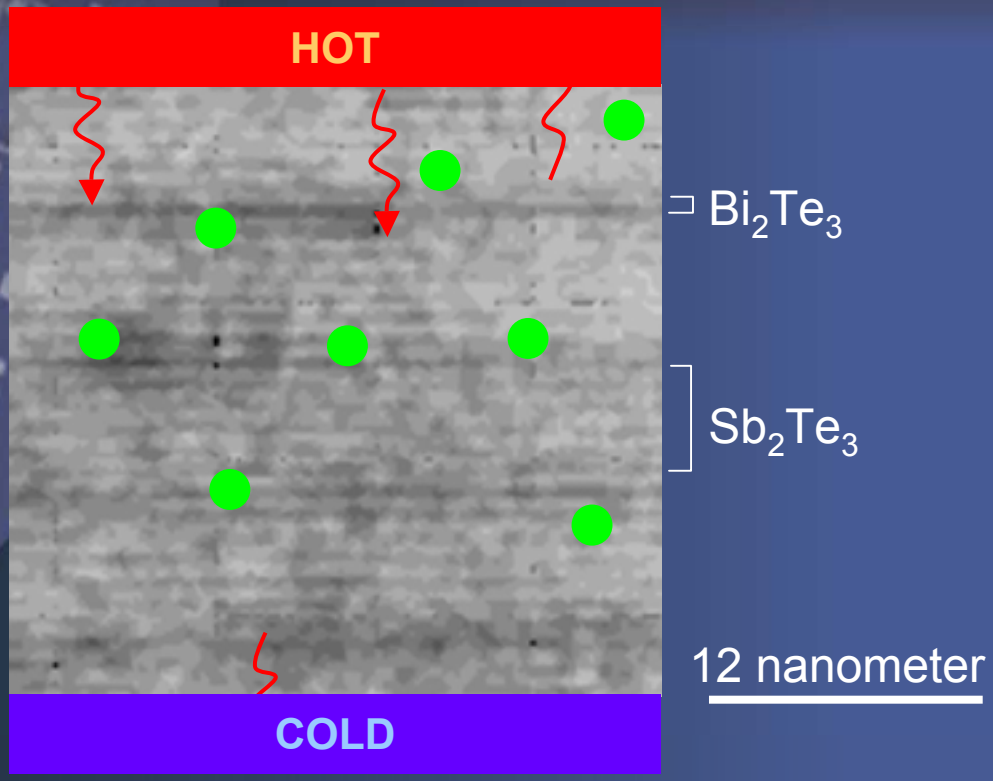

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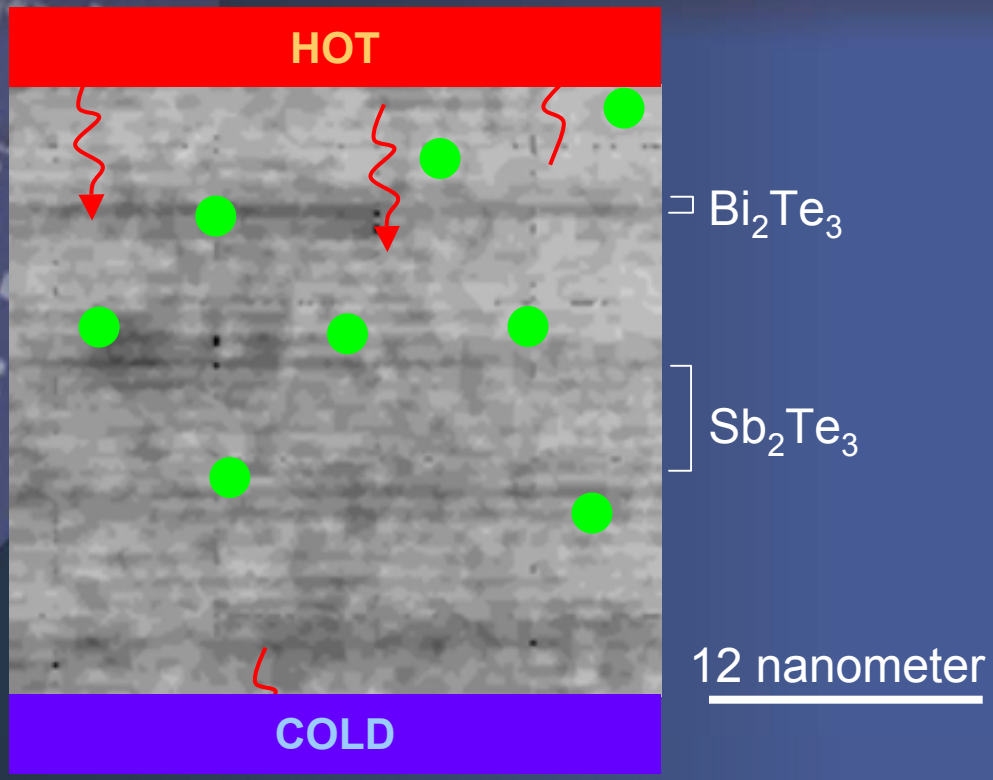

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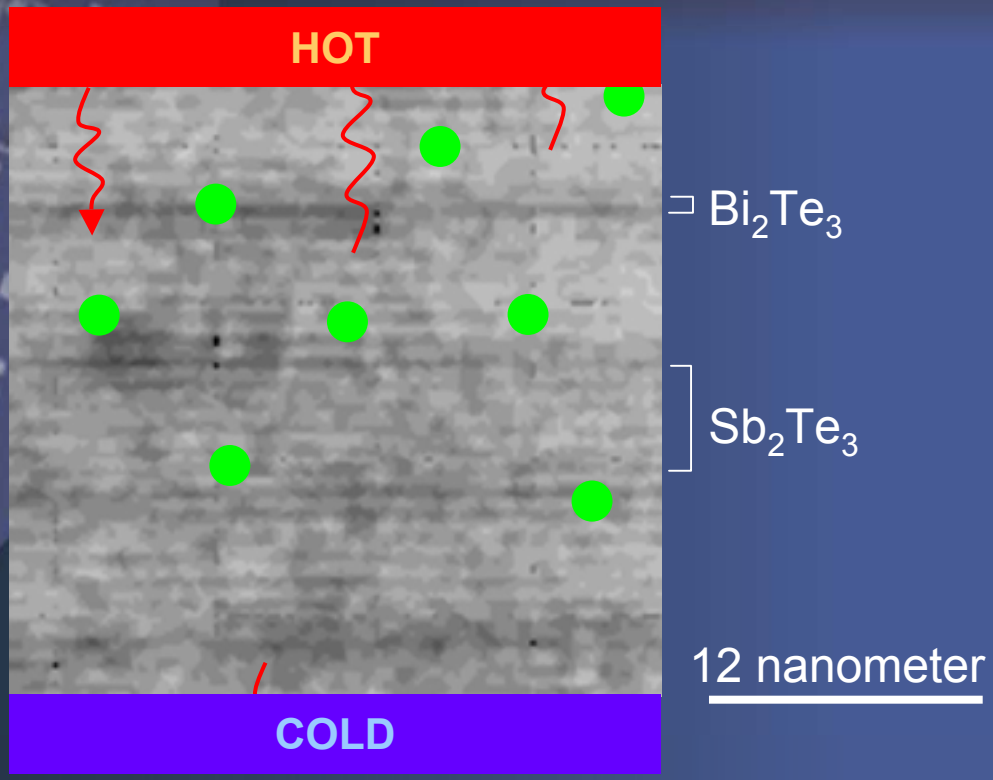

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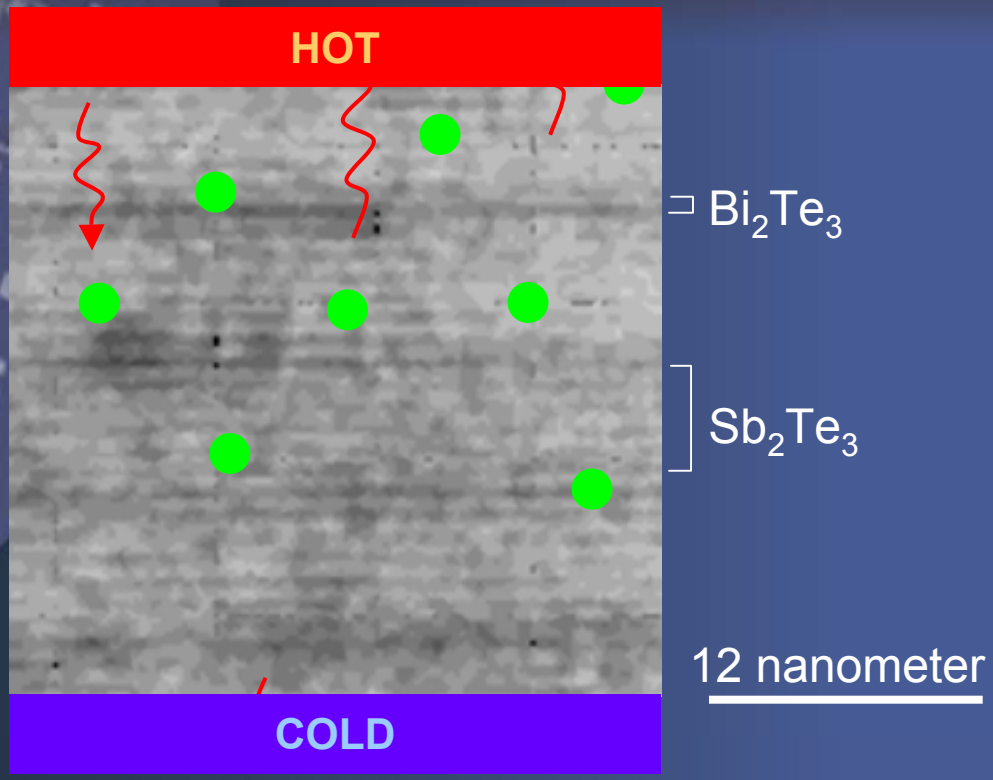

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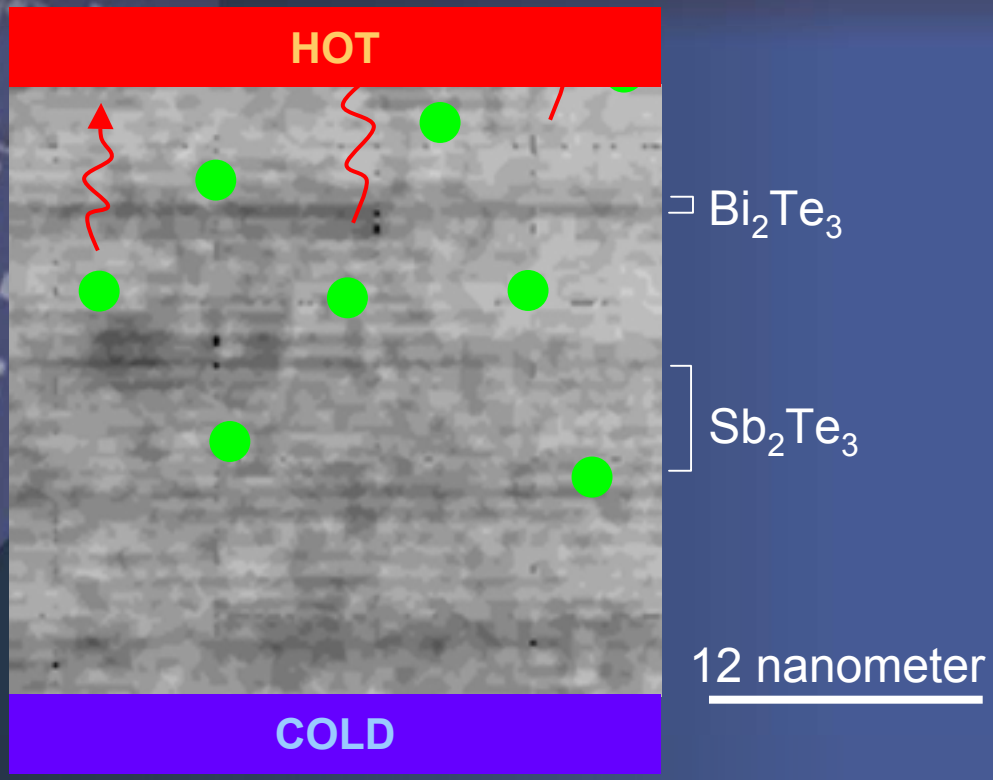

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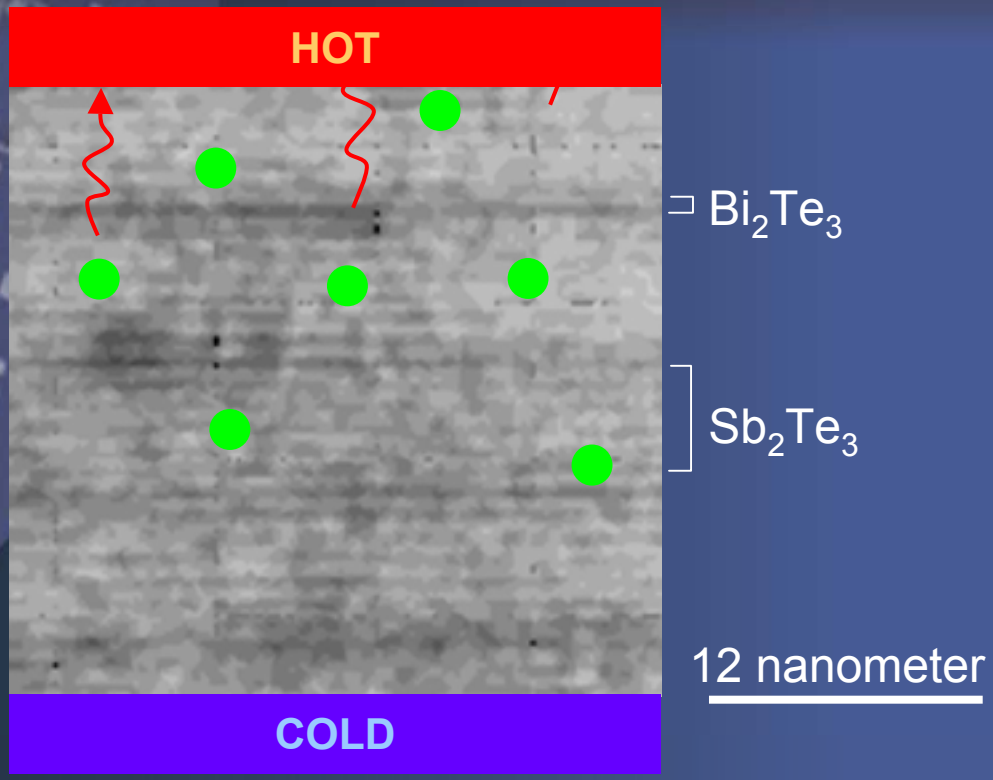

