Higher Efficiency Filaments for Incandescent Lamps

DE-FC26-99FT40636

**Final Report to
Dept. of Energy/NETL**

**February 26, 2002
Revised April 22, 2002**

Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140-2390

Reference 69471

◆ Arthur D. Little

- Eric Carlson
(Project Team Leader)
617-498-5903
carlson.e@adlittle.com
- Mehmet Rona
- Dmitri Novikov
- John O'Brien
- Joan Kertz
- Peter Stark
- Professor Clyde L. Briant
(Brown University)

◆ Department of Energy

- James R. Brodrick
(Office of Building
Research and Standards)
- Edward D. Petrow
(Technical Monitor)
- Eddie Christy
(NETL, Contracting Officer)

Agenda

1

Executive Summary

2

Emissivity Model

3

Filament Material Life

4

Conclusions

Appendices

1	Executive Summary
2	Emissivity Model
3	Filament Material Life
4	Conclusions
	Appendices

To significantly improve the light output of incandescent filaments in the visible region and the overall energy efficacy of light bulbs by modification of the emissivity properties of the filament.

Lighting Technology	Efficacy (Lumens/Watt)
Incandescent	7-15
Quartz Halogen	15-20
Fluorescent	75
Low Pressure Sodium	100 - 200
High Pressure Sodium	80-140
Metal Halide	80-100
S-Lamp	90 - 110

Current incandescent lamps have the lowest efficacy of available lighting technologies.

By not letting invisible radiation leave the filament, we decrease the electrical power needed to keep the filament hot.

The electrical power which is applied to a filament as heat can be lost through heat conduction, convection, or through radiation which is invisible to the human eye.

During the proposal process, modeling of the efficacy of tungsten filaments with the anticipated emissivity increase indicated energy savings of approximately 40 percent for an efficacy of 26 lumens per watt.

Assumption	Today	Proposal Projection	Projection Based on Project Learning
Efficacy (LPW)	15	25.5	23
Energy Savings (%)		40	35
Market Penetration		80	80
Cost Impact to Consumer		Negligible	

The projected energy savings in commercial and residential lighting using 23 LPW is 0.36 Quad relative to current consumption of 1.3 Quad or 28%.

In our proposal, we anticipated a rapid demonstration of feasibility followed by discussions with the major OEMs to commercialize the technology.

As we progressed through the project, our efforts were focussed on Task 1 and refinement of the emissivity and life modeling tools.

The project has led to an emissivity model that the lighting industry can use to develop new lamp technologies without large R&D investment.

- ◆ **Prediction of the emissivity of materials from first principles (quantum mechanics model) using only their crystal structure**
 - **Emissivity versus wavelength**
 - **Emissivity versus temperature (metallic like conductors)**
- ◆ **Conceptual model of incandescent filament to guide material selection**
 - **Enabler for accelerating discovery of new materials and empirical rules to combine materials**
- ◆ **Quantitative framework for estimation of filament life using thermodynamic properties and Langmuir sheath model**

Feedback from lighting developers suggests that the emissivity model is an industry first.

1	Executive Summary
2	Emissivity Model
3	Filament Material Life
4	Conclusions
	Appendices

The project has led to the development of a first principles (QM) model for the prediction of the emissivity characteristics of solids from their crystal structure and electronic properties.

- ◆ **Model Basis**
 - **Crystal Structure**
 - **Quantum Mechanics**
 - **Calculation of Complex Dielectric Constant**
- ◆ **Verification of Model with Literature Data**
- ◆ **Temperature Scaling**
 - **QM model describes ϵ at low temperature (at $T = 0$ K)**
 - **Estimation of emissivity at filament temperatures based on Drude relationship**

We have identified fundamental parameters to tailor the emissivity in the visible and IR regions.

Goal: Improve efficacy of tungsten filament in incandescent lamps

Approach: Apply coating to modify emissivity of the tungsten filament

**Desired Outcome :
Near Ideal Emissivity Curve**

Options:

- ◆ **Suppress IR, leave visible unchanged**
- ◆ **Increase visible, leave IR unchanged**
- ◆ **Increase visible, decrease IR**

We applied fundamental material insights gained from QM modeling to our search for optically tuned filament coating materials.

