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Enhanced thermionic energy conversion and thermionic emission from doped diamond films through methane exposure☆☆

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ABSTRACT

Thermionic electron emitters are a crucial component in applications ranging from high power telecommunication, electron guns, space thrusters and direct thermal to electrical energy converters. One key characteristic of diamond based electron sources is the negative electron affinity (NEA) properties of hydrogen terminated surfaces which can significantly reduce the emission barrier. Nitrogen and phosphorus doped diamond films have been prepared by plasma assisted chemical vapor deposition on metallic substrates for thermionic emitter application. Electron emission current versus temperature was measured and analyzed with respect to the Richardson–Dushman relation, with work function and Richardson constant deduced from the results. Initial emission measurements up to 500 °C in vacuum were followed by emitter characterization while the sample was exposed to methane. Vacuum measurements indicated a work function of 1.18 eV and 1.44 eV for phosphorus and nitrogen doped diamond films, respectively. Introduction of methane resulted in a significant increase of the emission current which was ascribed to contribution from ionization processes which increase charge transfer from the emitter surface. This phenomenon was utilized in a thermionic energy conversion structure by introduction of methane in the inter electrode gap where a two-fold increase in output power was observed upon introduction of the gaseous species.

1. Introduction

Recently, efficient electrical power generation alternatives have become a topic of intensified research [1,2]. With today's coal powered plants averaging 32% efficiency harnessing their waste heat could increase total electrical power output thus increasing plant efficiency [3–5]. While nuclear power plants produce heat of ~300 °C employing thermo-chemical cycles would allow thermal upgrade to 550 °C usable for thermionic devices [6]. Direct conversion of heat into electricity can then be achieved by a process termed thermionic energy conversion [7]. Here, an electron emitter is separated from a collector by a vacuum gap and held at a temperature sufficient for sustaining significant current densities. It has been shown that efficiency of such a device can exceed 30% but cannot surpass 90% of the Carnot cycle efficiency [8].

Crucial to operation is a thermionic electron source operating efficiently in the desired temperature range. For metallic electron emitters at low extraction fields and temperature, T, the emission current density, J(T), is related to the work function, φ, and the emission or Richardson constant, A_R, by the Richardson–Dushman relation [9].

$$J(T) = A_R T^2 e^{-\frac{\varphi}{k_B T}}$$
$$A_R = \frac{4\pi m_o k_B^2 e}{h} \quad (1)$$

With Boltzmann's constant, k_B, electron effective mass, m_0, electronic charge, e, and Planck's constant, h, a theoretical value of 120 A/cm^2 K^2 is obtained for the emission constant, A_R.

Practical electron sources often employ a thermionic cathode of metallic composites and oxides with a typical work function of 2 eV at an operating temperature of 1000 °C [10–12]. Initial demonstrations of thermionic energy converters operated at 1260 °C employing tungsten impregnated with $(Ba/Sr)CO_3$ electrodes in a close spaced configuration, i.e. gap distances of less than 25 μm [13].

Preparation of low work function electron sources is the crucial step in providing an approach to moderate temperature thermionic energy conversion. While practical metal based emitters employ adsorbates or oxides for reduced work functions, for semiconductor emitters lowering of the surface electron affinity reduces the emission barrier. The barrier to extracting an electron from the conduction

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band minimum (CBM) to the vacuum level away from the surface defines the electron affinity χ and contributes to the work function of the material. Elimination of this surface barrier results in a low effective work function and enables emission of electrons from the CBM into vacuum. While most semiconductors exhibit a positive electron affinity surface where electrons at the bottom of the conduction band are bound by several eV, diamond surfaces, as it has been well established [14–16], can obtain negative electron affinity (NEA) properties where the vacuum level is positioned below the CBM. Techniques most commonly employed to induce NEA characteristics in diamond include exposure to a hydrogen plasma, and the resulting H-termination establishes a dipole layer which modifies the electrostatic potential outside the surface [17]. The NEA character in conjunction with suitable donors can then be employed to engineer a low effective work function thermionic emitter based on diamond films [18].

