Diamond-based thermotunnel devices for hostile environment energy conversion

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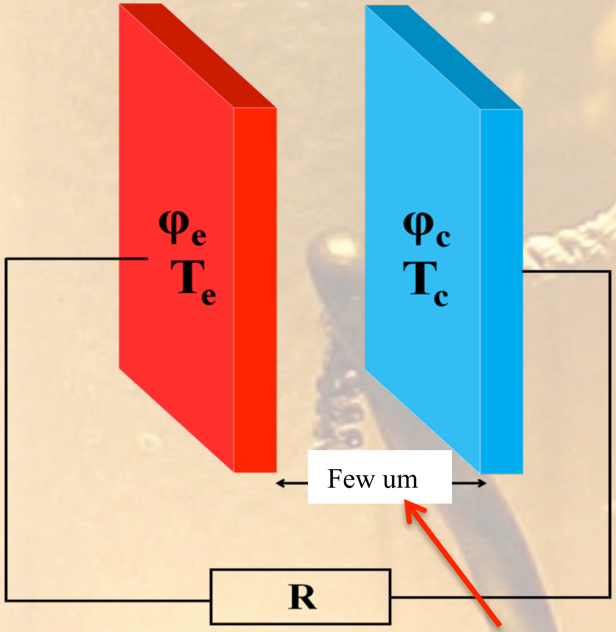
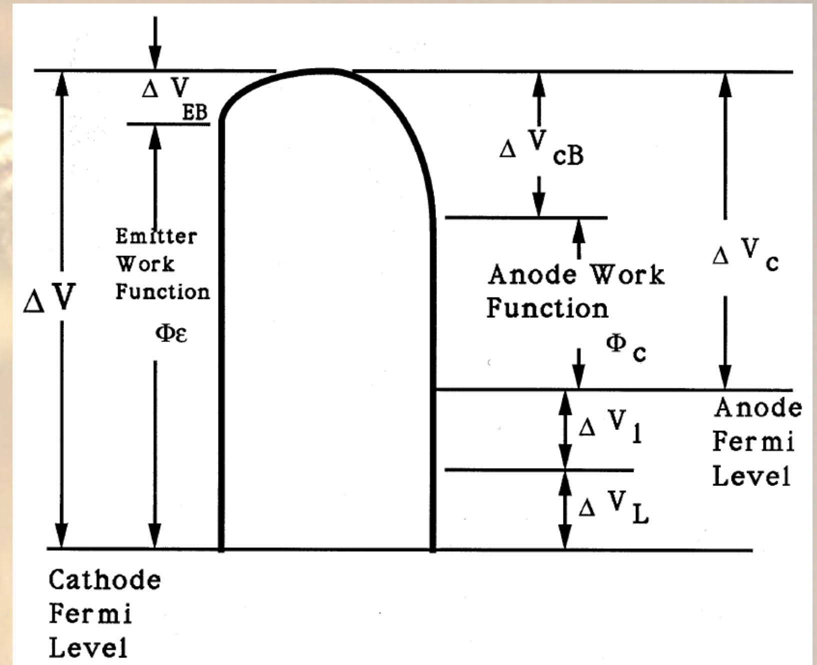
Thermionic energy conversion





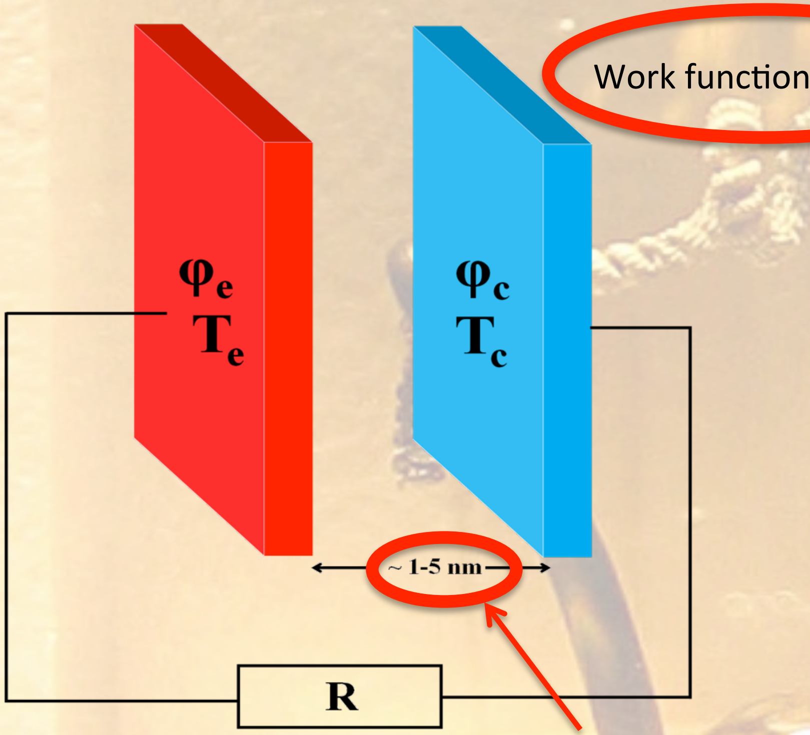
◆ A heat engine which utilises the electrons as a working fluid and converts the heat directly into electricity.

◆Performance is limited since a combination of high emission current and high output voltage (difference of electrodes work function) is desired for the high output power density.