QM Model	<ul style="list-style-type: none">◆ Gain insights from QM modeling of materials with available emissivity data
Conceptual Model	<ul style="list-style-type: none">◆ Develop understanding of controlling physical processes◆ Identify generic electronic properties needed to obtain desired optical properties

We developed a conceptual model based on simple physical considerations and the results of our QM modeling.

Conceptual Model:

- ◆ Has a limited set of independent parameters
 - Plasma frequency
 - Damping coefficient
 - Real and imaginary part of the band part of dielectric function
- ◆ Validated with experimental data from the literature for tungsten
- ◆ Provides clear relationship between its independent parameters and emissivity
- ◆ Provides easy connection with the results of our quantum-mechanical modeling

The conceptual model was then used to guide our search for materials with the desired emissivity behavior.

In the conceptual model, emissivity is calculated from the complex dielectric function. In turn, the *intraband* (Drude) and *interband* (band structure) components of the complex dielectric function are estimated from the QM model.

Complex dielectric function: $\varepsilon(\lambda) = \varepsilon_D(\lambda) + \varepsilon_B(\lambda)$

Contribution	Drude Part, ε_D	Band Structure Part, ε_B
Transition	Intraband	Interband
Parameters & Assumptions	$\varepsilon_D(\lambda) = \varepsilon_{1D}(\lambda) + i\varepsilon_{2D}(\lambda)$ $\varepsilon_{1D}(\lambda) = 1 - \frac{\omega_p^2}{\omega(\lambda)^2 + \gamma^2}$ $\varepsilon_{2D}(\lambda) = \frac{\omega_p^2 \gamma}{\omega(\lambda)(\omega(\lambda)^2 + \gamma^2)}$ <p>ω_p – plasma frequency</p> <p>γ - Damping parameter (related to resistivity)</p>	$\varepsilon_B(\lambda) = \varepsilon_{1B}(\lambda) + i\varepsilon_{2B}(\lambda)$ <p>Assume that ε_{1B} and ε_{2B} are constant</p>
Physical origin	Collective excitations of conduction electrons	Excitations of the valence electrons to the higher energy states (bands)

Conceptually, the band and Drude contributions to the dielectric function can be understood by considering the behavior of a liquid in a cup.

We calculated the optical indices and emissivity of candidate materials from their complex dielectric function.

Complex dielectric function (computed numerically): $\varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda)$

Complex index of refraction is calculated from dielectric function:

$$N(\lambda) = n(\lambda) + ik(\lambda)$$

$$n(\lambda) = \frac{1}{\sqrt{2}} \sqrt{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}} \qquad k(\lambda) = \frac{\varepsilon_2}{2n(\lambda)}$$

Emissivity of an opaque material is estimated as “1 – reflectivity”:

$$E(\lambda) = 1 - R(\lambda) = 1 - \frac{(n(\lambda) - 1)^2 + k(\lambda)^2}{(n(\lambda) + 1)^2 + k(\lambda)^2}$$

The emissivity behavior of tungsten as a function of temperature has been studied extensively.

Additionally, as temperature varies, the emissivity curves pass through a point of constant emissivity at a wavelength of 1.25 microns.

We used the QM model to estimate the ϵ_{1B} and ϵ_{2B} parameters for tungsten and candidate materials.

Step 1.

The band structure (*interband*) part of the complex dielectric function was numerically computed by the quantum-mechanical approach.

Step 2.

We assumed that the dielectric function does not depend on wavelength in our model.

We used the mean values ($\epsilon_{1B} = 20$ and $\epsilon_{2B} = 18$) for the calculation of tungsten emissivity.

Using the conceptual model, we were able to simulate the temperature dependent emissivity characteristics of tungsten and the constant emissivity point found at 1.25 microns.

- ◆ Fixed plasma frequency of 6 eV assumed for tungsten
- ◆ Varying the damping factor (γ) simulates temperature changes

λ (μm)

The conceptual model captures the general shape and temperature dependence of tungstens emissivity.

