# NOVEL ENERGY CONVERSION DEVICES OF ICOSAHEDRAL BORIDES

**ICOSAHEDRAL BORIDES** ARE **DISTINCTIVE SOLIDS**

THE **UNUSUAL PROPERTIES** OF THESE BORIDES
OFFER THE PROMISE OF THEIR
SERVING AS THE BASIS OF
**NOVEL ENERGY CONVERSION DEVICES**

PRESENTATIONS

I. Background: Science of icosahedral borides

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II. Progress: Feasibility of energy conversion devices

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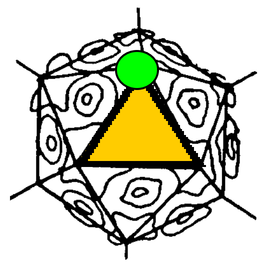
# ICOSAHEDRAL BORIDES' UNUSUAL STRUCTURES

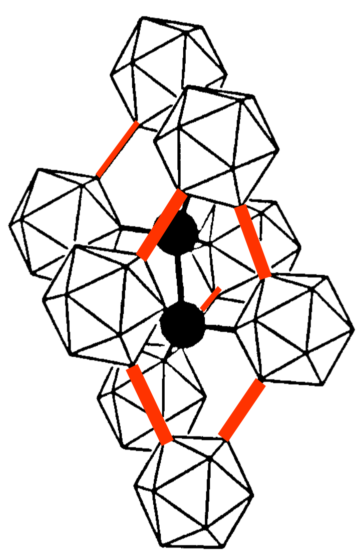
• Based on icosahedral borane molecule: $(B_{12}H_{12})^{2-}$

- **Boron atoms** in **six-fold coordination**
- Bonding charge is centered on **triangular faces**
- $(B_{12}H_{12})^{2-}$ are **dianions**



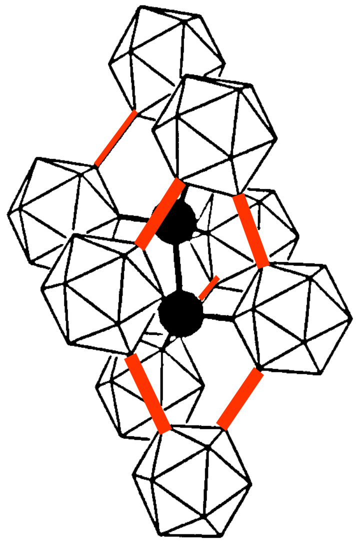
• **Stable and hard**, **high-melting-point** solids (> 2000 C)

- $B_{12}$ clusters become **dianions: $(B_{12})^{2-}$**
- Some icosahedral borides are **wide bandgap semiconductors**:
  e.g. $(B_{12})^{2-}(As^{+})_2$



# ICOSAHEDRAL BORIDES' DISTINCTIVE BONDING

*Boron atoms' second-shell electrons participate in*
***both covalent** and **electron-deficient bonding***



$(B_{12})^{2-}(As^{+})_2$

- **External bonding**:
  - **Two-center covalent bonds** emanate from icosahedral atoms

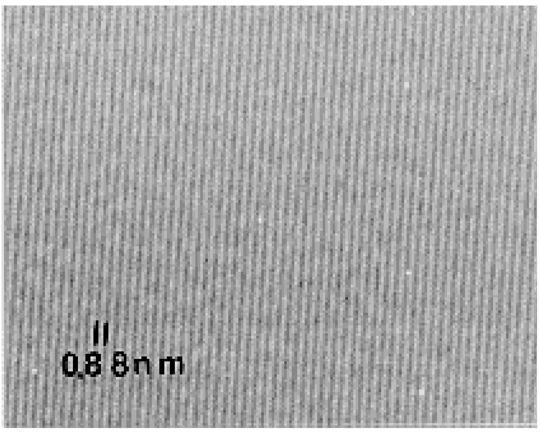
- **Internal bonding**:
  - **"Electron-deficient"** - electrons extend over icosahedron's surface
  - **Superatoms**: electrons in s,p,d,f (split) molecular orbitals
  - **Bielectron affinity**: high density of unshielded nuclear charge **binds two electrons** - $(B_{12})^{2-}$

- **Inverted** molecular solids:
  - **External bonding** is **stiffer** than **internal bonding**

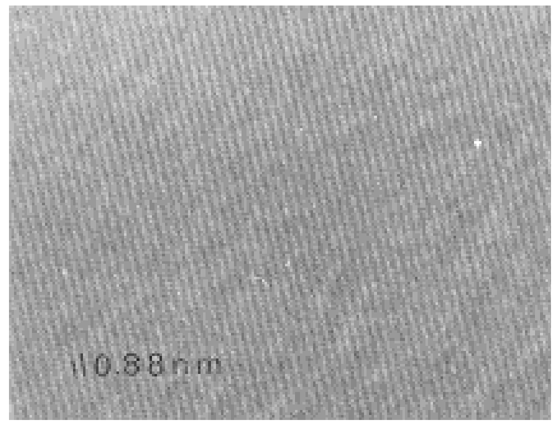
D. Emin, Physics Today, January 1987.