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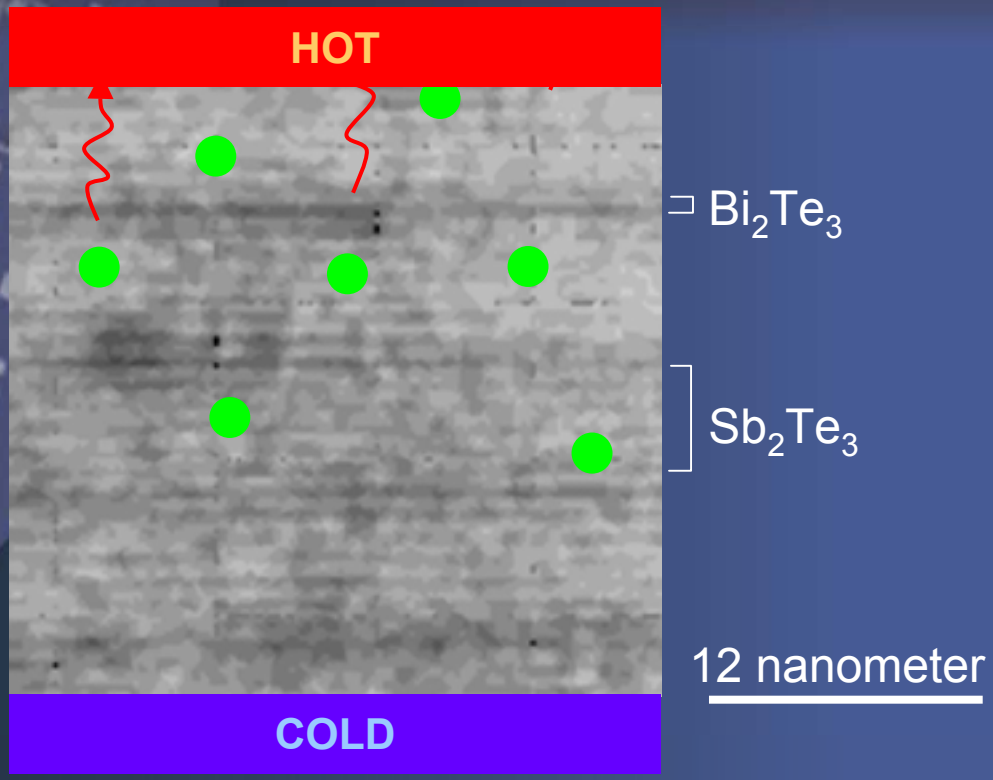

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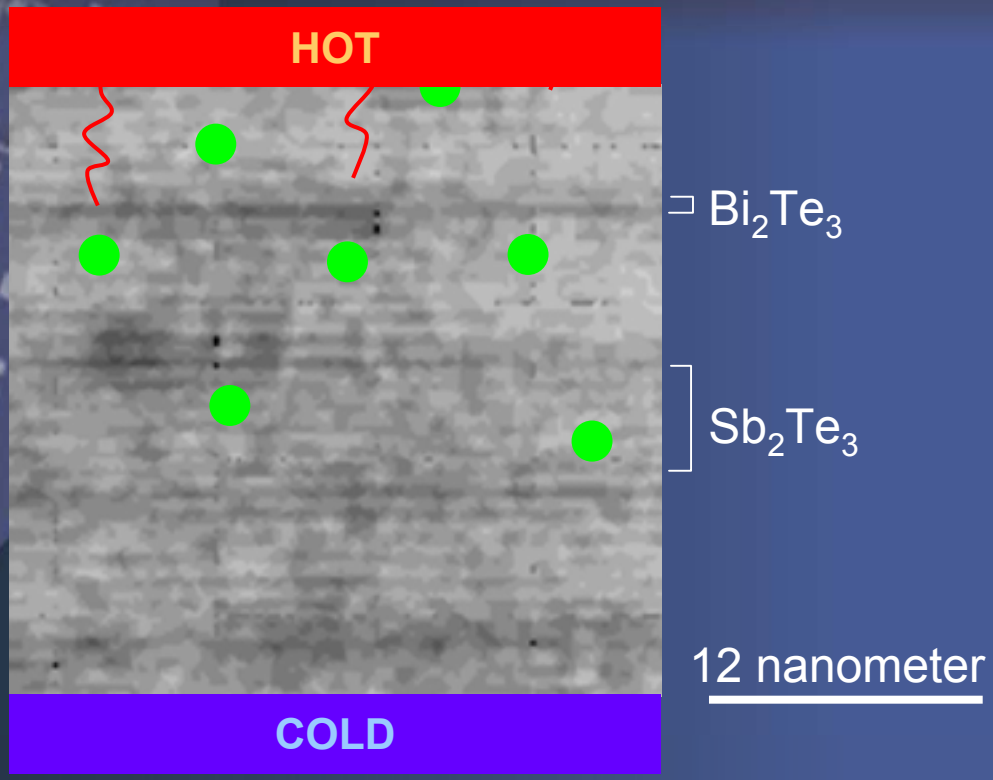

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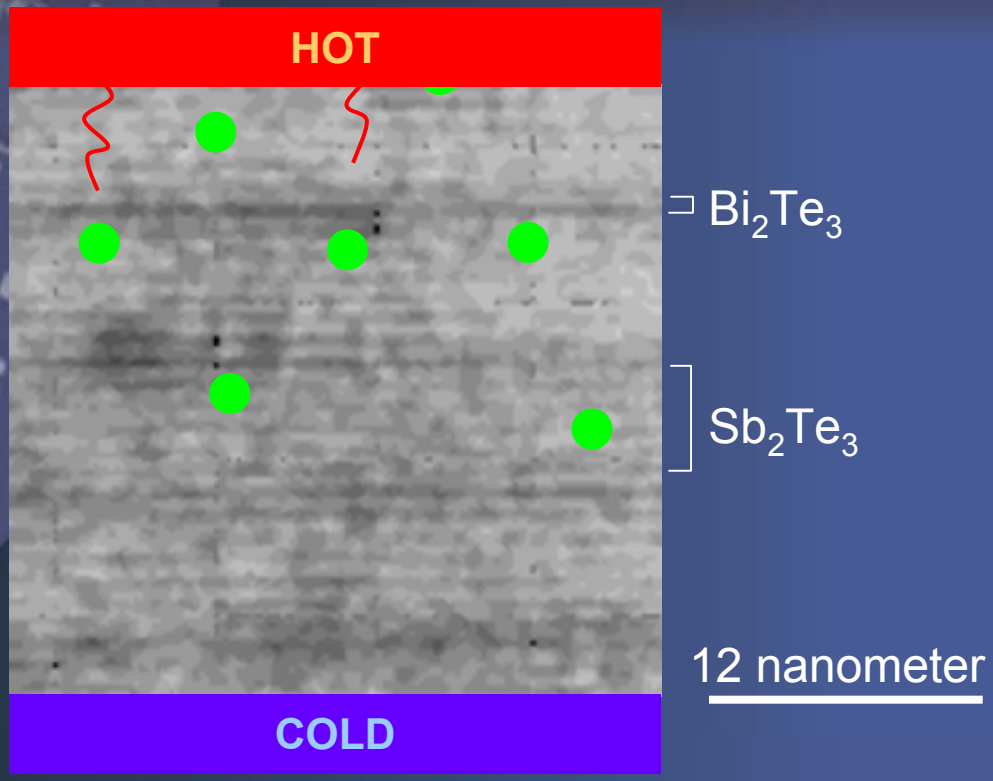

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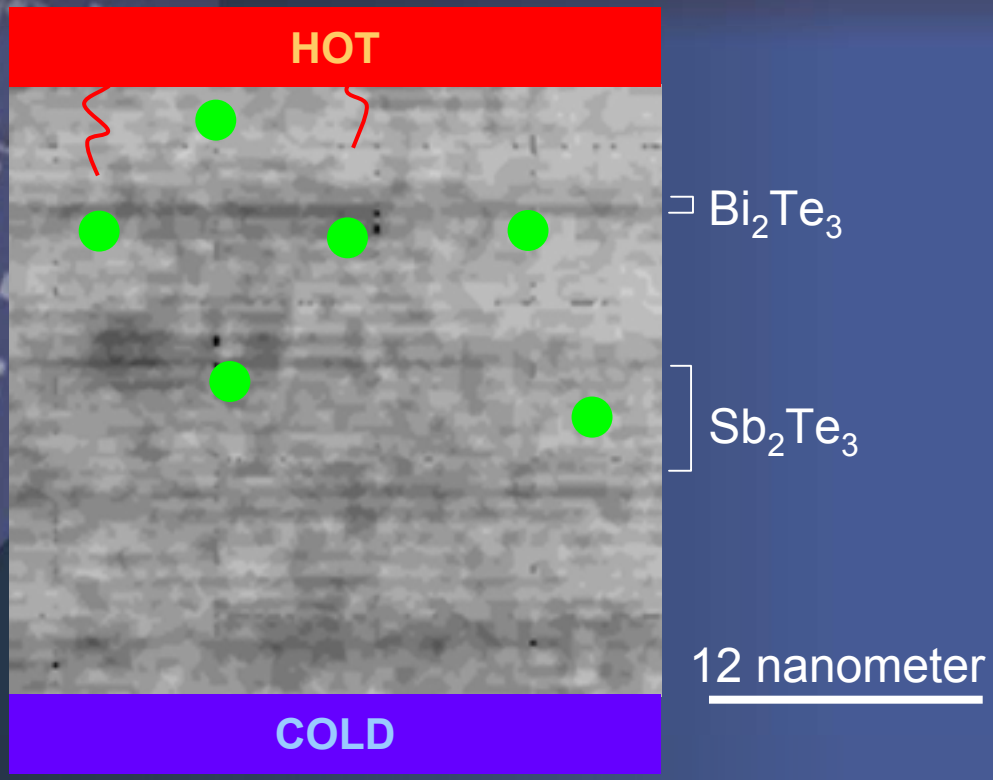

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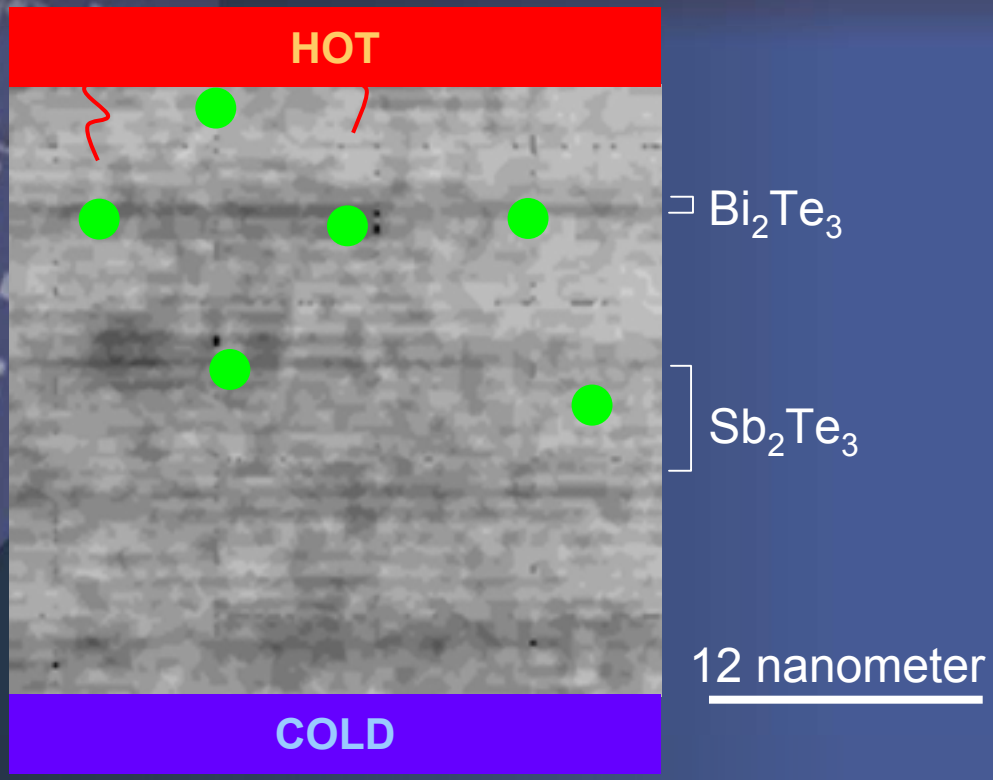

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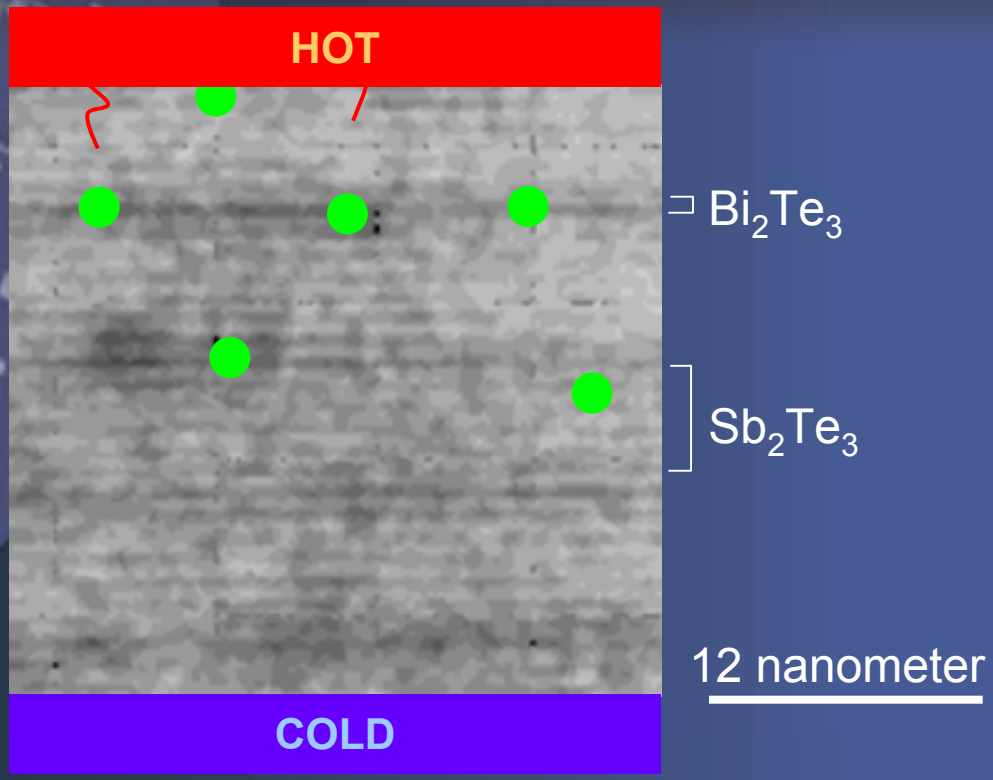

