1 Project Statement

Manned interplanetary missions will only be desirable once the ability to return is established. Even using improved fuel technologies we have not resourced the fuel requirement for return missions to our nearest terrestrial neighbors. Energy harvesting in Outer Space or on another planet is imperative for return mission success, as it is impossible with current Earth-based fuel technologies to supply an outgoing mission, to even our closest neighbor planets, with enough fuel for return. Thermophotovoltaic (TPV) devices, with a theorized maximal efficiency of 85% conversion of incident sunlight to electricity [1, 2], are ideal for such harvesting. **Thus, the work I propose will investigate performance parameters of select TPV materials. Specifically, I will study how the optical absorption, thermal emission, energy conversion efficiencies, and thermal transport properties are related to the structural features of TPV materials in the presence of photon wavelengths abundant in the Universe.** Through an in-depth, coupled experimental and theoretical, study the relationship between amorphous material structure (i.e., atomic density and fractal dimension [3]) and optical absorption, thermal emission, electronic conversion and thermal transport properties will be determined. The results will establish the governing materials physics to further guide material selection and device design for efficient electromagnetic harvesting cells to be used for constant refuel on interplanetary missions.

2 Introduction and Overview of Proposed Work

Solar energy is a clean and renewable energy source consistently available in Outer Space, on Earth and on neighboring terrestrial planets. Optimization of electromagnetic harvesting devices that convert light into electricity offers the potential for a perpetual and reliable source of fuel both on Earth and on interplanetary missions. It is theorized that TPV devices, which ideally absorb and convert all incident solar radiation to a spectra of thermal emission finely tuned for conversion to electricity by a photovoltaic (PV) cell, can reach a maximum efficiency of 85% [1, 2]. The effects of component material morphology (i.e., amorphous or crystalline) [4, 5, 6, 7], material family (i.e., inorganic, organic, or hybrid) [8, 9, 10, 11], and processing [12, 13] on performance parameters affecting ultimate power conversion of these devices continue to be investigated. Yet, we remain far from the theorized maximum efficiency of these devices, thus, further investigation of the structural parameters of TPV materials is warranted.

The intention of this proposed project is to arrive at an energy harvesting material system that is functionally optimized for yield and efficiency in Outer Space and on Mars. Through coupled experimental and theoretical thrusts, this initiative will elucidate relationships between component materials structure and electromagnetic absorption, thermal emission, electronic conversion, and thermal transport properties. The underlying relationships between the parameters affecting energy conversion efficiency and the structural details of amorphous systems (i.e., atomic density and fractal dimension) will be established by experimental exploration of these quantities; development of models detailing the dependences of these properties on the structural aspects of amorphous systems will support these studies.

This joint experimental and modeling initiative will address the following questions, focusing on the independent and dependent optimization parameters outlined in Fig. 1, with the aim of developing theory to improve energy harvesting capabilities:

1. **Atomic Density:** What are the characteristic interatomic spacing scales of amorphous materials that give rise to peak electromagnetic energy absorption (of the full spectrum or of finely tuned spectra) and electronic conversion? Can finely tuned porosity or local differences in atomic density, provide pathways for electron transfer while maintaining efficacy of optical absorption? To what degree can the thermal emission spectra and the thermal transport properties be optimized by changes to atomic density? How do atomistic models predict these properties?

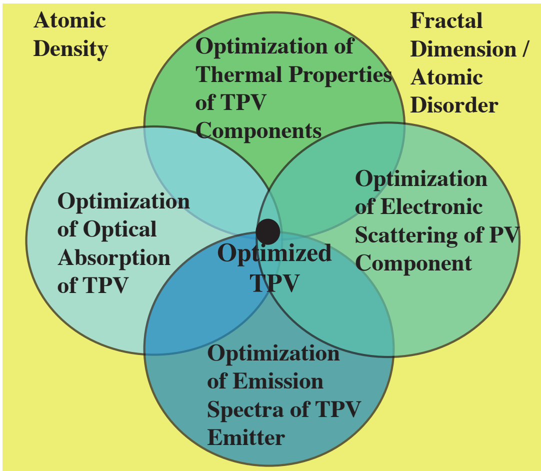

FIGURE 1. Schematic pictorially representing the independent parameters that will be investigated to determine the structural arrangements that simultaneously optimize optical absorption, electronic conversion, and the emission spectra of TPV materials.