While low effective work functions are generally preferred for electron emitters, thermionic emission is also limited by space charge that develops from electrons accumulating at the emitter–vacuum boundary. This space charge layer impedes successive charge carriers from being released into the inter-electrode gap and substantially reduces the collected electron current and thus converter efficiency. Two approaches have been considered for mitigation of the space charge layer: employment of a narrow gap configuration or incorporation of positive ion species to neutralize the negative charge cloud adjacent to the emitter surface. However, the narrow gap spacing (<5 μm) required to overcome space charge limitations results in systems difficult to manufacture. Neutralizing space charge by introduction of cesium vapors has been successfully used in thermionic energy converter applications and made practical apparatus feasible as macroscopic electrode separations of 0.5–2.4 mm could readily be engineered [19]. Introduction of cesium vapor had a secondary advantageous effect of reducing the work function of the metallic emitter surface. For clean tungsten [110] with a work function of 5.25 eV a significantly reduced emission barrier of ~1.45 eV was observed under cesium exposure [20]. Similar observations of molybdenum electrodes exposed to cesium vapor at 1 mTorr in a converter configuration presented an emitter work function of 2.2 eV at 1200 °C while the collector at 550 °C was characterized by a work function of 1.7 eV [21].

In this study we describe a new approach to mitigate the space charge layer and enhance the efficiency of a moderate temperature thermionic energy converter. The new concept is to incorporate molecular assisted charge transport between the doped diamond emitter and collector surfaces. Inter electrode molecules will acquire an electron at the emitter surface establishing a transient negative ion and then transport the charge across the gap to the collector surface. For low work function cesiated metallic surfaces charge transfer to positive hydrogen ions or neutral hydrogen atoms by scattering has been reported with efficiencies up to 40% [22]. As nanostructured NEA doped diamond constitutes a low effective work function material, exposure of its emitting surface to suitable gaseous species should result in enhanced emission due to surface ionization processes. Additionally, electron transport by negative ions should reduce space charge and mitigate limitations due to this effect.

2. Experimental

In this study thermionic emitters were prepared by deposition of phosphorus or nitrogen doped diamond films on 25 mm diameter metallic (molybdenum) substrates.

Phosphorus doped diamond layers were synthesized at Hasselt University by plasma assisted chemical vapor deposition utilizing phosphine as dopant source. Film growth was performed at 1130–1200 °C. Exposure of the doped diamond film to a hydrogen plasma resulted in NEA surface properties.

Nitrogen doped diamond films were prepared at Arizona State University by a similar technique utilizing nitrogen as dopant source. The complete emitter structure comprised a nitrogen incorporated nanocrystalline diamond interface layer, a top nitrogen doped diamond layer and hydrogen surface termination. Ultrasonication of the metallic substrate in a nanodiamond suspension promoted nanocrystalline morphology for the initial layer. Under the addition of Ar in the gas phase renucleation was enhanced during growth of the nanocrystalline layer [23]. Low emitter resistance was established with concurrent introduction of methane and nitrogen. For the top doped diamond layer adjustment of growth parameters included establishing hydrogen gas flow while eliminating argon and reducing methane flow. An optical pyrometer recorded growth temperatures of 860–900 °C during deposition. Film growth was concluded by hydrogen plasma treatment of the final structure.

Thermionic electron emission measurements were conducted in a UHV system with base pressure $<2\times10^{-10}$ Torr. The diamond emitter was mounted on a radiatively heated sample stage, and an optical pyrometer was employed to control sample temperature. In measurement configuration the 1 cm^2 emitter and collector were separated by a 50 μm BN spacer. Electrical contacts were then made in vacuo and electron emission was recorded with a Keithley 2400-LV source-measurement unit. Measurement of uncoated surfaces in the same configuration established a background current of less than 10 pA up to 950 K with an applied bias of 20 V. The same system allowed introduction of various gaseous species during emission measurements. Pressure in the measurement chamber was controlled by adjusting gas flow rate through a mass flow controller and pump rate by a turbomolecular pump. The baseline noise level was determined by applying a potential of 20 V between two uncoated substrates positioned as emitter and collector and an electrical noise of less than 10 pA was observed in a methane ambient up to 700 mTorr and temperatures up to 950 K.

Electron emission data was acquired versus temperature and analyzed with respect to the Richardson–Dushman relation for both vacuum gap and with inter electrode gaseous species for molecular transport. For vacuum measurements data evaluation allowed extraction of material work function φ and Richardson constant A_R by a fitting procedure.