# EXTRAORDINARY RADIATION TOLERANCE
# OF ICOSAHEDRAL BORIDES

- **Intense light-ion bombardment (sufficient to amorphize standard semiconductors) fails to damage icosahedral borides**




(a)




(b)

HRTEM images of β-rhombohedral boron (a) before, and (b) after bombardment by 160 keV $N^+$ ions at 80 K.

- Even though each boron atom is estimated by TRIM to be **displaced on average 36 times** during this bombardment, **no defect clusters or loss of crystallinity** is observed in (b).

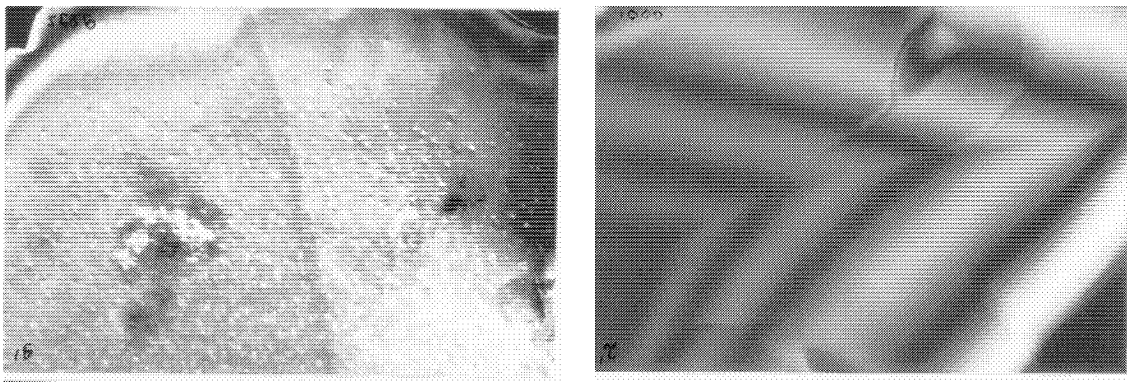
- Similar results obtained:

  - with ions of **higher mass** (to Ar, Z = 18)
  - with ions of **higher energy** (1 MeV He ions)
  - at even **lower temperatures** (12 K)


L. Schmirgeld, L. Zuppiroli, M. Brunel, J. Delafon, and C. Templier, in *Boron-Rich Solids*, D. Emin, T. Aselage, A. Switendick, B. Morosin, and C. Beckel eds. AIP, (1991) pg. 630.

# "SELF-HEALING"
# OF ICOSAHEDRAL BORIDES' RADIATION DAMAGE

- Diborides, octahedral borides and icosahedral borides were intensely bombarded with electrons
  - **ONLY icosahedra borides** remain **undamaged**
  - **ALL icosahedral borides** remain **undamaged**



(a) (b)

TEM images of 200 keV-electron-bombarded borides

(a) **$TiB_2$** is rapidly damaged by the electron beam
- **9 minutes** of exposure produces **very many defect clusters**

(b) **$B_{12}P_2$**, a boride based on $B_{12}$ icosahedral units,
- **2 hours** of exposure produces **no damage**

- **Self-Healing** of radiation damage:

  **Radiation-induced interstitials and vacancies rapidly recombine**

  - **Bielectron Affinity**: **icosahedra retain internal bonding electrons** even when "degraded" by loss of an atom
  - **Electron taken** from departing boron atom
  - Departing **cations** attracted to **residual negative charge**:

$$(B_{11}\text{-}B{:}B\text{-}B_{11})^{-4} \rightarrow (B_{11} \quad B\text{-}B_{11})^{-5} + (B{:})^{+}$$

  - Fast cation diffusion ensures **rapid recombination**

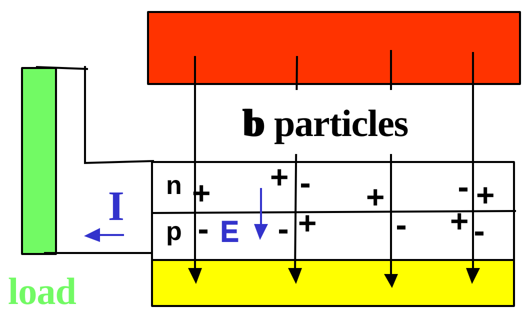
M. Carrard, D. Emin, and L. Zuppiroli, Phys. Rev. B, 51, 11270 (1995)

# NOVEL ENERGY CONVERSION DEVICES OF ICOSAHEDRAL BORIDES

***Does self-healing of damage in icosahedral borides render direct nuclear-to-electric energy conversion feasible?***

**Solar-Cell-Type Device**

**Radioisotope source**




- Passage of each β-particle generates $10^4$ to $10^5$ electron-hole pairs
- Device's internal field separates pairs
  - **High-mobility carriers required**

    **Radiation destroys conventional-semiconductor devices**
  - **High-mobility** (50 $cm^2$/V-sec) holes reported in $B_{12}P_2$