2. **Fractal Dimension / Atomic Disorder:** How do complex geometric arrangements, and the associated induction of localization of energetic carriers, affect the performance parameters of amorphous TPV materials? To what degree can the fractal dimension of the material be separated from atomic disorder in amorphous materials, and what magnitude of change to performance parameters can be realized through this independence of structural details?

To provide a mission-specific description of the effects of atomic density, fractal dimension and atomic disorder on electromagnetic absorption, electronic conversion, thermal emission spectra and thermal transport properties the materials chosen for investigation not only exhibit ideal physical properties but also have proven facility for use on interplanetary missions [14]. We will investigate organic semiconducting polymers including but not limited to: PCBM, P3HT, and P3HT:PCBM blend thin films. Due to their small band gaps [16] these materials have an extremely high capacity for absorption in the visible and near-IR spectra [15], wavelengths abundant on the Martian surface and in interplanetary space [22]. They also offer low thermal conductivities [17] and controllable fractal-dendtritic growth [18, 19, 20]. With further improvements to energy conversion efficiency, these amorphous organic materials offer cost-effective and reliable alternatives to current state-of-the-art TPV device materials.

Optical absorption coefficients and electronic scattering rates, the limiting factor on the length of time excited electrons remain in the conduction band offering usable current, will be measured with sub-picosecond optical techniques and will be mapped to precise spatial locations that are well characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Thereby, direct correlations between the performance parameters and roughness intrinsic to amorphous fractal systems will be made. The sub-picosecond resolution of absorption and electron scattering rate measurements will offer direct insight to the optical and electrical processes. Emission spectra will be monitored simultaneously with optical emission spectrometry (OES).

3 Background

3.1 Radiation on Mars and in Outer Space

Beyond Earth's protective atmosphere there exists an abundance of radiation. Radiation, defined as energy in transit, may be classified as either non-ionizing or ionizing dependent on its magnitude of energy. More specifically, ionizing radiation carries enough energy to eject electrons from matter that it interacts with. While it is conceivable that all forms of radiation may be harnessed for usable energy in the form of heat, electricity or pressure, the energy harvesting device to be improved upon by this proposed research readily converts only non-ionizing radiation. Furthermore, the functionality of TPV devices may be negatively affected by ionizing radiation and, therefore, it is expected that the device will be properly shielded from such incident rays and particles; the necessary shielding is not an initiative of this proposal.

The intensity and spectra of non-ionizing radiation present on the Martian surface differs from that in orbit or, as a point of reference, on the Earth's surface. In orbit or in interplanetary space, the blackbody radiation of the Sun pervades across most of the electromagnetic spectrum (gamma rays are converted to lower energy photons before they reach the Sun's surface) with the limiting factor on intensity of the spectra being inversely proportional to the distance from the source. At Mars, the absorbance and collisions that the Sun's irradiance will have experienced on its travel leaves the density of incident solar radiation to be approximately half that reaching Earth's surface. Based on recent observations from the Curiosity rover on Mars, the overall radiation dose rate is also approximately half that of the average experienced on the cruise to the planet; this is explained by the rover being on the planet versus in space where it would have exposure to radiation from all directions [21]. However, despite the diminished radiation rate experienced on Mars the planet's minimal atmosphere, consisting mainly of CO_2 and dust, does not abundantly scatter and absorb solar radiation in the visible spectra [22]. Additionally, the planet's lack of an ozone (O_3) allows for drastically lower UV absorption and scattering than compared to that of Earth's atmosphere. It has been reported that the surface of Mars, during periods of daylight, receives a total UV flux between 200-400 nm that is comparable to that incident upon the Earth's surface [23]. However, CO_2 clouds do readily reflect and absorb wavelengths less than 204 nm [22, 23, 24] and a small fraction of wavelengths in the IR range [25]. Likewise, these clouds partially reflect the upwelling of IR radiation from the planet surface back towards the surface [26]. Focusing on the wavelengths prevalent on the Martian surface, this study will investigate a range of frequencies in the near-UV, visible and near-IR spectra.

