Novel Low Workfunction Semiconductors: Dark Matter, ν- Phenomena, x-ray Astronomy

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Novel Low Workfunction Semiconductors: Dark Matter, Neutrino Phenomena and X-ray Astronomy

- Precision calorimetry via absorbed energy has lead to major discoveries.
- Energy Resolution + very low detection thresholds:
  - dark matter searches;
  - Cosmic, solar and reactor ν: oscillations, mass measurements, coherent interactions
- Key Challenge for homogeneous semiconductor detectors: 0.1-1 eV energy resolution.
- Semiconductor detectors: benefit from high atomic number (Z), high density (ρ), low electron-hole pair production energy E_{pair} or E_p (also called $E_{threshold}$ for e-hole pair production).
- Applications to large sampling calorimeters may have superior radiation resistance and temporal properties.

Semiconductor Calorimetry- 1

- For the lowest bandgaps E_g, operation must be cooled to LHe or lower to avoid thermal noise generation in the lowest deposited energy regimes.

- Probability per unit time for thermal electron-hole pair:

$P(T) = CT^{3/2} e^{-Eg/2kT}$ Eg: band gap energy, k: Boltzmann constant and C is a proportionality constant characteristic of the material.

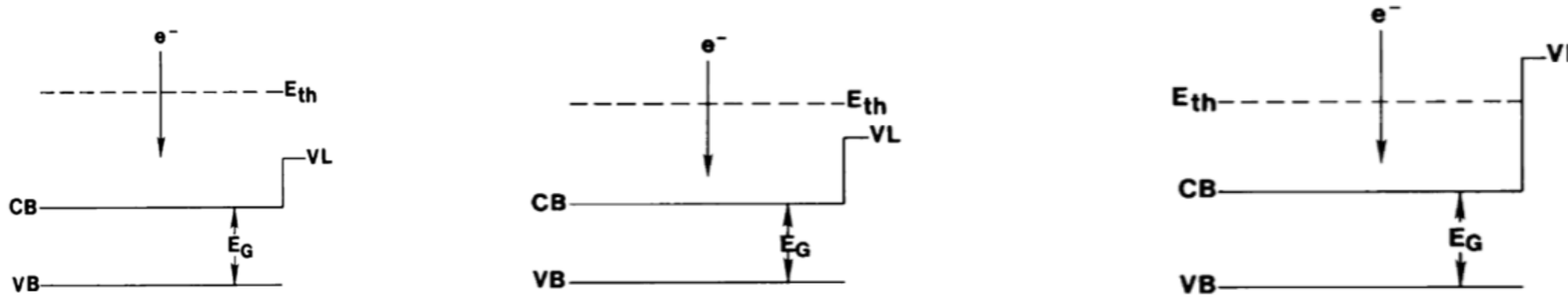
- Room temperature Operation: Typically a Bandgap E_g > ~1.3 eV necessary so thermally generated carriers do not dominate detection of low energy events.

Example: Si (E_{gap} ~ 1.1 eV) SiPM often requires T< -20 C° for sufficiently low noise for single p.e. detection or good energy resolution

- High Resolution: low e-hole pair energy Ep is given by Ep=Eg +Ea (Ea=electron affinity), also called by some authors the threshold energy E_{th}. E_{th}(=Ep) is similar to/related to the work function ϕ but can be more or less than the vacuum level VL.

Semiconductor Calorimetry- 2

Generic energy bands levels fall into 3 classes.

- 

VB=Valence Band, CB=Conduction Band, VL=Vacuum Level, E_G=Band Gap, E_{th} is Ep, the threshold energy to produce electron-hole pairs.