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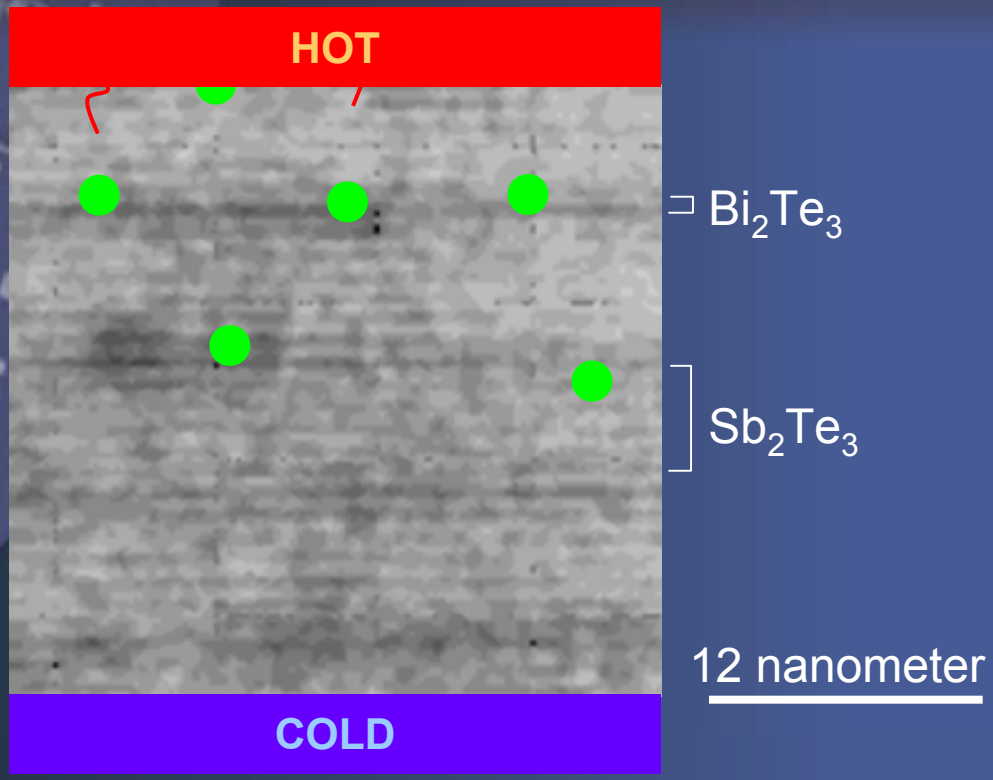

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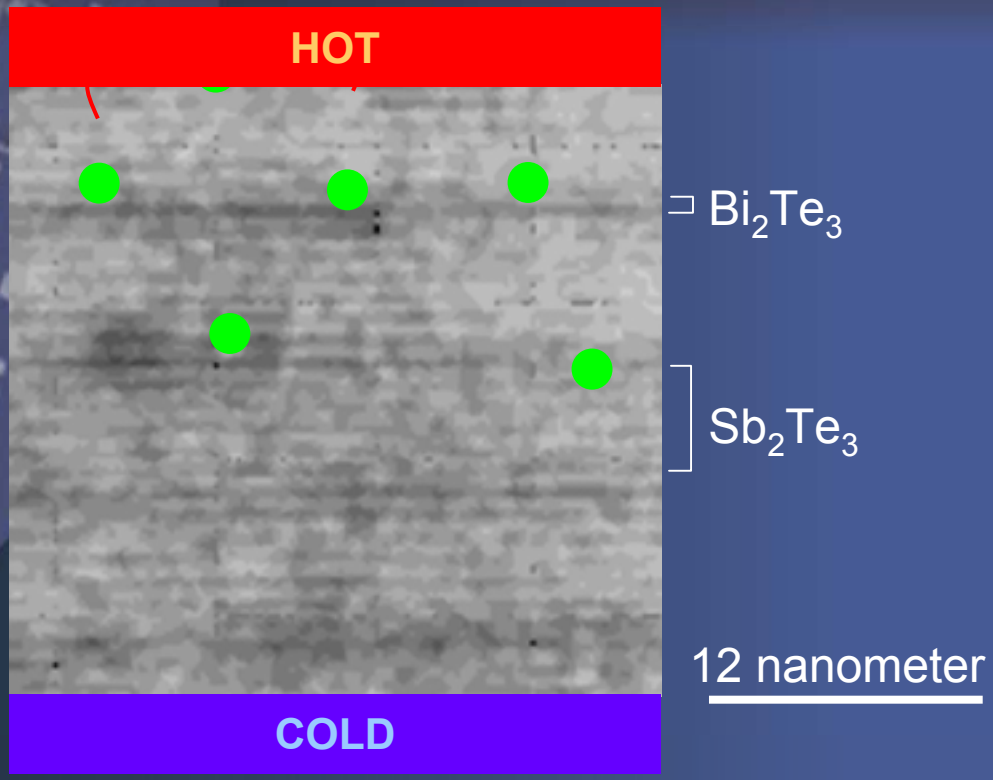

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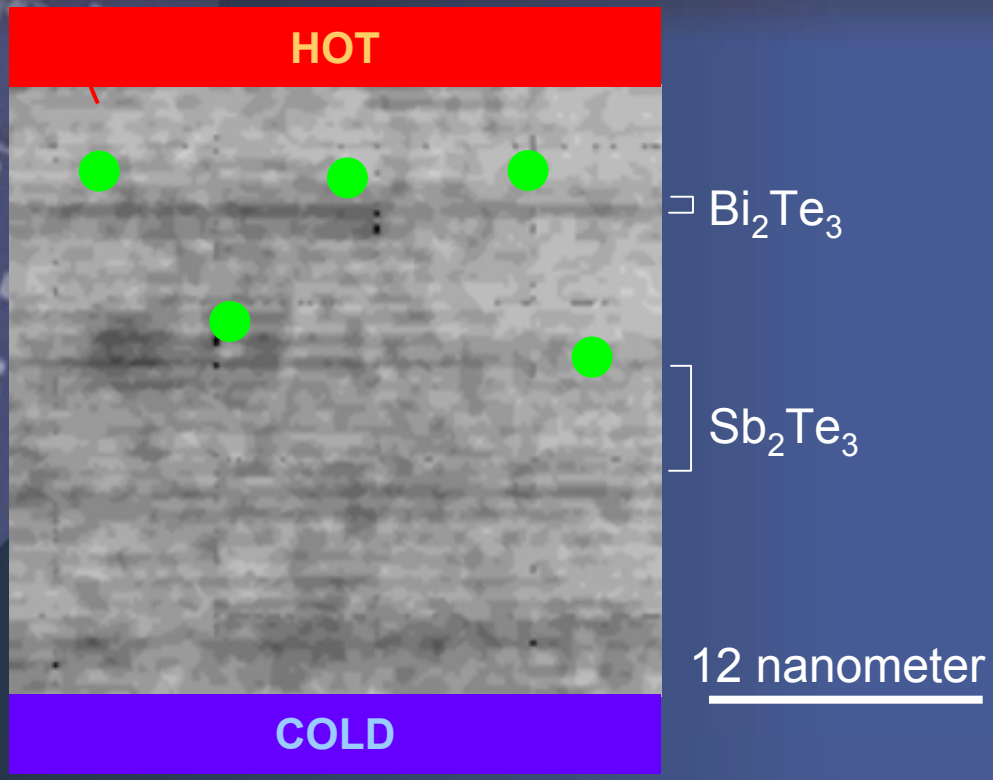

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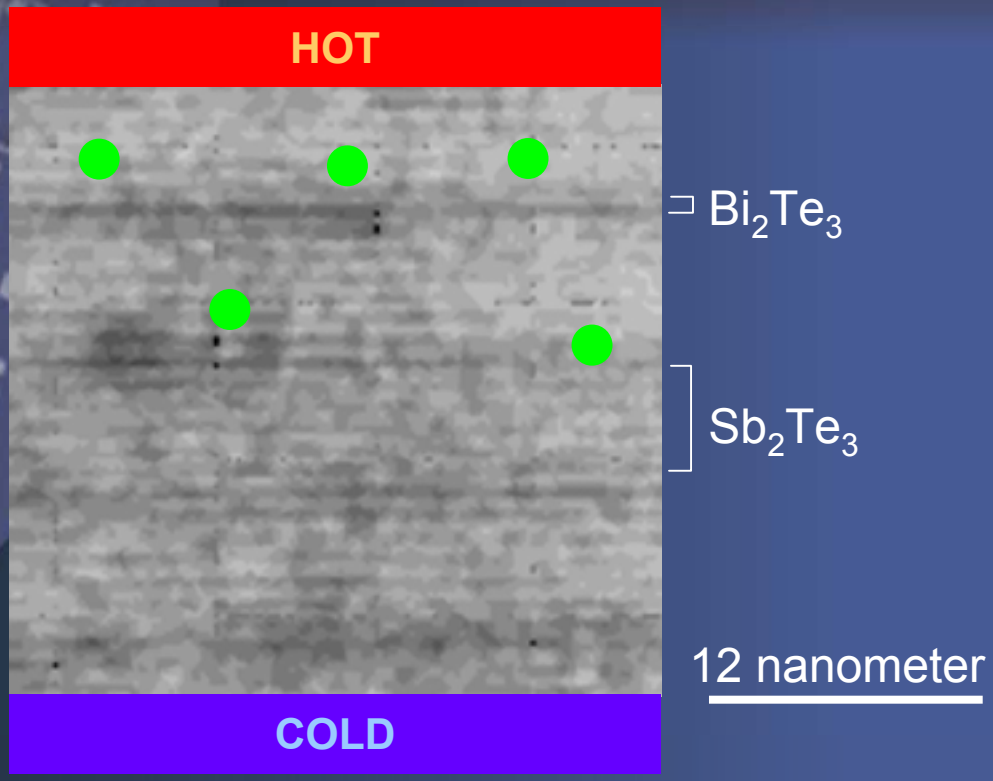
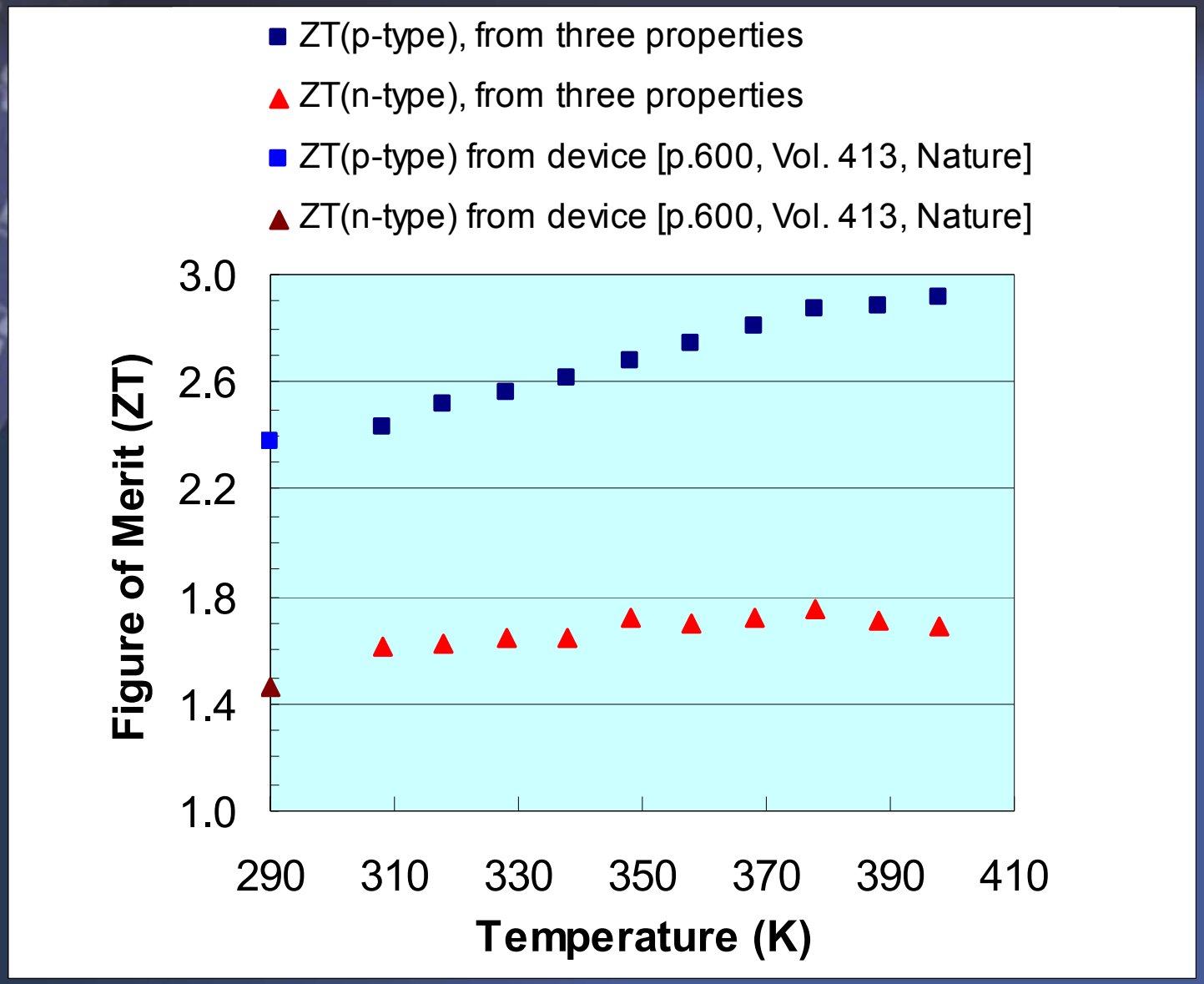
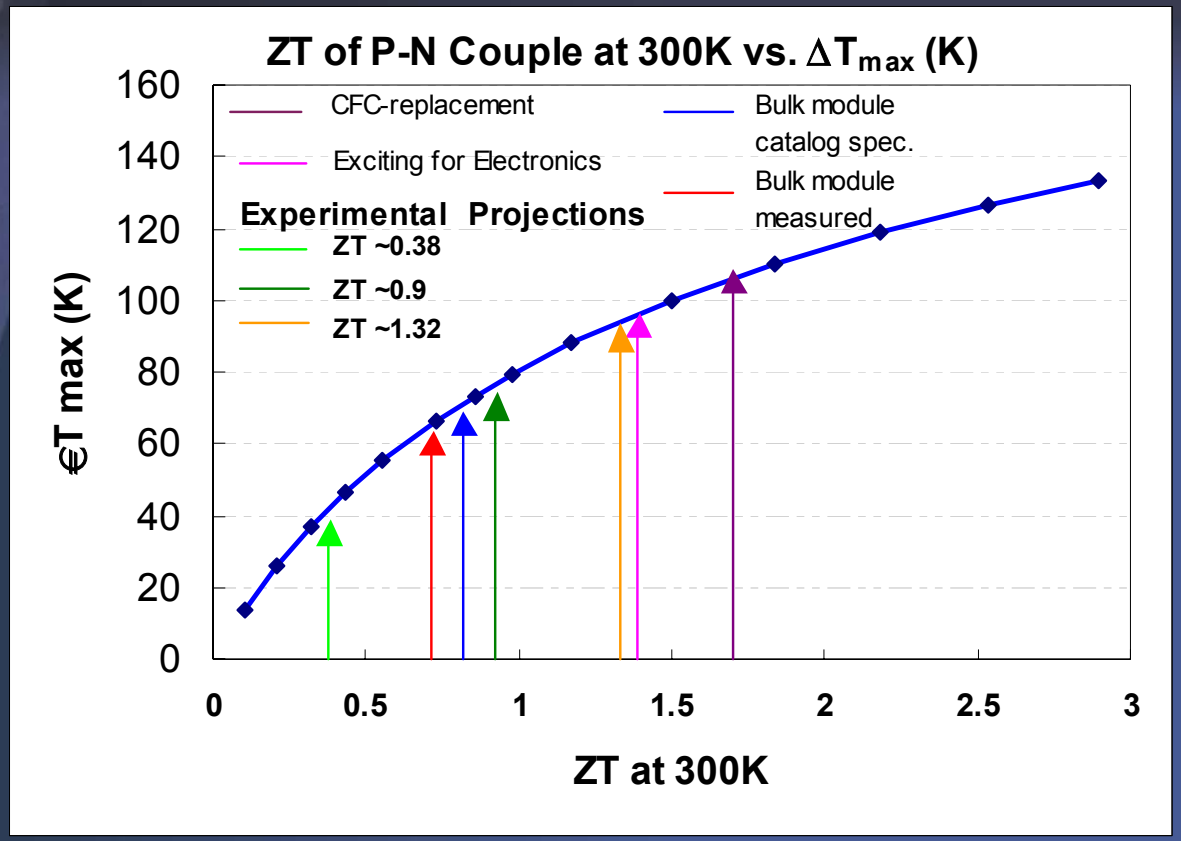