- ◆ The model results suggest that the point of constant emissivity must exist for any material that has a Drude part in its dielectric function, i.e. in any metal-like material
- ◆ The position of the point of constant emissivity strongly depends on the plasma frequency
- ◆ The models allows one to speculate on the physical reasons for existence of the point of constant emissivity

The models allows one to speculate on the physical reasons for existence of the point of constant emissivity.

- ◆ Existence of the point of constant emissivity means that the absorption of photons at this specific wavelength does not depend on temperature
- ◆ Our model incorporates the effect of temperature changes by changes in the damping parameter (or the relaxation time)
 - the damping factor is related to the strength of electron-phonon interactions.
 - If emissivity does not depend on the damping parameter, it means that the Drude term effectively does not contribute to the optical properties at this wavelength
 - ◆ This means that a photon with such a wavelength does not interact with conduction electrons and the absorption process takes place only due to the band structure part of dielectric function.
 - ◆ That might happen if a photon participates only in an instantaneous interband transition.
- ◆ One can argue that at point of constant emissivity a photon has exactly the amount of energy needed to initiate an interband transition, leaving plasma electrons unperturbed.

The fall-off in emissivity can be kept within the visible range by adjusting the plasma frequency.

- ◆ A higher plasma frequency is needed to keep the CEP in the region of 1 micron the larger the real part of the dielectric constant (band)

Generated from conceptual model

The constant emissivity point defines the λ at which the emissivity falls off.

The band structure contribution to the dielectric constant is critical to maximizing emissivity in the visible region.

- ◆ To get higher emissivity in the visible range we need smaller ϵ_{1B} values
- ◆ ϵ_{1B} is directly proportional to the number of bands in the vicinity of the Fermi level

In the model, it is always possible to find a combination of plasma frequency (ω_p) and ϵ_{1B} that confines the emissivity step within the visible range.

We found that the optimum plasma frequency is related to ϵ_{1B} through a quadratic form:

$$\epsilon_{1B} \approx -3.4 + 0.9\omega_p + 0.2\omega_p^2$$

Several empirical rules were formulated from the conceptual model for the desired relationship between parameters.

- ◆ The emissivity step can be kept within the visible range by adjusting the plasma frequency
 - Plasma frequency defines the cut off wavelength at which conduction electrons inhibit emissivity.
 - There is always a combination of plasma frequency (ω_p) and a real part of the band structure part of dielectric function (ϵ_1) that confine the emissivity step within the visible range.
- ◆ The damping parameter can be used to model temperature dependence of the emissivity function.
- ◆ The imaginary part of the band structure related dielectric function (ϵ_2) mostly affects the emissivity in the visible range
 - The larger ϵ_2 is, the lower is the emissivity

Insulating oxides, in particular hafnia, were the most promising materials found.

	QM Modeling	Implications
Metals and Metal-Like Materials (borides, nitrides, carbides, silicides)	<ul style="list-style-type: none"> ◆ Ta and HfN show enhanced emissivity characteristics relative to W 	Difficult to get further improvements by tailoring properties
Semiconductors	<ul style="list-style-type: none"> ◆ Good IR emitters ◆ At higher temperatures become more metallic 	Low plasma frequency results in high IR emissivity
Insulators (oxides)	<ul style="list-style-type: none"> ◆ Al_2O_3 doped with Cr_2O_3 shows reduced IR emissivity. ◆ Insulating oxides doped to induce conductivity may show desired emissivity properties 	Doping of metal or oxygen sites by elements with higher electron count. For example, <ul style="list-style-type: none"> • W/Ta for Hf • F, Cl, Br for O

Metals and semiconductors were deemed not to be a viable pathways to optically tunable filament coating materials.

Doped insulators, e.g. doped transparent oxides, having a wide band gap are good candidates for the “ideal material”.

- ◆ Band structure of the “ideal material” should have a wide band gap below the Fermi level
- ◆ One should be able to control electronic conductivity of such a material by doping to optimize plasma frequency

	Value		Band Structure
ϵ_{1B}	Low in visible range	3 - 10	Band gap close to Fermi energy
ϵ_{2B}	Low in visible range	Minimize in visible	Conduction band in the band gap of the insulating oxide material
ω_p	Adjust through doping	Emissivity drop-off at 0.75 μm	Conductivity controlled by the number of bands in the gap

The damping parameter, γ , is proportional to temperature and can not be optimized in a manner similar to the plasma frequency or ϵ_{1B} .