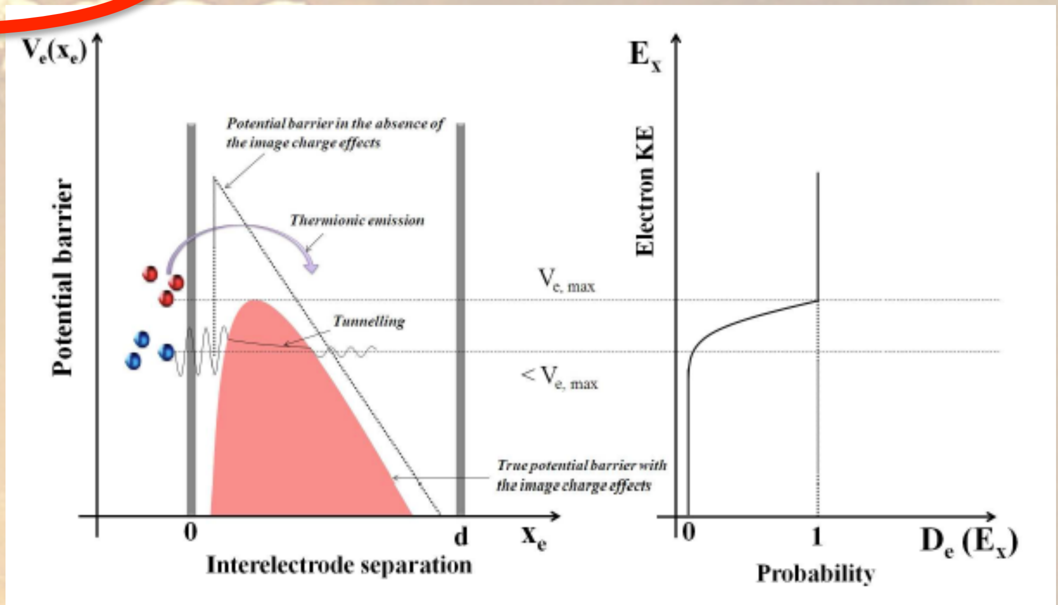
◆Lowering the surface barrier in conventional designs doesn't always help. Although the electron emission dramatically increases, the difference in the electrodes work function also reduces in addition to increment in severe space charge effects.

Angelo and Buden, Space Nuclear Power (Orbit Book Comp., Malabar, Florida, 1985).

Thermo-tunnelling device



Work function <1.5 eV



◆Very much identical to conventional thermionic converter; however the inter-electrode spacing lies in nanometer regime, which allows the tunnelling of electrons.

◆Temperature has even stronger impact upon the tunnelling in comparison to emission and thus without much compromising with the output voltage, a very high output power density is achievable.

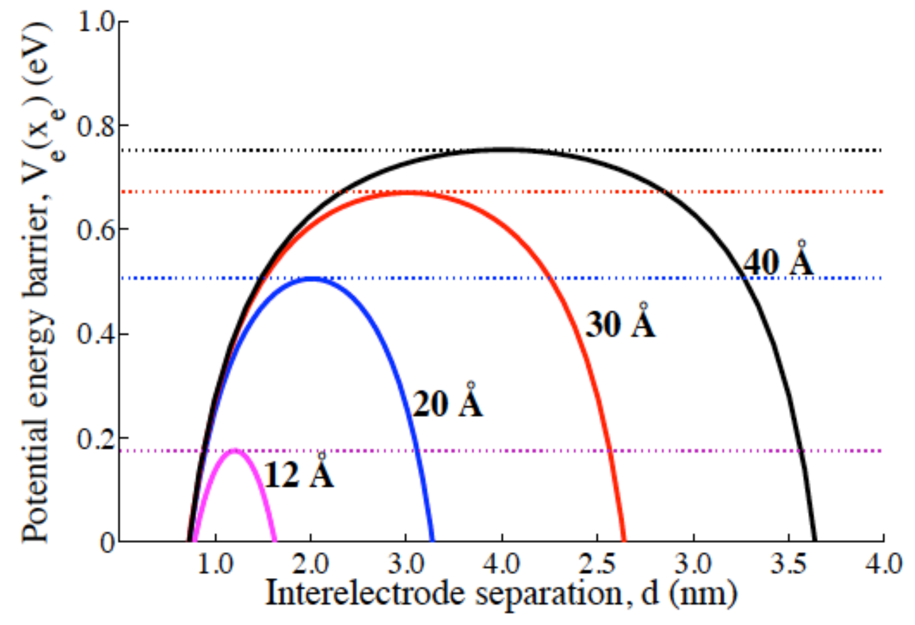
◆ The space charge effects are absent and even a minor reduction in the emission barrier can significantly improve the device performance.

◆Major problem is achieving and maintaining the nanometer vacuum gap, at high temperatures swelling of surface and closing the vacuum gap.