- Left + Middle Cases: semiconductors where E_{thresh} for e-hole production > vacuum level VL. When e-hole pairs are produced, the electron has a chance to escape, as its energy can be above the vacuum level, and can be a photoelectron (p.e.) or photoconducted electron.
- semiconductor material for photoemission (photocathodes) have energy levels qualitatively similar to the left figure; once a pair is made, over a large range of energy depositions, the electron can escape, while the middle diagram describes photoemitters with a restricted range of emissions.
- Right Case: Multi-alkali and GaAs photocathodes are like the left most diagram, most mono-alkali PC are like the middle diagram and Si or Ge are like the diagram on the right.
- The electrons produced only need to be near the top of the conduction band for operation as a diode.
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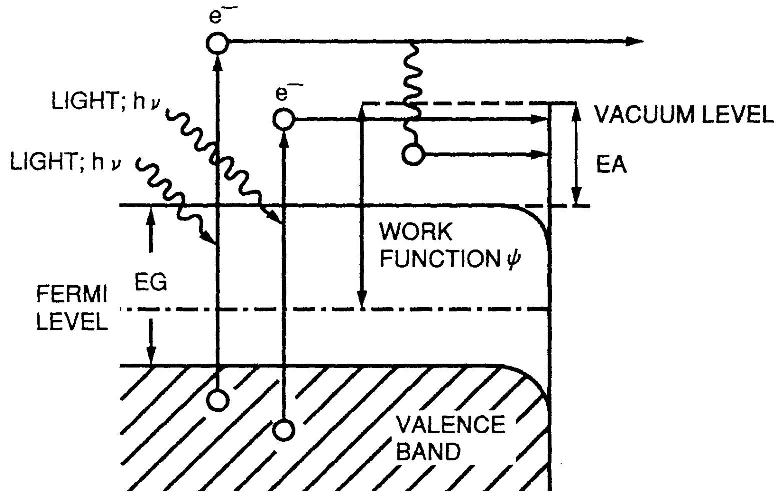
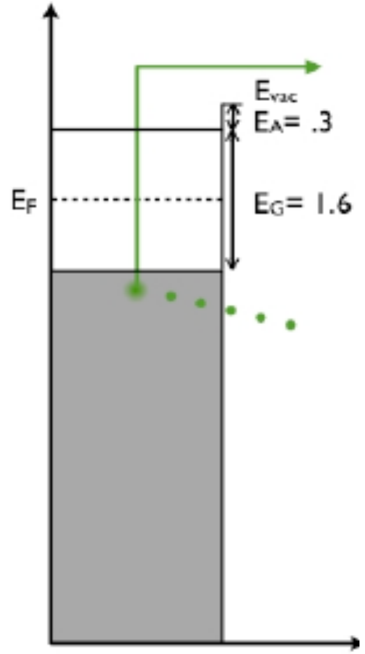
Semiconductor Calorimetry- 3





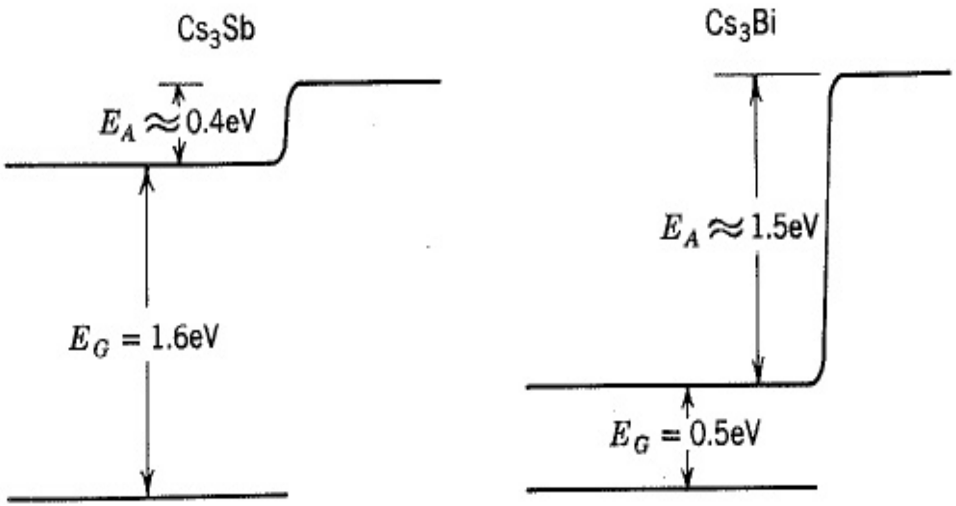
Left: Schematic of the Energetics for alkali photocathode vacuum emission – the pair energy Ea+Eg is near the vacuum level.

Right: Cs_3Sb semi-conductor energy level band diagram – the energy for pair production is ~Ea+Eg= 1.9-2.0 eV, near the vacuum level

Semiconductor Calorimetry- 4

A Guiding Example:

Cs_3Sb vs Cs_3Bi



• Cs_3Sb and Cs_3Bi : *nearly equal pair energies* Ep ~ Ea+Eg ~2 eV; Cs_3Sb slightly lower

• Yet Cs_3Sb Eg ~1.6 eV, considerably larger than Eg ~ 0.5 eV of Cs_3Bi.