We looked for dopants to increase the electron concentration in HfO_2 in order to induce metallic conductivity.

Periodic Table of the Elements

I A																	0															
1	H																	2	He													
2	3	4																	5	6	7	8	9	10	11	12	13	14	15	16	17	18
2	Li	Be																	9	B	C	N	O	F	Ne							
3	11	12																	13	14	15	16	17	18								
3	Na	Mg	III B	IV B	V B	VI B	VII B	VIII					IB	II B	13	14	15	16	17	18												
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36														
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr														
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54														
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe														
6	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72														
6	Cs	Ba	* La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn														
7	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104														
7	Fr	Ra	+ Ac	Rf	Ha	106	107	108	109	110																						

Metal electron donors (W and Ta) substituted in the Hf sites increased emissivity in the visible region; however, the fall-off in the infrared occurred at around 1.5 μm .

Consequently, emissivity in the infrared region is still too high.

The number of bands in the vicinity of the Fermi level observed in Ta and W doped HfO_2 are small enough to give favorable ϵ_{1B} .

- ◆ To get higher emissivity in the visible range we need smaller ϵ_{1B} values
- ◆ ϵ_{1B} is directly proportional to the number of bands in the vicinity of the Fermi level

HfO_2 is the host material.

Emissivity of HfO_2 containing oxygen vacancies is higher than that of W in the visible range as well as in the IR range.

50% vacancies used in calculation

Therefore, filament environments should be designed to inhibit formation of vacancies.

Substitution of halides, e.g. F, Cl or Br, increases emissivity in the visible region and moves the cut-off wavelength to the visible/IR edge .

- F doped hafnia has an undesirable peak in the infrared
- QM model is too complex to provide a simple explanation

Doping with elements to the left of oxygen, e.g. N, does not improve the emissivity profile.

- ◆ Elements to the left decrease the Fermi level
- ◆ This decrease is insufficient to take the Fermi level outside the region where there is a multitude of overlapping bands producing a large ϵ_{1B}

Numerical experiments confirmed that a wide gap below the Fermi energy and a controllable number of conducting electrons are required to obtain the desired emissivity profile.

However, the QM modeling of the F-doped case shows that our conceptual model does not capture all details.

Cl and Br doped hafnia were the most attractive materials identified by our conceptual model of emissivity and confirmed by QM modeling.

- ◆ Smaller values of ϵ_{1B} and ϵ_{2b} produce higher emissivity in visible
- ◆ In addition, plasma frequencies must be large enough to suppress IR emissivity

Dopant	Dopant	ϵ_{1B}	ϵ_{2B}	Plasma Frequency (eV)	Relative Performance to W	
					Vis	IR
Benchmarks	W (baseline)	~ 15	~ 18	~ 7.2	O	O
	HfN	~ 5	~ 2	~ 8.7	+	+
Hf site	Ta	~7	~0.5	2.3	+	-
	W	~ 7	~ 1	~ 1.9	+	-
O site	N	~17	~1	5.7	+	-
	F	~2	~1	3.	+	-
	Cl	~4	~4	5.03	+	++
	Br	~5	~5	5.22	+	++

1	Executive Summary
2	Emissivity Model
3	Filament Material Life
4	Conclusions
	Appendices

The high temperature environment of the filament (2600-2800 K) presents significant challenges to achieving long coating life.

Additionally, application requirements further increase the challenge of finding an acceptable coating.

Requirements:

- ◆ Target life of 1000 hours for consumer incandescent lights
- ◆ Withstand mechanical stresses arising from rapid heat-up
 - Temperature increase from ambient to 2800 K in seconds
 - Coating thickness limited by mismatch in thermal expansion between the coating material and the tungsten substrate (GE estimates that this places a practical limit of $\sim 5 \mu\text{m}$ to coating thickness)
- ◆ Evaporation rate must be less than $0.005 \mu\text{m/hr}$.