3.2 Thermophotovoltaic Technology

TPV devices consist of an absorber to collect and convert non-ionizing radiation to thermal emission and a PV cell that converts the received wavelengths into electronic energy. Ideally, the absorber will absorb all wavelengths and convert them, without loss through waste heat and emission, to a wavelength spectra finely tuned for absorption by a PV cell. Ideally, this wavelength spectra will be completely absorbed by the PV cell that is optimized to convert this incident radiation to electronic energy. This electronic conversion is optimal when the excited electrons remain in the conduction band for long enough to extract usable current while minimizing electron scattering, caused by waste heat, and heating effects. For ideal components with no optical losses and only radiative recombination in the solar cell, theoretical maximal efficiencies are found to be 85% for full concentration of the incident sunlight on a black absorber [1, 2]. Therefore, the initiative of this proposal is to achieve near blackbody optical absorption, finely tuned thermal emission, long electron excitations, minimal electron scattering, and efficient waste heat removal through exploiting the structural morphology of amorphous TPV materials.

3.3 Organic Polymer Semiconductor Thin Films

Organic polymer semiconducting materials exhibit many electronic properties and manufacturing advantages that make them ideal for use as energy conversion materials. Additionally, thin film morphology offers improved flexibility [27, 28], manufacturing cost reduction [27, 28], and control over the fractal dimension of the material [18]. These materials have small band-gaps, absorbing and emitting in the visible and very near-IR spectra, making them ideal candidates for energy harvesting on Mars and in Outer Space. Much work has been done to optimize the parameters affecting overall power conversion efficiencies, these being: photon absorption [4, 6, 29, 27], electron excitation [10, 11, 27, 7, 30, 31, 29], diffusion of the electron-hole pairs to their respective electrodes for collection [11, 30, 31, 29, 27], thermal emission spectra of the emitter [32, 33, 34] and waste heat removal [35]. However, these parameters are not yet fully optimized. The current low TPV power conversion efficiencies of organic semiconductor materials can be attributed mainly to incurred resistances due to improperly spaced electron energy levels for the charge generation, transportation, and collection at the TPV electrodes caused by poor spatial geometries [36, 37].

4 Technical Approach and Methods

4.1 Materials and Characterization

As outlined in Section 2, this proposed work will explore the optical absorption, thermal emission, electronic excitation and scattering rates, and thermal transport properties of an array of organic semiconducting polymer thin films. The carbon-based films will be grown in the microfabrication laboratory at U.Va with a spin-coating process. Each set of identical material parameters will be fabricated on two different substrates, glass and aluminum, to facilitate the experimental investigations of this study. The characterization of the fractal dimension of these films will be performed by Professor Petra Reinke, a close collaborator at U.Va. in the Materials Science and Engineering Department. Professor Reinke has detailed the growth mechanism [19] of carbon-based thin films which are confirmed to adopt a fractal-dendritic shape [18]. Facility to control this growth and the resulting fractal dimension of the material is proven [18]. Furthermore, her team has developed a box-counting characterization technique to calculate the fractal dimension of the system, found to be in agreement with a diffusion limited aggregation model [18]. Additionally, the atomic density of the monolayer materials will be controlled through growth and will be directly measured with TEM and AFM for each sample.

4.2 Optical absorption, Electron conversion, and Optical Emission Measurements

The incident electromagnetic energy absorption and resulting electronic scattering processes of the various systems will be measured with time-domain thermoreflectance (TDTR) [38, 39, 40]. Briefly, TDTR is a non-contact optical "pump-probe" technique that monitors the temperature change on the surface of a sample with femtosecond resolution following a short-pulsed heating event. A schematic of the TDTR experimental set up in our Nanoscale Heat Transfer lab is shown in Fig. 2.