3. Results and discussion

The major focus of this study is the role of inter electrode gas species to enhance electron emission through molecular transport in an energy conversion device. Highly engineered low effective work function emitters based on phosphorus or nitrogen doped diamond thin films have been prepared with negative electron affinity (NEA) surface characteristics and we will elaborate on NEA effects and doping in the following sections.

3.1. Vacuum thermionic electron emission results

Evaluating nitrogen and phosphorus doped diamond films with respect to the law of Richardson–Dushman indicates the significance of electronic material parameters to thermionic electron emission.

Fig. 1 displays data plots and their corresponding fit (line) for thermionic electron emission from a nitrogen and phosphorus doped diamond film on a metallic (molybdenum) substrate. Two key aspects are evident. The phosphorus doped diamond film exhibits a significantly lower work function of 1.18 eV compared to a value of 1.44 eV for the nitrogen doped film. Conversely, the nitrogen doped diamond emitter exhibits a significant Richardson's constant of 4.05 $A/cm^2\,K^2$ while the phosphorus doped film shows a value of 0.003 $A/cm^2\,K^2$.

Addition of nitrogen during UNCD film growth will result in preferred incorporation of nitrogen into its sp^2 bonded carbon grain

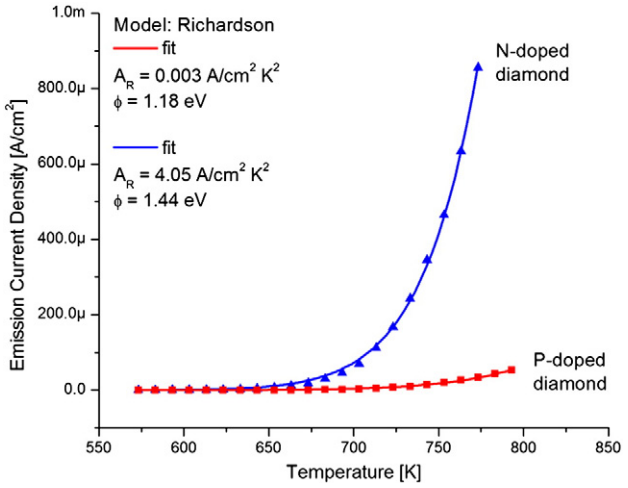

Fig. 1. Thermionic emission data from typical phosphorus and nitrogen doped diamond films and corresponding fit to the data using the Richardson–Dushman expression. The deduced work function and Richardson's constant are indicated.

boundaries not necessitating substitutional donor states of nitrogen into the crystal lattice [24]. With accumulation of nitrogen in the grain boundaries abundant states in the band gap increase conduction which has been shown to be of semimetallic nature [25]. For the top diamond layer nitrogen is incorporated into single substitutional sites producing donor levels 1.7 eV below the conduction band minimum. The high density network of conducting grain boundaries can then effectuate efficient means of electron injection into the ~50 nm thick, top doped diamond layer. Phosphorus doped diamond films, directly synthesized on a metallic substrate are characterized by high sp^3 bonded carbon concentration and exhibit increased electrical resistivity with correspondingly lower Richardson constant. Employing a similar nitrogen incorporated nanocrystalline layer for phosphorus doped diamond emitter structures did not show an increase in the Richardson constant which was in part attributed to a compensation of donors through defects [26,27].

We note that for a semiconductor the theoretical value for Richardson's constant, A_R, should be modified by substituting the electron effective mass for the free electron mass, m_0 [28]. For diamond, longitudinal and transverse electron masses were determined to be 1.3 m_0 and 0.36 m_0, respectively [29]. Replacing m_0 in A_R with the suggested lower effective electron mass yields a significantly reduced emission constant of 43.2 A/cm^2 K^2 for diamond. Experimental data from phosphorus doped diamond indicated a slightly smaller value for the transverse effective mass of 0.306 m_0 [30]. Even with these corrections it seems likely that effective mass effects are not the most significant effects in the measured results for the doped diamond films. This has led us to suggest that the resistance of the film limits the emission and is reflected in a reduced Richardson's constant.