The need to maintain equivalent light output limits the freedom to lower temperature and alleviate material issues.

We developed a quantitative framework to assess the life of candidate materials.

- ◆ Identify and assess physical processes, kinetics, and thermodynamic factors governing coating life
- ◆ Specifically, our efforts focussed on hafnia (HfO_2) as a coating material on tungsten in incandescent light bulbs. Among the known oxides, hafnia has
 - the second highest melting point
 - the lowest vapor pressure

Our analysis also provided insight into potential life extending lamp modifications.

The lighting industry uses a combination of gas pressure, fill gas molecular weight, and filament temperature to tune filament life.

Function of Pressure and Gas Species
(W Filament, $T = 2854\text{ K}$)

Function of Pressure and Temp.
(W Filament, Fill Gas Ar)

Data from Vukcevic

In incandescent lamps, light output (proportional to T^4) and color balance are additional factors influencing the selection of filament temperature.

We considered both thermodynamic and kinetic processes in assessing the viability of candidate coatings.

At these temperatures, all reactions are assumed to be at equilibrium.

The filament coating may be lost through two surface reactions, decomposition and sublimation.

- ◆ $\text{HfO}_2 (\text{s}) \rightarrow \text{Hf} (\text{g}) + \text{O}_2$ also occurs, but this reaction is not considered in our analysis because the vapor pressure of Hf is low in comparison to that of HfO_2 or HfO .
- ◆ The parameters (P, T, composition) of the gas envelope surrounding the filament can have a significant impact on the evaporation behavior.

Hafnia decomposition to HfO depends on the oxygen partial pressure.

Literature values (experimental data and empirical model calculations) for HfO vapor pressure agree.

Oxygen Pressure

- ◆ Panish: 1.3×10^{-9} bar
- ◆ Semenov and Marushkin: not stated
- ◆ Sasamoto calculations: $P_{\text{O}_2} = 1 \times 10^{-9}$ bar

Sasamoto Expression

$$\text{Log } P_{\text{HfO}} (\text{Pa}) = -61,850/T + 20.747 - 0.5 \log P_{\text{O}_2}$$

Calculated values differ from experimental as temperature decreases, but agree well near temperature range utilized in our model ($1000/T < 0.41$).

The limited literature data available for HfO_2 vapor pressure are consistent.

The vapor pressure of HfO_2 , unlike that of HfO , is independent of oxygen pressure.

At elevated temperatures, a Langmuir sheath or “boundary layer” surrounds the filament, and diffusion through a surrounding plasma governs the loss of material.

- ◆ Diffusion through the Langmuir sheath is controlled by:
 - concentration gradient, $n \sim D (\Delta C/\delta)$, where $D = f(\text{concentration, species})$
 - e^- field gradient, $n \sim m (\Delta V/\delta)$
- ◆ Effective diffusion, $n \sim D(\Delta C/\delta) + m(\Delta V/\delta) = D_{\text{eff}} (\Delta C/\delta)$

Evaporation through the Langmuir sheath is calculated using the expression below.

$$N = \frac{2\pi D N_o}{\ln(\delta/d)}$$

Langmuir Expression

N = number of atoms evaporating per second per unit length

D = effective diffusion coefficient

N_o = vapor pressure of the evaporating material

δ = diameter of the Langmuir sheath

d = diameter of the material

◆ **Assumptions:**

- 1 No convection within the sheath.
- 2 At the filament surface, concentration is determined by its vapor pressure.
- 3 At the sheath outer surface, concentration of the material is effectively zero.
- 4 The evaporating material moves through the sheath primarily by diffusion through a concentration gradient.
- 5 Outside the sheath, convection transports the material.

◆ Pressure comes into the calculation through the boundary layer thickness and the diffusivity.

See appendices for a summary of model validation and calibration.

The thickness of the Langmuir sheath, δ , is a strong function of pressure.

- ◆ As pressure approaches zero, δ becomes infinitely large.
- ◆ Sheath thickness approaches an asymptotic value as pressure increases.

In a 1 bar atmosphere, pressure has a second order impact on sheath thickness.