Inter-electrode potential profile: effect of spacing and work function

$$V_e(x_e) = \phi_e - \frac{x_e}{d}\left(eV_{\text{bias}} + \phi_e - \phi_c\right) - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{4x_e} + \frac{1}{2}\sum_{n=1}^{\infty}\left(\frac{nd}{n^2d^2 - x_e^2} - \frac{1}{nd}\right)\right]$$

X_e, distance of an electron from emitter



$\Phi_e=\Phi_c=1$ eV

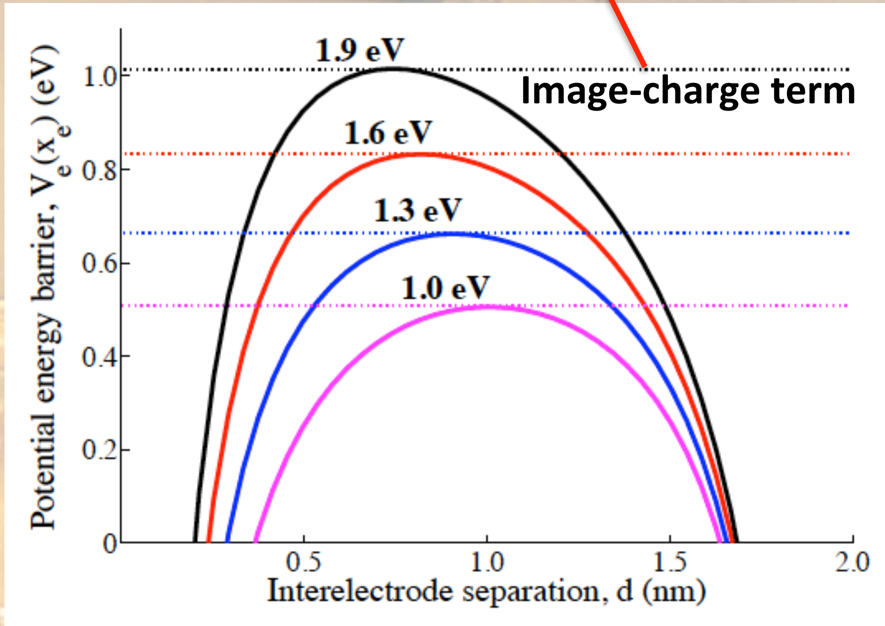


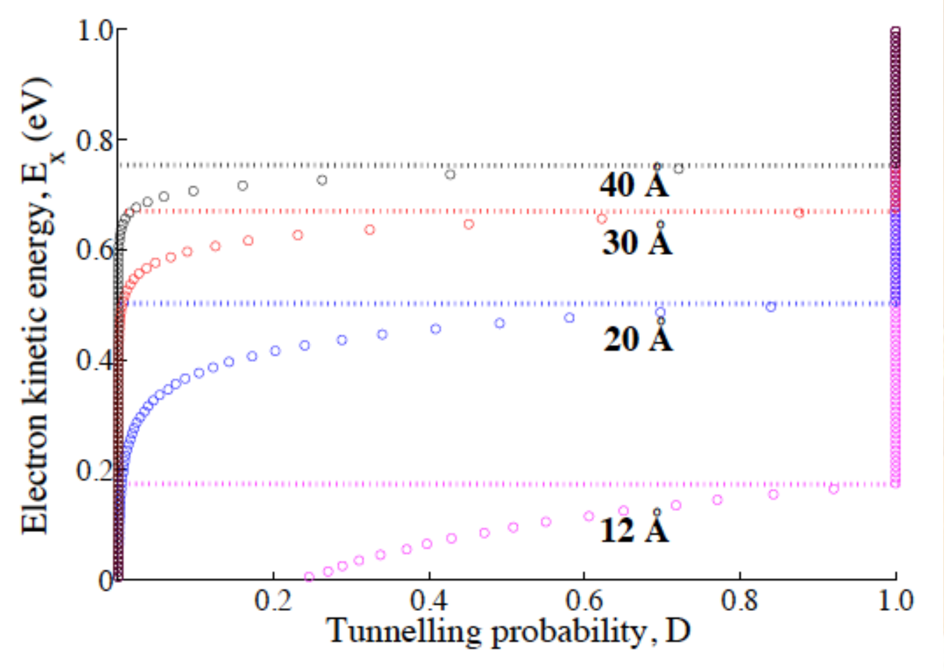
Image-charge term

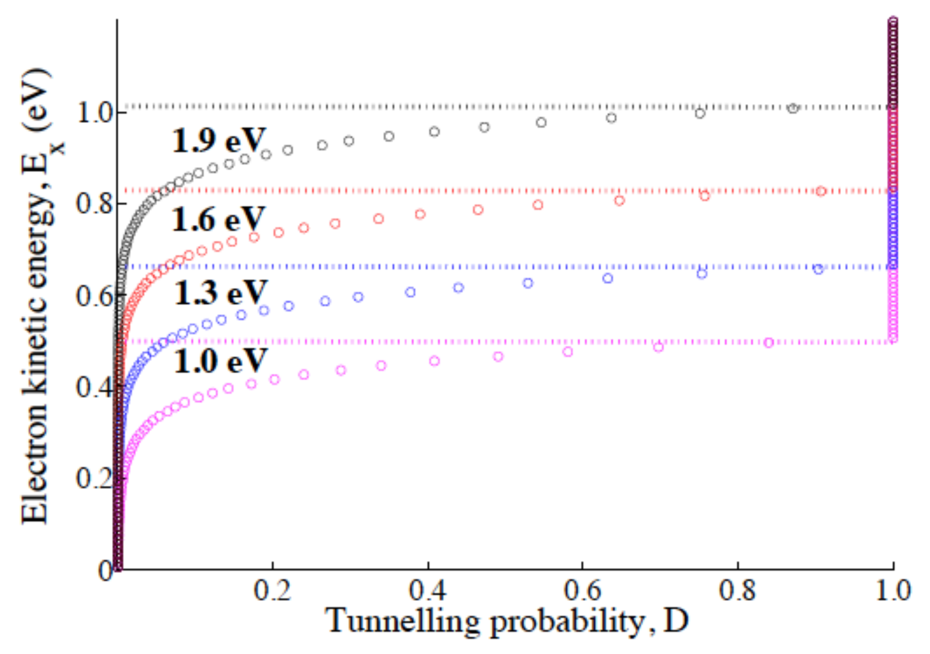
$\Phi_e=\Phi_c= \Phi$, d=20 Å

Electron tunneling probability as a function of KE: effect of spacing and work function

