Abstract – We report the first demonstration of optical detection by thermoelectric nanowire junctions. We employed devices composed of bismuth nanowire arrays (NWAs) which are capped with a transparent indium tin oxide electrode. The incident surface features very low optical reflectivity and enhanced light trapping. The unique attributes of the thermoelectric arrays are the combination of strong temporal and optical wavelength dependences of the photocurrent. Under infrared illumination, we detected a pure thermoelectric photoresponse where the photocurrent increases with the square root of the illumination frequency for frequencies above the cutoff frequency of 400 Hz where cutoff is caused by nanowire thermalization. We discuss theoretical and experimental operations.

Index Terms – nanowire, thermoelectric, detector.

I. INTRODUCTION

Boeing communications systems increasingly rely on higher bandwidth communications in all segments of the electromagnetic spectrum. As a result, systems involving high speed optical communications and imaging require ever more sensitive detection systems. This is increasingly true in the opto-electronic regime, in which rapid conversion of optical signals to electrical signals and the inverse must occur at high bandwidth to avoid communications and informational bottlenecks. For general semiconductor devices, photocurrent generation is due to the separation of excited electron-hole pairs by a built-in electric field or photovoltaic effect (PV) [1]. For semiconductor-based optoelectronic devices, such as silicon solar cells, photon absorption leads to the transfer of charge between different electronic bands, resulting in a photocurrent (PC). If a temperature gradient is generated by light across the interface between two materials that have different thermoelectric powers, there is photocurrent generation by the thermoelectric (TE) Seebeck effect. Recent work in two dimensional graphene demonstrated a hot carrier thermoelectric (TE) photoresponse, in which an electrical response was generated by the thermal heating caused by light absorption at the nanoscale [2, 3]. However, there have been no reports of this effect in other nanoscale systems.

Boeing has on-going experimentation at strategic universities in the various areas of nanotechnology. One of these nanotechnologies has to do with thermo-electric optical detection. From this relationship, we report on the first demonstration of thermoelectric optical detection in bismuth nanowire arrays (NWA). These devices are composed of thermoelectric bismuth nanowire arrays that are capped with a transparent indium tin oxide electrode. The incident surface features very low optical reflectivity and enhanced light trapping. The unique attributes of the thermoelectric arrays are the combination of a strong temporal and optical wavelength dependence of the photoresponse. Here, we report the first demonstration of TE response in an array of junctions of nanowires. We discuss the nanoscale optical and
TE properties that give rise to the effect. Finally, we offer comment on potential effects to Boeing platform subsystems and payloads. We report on the fabrication of TE devices composed of Bi NWAs and its photoresponse. We find that under illumination there is a photoresponse in both near infrared (NIR) and visible spectral regimes. Under infrared illumination, the photoresponse is simply governed by heat diffusion and can be uniquely attributed to TE effects. However, under visible illumination, the photo response is a combination of TE and PV effects.

II. ANALYTICAL MODEL: THERMOELECTRIC EFFECT

TE effects are caused by the difference in the broadening of the energy distribution in the electronic bands caused by a temperature gradient. The efficiency of TE power conversion is characterized by a figure of merit Z, defined by

\[ Z = \frac{\alpha^2 \sigma}{T \kappa} \]  

where \( \alpha \) is the thermopower, \( \sigma \) is the electrical conductivity, \( \kappa \) is the thermal conductivity, and \( T \) is the absolute temperature. Some traditional TE materials, such as bismuth, have unusually high thermopower values and a large \( \sigma / \kappa \), leading to exceptionally large \( Z \) values [4] and high efficiency. However, although it is almost counter intuitively, bulk TE crystals are not good candidates as TE photoresponse detectors, because the same properties that create high \( Z \) values cause the material to have high thermal conductivity. As a result, the energy dissipates quickly in these systems. We chose to address this problem by working in a nanowire geometry. We anticipated that this geometry would show enhanced thermoelectric performance because \( \kappa \) is less in nanowires than in the bulk [5]. In addition, bulk thermoelectric materials have large refractive indices relative to air. This causes large Fresnel reflection at the incident surface of bulk thermoelectrics, which is not conducive for efficient conversion. In fact, in a variety of bulk systems, including bulk crystalline semiconductors and Bi, light induced thermoelectric responses are so weak that they have only been observed under pulsed illumination [6, 7]. In investigations of PV in solar cells, researchers have discovered that the nanostructuring of bulk materials into wires or sharp points aligned along the optical incident direction results in reduced optical reflection and induced light trapping [8, 9]. There are many mechanisms that may play a role in this effect. The optical reflection of a nanowire array (NWA) is greatly reduced relative to the well ordered surface because the electromagnetic field penetrates deep in the material. This property has been attributed to dipole effects because the wires point parallel to the light wave vector and the photon electric field is perpendicular to the wire length [10]. NWA optical properties have also been discussed in the context of optical meta-materials [11, 12, 13, 14].