The Langmuir sheath model shows that addition of oxygen to the gas envelope suppresses HfO_2 decomposition.

Chemical Reactions

- ◆ **Decomposition:**
 $\text{HfO}_2 (\text{s}) \rightarrow \text{HfO (g)} + \frac{1}{2} \text{O}_2 (\text{g})$
- ◆ **Sublimation**
 $\text{HfO}_2 (\text{s}) \rightarrow \text{HfO}_2 (\text{g})$

Sublimation of HfO_2 is negligible relative to total evaporation at $P_{\text{O}_2} < 10^{-6}$ bar.

Lowering the temperature 100 K can decrease the decomposition rate by almost an order of magnitude and the sublimation rate by a factor of 3 - 4.

- ◆ Both decomposition and sublimation are reduced when the filament temperature decreases.
- ◆ At a given pressure, sublimation becomes more important at lower temperatures.

For typical filament temperatures, an oxygen concentration on the order of 10^{-3} - 10^{-5} bar would be needed to minimize HfO_2 decomposition.

- ◆ The threshold oxygen pressure between sublimation- and decomposition-controlled regimes decreases with decreasing temperature.

Once evaporation becomes controlled by sublimation, increasing the oxygen content has little effect on the overall evaporation rate.

In the presence of O_2 , the oxide coating must be a sufficient barrier to prevent loss of W via formation of WO_2 ,

- ◆ Langmuir sheath calculations predict that at 2700 K, a 5 μm HfO_2 coating in a 10^{-4} atm O_2 , 1 atm Ar environment may be suitable ($r_{\text{evap}} < 0.005$ $\mu\text{m/hr}$)
- ◆ At this oxygen concentration, oxidation of tungsten is a concern

Modification of gas composition (O₂ addition) and lowering of filament temperature may lead to acceptable life of the HfO₂ host.

- ◆ A gas envelope containing 1 atm Ar + 10⁻⁴ bar O₂ may be sufficient to stabilize a thin coating at 2700 K.
- ◆ Lowering temperature by as “little” as 100 K could increase life by an order of magnitude.

Our calculations have assumed 1 atm argon because the type of gas fill has only a slight effect on the evaporation rate of HfO_2 .

In the Langmuir sheath, larger atomic radii (r) gases physically suppress evaporation.

The behavior of doped oxide coatings on tungsten should be assessed experimentally.

- ◆ In order to study the stability of doped oxide coatings, experiments should be conducted with doped coatings in appropriately modified gas envelopes
- ◆ Compatibility of the filament coating approach with current lamp design and processes must be assessed
- ◆ Attention must be given to the aesthetic appearance of the bulb, e.g. color balance

1	Executive Summary
2	Emissivity Model
3	Filament Material Life
4	Conclusions
	Appendices

The project has led to the development of a powerful tool for discovery of new materials for optical applications.

- ◆ Emissivity model
 - A first principles (QM) model was developed to predict the emissivity (optical) properties of materials
 - Use of the QM model within a conceptual framework of how a filament works led to the development of generic solid state property criteria for the “ideal” material
 - Use of the model and criteria guided our search of the periodic table for dopants or alloying components for hafnia
- ◆ Material life analysis
 - Hafnia oxide was identified as the best matrix for the filament coating
 - The Langmuir Sheath model and thermodynamic data for hafnia were used to estimate the life of coatings as a function of temperature and gas envelope composition

Addition of oxygen to the lamp could provide the desired life for the hafnia matrix, however, the stability of the halogen alloyed hafnia is suspect.

The new materials face daunting stability issues, and for any chance of success, they would probably require re-engineering of the bulb.

Critical Lamp Design Modifications

- ◆ Doped hafnia **bulk emitter** rather than coating on tungsten filament
- ◆ Tungsten **heating element** not exposed to gas envelope
- ◆ **Gas envelope chemistry** to stabilize filament

The lighting industry is aware of this type of design.

We believe industry feedback is critical to assessing the benefit of the project results to incandescent lamp technology.