The RTI breakthrough arises from reducing heat transmission without disrupting electron flow

Best Intrinsic ZT Values in Bi_2Te_3-based P-type and N-type Superlattices for Power Conversion (300K- 420K)



Correlation Between ZT and ΔT_{max}

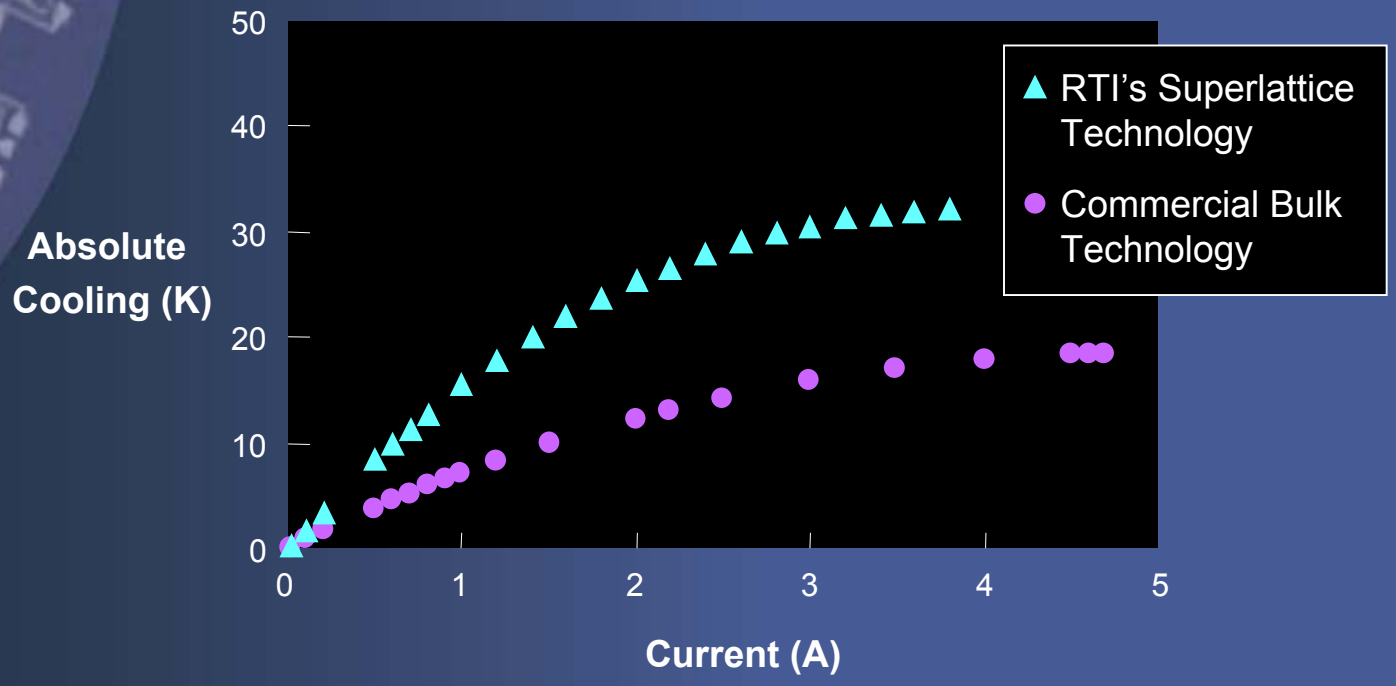


- Current focus of program to translate ZT of material closer to system-level external cooling or efficiency

Advantages and Thin-film Cooling Examples

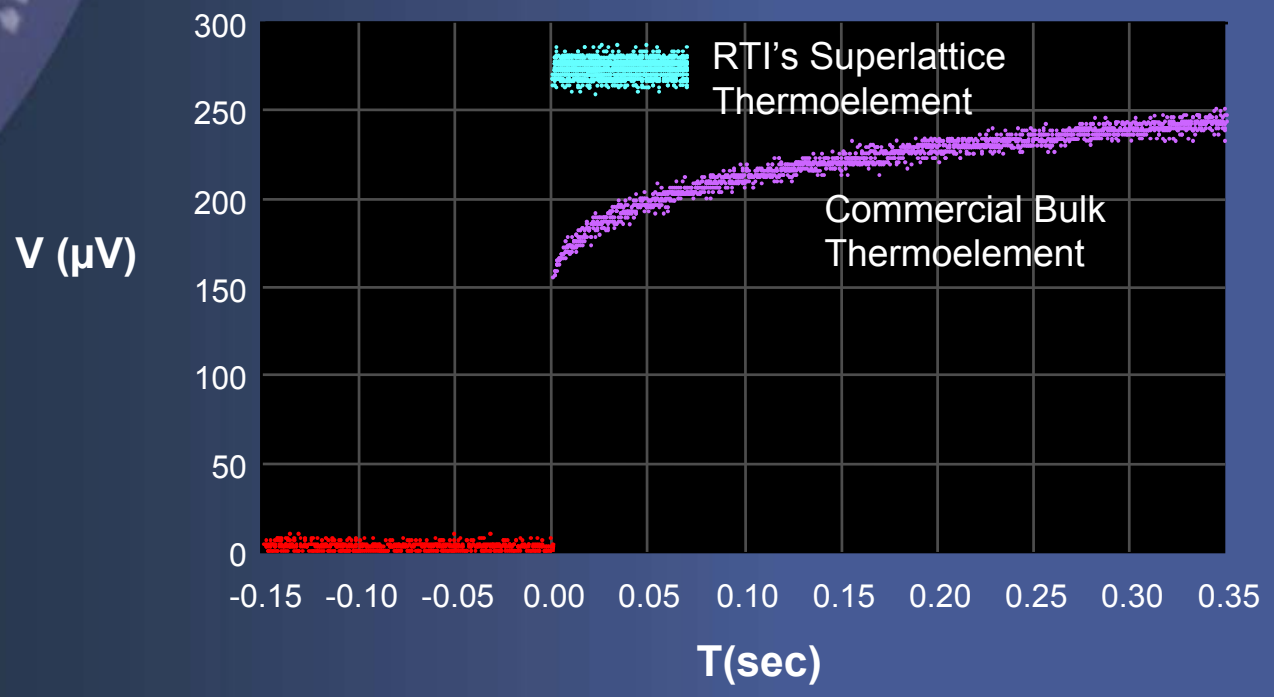
Advantages of RTI's Superlattice Thermoelectric Technology

- Enhanced cooling



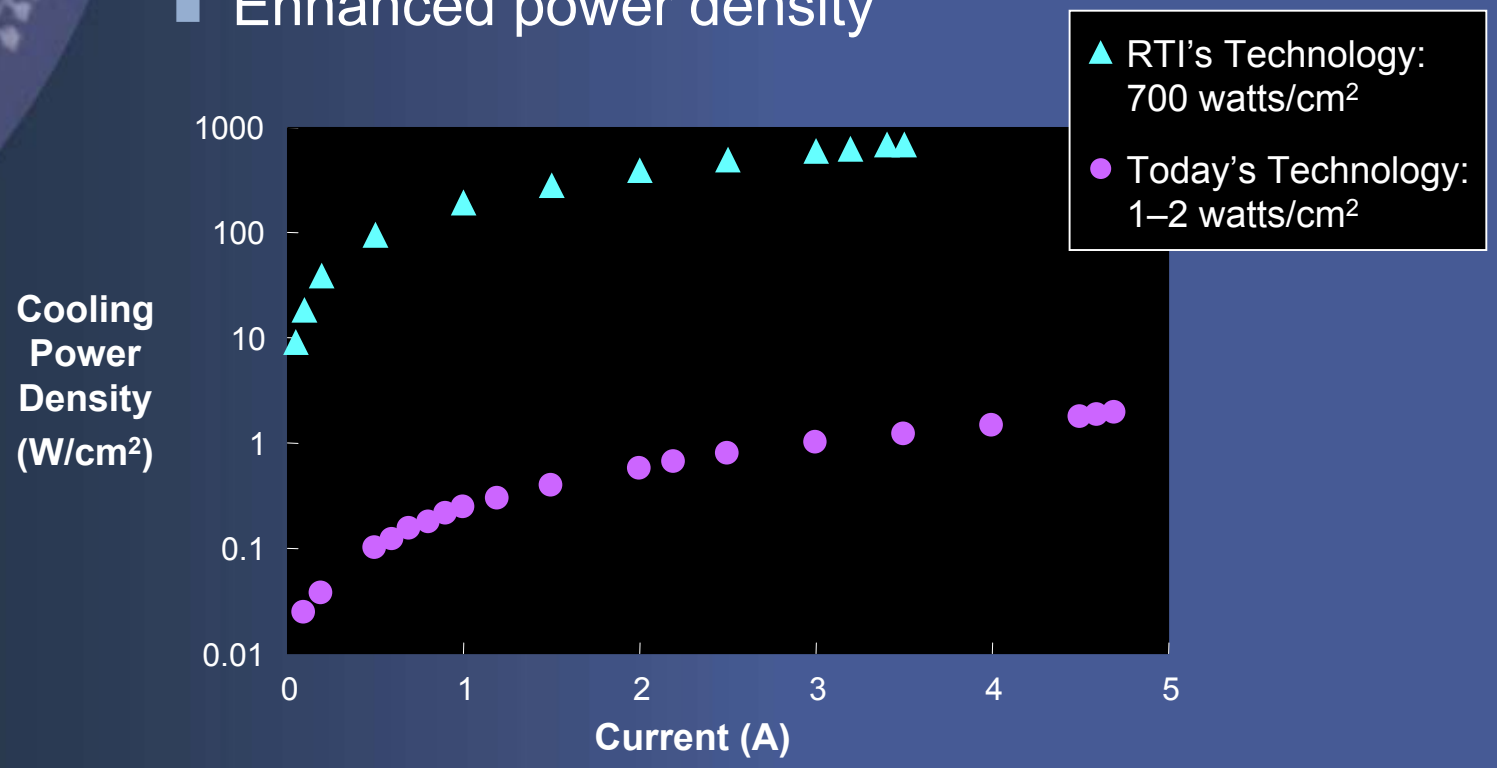
Advantages of RTI's Superlattice Thermoelectric Technology

- Enhanced cooling
- Super-fast cooling and heating



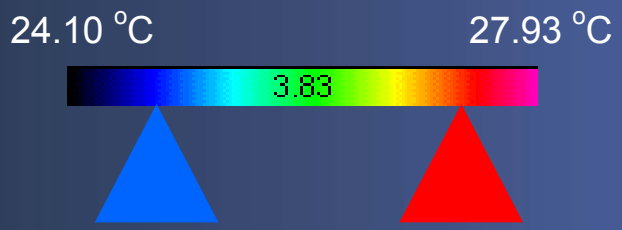
Advantages of RTI's Superlattice Thermoelectric Technology

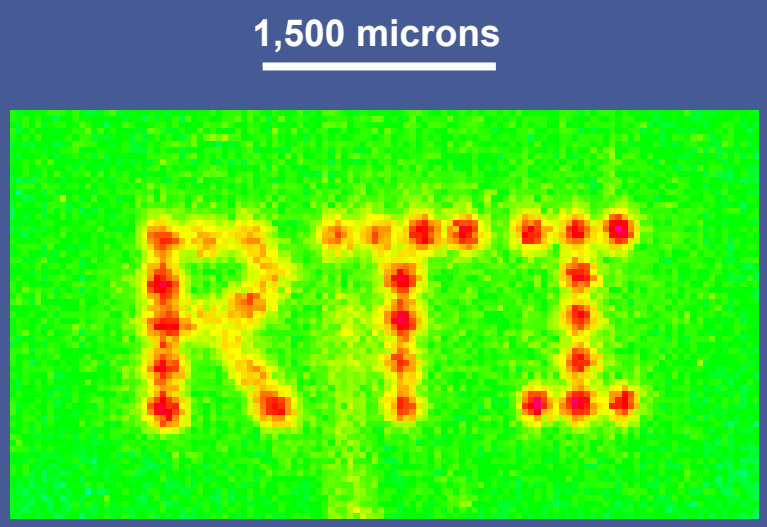
- Enhanced cooling
- Super-fast cooling and heating
- Enhanced power density