The optical absorption of the pump pulse and resulting excited electron scatter rates will be monitored by the time delayed probe pulses. Femtosecond resolution of pulse and probe beam events allow for the precise measurement of electronic scattering times as they relax to the valence band of unusable

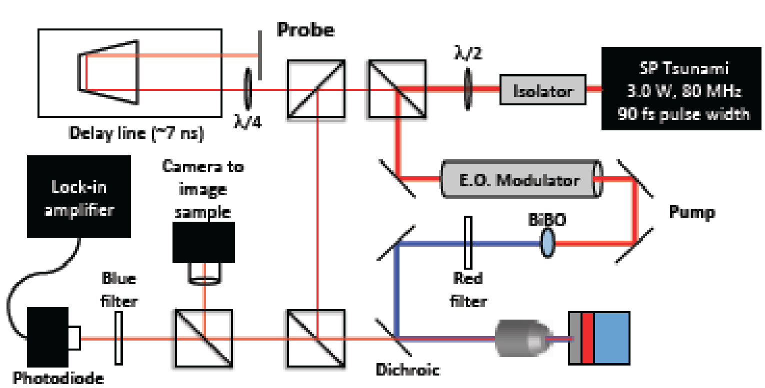

FIGURE 2. Schematic of the optical layout for the TDTR measurement system in the Nanoscale Heat Transfer Laboratory at U.Va.

energy states. Simultaneous measurements of optical emission spectra of the various materials under the conditions explored in this investigation will also be measured with OES. The sample set grown on glass substrates, ideal for optical absorption and conversion measurements, will be used for this set of results. Temperature dependent measurements will be conducted over the range of ≈ 10 – 1800 K as facilitated with an optically accessible cryostat.

4.4 Thermal Conductivity and Thermal Boundary Conductance Measurements

TDTR will be used to measure the thermal conductivity and the thermal boundary conductance (TBC) of the systems produced in this research. Both the sample sets, grown on aluminum and glass substrates, will be examined to explore the role of a heat sink layer on TBC. With these measurements the relationship between the electronic scattering processes and the thermal transport produced by these events will be evidenced. These measurements will be conducted over the range of temperatures explored in the investigations of electromagnetic energy conversion efficiency.

4.5 Model Development

Experimental data will be analyzed with atomistic models to develop analytical and phenomenological theories. The atomistic model development will focus on quantum mechanical non-equilibrium Green's functions (NEGF). As NEGF modeling constructs the material atomistically it is the perfect approach to study the effects of specific structural arrangements on electron scattering. The trends determined with the NEGF approach will be directly compared to the trends observed in the experimental data to determine the intricacies in the interplay between atomic arrangement and electron excitation and recombination on an atomistic level.

5 Work Plan

Following the work plan shown in Fig. 3, Ms. Gorham will present results at Materials Research Society (MRS) and American Society of Mechanical Engineers (ASME) symposia and conferences and will simultaneously publish findings and theory in advanced materials, chemistry, physics and engineering journals. The project management plan will include several interactions with supervisors and colleagues at different frequencies and formalities, including weekly meetings with her Ph.D. supervisor, Dr. Patrick Hopkins, monthly meetings with NASA contacts and the presentation of annual reports. Minutes and slides from all meetings will be documented and saved in a centralized location that is accessible to all parties on the project. Ms. Gorham also plans to spend time on-site at appropriate NASA facilities to work with lead researchers to advance the future stages of this initiative.

	Year 1				**Year 2**				**Year 3**			
Thrust I	**Optical Absorption, Electronic Scattering Times, Optical Emission Optimization**											
Sample Fabrication												
TDTR Testing												
Modeling												
Thrust II	**Thermal Transport Measurements**											
Sample Fabrication												
TDTR Testing												
Modeling												
On-Site Prototyping												
Project Management												
Annual Presentation/Report												

FIGURE 3. Project timeline.

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