- ◆ Industry Experience
 - Lamp engineering and design
 - Gas envelope development
 - Lamp components (e.g., tungsten parts, ceramics for vapor lamps)
 - Consumer preferences for lighting attributes
 - Lamp manufacturing and cost
 - New lighting technology commercialization
- ◆ The patent literature indicates that the industry (i.e., Westinghouse) considered ceramic emitters in the late sixties into the seventies.

1	Executive Summary
2	Emissivity Model
3	Filament Material Life
4	Conclusions

Appendices

Langmuir derived a theoretical expression for the maximum evaporation rate of a material in a vacuum.

- ◆ Langmuir's expression:

$$r_{\text{evap, max}} = \frac{P_V}{(2 \pi MW R T)^{0.5}}$$

MW = molecular weight of the filament material

R = the universal gas constant

T = temperature

(from Ragone, "Thermodynamics of Materials")

- ◆ Using vapor pressures of HfO and HfO₂ from literature (Marushkin paper), the evaporation rate of HfO₂ in a vacuum* was calculated.

	Species	
	HfO	HfO + HfO ₂
Vapor Pressure (bar)	4 x 10 ⁻⁶	4.02 x 10 ⁻⁶
Temperature (K)	2700	2700
r _{evap} (μm/hr)	182	183
r _{evap} (Å/s)	505	507

*P_{O₂} (assumed) = 10⁻⁹ bar

GE investigated several coatings for incandescent lamp efficiency improvement.

- ◆ GE looked at oxide coatings to stabilize filament surface morphologies.
- ◆ Thermodynamic partial pressures for W and candidate oxides were calculated at $P_{O_2} = 10^{-6}$ bar and at typical filament temperatures.
- ◆ These pressures were utilized to calculate a theoretical vaporization rate of hafnium oxide.

Solid compound, T_m (K)	Vapor species	Partial pressure (bar) of vapor species at $p_{O_2} = 10^{-6}$ bar and indicated temperature (K)				
		2400	2600	2700	2800	3000
BeO	Be			2.11E-04		
2851	BeO			3.80E-06		
	Be ₃ O ₃			1.49E-05		
MgO	Mg			3.27E-01		
3100	MgO			1.51E-03		
CaO	Ca			7.44E-03		
3172	CaO			3.86E-05		
SrO	Sr			3.70E-02		
2805	SrO			9.71E-04		
Sc ₂ O ₃	Sc	6.54E-11	9.46E-09	8.57E-08	---	---
2762	ScO	1.95E-07	5.19E-06	2.22E-05	---	---
	ScO ₂	5.81E-06	3.93E-05	9.11E-05	---	---
Y ₂ O ₃	Y	3.62E-12	6.13E-10	5.76E-09	---	---
2712	YO	9.07E-08	2.44E-06	1.01E-05	---	---
	YO ₂	1.62E-05	9.77E-05	2.08E-04	---	---
ZrO ₂	Zr	6.06E-15	3.71E-12	6.29E-11	8.68E-10	---
2983	ZrO	1.22E-09	9.93E-08	6.87E-07	4.11E-06	---
	ZrO ₂	7.67E-08	1.28E-06	4.36E-06	1.35E-05	---
HfO ₂	Hf	2.38E-16	1.54E-13	2.72E-12	3.88E-11	4.37E-09
3073	HfO	1.35E-10	8.79E-09	5.54E-08	3.04E-07	6.67E-06
	HfO ₂	2.27E-10	5.11E-09	2.01E-08	7.13E-08	7.11E-07
ThO ₂	Th	2.62E-18	2.69E-15	5.84E-14	1.02E-12	1.73E-10
3623	ThO	8.24E-11	7.23E-09	5.26E-08	3.32E-07	9.07E-06
	ThO ₂	1.91E-07	3.03E-06	1.03E-05	3.16E-05	2.37E-04
W	W	1.43E-11	3.96E-10	1.73E-09	6.80E-09	7.95E-08
3695						

*Report provided by the Department of Energy, courtesy of General Electric

In GE's study, a ratioing method was used to calculate vaporization rates.