3.2. Thermionic electron emission in gaseous environments

The new approach described here is to enhance thermionic electron emission current densities by charge transfer to molecular species in the inter electrode gap. Molecular species introduced adjacent to the emitter enables surface ionization and consequent charge transfer. In the ionization process an electron is transferred to an unoccupied molecular orbital establishing a negative ion state with lifetime τ.

If resonant electron capture occurs an electron will populate the species long compared to the transit time of an electron through regions of molecular dimensions. Traversing a distance of 3 Å for a 1 eV electron will take 5×10^{-16} s compared to vibrational periods of 10^{-14} s establishing a resonant process for charge transfer for the transient negative ion [31]. Evaluation of the neutral molecular state M with respect to its negative ion M^- is expressed through the electron affinity (EA) of their corresponding ground states. The EA of M is considered positive if its negative ion state M^- lies energetically below M, indicative of its stable anion. It also represents the binding energy of the excess electron in the negative ion.

In the following we explore using nitrogen and methane as gas species in the inter electrode gap. For the nitrogen molecule a negative electron affinity of −1.8 eV has been reported corresponding to an unstable negative ion [32]. Recording thermionic electron emission in nitrogen ambience from 10 mTorr to 1 Torr presents no clearly identifiable emission enhancement in agreement with the unstable N_2^- anion (Fig. 2).

With a slightly positive EA of 0.083 eV methane can produce stable negative ion states that significantly affect thermionic electron emission for doped diamond films [33]. Separating phosphorus doped diamond film emitter from a metallic collector by 50 μm and introducing methane at various pressures into the gap enhances thermionic emission behavior as shown in Fig. 3.

Thermionic emission from the hydrogenated NEA P-doped diamond film as plotted in Fig. 3a is characterized by significant current densities >100 μA/cm^2 at 450 °C with a small increase in emission current as methane pressure increases to 500 mTorr. In contrast, a much more significant increase is observed at 500 °C. Here, as emission current >200 μA is measured in vacuum and as the methane pressure is increased the emission current reaches ~700 μA at 500 mTorr indicative of efficient charge transfer from the emitter. Methane ionization can be accompanied by a dissociation process where a single hydrogen atom separates from the molecular species. Observation of methane dissociation on metallic surfaces has been reported with a corresponding energy barrier of 0.66–1.12 eV [34,35]. In the case of nitrogen doped diamond films a similar emission behavior upon methane exposure is observed (see Fig. 4).

The emission current density from nitrogen doped diamond as a function of temperature, as shown in Fig. 4, is fit with the Richardson–Dushman relation, and the work function, φ, and emission constant, A_R, are determined for the case of vacuum emission and emission in the presence of methane gas. Vacuum thermionic electron emission from the nitrogen doped diamond emitter displays a significant emission current density of ~3 mA/cm^2 at 520 °C corresponding to a low work function of 1.3 eV and Richardson constant of 1 A/cm^2 K^2. Applying the same analysis to the results for emission under

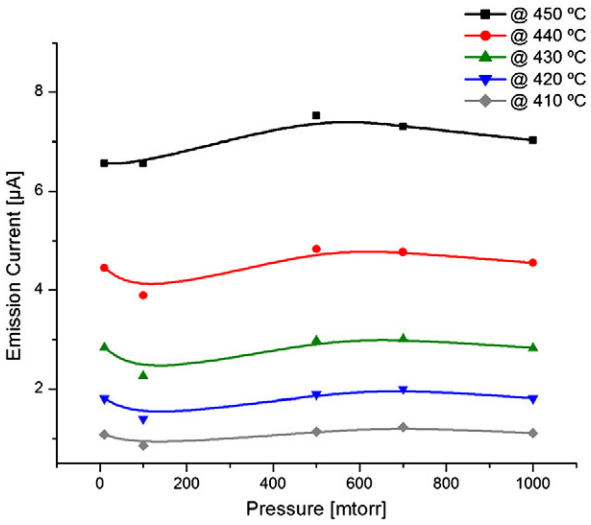

Fig. 2. Thermionic emission data from nitrogen doped diamond films as a function of nitrogen pressure and emitter temperature as parameter.