    **Icosahedral borides survive bombardment**

## Advantages

- **Reliable, self-contained** energy source
- **Enormous energy capacity**

**$10^7$ to $10^8$ W-hr per kg of radioisotope**

Pb-acid battery: 30 W-hr/kg

Li-polymer advanced battery: 200 W-hr/kg

Gasoline: $10^4$ W-hr/kg of fuel

- β-emitters offer **choice of power, lifetime, size**

# Useful b-Decay Sources

| **Beta Decay**<br>Highest Energies of Emitted Betas in Parentheses (MeV)<br>Blue: Isotope exists in reactor waste<br>Red: Isotope produced by bombardment of stable isotopes | **Nuclear Capacity** (MW-hr/mole) | **Half-life** (yr.) | **Beta Power** (kW/mole) | **Estimated Shielding for 1 $W_{th}$ source** (cm Pb) |
|---|---|---|---|---|
| $^{90}$**Sr** $\rightarrow$ $^{90}$Y $\rightarrow$ $^{90}$Zr + $\beta$(0.54) + $\beta$(2.27) | 20. | **28.** | 0.08 | 7 |
| $^{137}$**Cs** $\rightarrow$ $^{137}$Ba + $\beta$(1.18) 6%<br>$\rightarrow$ $^{137}$Ba + $\beta$(0.51) + $\gamma$(0.66) 94% | 4.7 | 30.2 | 0.02 | 8 |
| $^{144}$**Ce** $\rightarrow$ $^{144}$Pr $\rightarrow$ $^{144}$Nd + $\beta$(0.32) + $\beta$(3.0) + many $\gamma$'s. | **25.** | 0.78 | **3.6** | 15 |
| $^{147}$**Pm** $\rightarrow$ $^{147}$Sm + $\beta$(0.23) | **1.1** | 2.6 | 0.05 | **< 0.1** |
| $^{170}$**Tm** $\rightarrow$ $^{170}$Yb + $\beta$(0.97) 77%<br>$\rightarrow$ $^{170}$Yb + $\beta$(0.89) + $\gamma$(0.08) 23% | 6.6 | 0.35 | **2.2** | 3 |
| $^{204}$**Tl** $\rightarrow$ $^{204}$Pb + $\beta$(0.76) | 5.1 | 3.8 | 0.16 | 3 |

*U*

# NOVEL ENERGY CONVERSION DEVICES OF ICOSAHEDRAL BORIDES

**Three-part program to establish the *feasibility* of direct nuclear-to-electric energy conversion using icosahedral borides**

1. Confirm the "self-healing" of icosahedral borides' radiation damage

   Profs. Rod Ewing and Lumin Wang
   Dept. of Nuclear Engineering
   University of Michigan

2. Grow icosahedral boride films by chemical vapor deposition

   Prof. Steve Hersee
   Center for High-Technology Materials
   University of New Mexico

3. Measure and assess radiation-induced electrical response of films

   Drs. Terry Aselage and Wei Zhang
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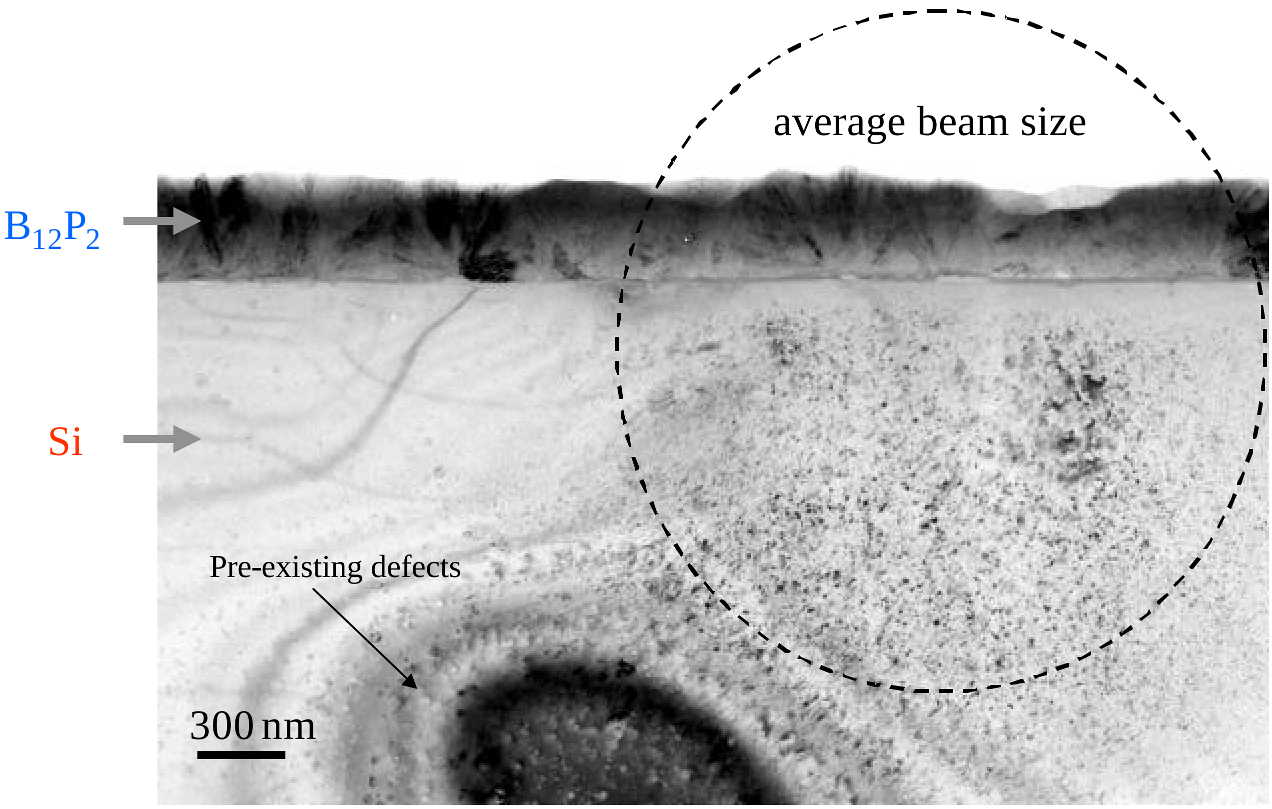
# ICOSAHEDRAL BORIDES ARE UNAFFECTED BY BOMBARDMENTS THAT SEVERELY DAMAGE SILICON