III. DETECTOR FABRICATION TECHNIQUE

We fabricated NWA devices composed of bismuth, integrated with electrodes consisting of a bottom bulk bismuth layer and a thin indium tin oxide (ITO) film (see Figure 1). The length of the nanowire array, \( L \), not including the bulk bismuth layer, was 50 \( \mu \)m and the active area, \( S \), of the array was approximately 1 mm\(^2\). The ITO film was composed of 90% \( \text{In}_2\text{O}_3 \) and 10% \( \text{Sn}_2\text{O}_3 \), and was 50 nm thick. It was deposited with a Cressington sputter coater. The measured current versus voltage (I-V) relationship of the detector was symmetric and ohmic without features that would have indicated the presence of Schottky barriers. The measured resistance was 6.3 k\( \Omega \). Because the contact resistance between the silver epoxy (Epotek 4110) and the bulk bismuth, and that between the bismuth nanowires and the bulk bismuth, was low (<1 \( \Omega \)), the measured I-V value was intrinsic to the front surface. The TE junction that detects the light energy is located at the front surface and is established at the nanowire array-ITO interface, and its temperature is designated \( T_f \). The back of the array is thermally grounded at ambient temperature \( T_0 \). Because the circuit is closed between the ITO film and the back of the array, the thermoelectric signal can be considered proportional to \( T_f - T_0 \).

![Figure 1. Schematic of experimental system.](image)

The arrays were fabricated using a template method—namely, the high pressure injection (HPI) method—in which the melt of the alloy of interest is injected in a porous insulator using high pressure [15]. We employed a commercial alumina membrane disk (Anopore, Whatman, MA, USA) with a thickness of approximately 55 \( \mu \)m (See Figure 2). It supports an array of parallel, largely non-interconnected, cylindrical channels of 200 nm in diameter parallel to the disk axis. To inject bismuth in the pores, we placed high-purity bismuth pellets (99.999 %, Sigma-Aldrich) in contact with the Anopore alumina membrane inside a high pressure reactor. The reactor was heated to a temperature of 400 °C, well above the melting point of Bi (270 °C). Next, the pressure was gradually increased to 1 kbar, forcing the molten material into the matrix channels. The injection is completed in a few minutes. The reactor was then cooled and the impregnate allowed to solidify inside the
channels. The sample was then extracted from the reactor, and standard mechanical polishing techniques were performed to remove the surrounding excess. A scanning electron microscope was used to generate an image of the side of the NWA (see Figure 3).

![Alumina templates Channel diameter from micron to 5 nm](image)

**Figure 2. Commercial alumina membrane disk**

**IV. ELECTRONIC PROPERTIES**

The array electronic properties were determined in separate experiments [14, 16]. X-ray diffraction (XRD) spectra show that the crystal grains were larger than the wire diameter and were oriented with the c-axis along the wire length (See Figure 3, inset). Electron and hole band parameters were determined via magneto-resistance experiments. As with bulk bismuth, the bismuth in the nanowires was determined to be a semimetal. Thermopower measurements show that the thermopower of the nanowires was diffusive in nature and negative (nanowires, as well as bulk, are n-type because electrons have greater mobility than holes). This value of approximately $-90 \text{ mV/K}$ did not differ significantly from that attained for single-crystal bulk bismuth along the diagonal orientation [4]. The room temperature $Z$ was estimated to be $2 \times 10^{-3} \text{ K}^{-1}$, 0.6 times the value for bulk bismuth.

![X-ray intensity (a.u.)](image)

**Figure 3. Scanning electron microscope side image of NWA. Inset: X-ray diffraction spectra showing presence of crystal grains oriented with the c-axis parallel to wire.**

We have not measured the number of wires that are connected to the ITO and have not made any attempt to measure the value of the contact resistance. However, the individual calculated [15, 16] Bi NW resistance $L \lambda(\sigma \varnothing)$, where $\varnothing$ is the NW cross-section) is $\sim 500 \text{ Ohm}$, and we found that the contact resistance is consistent with the measured total resistance (6 $\text{ K\Omega}$). At the NWA-ITO interface, the bismuth was paired with the ITO film. A sample of the ITO film of the same thickness was deposited on a glass substrate and its resistance and thermopower were measured. We measured the ITO sheet resistance to be 1.2 $\text{k\Omega/\mu m}$ and the thermopower to be $\sim 10 \text{ \mu V/K}$. Our measurements were consistent with those of previous research on the electronic transport properties of ITO films [17].