–> Cs_3Sb Eg inhibits 300°K thermal energy from promoting carriers above the Fermi level, and therefore can operate with minimal or no cooling for detecting many types of low energy events, which could include very low energy neutrino scatterings.

• Si is similar to Cs_3Bi: Eg = 1.1 eV –> requires more cooling for many applications (SiPM or Si diode detectors) compared with Cs_3Sb: Eg = 1.6 eV

• Si Ep=3.6 eV compared with Cs_3Sb Ep=2 eV.

Discussion

- 0^{th} order: *energy resolution limit* $\sigma \sim \sqrt{(F/n)}$, where n~E/Ep is the number of generated carriers; Fano factor F small for semiconductor detectors ~0.1 (Ge~0.06).

- *Figure Of Merit FOM energies ≤ 500 KeV:*

  - FOM ~ $\rho Z^{3.5}/\sigma$. (higher energy, Lrad scales ~ Z^{-2})

Example: Ge(Eg = 0.7 eV; Ep = 2.96 eV) superior detector σ_E/E~0.2% at 662 KeV; peak/Compton ratios of 30 or even higher

- Ge: Ep too large for extending present Dark matter, ν searches.
- Si: Ep=3.6 eV;
- GaAs: Ep also too large.

- By contrast:
  - Cs_3Sb (S-11 photocathode) ~ 2eV Ep.
  - Cs-Ag-O (S-1) spatial-averaged Ep=0.7 eV* in commercial tubes

**old studies: S-1 small patches (~1mm) in research studies a remarkable Ep= 0.4 eV.*

L.R.Koller, Phys Rev 36, 1639 (1930)

S.Asao, Proc. Math Phy – Math Soc. Japan 22, 448(1940)

A. Lallemand and M.Duchesnes, Z. angew. Math Phys. 1, 195 (1950)

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Table 1: Semiconductor properties for low energy deposition detectors.

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	Z	ρ(g/cc)	Egap(eV)	E_{pair}	μ_e, μ_{hole} $cm^2/V/s$	Lrad(cm)
Ge	32	5.3	0.7	2.98	≤3900, ≤1900	2.3
Si	14	2.3	1.1	3.6	≤1400, ≤450	9.4
GaAs	31,33	5.3	1.4	4.4	≤8500, ≤400	2.3
Cs_3Sb (S-11)	55,51	4.6	1.6	2.0	10,000-10^6	1.9
Ag-O-Cs (S-1)	55,47,8	7.1	<0.3	0.4-0.7	Predicted ~5,000	1.8-2.0

• In vacuum photocathodes: photoelectron escape depth ~100's of atoms thick; almost no electric field enhancement from ~100-200 V between cathode and nearest electrode/dynode.

• A biased drift or diode junction device would not have that restriction in thickness with an applied field (similar to GaAs-based photocathodes vs GaAs-diodes to collect e-hole pairs).

• Diodes Possible: metal electrode Schottky diode on p-type Cs_3Sb or Cs-Ag-O, or a few nm thick defect or low-doped layer could be deposited to form an n-p junction.

• Photocathodes S-1 S-11: rad-resistant in space and accelerator applications

Cesium antimonide (Cs_3Sb)

Cesium antimonide (Cs_3Sb) weakly bound cubic semiconductor:

Lattice Constant 0.915 nm;
Conduction: p-type if Sb excess defects;
Electron affinity Ea: 0.4-0.5 eV,
Resistivity ρ: ~1,000 Ω-m (T=300°K) ~ 10^8 times higher than Sb, (Ge 500 Ω-m at 77K).
Mobility μ: $\mu_e \sim \mu_{hole} \geq 10^4$ cm^2/V-s (thermal diffusion fabricated defect filled photocathodes).

• Theoretically μ could exceed 10^6 i.e. like InSb.

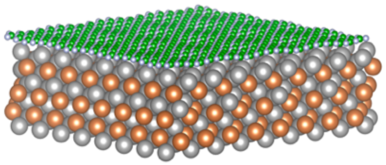
• The low polarizing of the material due to similar electron and hole mobilities and high mobility imply that high rates of ionizing events may be sustained.