The encircled area was bombarded with 800 keV electrons at 25K
Dose of $3 \times 10^{23}$ electrons/cm$^2$
equivalent to hundreds of years of exposure to intense radioactive β-emitters.

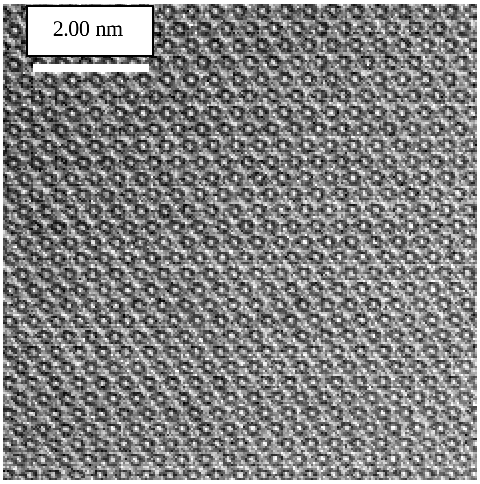
**The bombarded region (area within circle) of the Silicon crystal is extensively damaged.**

**No damage is detected in $B_{12}P_2$.**

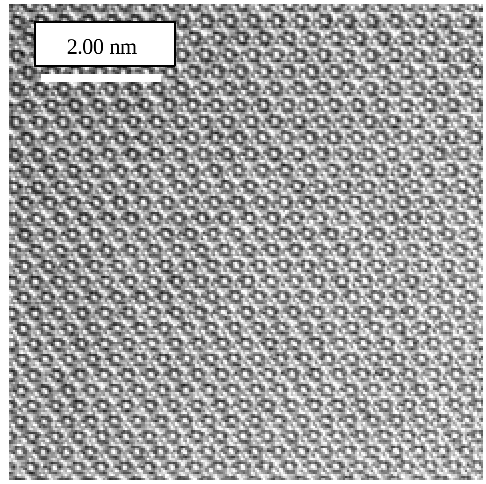
# SELF-HEALING HAS BEEN CONFIRMED

***One* illustration*:***

- **Very intense bombardment** with 400 keV electrons, **$10^{18}$** electrons/cm$^2$-sec (**$10^{12}$** electrons/cm$^2$-sec from **$^{90}$Sr** , **$10^{14}$** electrons/cm$^2$-sec from **$^{144}$Ce**)
- **Total dose » $10^{23}$ electrons/cm$^2$ exceeds hundreds of years of exposure**