Advantages of RTI's Superlattice Thermoelectric Technology

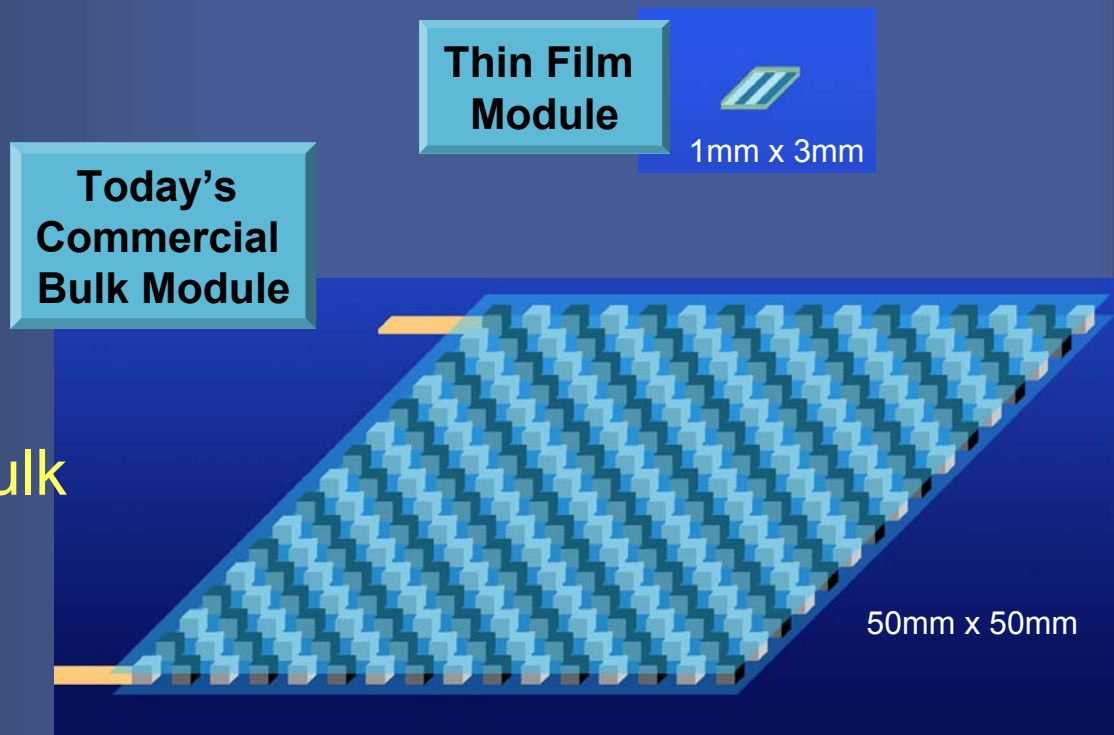
- Enhanced cooling
- Super-fast cooling and heating
- Enhanced power density
- Anywhere, any time cooling/ heating technology



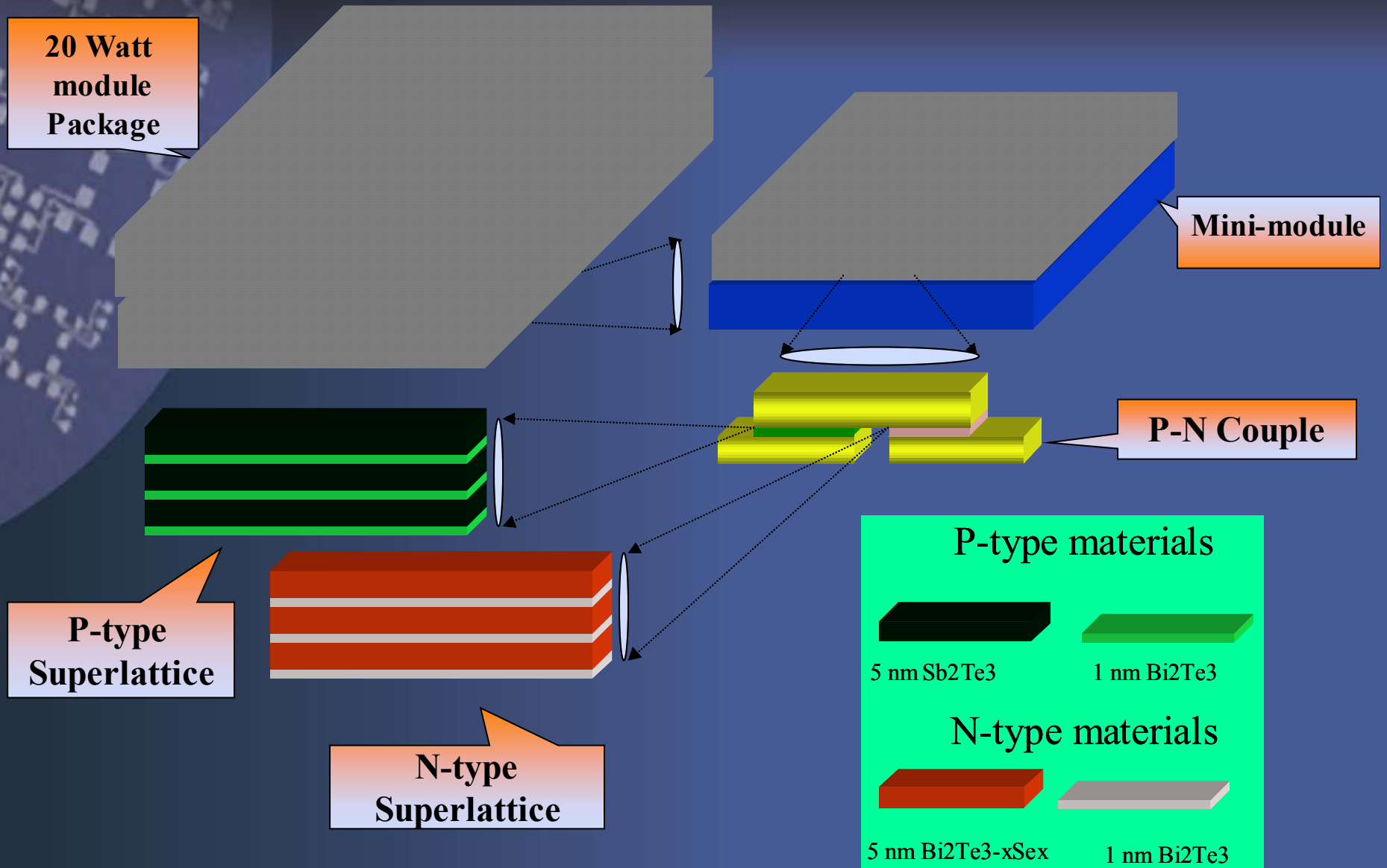


Advantages of RTI's Superlattice Thermoelectric Technology

- Enhanced cooling
- Super-fast cooling and heating
- Enhanced power density
- Anywhere, any time cooling/ heating technology
- 1/40,000th the actual TE material requirement of bulk technology – low recycle costs

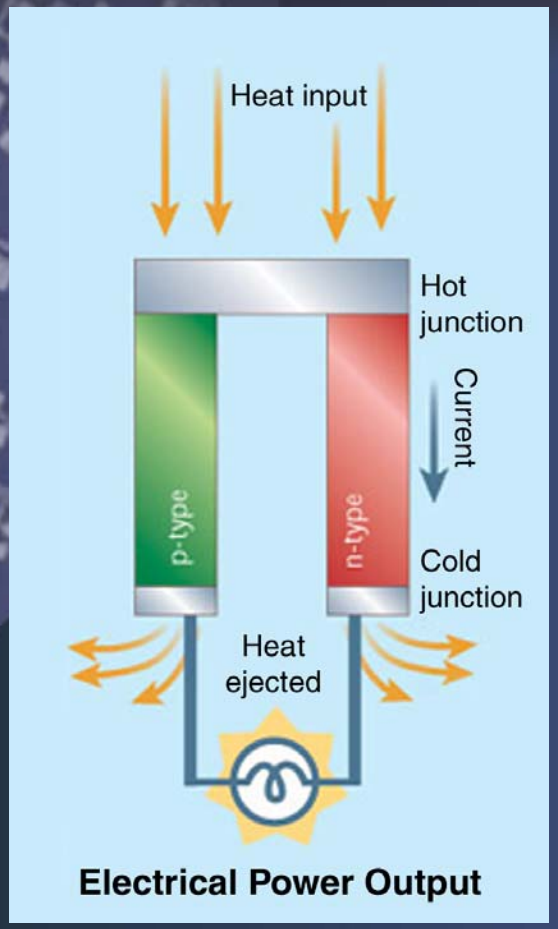


Thin-film Thermoelectric Module Fabrication



Thin-film Power Conversion Examples

Thermoelectric Power Conversion

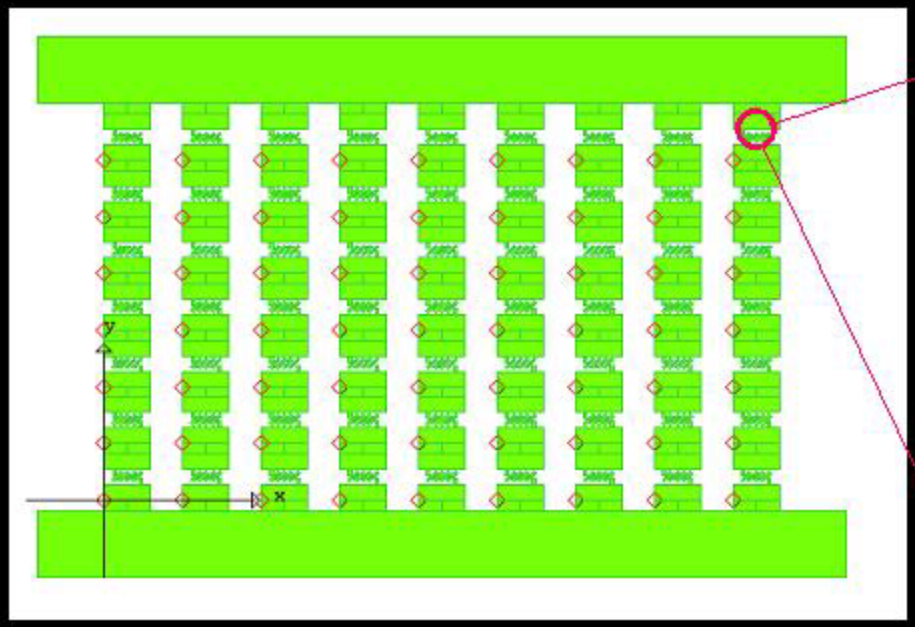


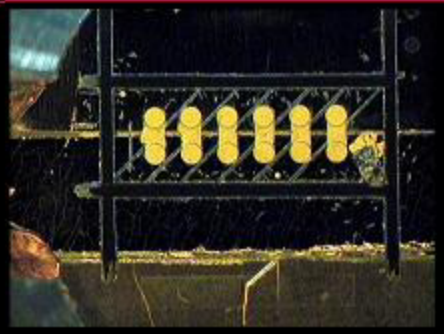
$$\psi = \frac{(T_h - T_c)}{T_h} \frac{\{(1+ZT)^{1/2} - 1\}}{\{(1+ZT)^{1/2} - 1\} + T_c/T_h}$$

- Power Conversion Efficiency critically dependent on the material Figure of Merit (ZT)

- Maximize ΔT
  - Thermal management (getting the heat out from the heat-sink) is important to generating the maximum ΔT

RTI's Gen-1 Power Module Design Using 63 Mini-modules (Area ~ 3.5 cm x 2.4 cm)

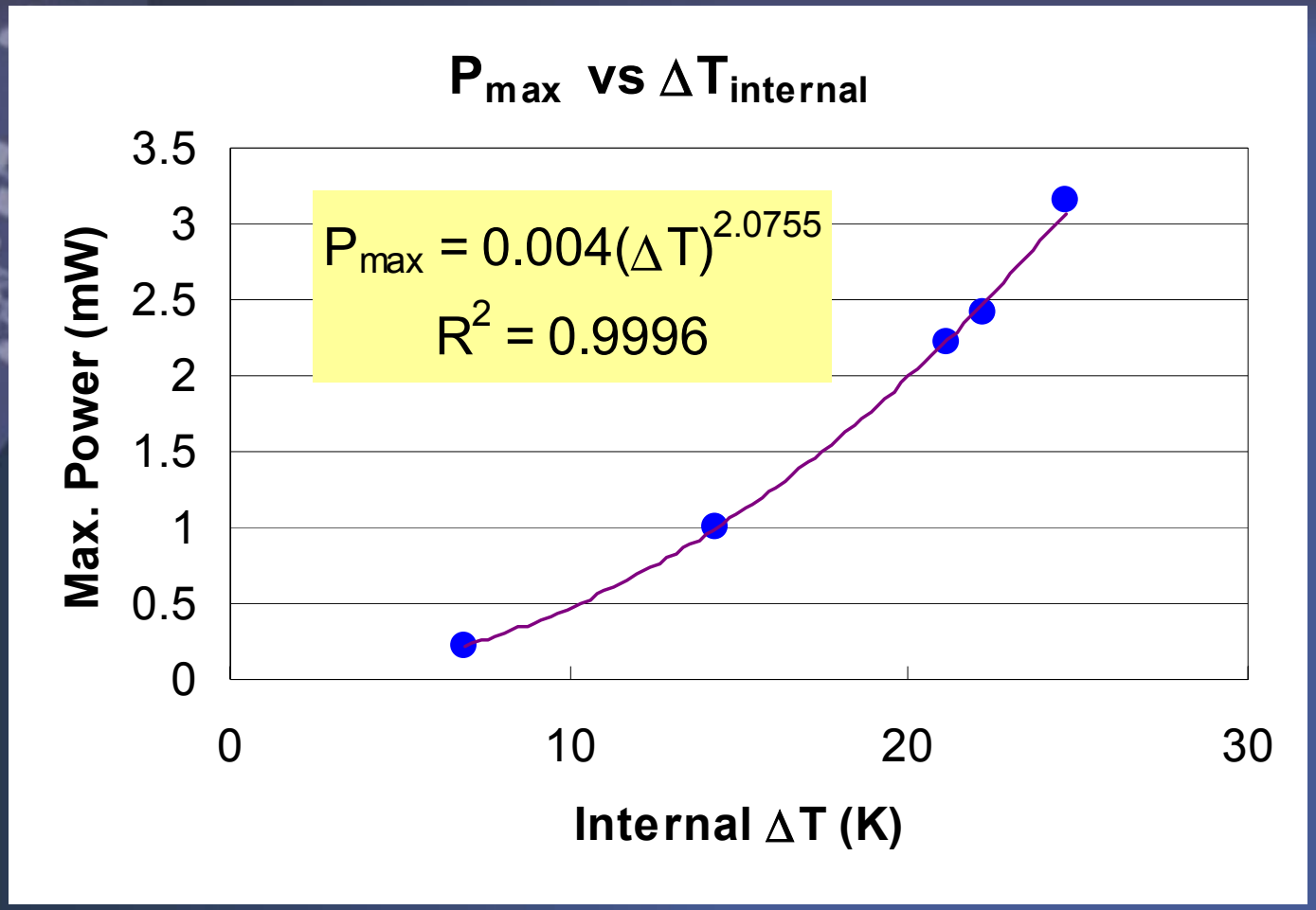




- **6x2 300-μm Series mini-module**
- **V_{oc} ~ 76 mV**
- **P_{max} = 3.160 mW**
- **ΔT ~ 25°C**