• Precision assembly of films or tiles using ALD or CVD displacement defects may be minimized –> may become more intrinsic, rather than p-type..

J.J.Scheer, P.Zalm, Philips.Res. Rept 14, 584 (1959)
Sommer, A., "Photoemissive Materials" sect6.5-6.8 [1968] J.Wiley

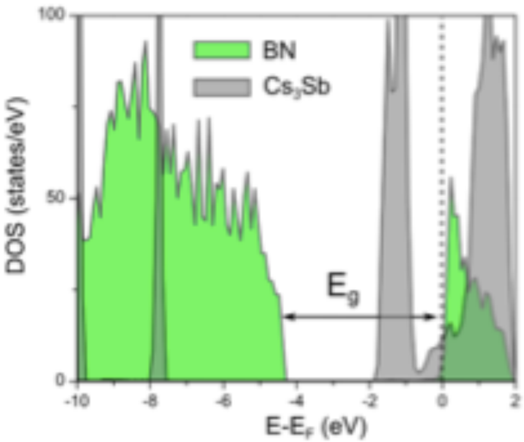
Cesium antimonide (Cs_3Sb) - 2

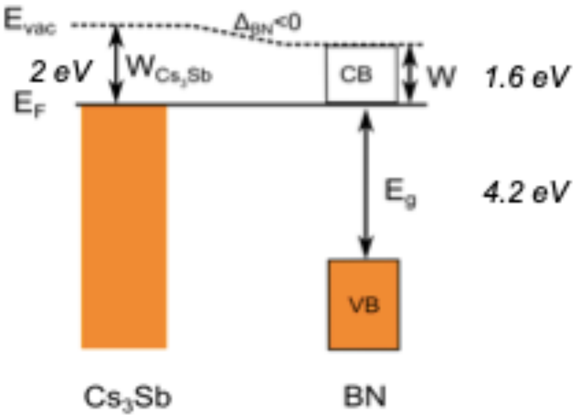
• One molecular thickness of boron carbide (BN) or one layer of graphene can protect Cs_3Sb from air, important for practical detectors.



Molecular model BN (boron nitride) single molecular layer covering atomically layered Cs_3Sb.

• Remarkably, a BN layer *lowers* the pair energy from 2 eV to 1.6 eV. Atomic layers of BN can be deposited at temperatures less than 100°C .





L: Energy bands Cs_3Sb, BN. ***R:*** Implied electrostatic potential *lowers* Ep from 2 eV –> 1.6 eV

Wang, Yang, Moody and Batista, NPJ 2D Materials and Applications 2, 1-9 (2018)
Wang , Pandey, Moody, Yang, Batista, J. Phys. Chem. C 121, 8399-8408 (2017)
Pavlenko, Liu, Hoffbauer, Moody, and Batista, AIP Adv. **6**, 115008(2016)
J.C. Sprenger et al, Electron-Enhanced Atomic Layer Deposition of Boron Nitride Thin Films Room Temperature and 100°C, J.Phys. Chem. C 122(17), 9455-9464 (2018)

Compare Cs_3Sb with Ge, Si, CdTe

- Ep: Ge (2.98 eV) <–> Cs_3Sb (2 eV) (1.6 eV/BN coating) –> ~50% more signal
- Intrinsic resolution/FOM: Cs_3Sb better than Ge by factor √(2.98/2)~1.22 or √(2.98/1.6)~1.36.
- Egap: Cs_3Sb (1.6 eV); Si (1.1 eV); CdTe (1.47 eV) –> *thermal noise is less for Cs_3Sb*
- Thermal noise current at room temperature is between 10,000-20,000 times lower in Cs_3Sb than Si, alone makes it interesting as a detector.
- Ep ~ 0.4 eV above Eg – the potential of this as a breakthrough material, quite unlike Si, Ge and the like.
- Density g/cc: Cs_3Sb(4.6); Ge(5.3) –> Ge 16% higher density….but
- Z: Cs_3Sb (55+51 -average~54), Ge(32) -> Photoelectric absorption, 662 KeV gamma ~4-5 times higher for Cs_3Sb compared with Ge for any given thickness.
- Peak/Compton ratio should exceed Ge, provided a low-defect crystal can be obtained.
- Xo(cm): Cs_3Sb (1.1), Ge(2.3)