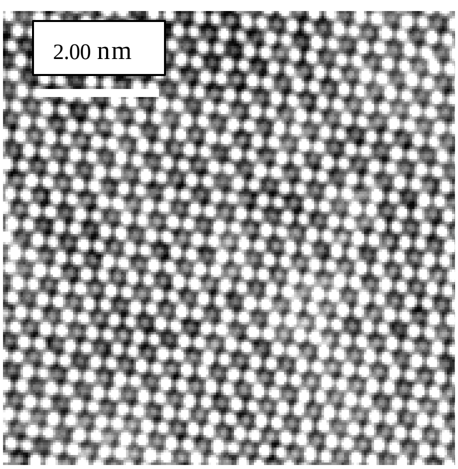



Before

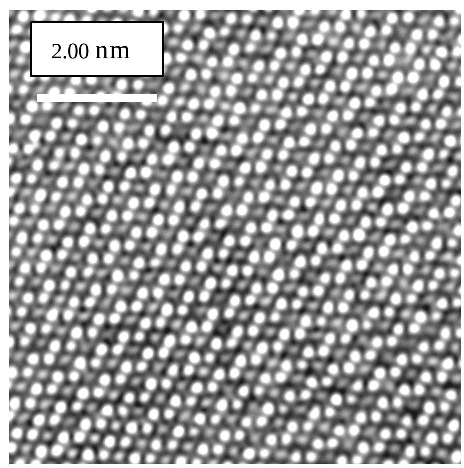



After

β-rhombohedral boron




Before




After

$B_{12}P_2$

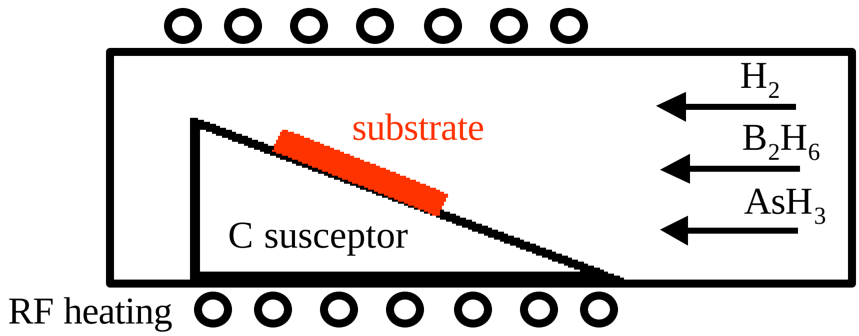
**No damage observed even with Very-High-Resolution TEM**
**Image features about the size of icosahedra**

# CVD GROWTH OF ICOSAHEDRAL BORIDE FILMS

***Solar-cell-type device requires semiconducting films***

**Chemical Vapor Deposition** of **$B_{12}As_2$**

$$6B_2H_6 + 2AsH_3 \rightarrow B_{12}As_2 + 21H_2$$




High volatility of **As** makes it **hard to contain**

- CVD can maintain As concentration at film surface

**Growth of $B_{12}As_2$ is difficult**:

- ***No established technology***
- Refractory solids, ***require exceptionally high temperatures***
  - Conventional CVD reactors operate only up to 1100 C

**CVD growth at CHTM:**

1100 C: crystalline β-rhombohedral boron

**1100C: amorphous "$B_{12}As_2$"**

**1150 C: some crystalline $B_{12}As_2$**

→ Reactor being modified for higher-temperature, reliable $B_{12}As_2$ growth

# ORIENTED, CRYSTALLINE $B_{12}As_2$ FILM ON SiC

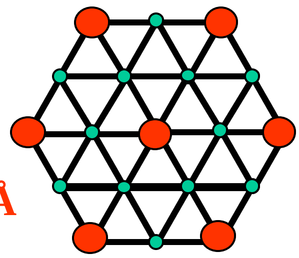
*Grown by CVD at 1150 C*

- **SiC** provides a **lattice-matched substrate** for $B_{12}As_2$ **hetero-epitaxy**