Tunneling probability (WKB approximation)

$$D_{\mathrm{e}}(\mathrm{E_x}) = \exp\left[-\frac{2}{\hbar}\int_{x_{\mathrm{e1}}}^{x_{\mathrm{e2}}}\sqrt{2m\left[V_{\mathrm{e}}(x_{\mathrm{e}})-E_{\mathrm{x}}\right]dx_{\mathrm{e}}}\right] \quad \text{if} \quad E_{\mathrm{x}} < V_{\mathrm{e,max}}$$
$$= 1 \quad \text{otherwise,}$$





Thermo-tunnel device operation

Emitter tunnelling current

$$J_{\text{etun}} = e \int_{-\infty}^{V_{\text{emax}}} N_{\text{e}}(E_{\text{x}}) D_{\text{e}}(E_{\text{x}}) dE_{\text{x}},$$

where

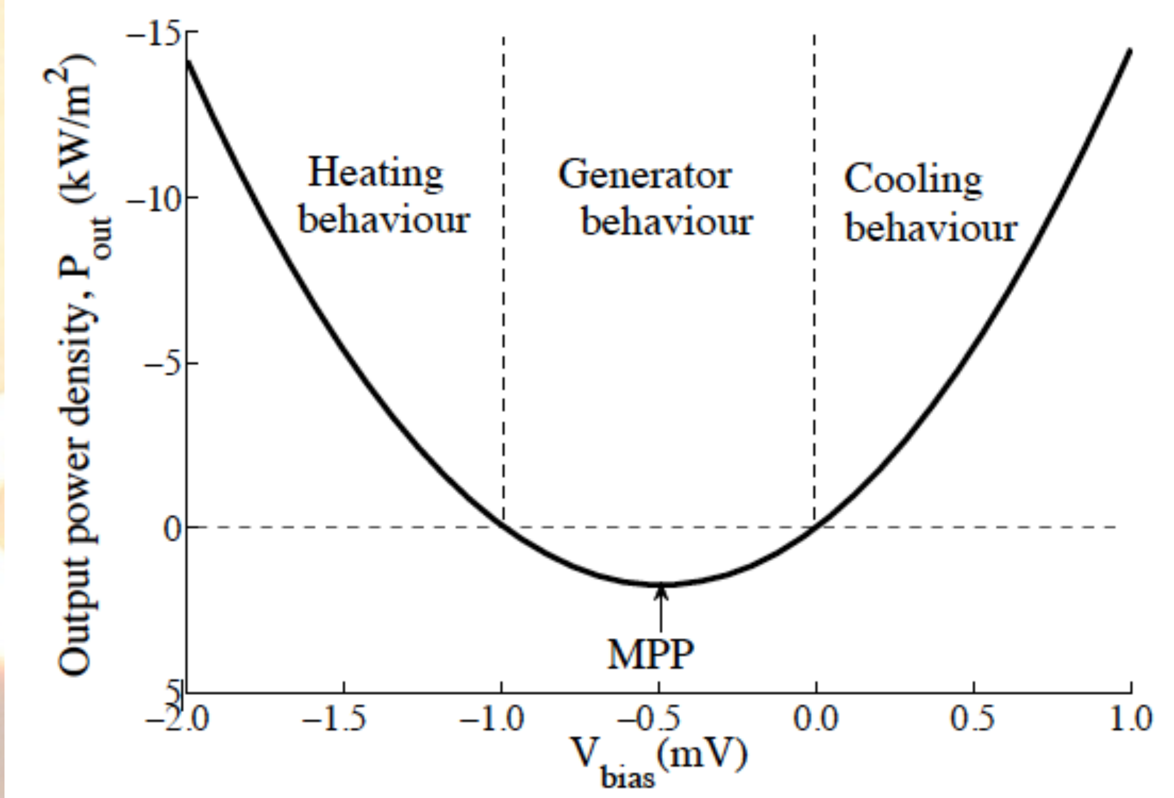
$$N_{\text{e}}(E_{\text{x}}) = \frac{4\pi m k_{\text{B}} T_{\text{e}}}{h^3} \ln\left[1 + \exp\left(\frac{-E_{\text{x}}}{k_{\text{B}} T_{\text{e}}}\right)\right]$$

Collector thermionic current

$$J_{\text{ether}} = e \int_{V_{\text{emax}}}^{\infty} N_{\text{e}}(E_{\text{x}}) D_{\text{e}}(E_{\text{x}}) dE_{\text{x}}$$

Thermal power density of emitter electrons (emitter cooling)

$$Q_{\text{e}} = \int_{-\infty}^{\infty} (k_{\text{B}} T_{\text{e}} + E_{\text{x}}) N_{\text{e}}(E_{\text{x}}) D_{\text{e}}(E_{\text{x}}) dE_{\text{x}}.$$



“Contribution of electrons can be calculated in the similar way.”