K.H.Jack and M.M.Wachtel, Proc.Roy.soc., A239, 46 (1957); Sommer, A., "Photoemissive Materials" page 94 [1968] J.Wile
L.Apker et al., J.Opt.Soc.Am. 43, 78 (1953) W.E.Spicer, J.Phys.Chem.Solids22, 365 (1961)

Cesium antimonide (Cs_3Sb) - 4

As a detector for low energy photons or dE/dx, Cs_3Sb may be superior Ge in many respects

- *Photoelectric Absorption:* peak to Compton ratio is larger, radiation length is shorter.
- *Energy Resolution:* - pair energy is lower.
- *Cooling:* For many applications at 300°K does not need to be cooled because its bandgap is large, even larger than for Si.
- *Rate/Timing:* Cs_3Sb detector could be 5-10x faster than Si; μ substantially larger - x7-700, with nearly equal e and hole mobility, making it able to take high rates without polarizing.
- *Cost:* compared to germanium, the cost of the highly purified raw material is negligible, *albeit the fabrication costs are at present high.*
- *A shortcoming:* - like NaI,must be protected from the atmosphere.

Cs_3Sb 5 - Melt Fabrication

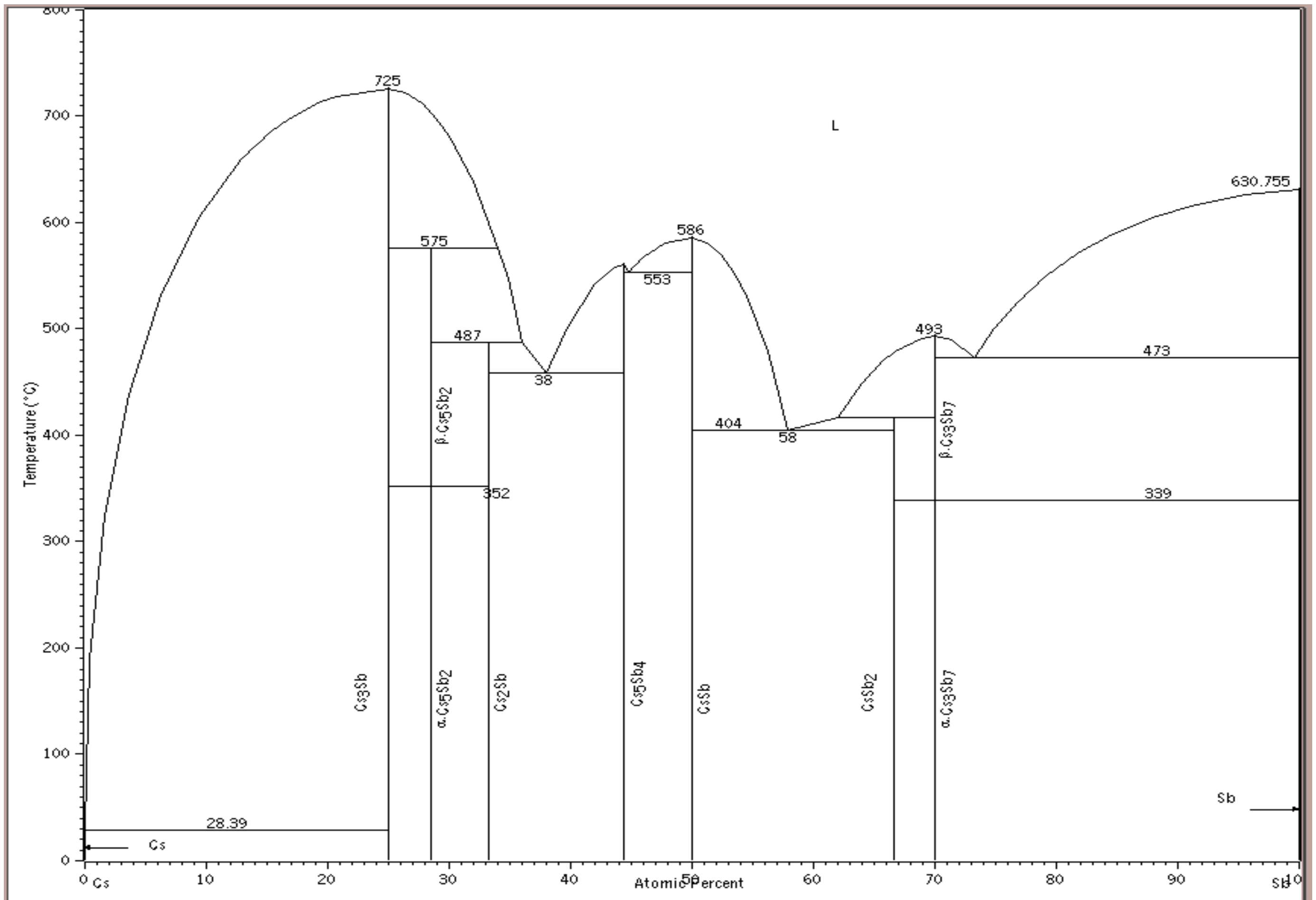
Cs_3Sb Crystals – inert atmosphere melt (Sb powder+Cs metal particles 725°C) similar to NaI/CsI.