- One year target of 5 Watts Module based on power from all 63 mini-modules, ΔT of 75°C, factor of three improvement in reducing internal series resistance and translating current material ZT to external ZT
  - 3.16 mW x 63 x $(75/25)^2$ x 3 ~ 5 W
- **Larger Immediate Powers Possible with Larger Area Modules for Immediate Applications as in RTI Thermoelectric Power Shields™**
- Three-year target of 20 Watt Based on ΔT of 150°C

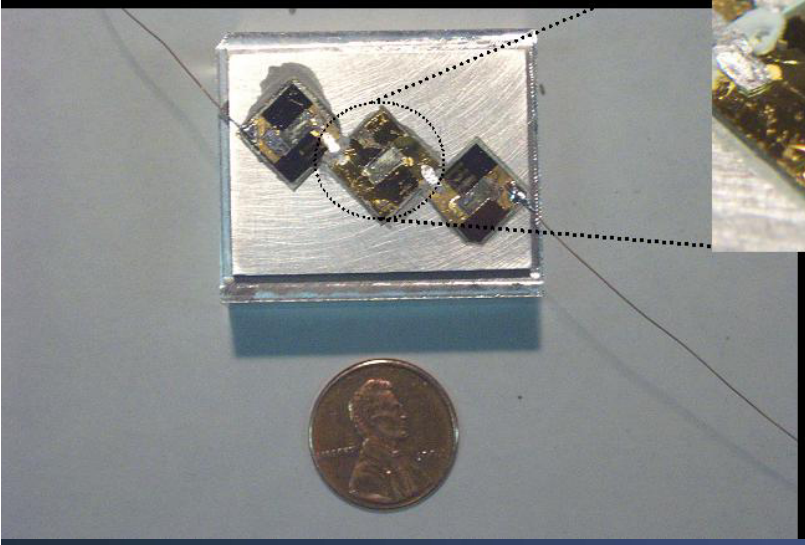
One of the next big focus areas - Reduce thermal interfaces to get more ΔT into the device

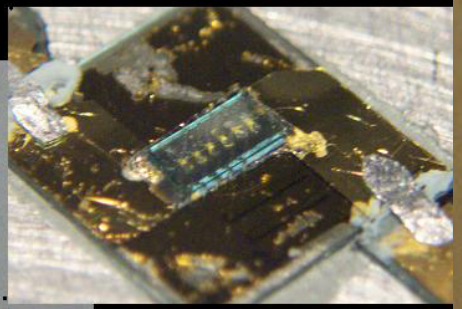


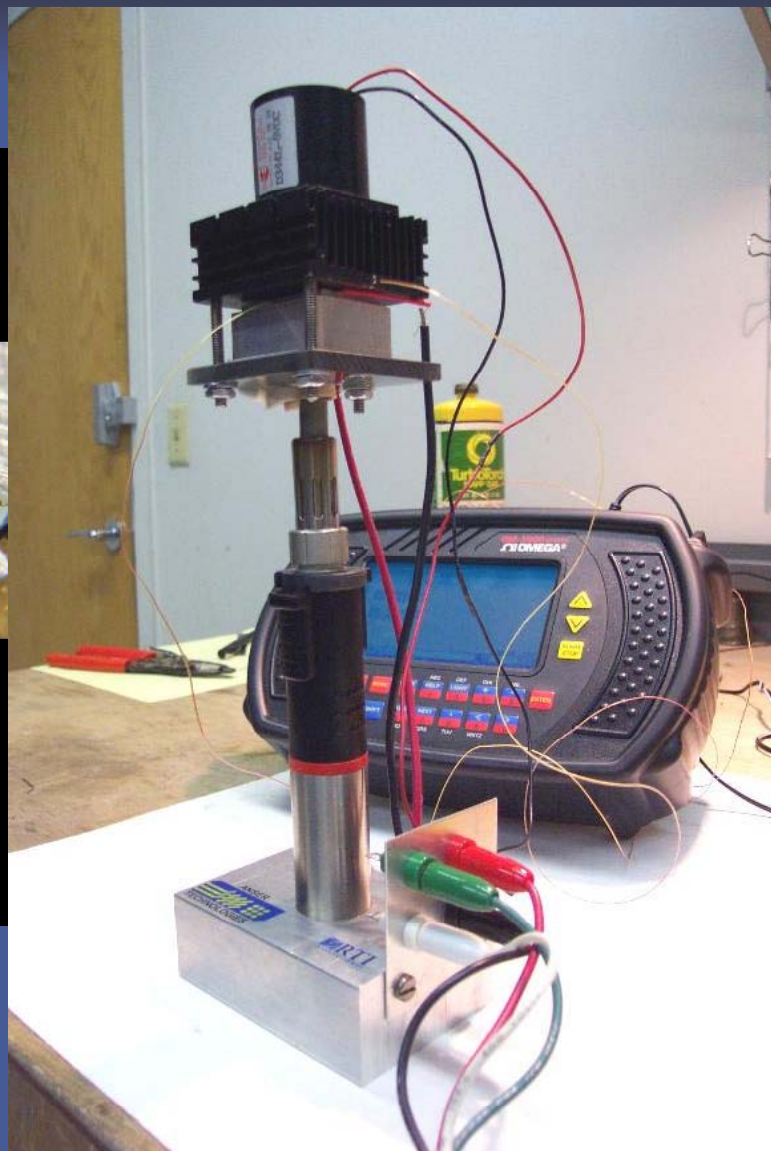
- Note square-dependence of P_{max} on ΔT across TE device

36–element, 0.025 cm^2-active area – enough power for a small fan

First thin-film power module using three mini-modules







Long-term Potential Efficiencies for Heat Sources at 660K and 750K

$T_{heat\text{-}sink}$ = 300K			$T_{heat\text{-}source}$ = 660K	$T_{heat\text{-}source}$ = 750K
			ΔT ~ 120K per stage	ΔT ~ 150K per stage
Very Optimistic Projection		ZT_{ave}	Efficiency (%)	Efficiency (%)
300K < **T** < 420K to 450K	Stage 1	2.75	10.1%	12.0%
420K to 450K < **T** < 540K to 600K	Stage 2	2.25	6.9%	7.9%
540K to 600K < **T** < 660K to 750K	Stage 3	2.25	5.6%	6.1%
Total Efficiency for 3-stage Cascade			**22.6%**	**26.0%**
Moderately Optimistic Projection		ZT_{ave}	Efficiency (%)	Efficiency (%)
300K < **T** < 420K to 450K	Stage 1	2.5	9.6%	11.4%
420K to 450K < **T** < 540K to 600K	Stage 2	2	6.5%	7.4%
540K to 600 K < **T** < 660K to 750K	Stage 3	2	5.2%	5.8%
Total Efficiency for 3-stage Cascade			**21.3%**	**24.6%**
Conservatively Optimistic Projection		ZT_{ave}	Efficiency (%)	Efficiency (%)
300K < **T** < 420K to 450K	Stage 1	2.25	9.1%	10.8%
420K to 450K < **T** < 540K to 600K	Stage 2	1.75	6.0%	6.8%
540K to 600K < **T** < 660K to 750K	Stage 3	1.75	4.8%	5.4%
Total Efficiency for 3-stage Cascade			**19.9%**	**23.0%**

Major Issues in Application to Waste-Heat Recovery from Heat Sources Operating at Various Temperatures

- High ZT Materials for higher temperatures
- Thermal Management at significant flux levels
- Low electrical resistivity metal-semiconductor Ohmic Contacts in the range of 300K to 750K
- Low resistivity metal-metal current injection and thermal transfer contacts in the range of 300K to 750K
- Low resistivity metal-dielectric thermal transfer contacts in the range of of 300K to 750K

Bulk versus Thin-film TE Cooling/Heating

Performance Parameter	Bulk Technology (ZT ~ 1)	Thin-film Technology (ZT ~ 2.5)
COP (Heat Pumped/Electrical Power in) for a **ΔT of 25°C**	1	2 to 2.5
Wight of TE module for pumping 50 Watts (without thermal management components)	~ 22 grams	< 3 grams
Cost of heat pumping	$ 0.5 to 1 per Watt as of today after 40 years of maturity	Long-term (three to five years) projected cost < $ 0.5 per Watt
Cooling Power Density Potential Maximum Cooling per stage	< 1 W/cm^2 ~ 60°C	> 700 W/cm^2 ~ 120°C

Bulk versus Thin-film TE Power

Performance Parameter	Bulk Technology (ZT ~ 1)	Thin-film Technology (ZT ~ 2.5)
Efficiency for a **ΔT of 150°C**	3 to 4%	10 to 11%
Specific Power excluding thermal management components	1 Watt/gram of TE module weight	570 Watts/gram of TE module weight
Cost	$5 per Watt as of today after 40 years of maturity	Long-term (three to five years) projected cost < $1 per Watt
Current Density	< 200 mA/cm^2	> 50 Amp/cm^2 possible
Voltage levels from <u>each</u> module	5 to 10 Volts	48 Volts achievable with microelectronically interconnected circuits
Power Density	< 1 W/cm^2	> 20 W/cm^2

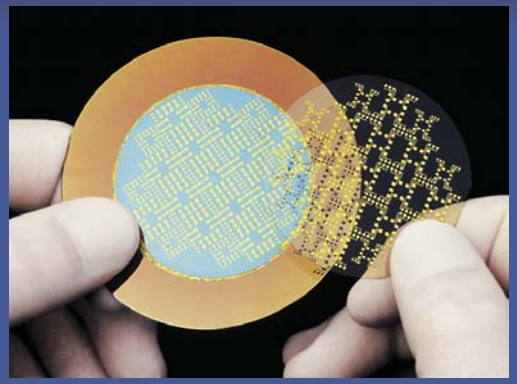
Low-cost, Efficient Fabrication of Large-Power Modules Using Standard Microelectronic Tools

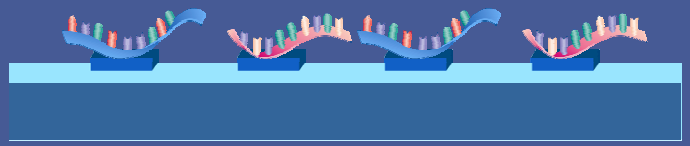
Standard Wafer Dicer and Pick-and-Place machines for Rapid Module Fabrication

Other Emerging Applications

Application in Genomics and Proteomics

- High-speed PCR for rapid DNA analysis
- Self-assembly of DNA and Protein molecules
- Today's analytical tools are inadequate
  to study proteins
  (2-D gel electrophoresis, liquid chromatography, and mass spectrometry)
- Wafer-scale thermoelectrics can enable "fingerprinting" of proteins and their interactions

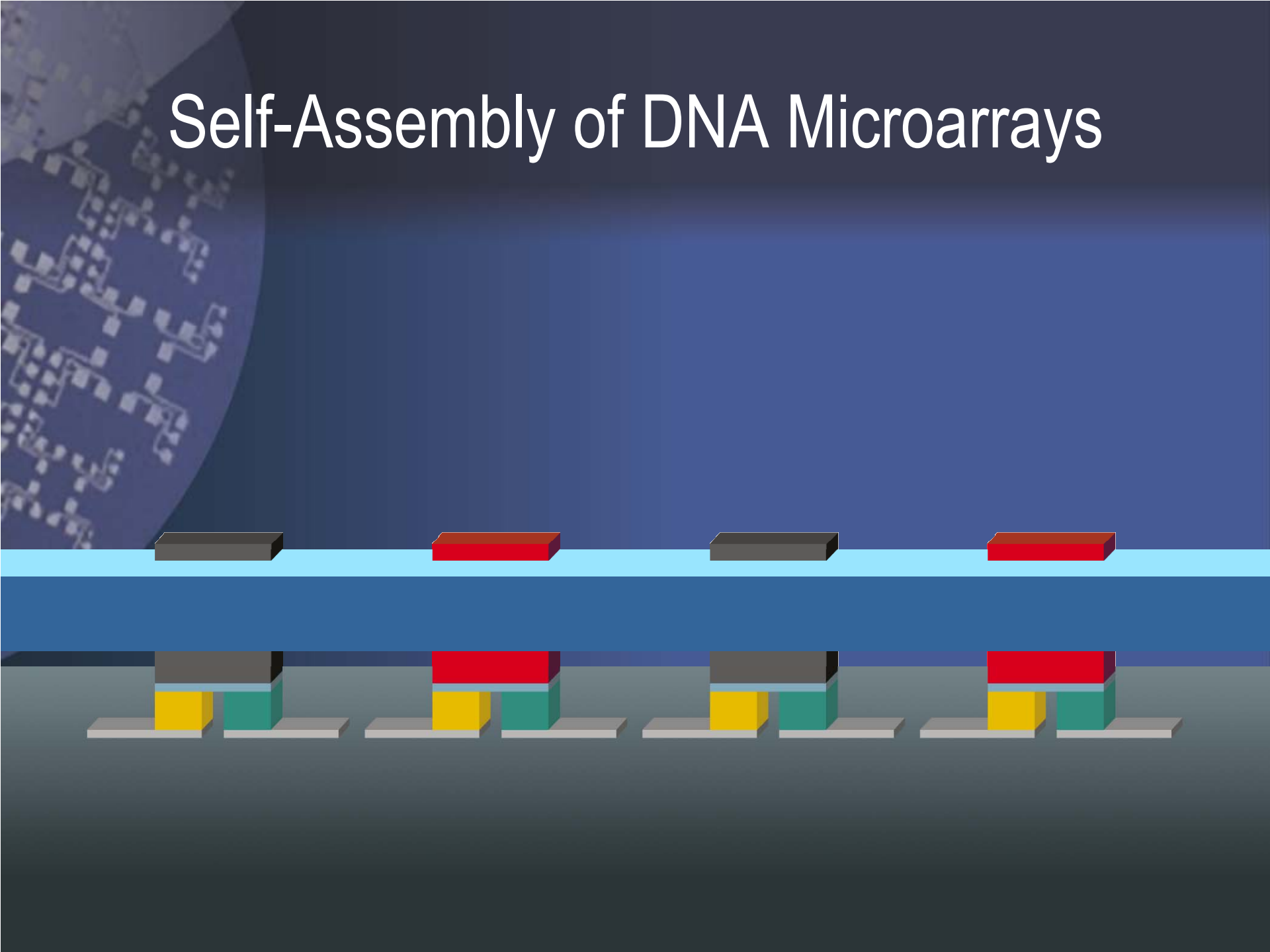




High-speed PCR

- Typical PCR- starts with double-strand DNA being split at 95°C, temperature lowered to where single strands can bind together with new strands
  - Two-step heating cycle is repeated n times, produces 2^{n} copies of target sequence
  - From a single starting molecule, 20 cycles yield over 1M, 30 cycles 1B, and 40 cycles 1T copies
  - Typically each cycle is 1 minute
- Reducing cycling time, efficient devices, and small-scale battery-operated systems can lead to field applications for DNA testing for pharmacology and bio-weapon detection