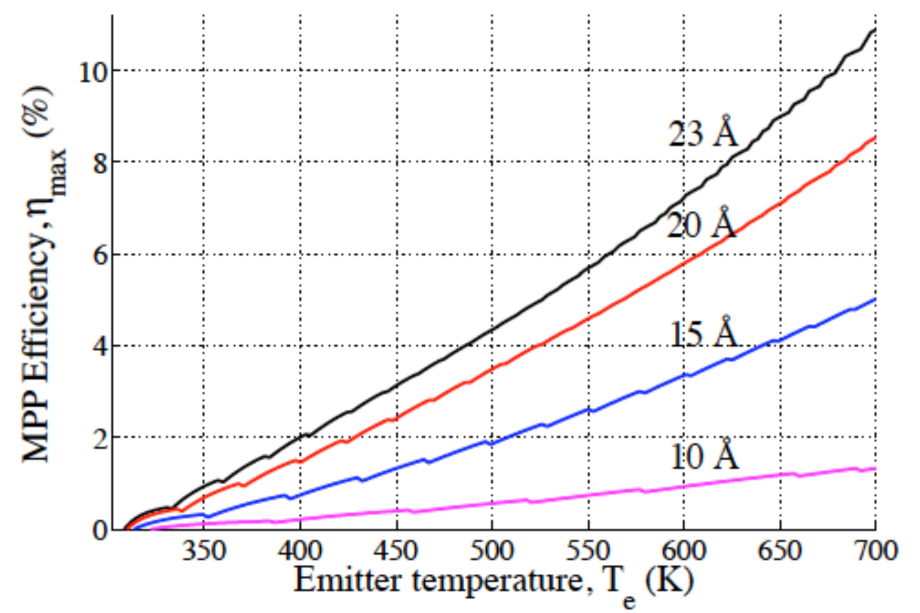
$$J_{\text{tot}} = J_{\text{e}} - J_{\text{c}}$$

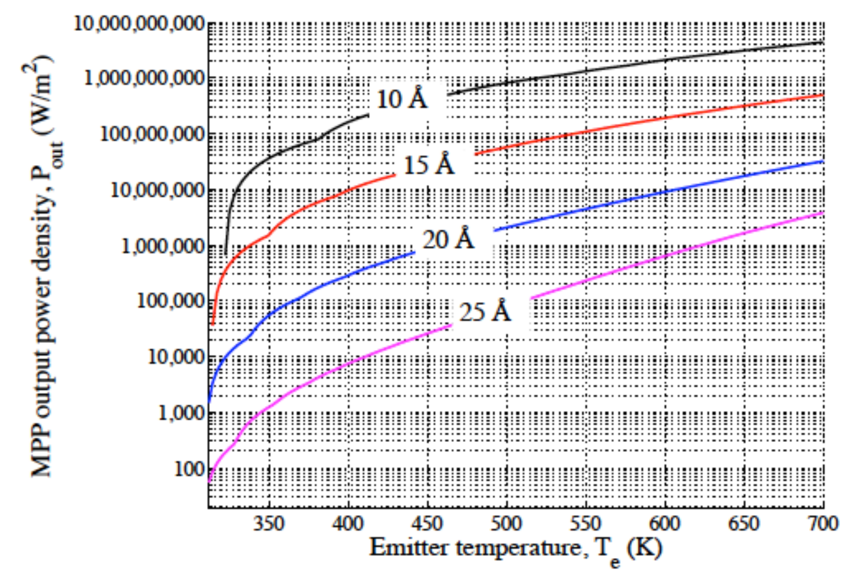
$$Q_{\text{net}} = Q_{\text{e}} - Q_{\text{c}}.$$