The Phase diagram for Cs_3Sb formation is shown below; perfect stochiometry forms at 725 °C.

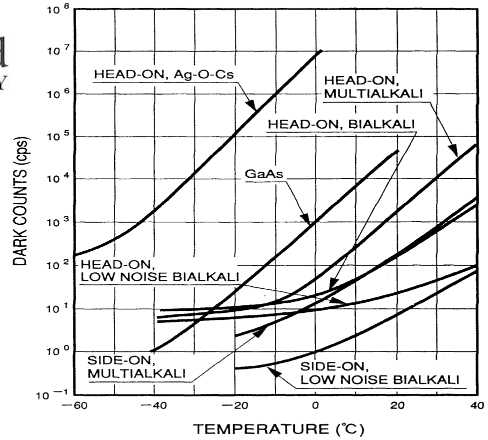
- Cs, Sb: much higher purities than experiments ~60 years ago.
- 2cc crystal our group made in a quartz vessel cracked to air before we could saw it open in a glove box ☹.

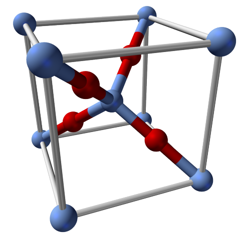
Phase Diagram

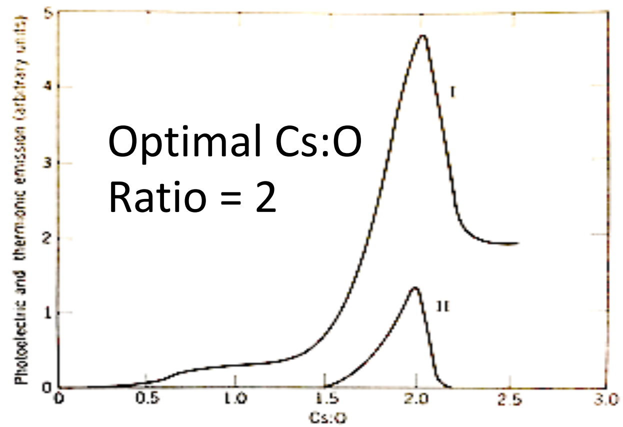
T(C°)
vs
% Sb



S-1 Ag-O-Cs (AGOCS)







Ag-O-Cs/S-1 photocathode seldom used: dark counts $10^{4\text{-}6}$ x bialkali photocathodes.

We propose turning that bug into a feature.

• Ag-O-Cs: lowest ϕ/Epair of any other(?) material: 0.7-0.4 eV. Basic reaction forming an Ag-O-Cs cathode

$$Ag_2O + 2\ Cs \rightarrow 2\ Ag + Cs_2O$$

- Optimal Cs:O ratio = 2:1; process proceeds at T ~ 100 C°-300 C°. Structure of Ag_2O amenable to incorporation of Cs. *Ag atoms remain in the lattice, essential for the energetics.*

• PMT S-1 formation: Ag deposition makes it difficult to be transparent to visible light or p.e. escape.

–>No need to preserve semi-transparency or electron escape; Optimize for semiconducting and Ohmic transport properties rather than semi-transparency and photoemission.

~mm's thick Ag-O-Cs tile cooled to <1K°: Dark Matter or coherent-ν detector(?) ~100 electrons for ~50 eV deposited. Deposition on Si may lower Ep by band bending or the electrostatic potential induced by protecting it with an atomic layer of BN, with a single layer graphene electrode on top of the BN.