**V. OPTICAL EXPERIMENTATION**

We characterized the NWAs under optical light illumination. The optical properties of the nanowire array were significantly different from those of bulk single crystal bismuth with its highly reflective front surface [18, 19]. In addition, the 50-$\mu$m thick alumina template, prior to processing, was translucent/transparent in the visible and infrared. By contrast, we found that the optical absorption by our NWAs was very high, broadband, and anisotropic. The array surface was black and dull without the reflective surface characteristic of single crystal bismuth. This finding is consistent with NWAs of many diverse materials (e.g. silicon nanowire arrays) and denotes low reflectivity caused by high levels of light trapping [8, 9]. We also observed that light reached deep inside the array. Under oblique illumination, that is to say, with the incident light propagation vector non-parallel to the nanowire orientation, the reflected visible light is highly polarized. This effect can be explained by modeling the wire array as a polarizing wire grid. For this polarization effect to occur, incident light has to penetrate a distance of the order of at least a wavelength $\lambda$. Based on these observations with $\lambda \sim 0.5 \text{ \mu m}$, we estimated that the optical penetration length $A$ exceeded 0.5 $\text{\mu m}$. By contrast, crystalline bismuth has an $A$ given by the skin depth of approximately 10 $\text{nm}$ in the visible range and only somewhat larger in the NIR [19].

We exposed the detector to a 633 nm HeNe 10-mW laser beam with a waist size of around 2 mm. The detector was 1 mm in size and the active area was 0.6±0.2 mm in diameter. As a result, the effective power on the active area was 0.09±0.06 mW. The device resistance was stable at 6.2 $\text{k\Omega}$. The responsivity was 0.20±0.13 V/W.

Because the signal arises in the absence of a bias current, we interpret it in terms of thermopower that is proportional to the $T_F - T_0$, the difference between the front surface temperature and ambient temperature $T_0$. When we measured the time-dependent photoresponse, we found evidence of a thermal flow as well as a major signal component that could be interpreted as PV. We performed the time-dependent
measurement with a quartz lamp whose output was chopped at frequency \( f \). This source beam had visible and infrared components. The signal \( I \), which is synchronous with the illumination, was measured via lock-in detection.

We measured the photoresponse under visible/infrared, and infrared-only exposure. The results we measure for \( I \) versus \( f \) for visible/infrared and infrared light are shown in Figure 4. The signal increases non-monotonically with increasing frequency \( f \). There is significant difference in the experimental behavior between the case of vis/infrared light and the pure infrared illumination. The latter clearly shows an inflection point at \( f_0 = 400 \pm 100 \) Hz, where \( I \) is constant for frequencies below the inflection point. This photoresponse is caused by both the time dependency of heat diffusion from the front to the heat sink in the back of the sample and to the deposited heat conversion from the incident pulse into electric power via TE effects in the nanowire array.

VI. PHYSICAL INTERPRETATION

Interpretation of this data can draw upon prior TE theoretical work. The diffusion of heat through a sample is characterized by the diffusion constant \( D \), given by \( \kappa / \rho \), where \( \kappa \) is the NWA thermal conductivity, \( \rho \) is the density, and \( c \) is the NWA specific heat. Parker et al. [18] presented an analysis of heat diffusion through a plate of thickness \( L \) showing that there is a thermal time constant \( \tau = 1.38 \) \( L^2/(\pi^2 D) \) for equilibration of the front temperature \( T_F \) and back temperature. For low frequencies \( f < 1/\tau \), the deviation of the front surface temperature, \( T_F \), from the back temperature decreases with decreasing \( f \) because thermal contact through the plate increases. The optical method introduced by Parker et al. [20] can be used to measure \( D \); this method involves applying a light pulse, or chopped beam illumination, to the front of an insulated slab and measuring the back temperature with a fast thermometer. This optical method was successfully applied to thermoelectric Bi\textsubscript{2}Te\textsubscript{3} and bismuth nanowire arrays by Borca-Tasciuc, Chen, Lin, Rabin, Dresselhaus, Borshchevsky, Fleurial, and Ryan [21, 22].