Self-Assembly of DNA Microarrays



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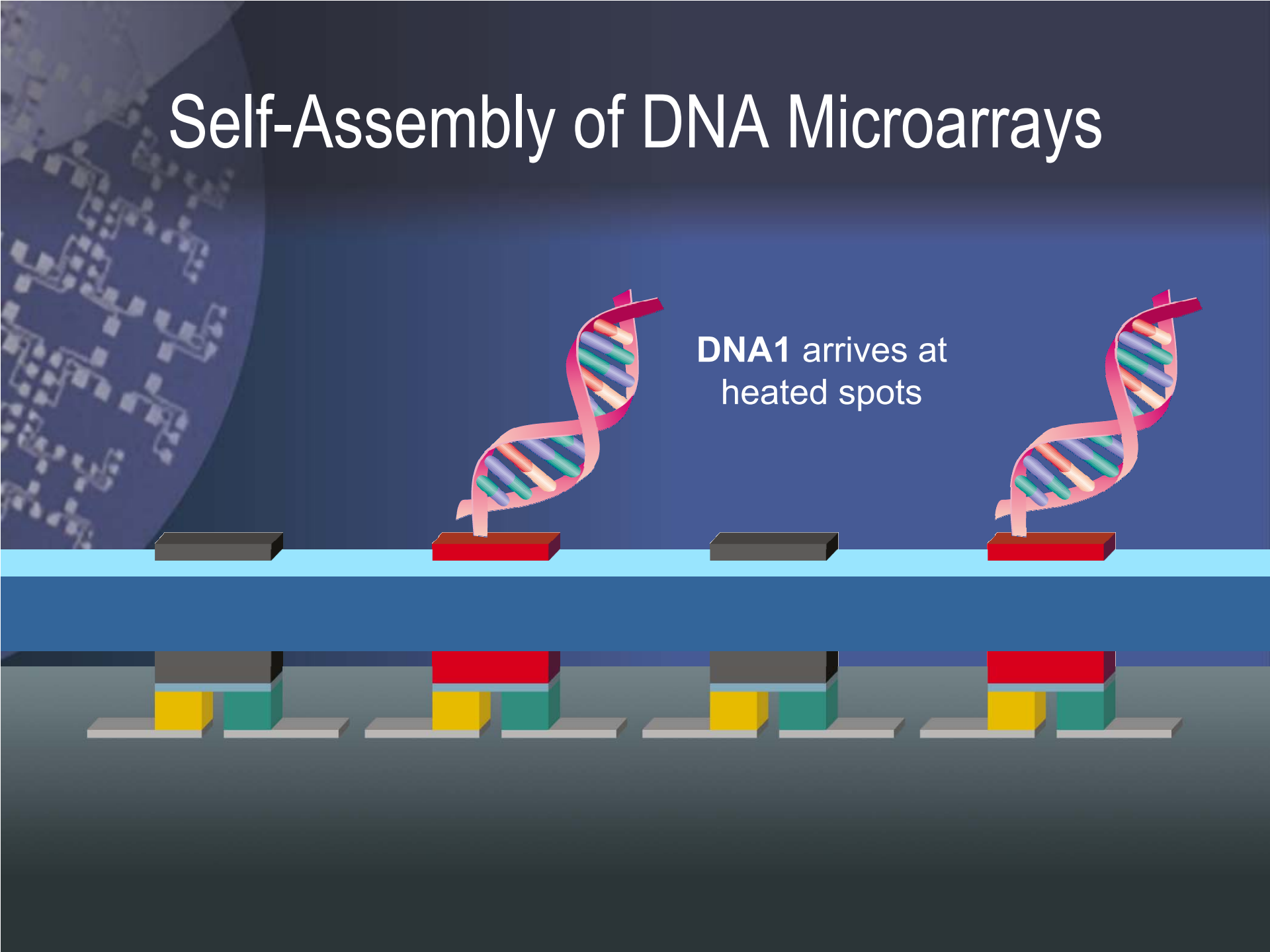

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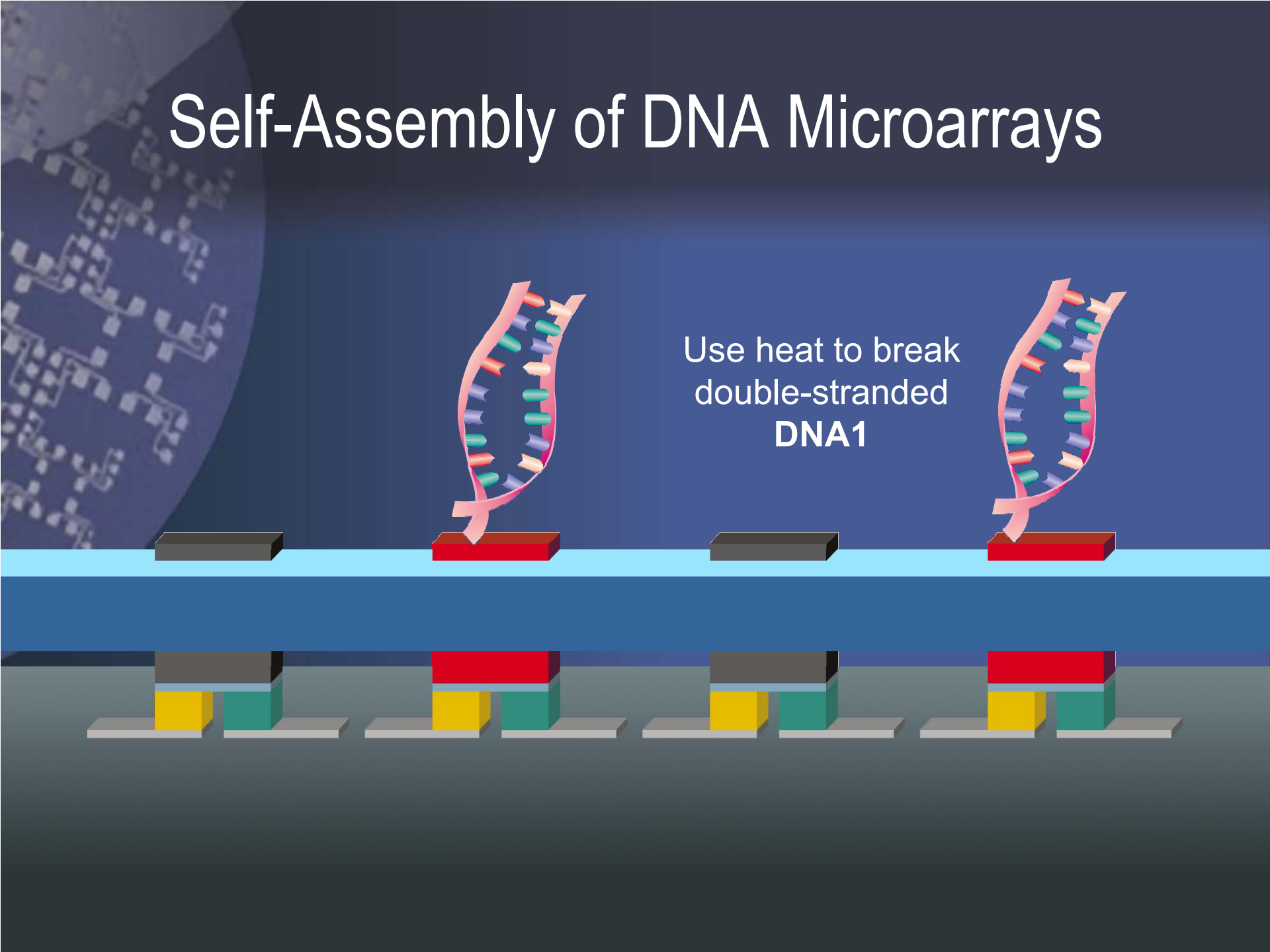
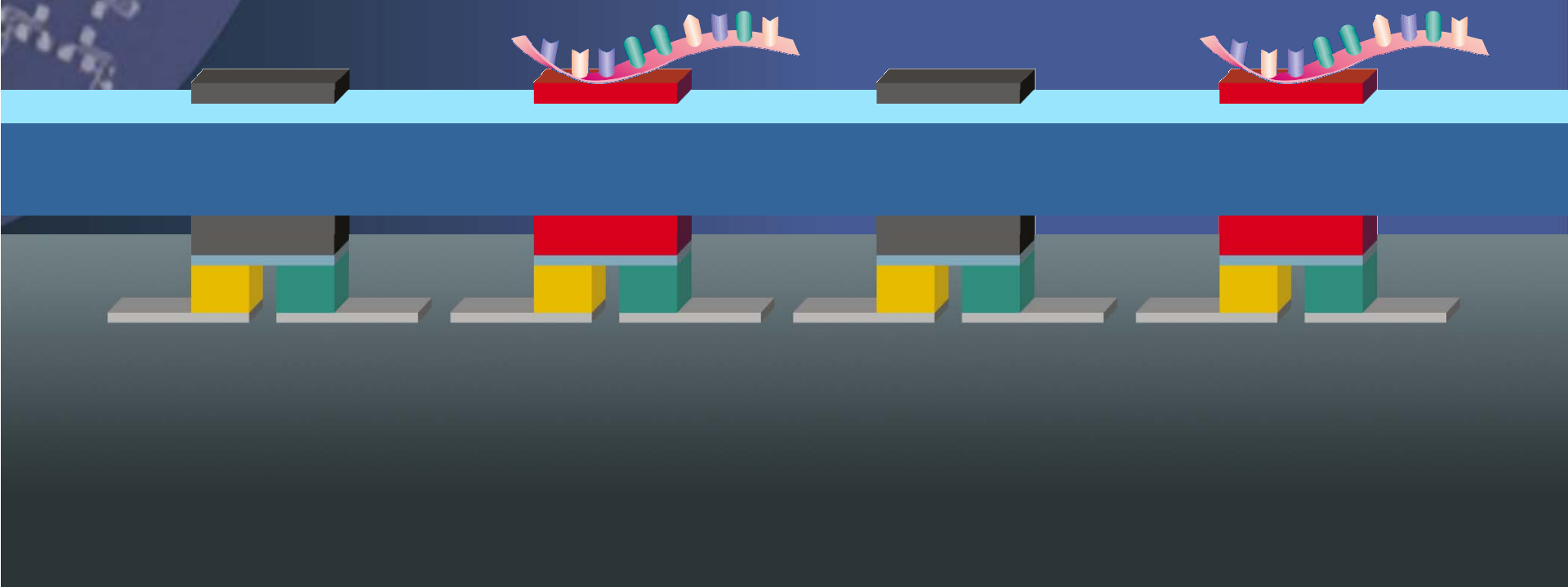