◆ *Calculation:*

$$r_{\text{evap1}} = \frac{P_{V1}}{P_{V2}} r_{\text{evap2}}$$

- Vaporization rate of W at 2700K in 1 atm Kr was calculated from GE's software GASLOSS (r_{evap2})
- Vapor pressures of W (P_{V2}), HfO_2 , and HfO ($P_{V1} = P_{\text{HfO}_2} + P_{\text{HfO}}$) calculated as shown previously
- Calculate vaporization rate of HfO_2 (r_{evap1})
 - » GE estimated that a 3-10 μm thick HfO_2 coating might survive 1000 hr
- ◆ *Experiment:* GE found that the HfO_2 coating on a roughened surface broke up into small islands and quickly vaporized above 2700 K.
 - No explanation was offered for the discrepancy between calculation and experiment.

In GE's study, hafnia was not long lived in the experiments conducted.

Using the Langmuir expression for maximum evaporation rate in a vacuum, GE's method of determining the evaporation rate of HfO₂ is validated.

- ◆ GE compares HfO₂ and W by making a ratio of their evaporation rate.
 - The denominator, $(2 \pi MW R T)$, is relatively equal for the two materials.
 - Thus, at equilibrium,

$$\frac{r_{\text{evap, max}}(\text{HfO}_2)}{r_{\text{evap, max}}(\text{W})} \sim \frac{P_V(\text{HfO}_2)}{P_V(\text{W})}$$

Comparison of the Langmuir sheath model calculations with experimental literature data for tungsten evaporation validated the model.

- ◆ Calculated values are within an order of magnitude of literature data and follow similar trends.
 - Differences may be due to input values for W vapor pressure.

Calculated model predictions of evaporation rates as a function of filament thickness further validated the approach.

Comparison of our Langmuir sheath calculations with literature data for W evaporation in different fill gases validated the approach.

◆ $\otimes$ indicates Vukcevic pressures at 1000 hours of lamp life:

- Argon: 595 torr
- Krypton: 410 torr
- Xenon 325 torr

◆ Langmuir sheath predictions:

- Argon: 595 torr (fit)
- Krypton: 500 torr
- Xenon 380 torr

Comparison shows that calculations performed for various fill gases are consistent on a relative basis.

Under the same physical conditions of gas composition, pressure, and temperature, the Langmuir sheath model and the GE ratioing method result in identical evaporation rates.

Evaporation (HfO ₂ + HfO) Rates at T = 2700 K		
Environment	1 atm Kr+10 ⁻⁶ atm O ₂	1 atm Kr+10 ⁻⁶ atm O ₂
Method	Langmuir sheath	GE (calc)
r _{evap} (μm/hr)	0.0102	0.0113

Experimental evaporation rates of HfO_2 in air are significantly higher than the Langmuir sheath predictions.

- ◆ Discrepancies in the results are unknown, as little information is given regarding the procedures used to obtain the experimental data.

HfN Vaporization Rate and Activation Energy

- ◆ GE reported experimental vaporization rates of HfN in different gases
- ◆ Rate is a function of temperature and gas species
 - increase T, increase rate
 - increase N₂ content, decrease rate
- ◆ Activation energy:
 - incorporates both surface events and diffusion through the Langmuir sheath
 - increases with decreasing vaporization rate

Temperature (K)	Vaporization Rate (mm/1000 hr)			
	Pure N ₂	50/50 Kr/N ₂	75/25 Ar/N ₂	95/5 Ar/N ₂
2600	1.4	2	3	4.5
2700	8.2 *	11.1	14	19.1
2800	43.1	51.3	58.1	73.1
Activation Energy H/R (K)	125,000	118,000	108,000	101,000
* GE theoretical value = 7.3 mm/1000 hr				

Based on evaporation rates and activation energy, HfO_2 is an inherently less stable material than HfN.

- ◆ Using experimental data (Karaulov) for evaporation of HfO_2 in air, activation energy for HfO_2 can be determined from an Arrhenius plot

Comparison of HfN and HfO_2		
Material	HfN	HfO_2
Environment	Pure N_2	Air (0.8 N_2)
Rate ($\mu\text{m}/1000 \text{ hr}$) at 2700 K	8.2	1470
Activation Energy H/R (K)	125,000	18,350

- ◆ From a stability standpoint, a combination of HfO_2 and HfN would most likely result in an inferior material