**$2a_H(SiC) = a_H(B_{12}As_2)$**

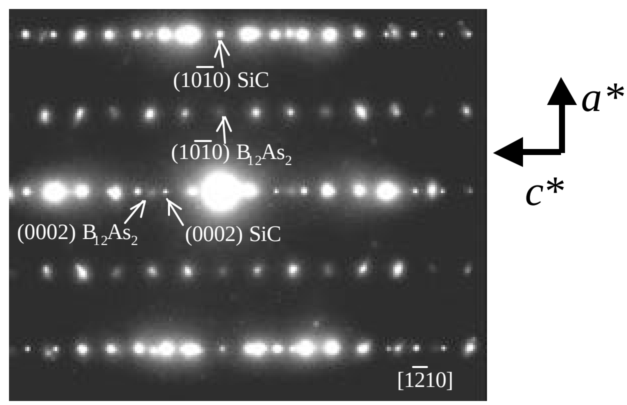
**$a_H(SiC) = 3.078$ Å**

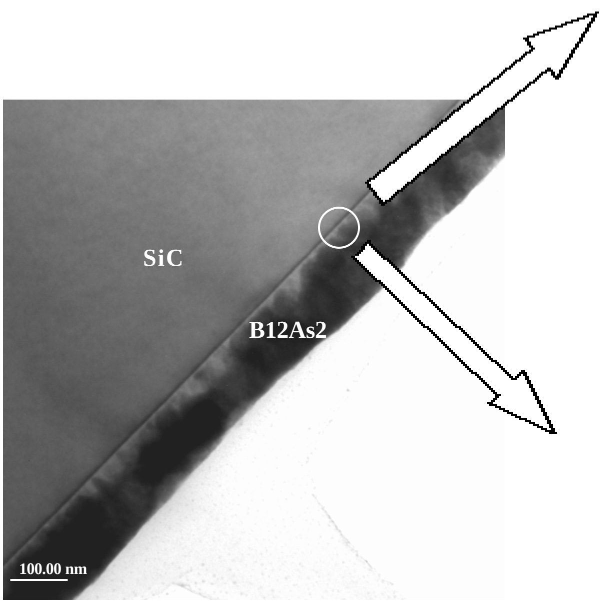
**$a_H(B_{12}As_2) = 6.156$ Å**

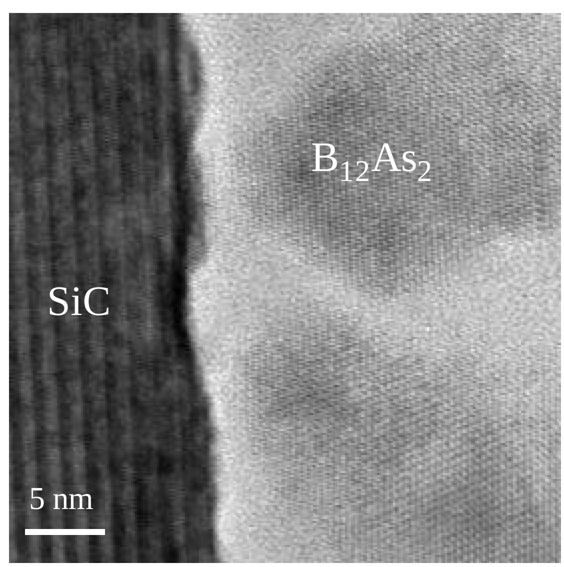


Schematic of (0001) planes

Electron diffraction confirms same orientation of film and substrate




TEM image shows films' imperfections

***Film quality should be further improved by higher-temperature growth***

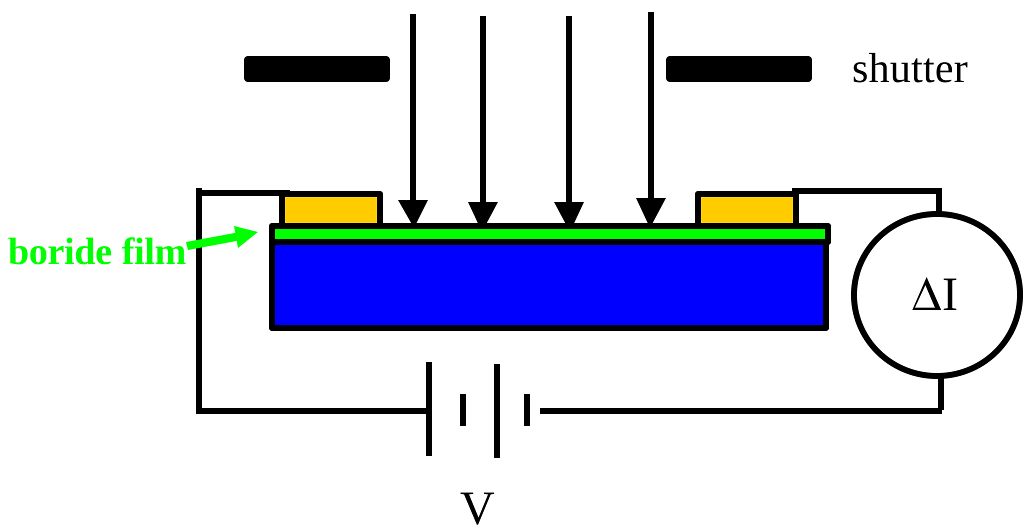
# ELECTRICAL RESPONSE OF SEMICONDUCTING ICOSAHADRAL BORIDES UNDER INTENSE BOMBARDMENT

- Simulate β-particle flux from radioisotope sources with:

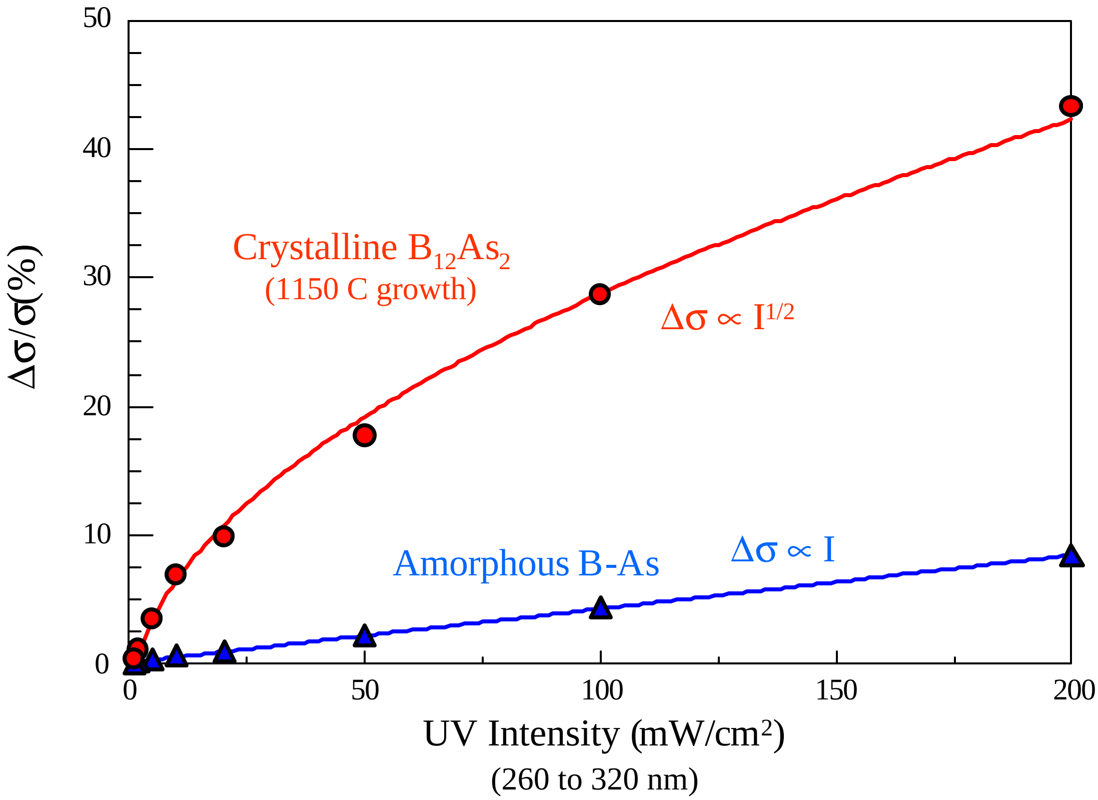
  Ultra-violet photons
  Electron beams

- Assess film quality required for solar-cell-type device

- Measurement of bombardment-induced conduction



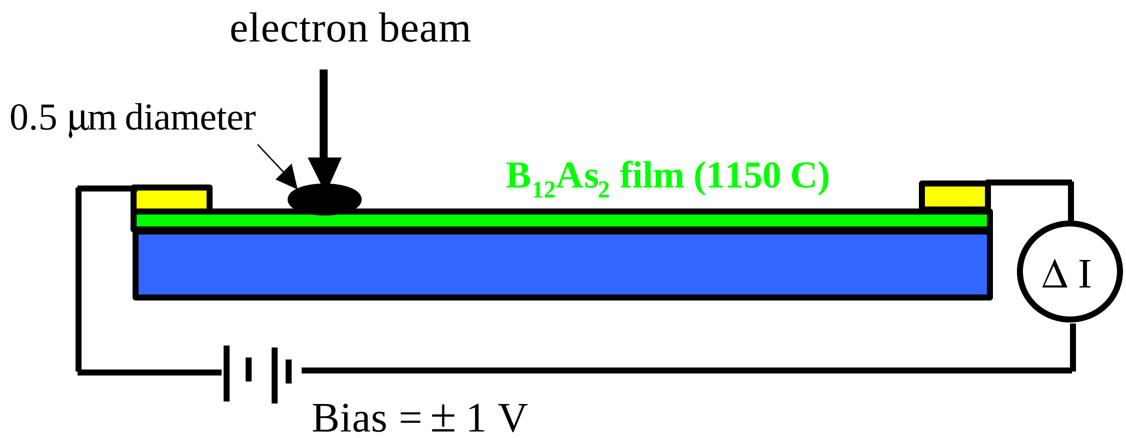
# PROMISING PHOTO-RESPONSE MEASURED WITH CRYSTALLINE $B_{12}As_2$ FILM



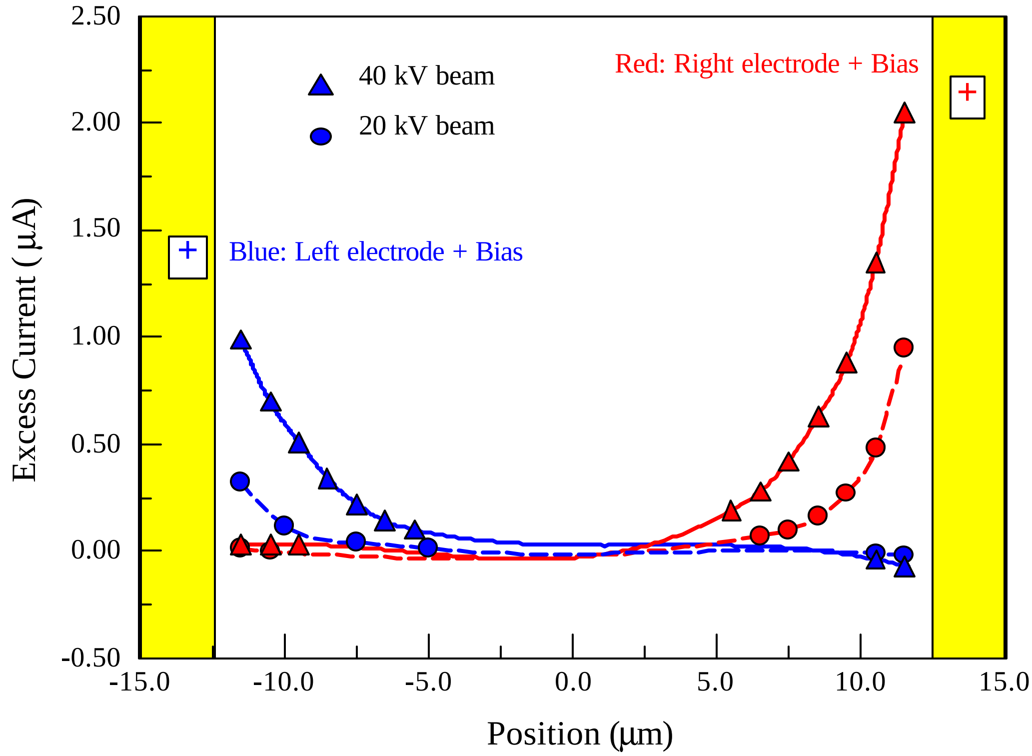

- **Amorphous B-As and b-rhombohedral boron**
  - Very low-mobility photocarriers(≈ $10^{-7}$-$10^{-8}$ cm$^2$/V-sec)
  - $\Delta\sigma \propto I$ : trap-dominated recombination

- **Crystalline $B_{12}As_2$** **<u>conventional semiconductor transport</u>**
  - High-mobility photocarriers ($10^1$ to $10^2$ cm$^2$/V-sec)
  - $\Delta\sigma \propto I^{1/2}$: intrinsic recombination
  - $\Delta n \approx 10^{15}$ to $10^{16}$/cm$^3$
  - Photocarrier lifetimes ≈ 0.1 μsec
  - Photocarrier diffusion lengths = $(\mu\tau k_B T/e)^{1/2}$ ≈ several microns

# ELECTRON-BOMBARDMENT-INDUCED CURRENTS




*Current as a function of beam position*

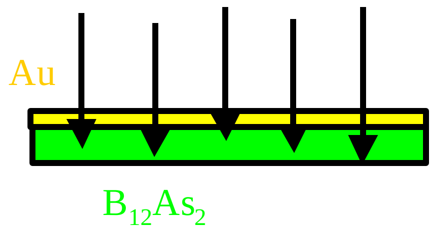