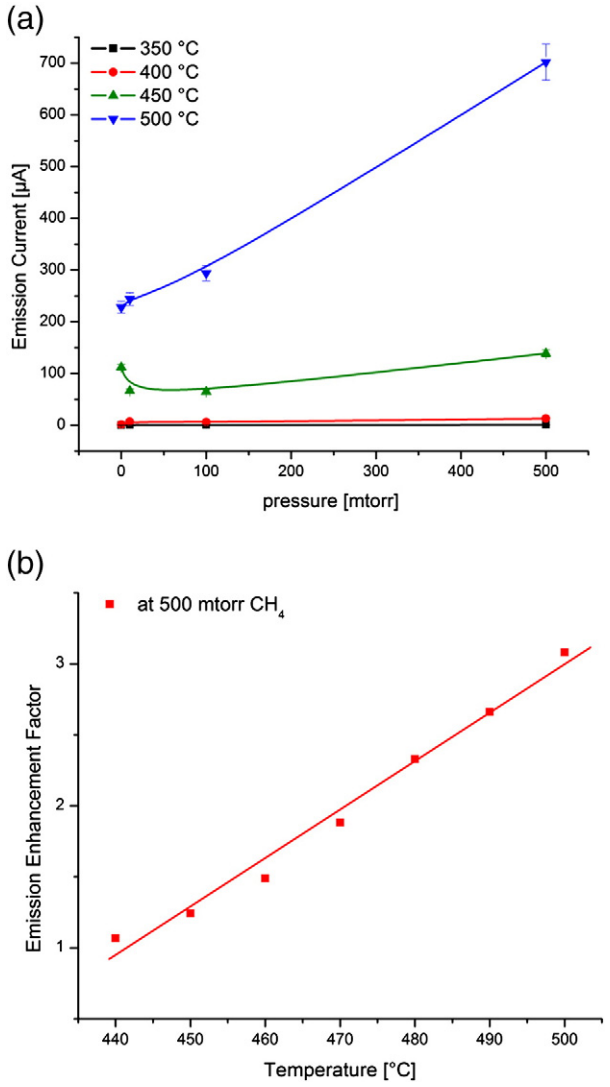

Fig. 3. Thermionic emission data from phosphorus doped diamond films as a function of methane pressure and emitter temperature as parameter (a), and normalized emission enhancement at 500 mTorr as a function of temperature (b). The lines are to more clearly show the trends.

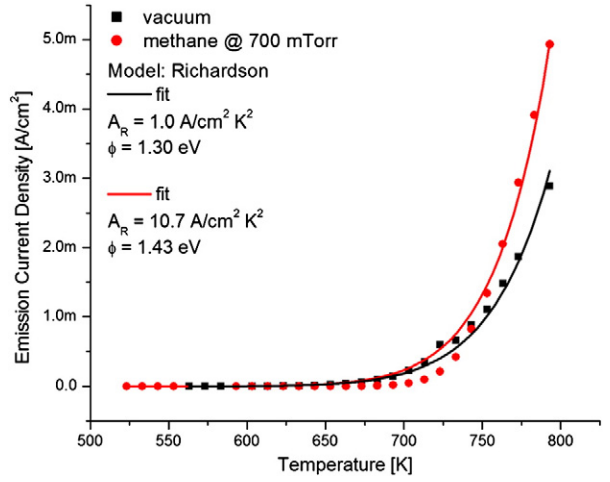

Fig. 4. Thermionic electron emission from nitrogen doped diamond in vacuum and under methane ambience and the corresponding fit to the data using the Richardson–Dushman expression. The deduced work function and Richardson's constant are indicated.

700 mTorr of methane indicates a small increase in the emitter work function from 1.30 to 1.43 eV.

More importantly, the analysis indicates an order of magnitude increase in the Richardson constant to 10.7 A/cm^2 K^2, where the emission current density reaches 5 mA/cm^2 at 520 °C. Temperature dependent emission enhancement also observed for the P-doped film as plotted in Fig. 3b suggests a thermal contribution to the ionization process of methane with increasing efficiencies at elevated temperatures. As the Richardson constant can be considered a measure for emission current saturation at the emitter surface plane, its increase indicates efficient charge transport from the emitter by molecular ionization.

3.3. Thermionic energy conversion results

In a vacuum thermionic energy converter configuration the potential difference is due to thermionic emission from the hot side and electron collection at the opposed cold surface. In the case described here, thermionic emission is augmented by molecular ionization at the emitter surface and electron detachment at the collector surface. To explore the charge transfer process for both vacuum and molecular transport enhanced configurations a cell was assembled that comprised two N-doped diamond surfaces separated by a gap of 50 μm. Electrical contacts to the metallic substrates were designed with equivalent materials to avoid thermo-electric artifacts.