Applying these concepts to our system, we interpret the observation of an inflection point at \( f_0 \) as the point where equilibration is reached between the front temperature \( T_F \) and back temperature, maintained at \( T_0 \) in our device, therefore, \( \tau = 1/f_0 \). This is the NWA thermalization time. The inflection point frequency of 400 Hz in Figure 3 gives \( D = (1.1 \pm 0.2) \times 10^2 \) cm\(^2\)/s. Our experimental result for \( D \) is in excellent agreement with the experimental result of 1.3 \( \times \) 10\(^2\) cm\(^2\)/s of Borca-Tasciuc et al. [22]. \( D \) is much lower than the thermal diffusivity of bulk Bi because \( \kappa \) is decreased in nanowires due to geometric effects on thermal carriers. This interpretation of \( \tau \) as the array thermalization time is confirmed by our observation that the electrical potential between the front and back surfaces, and, analogously, the signal can be interpreted as the thermoelectric signal proportional to \( T_F \) that is generated by the heat current. The observed signal plateau versus \( f \) arises because, under quasi-equilibrium conditions (i.e., \( f < f_0 \)), \( T_F - T_0 = \dot{Q} L / \kappa S \), where \( \dot{Q} \) is the absorbed optical power, is independent of \( f \).

Additional information about the TE processes in the sample can be obtained from the signal dependence with \( f \) for \( f > f_0 \). The heat diffuses a distance characterized by \( \sqrt{D/f} \), which is normally less than \( L \). Therefore, the thermal contact becomes decreases with increasing \( f \). Consequently, \( T_F - T_0 \) increases with \( f \), proportional to \( \sqrt{f/D} \). As shown on the dashed line in Figure, we observe that, under infrared illumination, the signal shows this \( \sqrt{f} \) proportionality. Therefore, the signal is interpreted as a pure TE response. Also, since the time dependent thermoelectric response corresponds to the thermal model, we interpret the result to indicate that electron-phonon thermalization dominates in the time domain and we can therefore rule out so-called hot electron processes [2, 3, 6, 7] in the case of infrared light. We obtained another estimate of the response frequency by measuring the photoresponse induced by a flash lamp with pulse duration of 100 \( \mu \)s. We observed a response time of \( \sim 150 \mu \)s, corresponding to a frequency of \( \sim 7 \) kHz. (See inset on Figure 4.)

Figure 4. Measured spectral response of NWA to optical excitation: The red dashes are included to emphasize the \( f^{1/2} \) frequency dependence.

The assignment of the signal to TE effects is appropriate in the case of infrared-only illumination. Under visible/infrared illumination, which includes visible light, the inflection point is barely noticeable, and the signal strength is nearly independent of frequency. This behavior strongly suggests that part of the signal is not strictly thermal, indicating the presence of PV or hot electron component in this case.

The measured responsivity of our device was 0.2 V/W. As reported by St-Antoine et al. [23] the nanotube thermopile has a higher responsivity of 0.9 to 1.8 V/W but with a long time constant (1 ms). By contrast, the photoresponse of
Ca$_2$CoO$_2$ thin (~100-nm thick) films with an off-diagonal TE effect were designed to be very fast (~10 ns), but the conversion is very inefficient [24]. In our system, we have demonstrated fast response mechanism, and response up to 7 kHz was achieved. According to our thermal model, the TE response is limited in speed only by thermal diffusion through the optical penetration length $A$. In the present device, $A \sim 500$ nm for visible light implying a potential response frequency as high as $2\pi D/A^2 = 3$ MHz, two orders of magnitude higher than $f_0$. This discrepancy may arise because $A$ is likely longer in the infrared than in the visible in our device [9].

Semiconductors used in solar cells cannot convert the infrared part of the solar spectrum, which represents approximately half of the total solar energy output, because in PV processes the absorption of a photon with energies below the bandgap energy cannot readily produce electron-hole pairs. Devices based on TE nanowires can convert the infrared radiation part of the spectrum into usable electrical power, which suggests that their integration in solar cells may increase overall solar energy harvesting efficiency.

### VII. BOEING APPLICATIONS

[The text in this section has been removed for trade secret protection.]

### VIII. CONCLUSION

In conclusion, we report on the fabrication and photoresponse of a device composed of a nanowire array of TE bismuth, which is capped with a transparent electrode consisting of a film of ITO. The front surface is highly absorbing over a broad band because of the light-trapping property of the nanowire array. We have shown that, under infrared illumination, the photoresponse can be completely described by thermoelastic effects. At low $f$, quasi-equilibrium is achieved and the signal is $f$-independent. At high frequencies the absorbed heat is not dissipated in the back electrode during the illumination cycle, and the signal can rise proportionately with $f^{1/2}$ to much higher values because the energy is delivered to a thin layer on the front of the sample where the junctions are located. The TE effect that completely describes the infrared-only illumination appears to be complimented by PV and hot-carrier processes under visible illumination. The TE signal can be fast, with a response time much shorter than the array thermalization time, only limited by optical penetration. The resulting detection arrays may find future optoelectronic application as fast nanoscale thermopiles. We hope that our work will stimulate work with TE junctions in individual nanowires.

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### REFERENCES

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