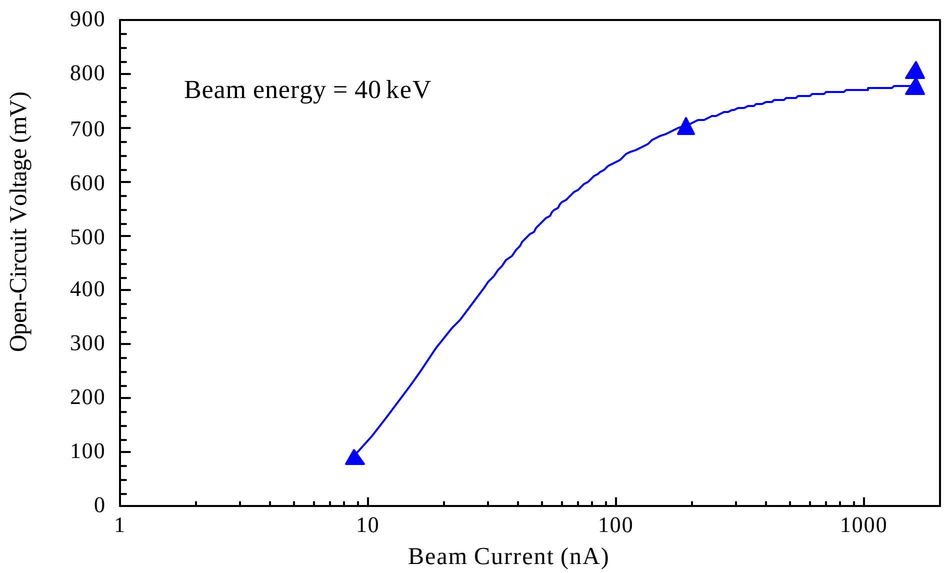

- Beam-induced current falls with distance from + electrode
- Collection length of mobile electrons ≈ $\mu \tau E$ ≈ 5 microns

Electron-bombardment conductivity agrees with photo-conductivity ($\mu\tau \approx 10^{-6}$ $cm^2/V$)

# DEMONSTRATION OF A SIMPLE DEVICE

***Schottky-barrier subjected to electron bombardment***




Direct bombardment of Au/$B_{12}As_2$ Schottky junction:

**- Generates open-circuit emf**

# NOVEL ENERGY CONVERSION DEVICES OF ICOSAHEDRAL BORIDES

## *Appears Feasible:*

- Self-healing of radiation damage has been **confirmed**
- Semiconducting $B_{12}As_2$ films **can be grown**
- Promising radiation-induced **electrical response measured**

## Objectives for the remainder of this program:

- Improve film quality and growth reliability

  CVD growth of $B_{12}As_2$ at higher temperature (to 1350 C)

- Assess electrical response of improved films
- Study of additional devices

Return to Agenda

Next Presentation