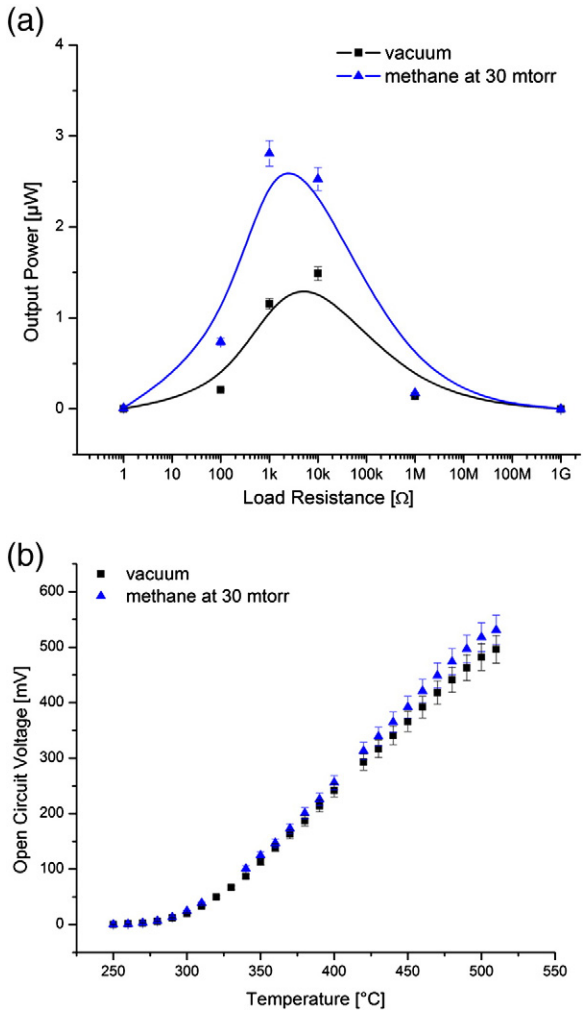

Fig. 5. Power output for a thermionic energy converter comprised N-doped diamond emitter and collector with a 50 μm separation in vacuum and under methane at 30 mTorr (a) and corresponding open source voltages (b).

The emitter temperature was then stabilized at 500 °C and the collector surface temperature rose to about 100 °C. Power output was determined by measuring the voltage drop across a variable ohmic load. Following the vacuum measurement, methane was introduced at room temperature and a pressure of 30 mTorr was established. Identical data acquisition procedures for the vacuum case and gaseous ambience were performed and both recordings are plotted as shown in Fig. 5. A significant increase is observed in output power upon methane introduction which evidences advantageous effects in converter performance attributed to mitigation of space charge and molecular charge transport. At an operating temperature of 500 °C an open circuit voltage of ~0.5 V is established for the vacuum gap configuration with a small increase upon introduction of methane.

4. Conclusion

Thermionic electron emission from phosphorus and nitrogen doped diamond films was evaluated with respect to the Richardson–Dushman formalism. For the films used in this study, work functions of 1.44 eV and 1.18 eV were determined for nitrogen and phosphorus, respectively. Introduction of methane results in enhanced emission current indicating ionization of the molecular species and enhanced charge transfer from the emitter surface. Ionization is a result of resonant electron capture which establishes a transient negative ion. Nitrogen- and phosphorus doped diamond films exhibit significant amplification of emission current densities. This enhancement is expressed in an order of magnitude increase of the value for the Richardson constant to 10.7 $A/cm^2 K^2$ for the N-doped diamond. A thermionic converter configuration was assembled with N-doped diamond emitter and collector surfaces separated by 50 μm and used to demonstrate direct heat to electricity conversion at 500 °C. Upon introduction of methane a significant increase in power output with a concurrent shift of maximum power to lower load resistance was observed evidencing space charge mitigating ionization processes of the gaseous species.

Further improvement of the diamond surfaces and optimization of the molecular transport properties indicates the potential for highly efficient, moderate temperature, thermionic energy conversions cells.

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