$$P_{\text{max}} = J_{\text{max}} \times V_{\text{max}}$$

$$\eta_{\text{max}} = \frac{P_{\text{max}}}{Q_{\text{tot}}}.$$

Efficiency and output power density-I

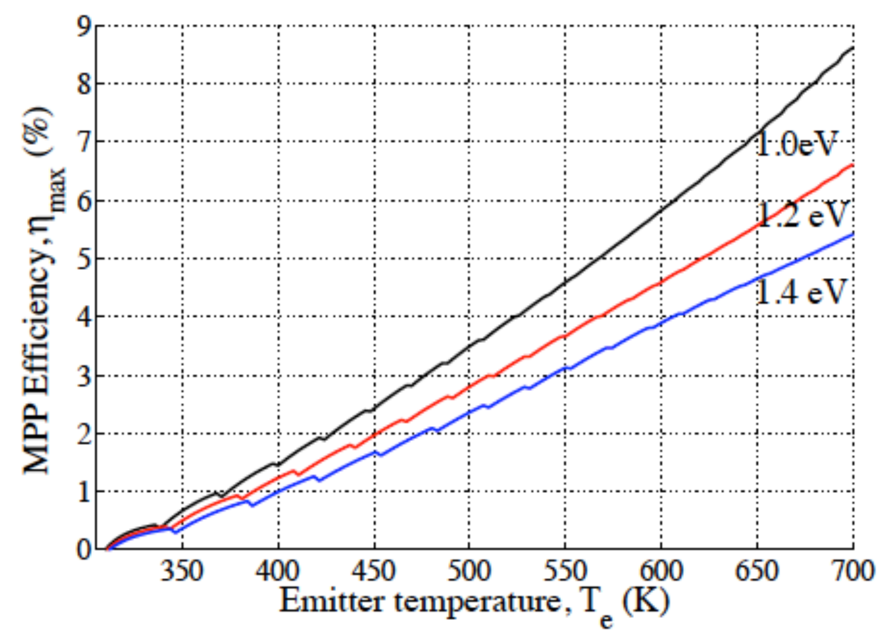


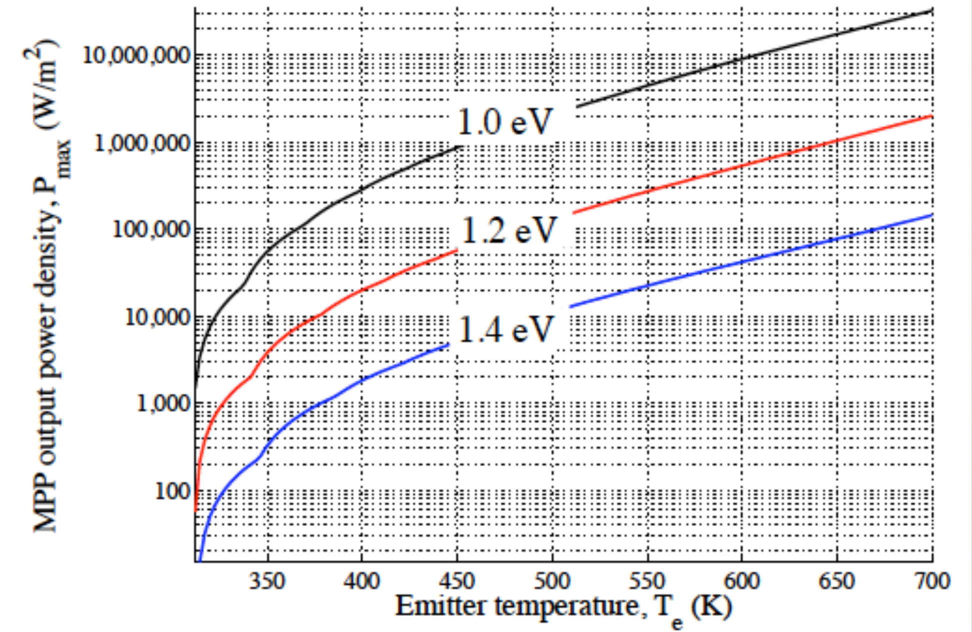


$\Phi_e=\Phi_c=1$ eV and $T_c=300$ K

- Efficiency increases with the vacuum gap thickness but the output power density goes down.
- Increase in the emitter temperature improves the efficiency as well as output power density; however, not necessarily suitable for thin vacuum gap.

Efficiency and output power density-II

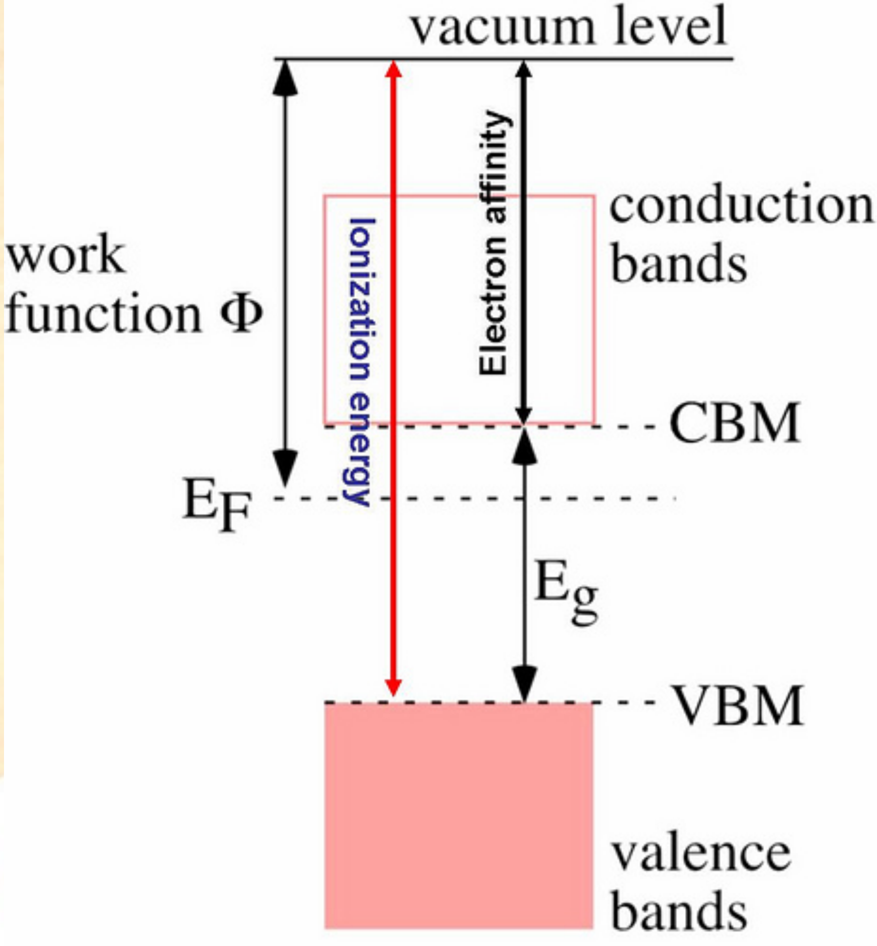




$\Phi_e=\Phi_c=\Phi$, d=20 Å and T_c=300 K

- High work function of the emitter electrode reduces the efficiency and output power density and therefore low work function electrodes are highly recommended.