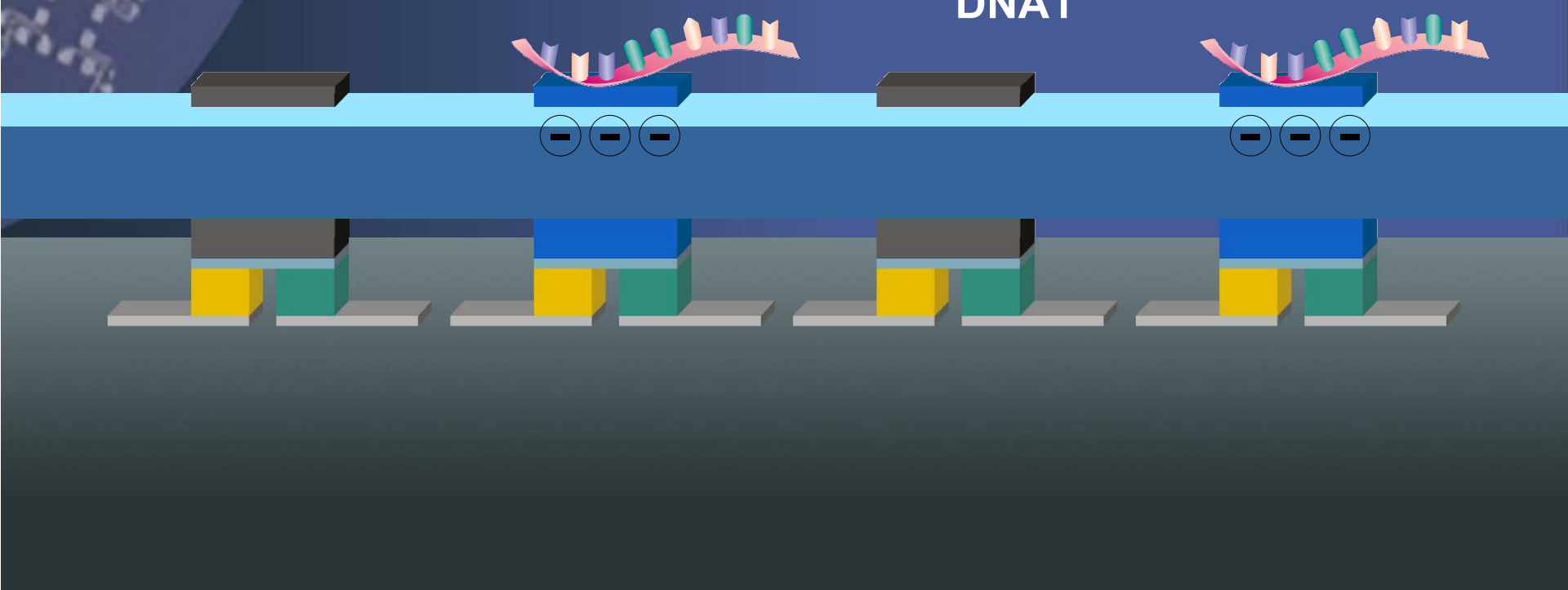
Self-Assembly of DNA Microarrays

A single-stranded
DNA1 is created

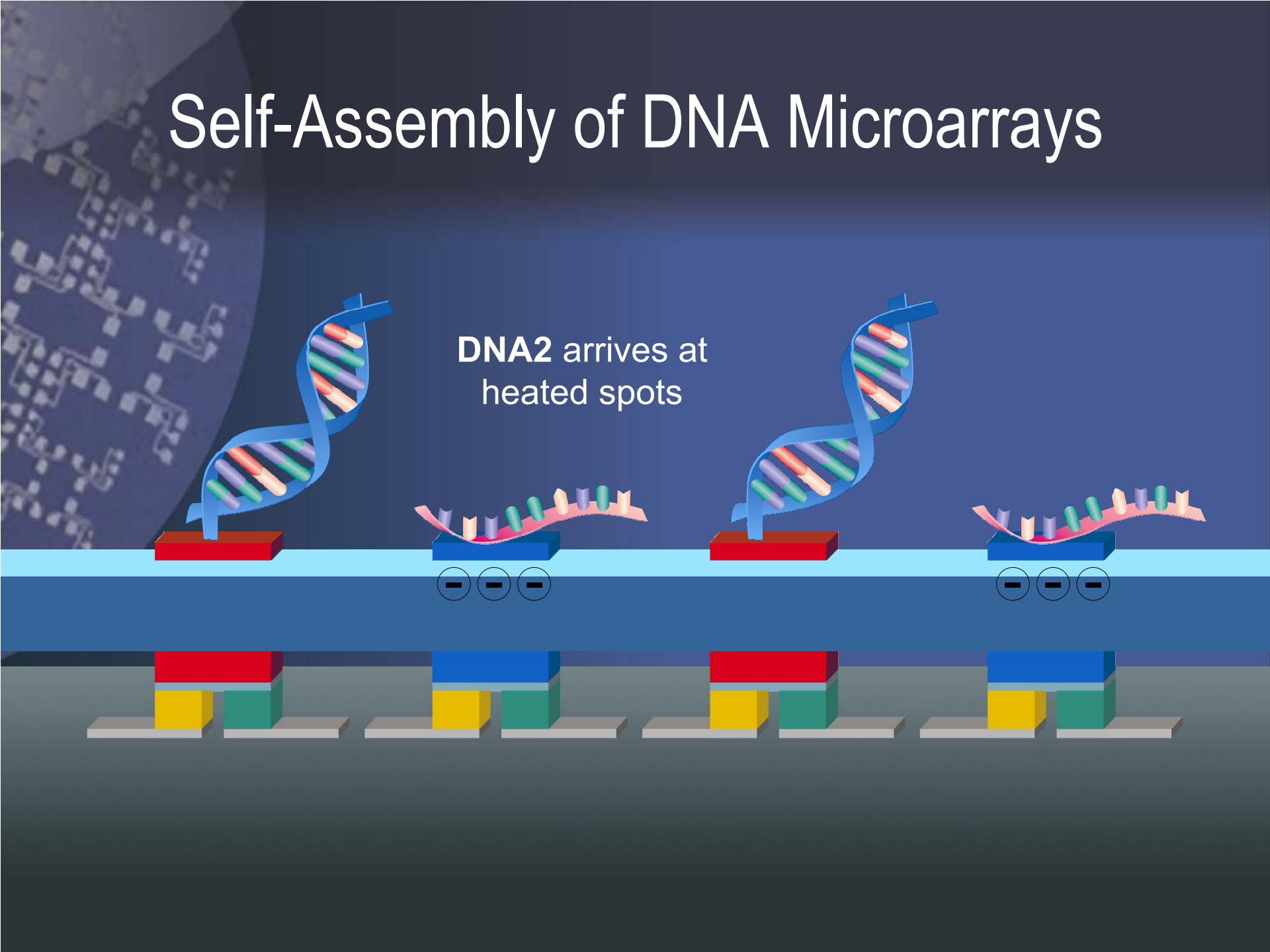


Self-Assembly of DNA Microarrays

Use charge and cooling to trap single-stranded **DNA1**



Self-Assembly of DNA Microarrays



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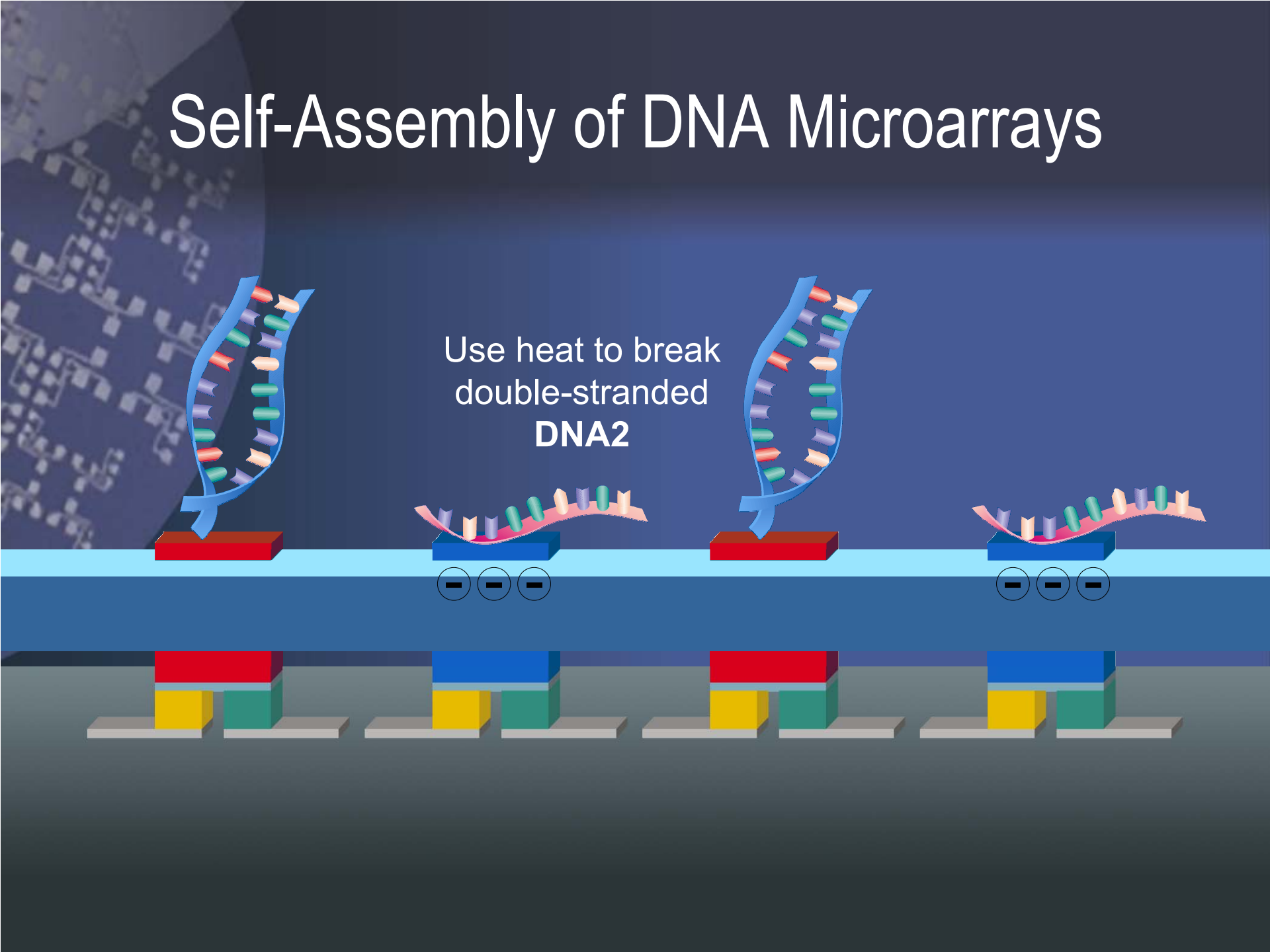
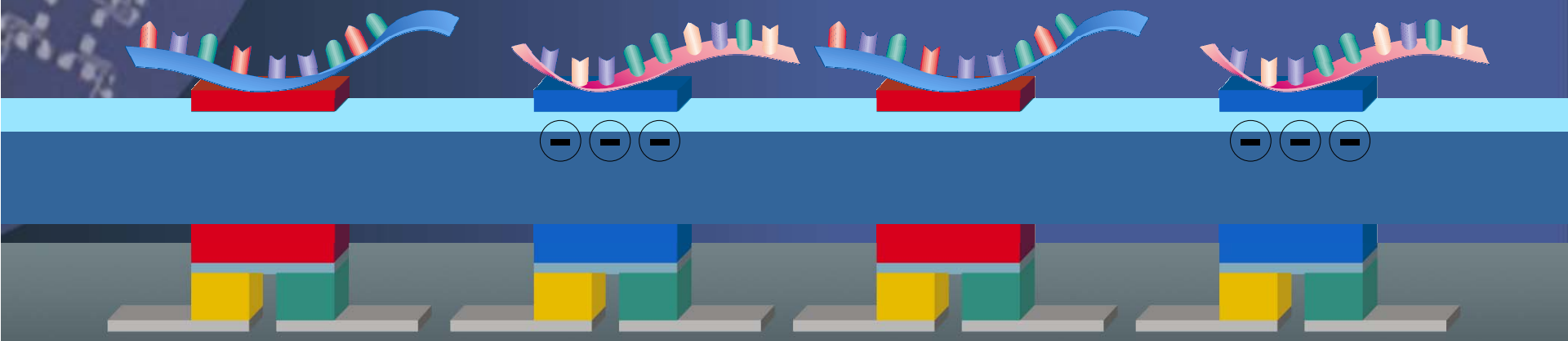


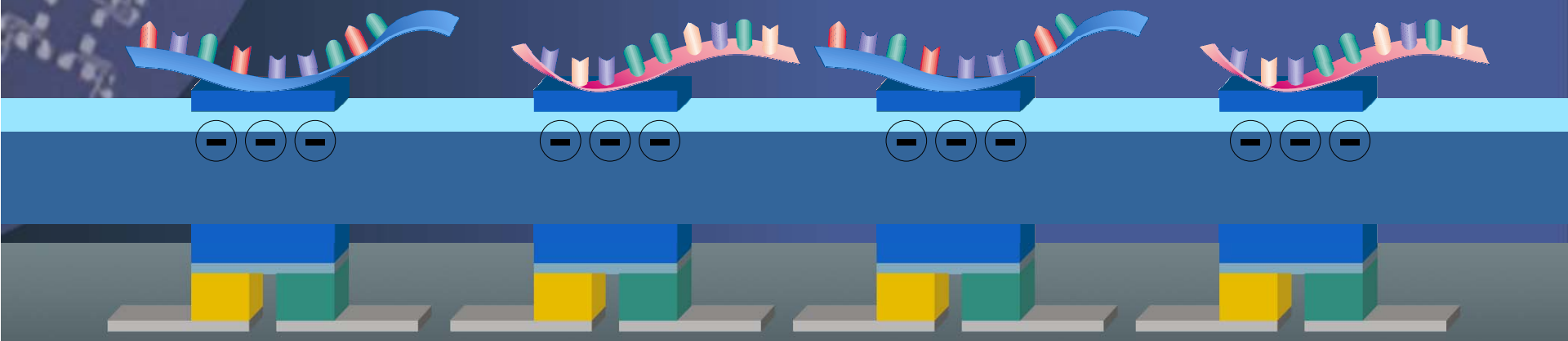
Self-Assembly of DNA Microarrays

A single-stranded
DNA2 is created



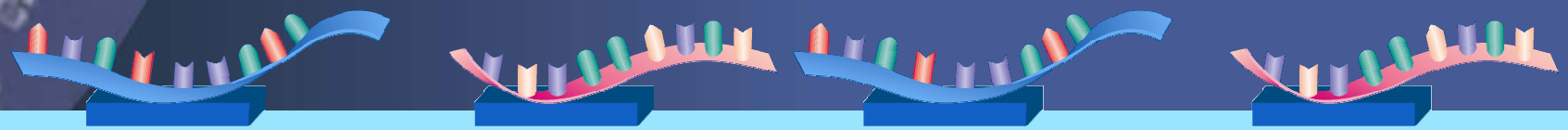
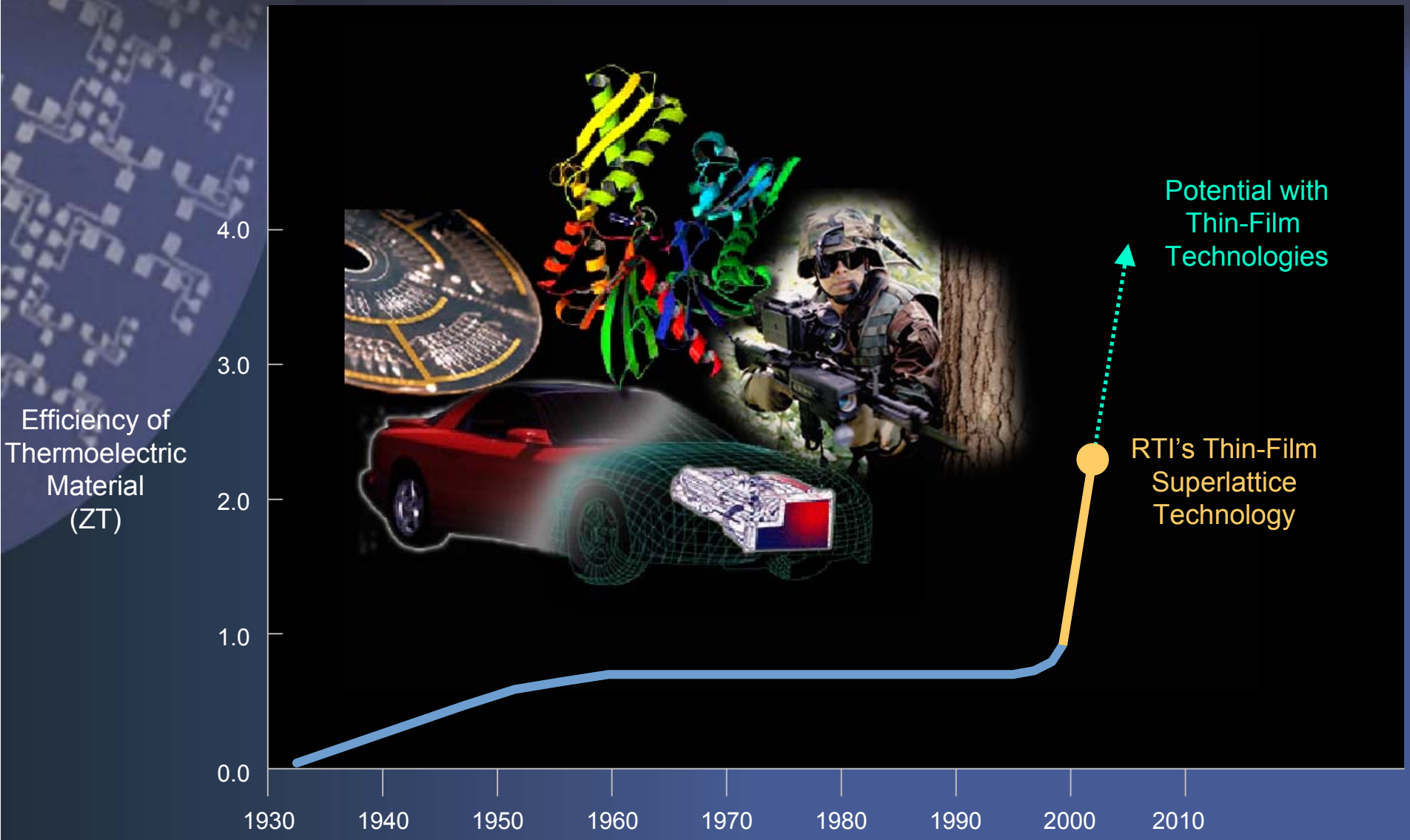
Self-Assembly of DNA Microarrays

Use charge and cooling to trap single-stranded **DNA2**



Self-Assembly of DNA Microarrays

Self-assembled DNA-array ready
for experiments



40-Year Breakthrough — A Multitude of Opportunities