A. Lallemand and M.Duchesnes, Z. angew. Math Phys. 1, 195 (1950)
N.A. Sloboleva, Radio Eng. Electron. 4, 11, p204 (1959)
Sommer, A., "Photoemissive Materials" pages 133-144 [1968] J.Wiley

Stochiometric Melt Growth

Cs_3Sb Melts: crystals have been made through stochiometric melts – see the phase diagram as shown above – our test melt looked good but the quartz vessel cracked before we could saw it open in a glove box. *Melts likely full of defects without extremely long, gradual processing and very pure reagents.*

Ag-O-Cs Melts: Calculated Phase diagrams for Ag_2O + 2Cs have similar melt properties but to our knowledge have not been made into crystals.

- The forming temperatures for Ag-O-Cs are low – between 100-200 °C.
- Care is required as silver oxide can be dissociated with visible light.
- Reagent grade (99.995) silver oxide costs ≤$1k per 200g. Reagent grade Cs(99.995) as metal pieces is ≤$80/g (reagent grade Sb(99.999) in mm beads is ≤$10/g.)

J.Scheer and P.Zalm, Philips Res.Rept. 14, 143 (1959)

ALD

Atomic Layer Deposition

- ALD (atomic layer deposition) fabrication is now standard in many VLSI fabs.

- 30cm wafer tools are standard

- ALD tools to coat very large areas (~1-2m^2) have been developed for advanced image displays(TV/video).

- ALD is the best method to create pure conformal atomic films.

- ALD Alternatives:

- MOCVD (metal-organic chemical vapor deposition) nearly as good, is faster, and cheaper but does not create as pristine a material.

- Approximate atomic layer PVD (physical vapor deposition) tools are being developed for introducing materials not amenable to ALD precursors, such as Cs.

ALD-2

Cs_3Sb/S-11: Normally Sb is thermally deposited to a desired thickness, and then Cs vapor diffuses into the Sb so that there are Cs and defect density gradients through even a very thin film. This cannot create a perfect semiconducting material, in contrast to ALD or CVD.

- Conformal atomic films of elemental Sb: $SbCl_3$ and $(Et_3Si)_3Sb$ as precursors.
- Substrates include SiO_2 or SiN film coated w/ (preferably) nichrome as a back electrode.
- Cs introduced as a vapor after each Sb layer only as sufficient for a single Cs_3 layer -far more ideal than the usual way of photocathode fabrication.

Zhuiykov S, Kawaguchi T, Hai Z, et al. Interfacial engineering of two-dimensional nano-structured materials by atomic layer deposition. Appl Surf Sci. 2017;392:231–243.

Ag-O-Cs/S-1: Cs is applied by PVD alternating with 2 ALD films of silver oxide Ag_2O.

- pseudo-lattice match on n-type or p-type Si electrodes, depending on Ag-O-Cs layer is p- or n- (nominally due to dislocations) to form a diode detector..
- AgO deposited by pulsed organometallic precursor (hfac)Ag(PMe_3) + O_3 200 °C
- Growth rate 0.33 Å/cycle. Cycle~0.3s with Cs deposition
- ~30s/nm, realistically 2 µm per 24 hour day, over 1-2 m^2 areas.
- Cs vapor must be stochiometrically precise to form the weakly bound semiconductor with as few defects as possible. A ~30 µm x $2m^2$ film could be made in about 3 weeks of 75% continuous operation.

T.V. Ivanova et al. Catalytic Performance of Ag2O and Ag Doped CeO2 Prepared by Atomic Layer Deposition for Diesel Soot Oxidation, Coatings 2018, 8, 237; doi: 10.3390/coatings8070237

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Summary:

• Low Workfunction Semiconductors normally used as photocathodes: potential as low energy calorimetric diode or drifted ionization detectors

• Cs_3Sb has potential to be a room temperature alternative to Si diodes or even Si APD. A "Cs_3SbPM" alternative to SiPM would not need much cooling in many applications.

• Cs_3Sb and Ag-O-Cs have potential to be higher rate detectors than Si due to the high mobility and nearly equal electron and hole mobilities.

• Ag-O-Cs may offer sub-eV energy deposition detection.

• Cs_3Sb and Ag-O-Cs - in thin film photocathodes – are radiation resistant.