Lowering of electron emission barrier of diamond



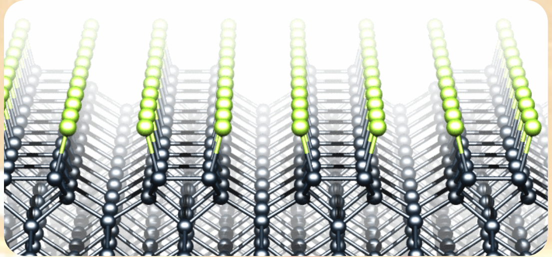
$$\Phi = \chi + (E_{CBM}-E_F)$$

Some common examples of + and – electron affinites:

◆Halogens (F, Cl), oxygen: PEA (1.5-3.5 eV)

◆H-termination: NEA of ~1.3 eV, stable upto 600 °C (in vacuum)

◆Alkali halides and oxides: NEA upto -3eV, weakly stable



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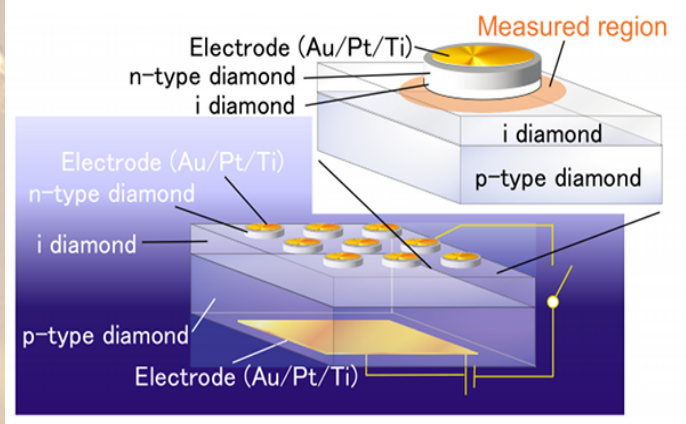
Ultra thin coatings of metals and their oxides

- Compatible with semiconductor device fabrication techniques.
- Due to smaller electronegativities in comparison to those of C and O atoms, there is a possibility of significant reduction in electron affinity (χ).
- Chemically and thermally stable.



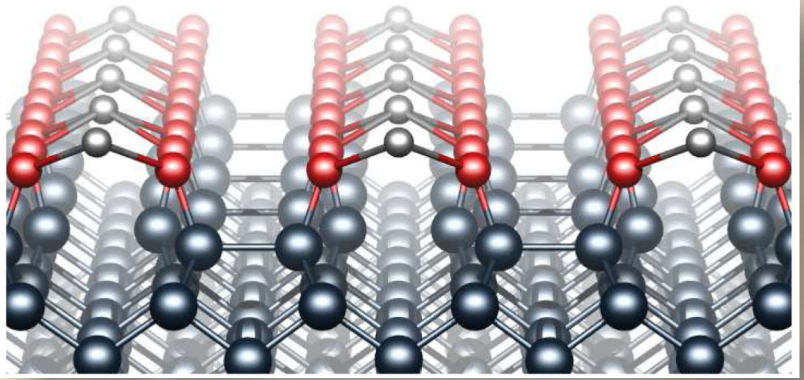
Metals: Cu, Ni, Ti, V, Ag, Al, Ga, Co, Fe, Au, Zn, Zr
Oxides: Cu, Ni, Al, Ti, Zn, Zr

Schmid, et al., Phys. Rev. Lett. 99, 196104 (2007).
Baumann, et al. , J. Appl. Phys. 83, 2072 (1998).
Weide, et al., Phys. Rev. B 49, 13629 (1994).
Tiwari, et al., Phys. Rev. B 86, 155301 (2012).

Predicted affinity and stability of new metal oxide-based coatings

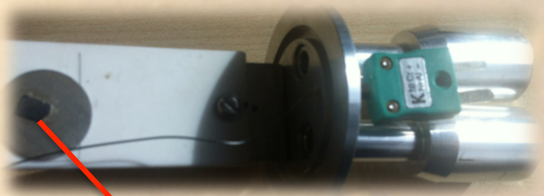
Metal	Oxide Stoichiometry (O:TM)	Adsorption Energy E_{ads}(eV)	Electron affinity χ
Cu	**1:2**	**—2.35**	**—1.28**
Ni	**1:2**	**—3.80**	**—0.16**
Ti	**1:4**	**—7.60**	**—3.10**
Zn	**1:2**	**—1.13**	**—3.05**

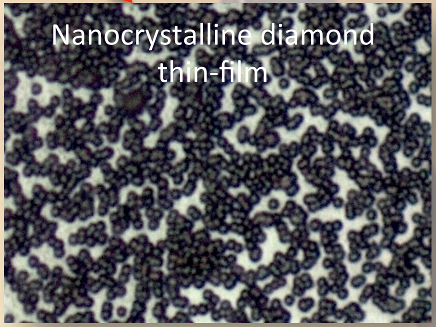
Calculated using the ‘AIMPRO’ DFT code



1. Tiwari, et al., Europhys Lett. (in press).
2. Tiwari, et al., MRS proceedings 1511, (2012).
3. Tiwari et al., Mat. Sci. Forum 717, 1311 (2012).

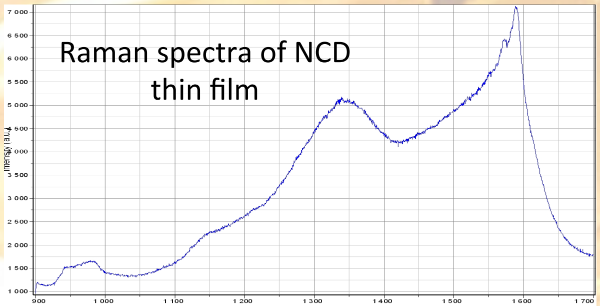
Aims of ongoing experimental investigation





Nanocrystalline diamond thin-film

- ➢ Lowering the work function of diamond to an acceptable level, ideally ~1 eV to enhance the electron emission at low temperatures.
- ➢ Examination of temperature induced surface roughness of diamond surface, critical for maintaining the nanometre vacuum gap above room temperature.

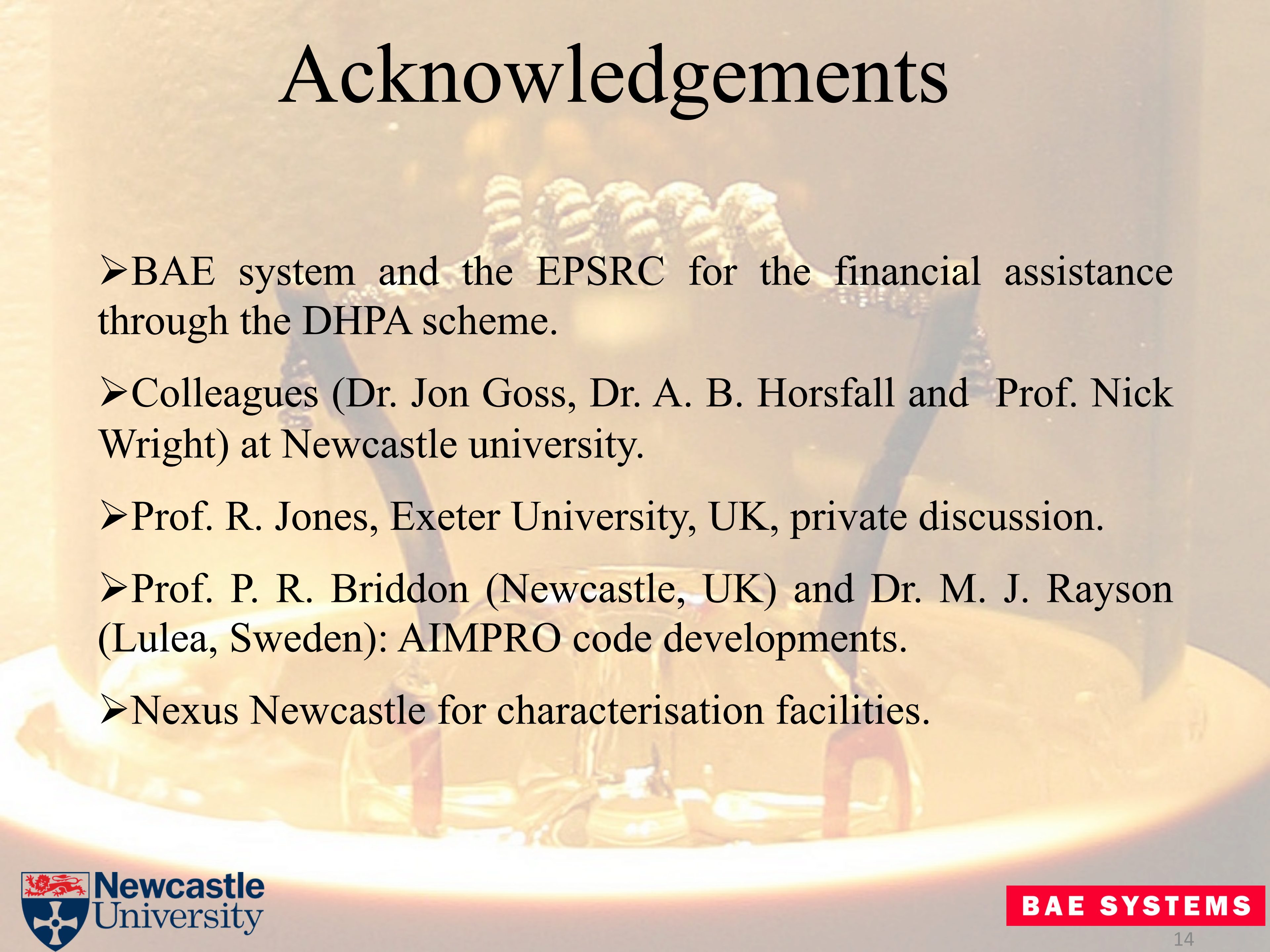


Raman spectra of NCD thin film

- ➢Realisation of solid-state device structures with an acceptable power density and efficiency.

Concluding remarks

- A physical modelling has been developed and evaluated for the functioning and parameter optimisation of thermo-tunnelling devices.
- Thermo-tunnelling devices possess considerable potential since the tunnelling effect allows a high emission current density while retaining the substantial voltage output. Such devices, if realised experimentally, have the capability of outperforming the thermoelectric devices.
- However, in addition to maintaining a very small inter-electrode vacuum gap (few nanometers), low work function diamond electrodes are required.
- DFT analysis suggest that use of ultra-thin coatings of transition metals oxide can substantially lower the emission barriers (3 eV) of diamond electrodes and exhibit good thermodynamic stability.
- A detailed experimental investigation is continued to deal with several challenges involved in the realisation of thermo-tunnelling devices.



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