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Infrared and thermoelectric power generation in thin atomic layer deposited Nb-doped TiO₂ films

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Infrared radiation is used to radiatively transfer heat to a nanometric power generator (NPG) device with a thermoelectric Nb-doped TiO₂ film deposited by atomic layer deposition (ALD) as the active element, onto a borosilicate glass substrate. The linear rise of the produced voltage with respect to the temperature difference between the “hot” and “cold” junctions, typical of the Seebeck effect, is missing. The discovery of the violation of the Seebeck effect in NPG devices combined with the ability of ALD to tune thermoelectric thin film properties could be exploited to increase the efficiency of these devices for energy harvesting purposes. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4901457]

I. INTRODUCTION

With the harmful environmental impacts brought on by strip mining, fracking, and burning of fossil fuels, there is need for research into clean energy production. Similar to the capture of visible light, as done by solar panels, also the capture and conversion of infrared (IR) radiation is an important and promising opportunity for energy harvesting purposes. The interest in this range of the electromagnetic spectrum stems from its unique property to be present during the day in the sun’s emitted radiation, and during the night in the rays emitted by the earth. In order to capture IR radiation and convert it into usable electricity, the ability of thermoelectric (TE) devices to produce a voltage when irradiated was demonstrated in various reports.¹⁻³ Commerically available bulk TE devices produce a voltage $\Delta V(t)$ when a temperature difference $\Delta T(t)$ is established between its “hot” and “cold” junctions. This phenomenon is TE power generation, which obeys the Seebeck effect, where $\Delta V(t) = -S \Delta T(t)$ and $S$ is the Seebeck coefficient. According to recent studies, $\Delta V(t)$ and $\Delta T(t)$ are not linearly related when heat is transferred radiatively from the IR radiation to a bulk TE device.¹¹ More specifically, $\Delta V(t)$ raises at least one order of magnitude faster than $\Delta T(t)$. In addition, in certain circumstances $\Delta V(t)$ decays while $\Delta T(t)$ does not. These phenomena in which the Seebeck effect is violated is IR power generation.¹¹⁻¹³ The goal of the research presented here is to determine whether the violations summarized above apply in a nanometric power generator (NPG) device in which the active element is a thin TE film deposited by atomic layer deposition (ALD). If the violation of the Seebeck effect applies, then voltage production is not limited by the Seebeck coefficient. Thus, thin film engineering could be exploited to improve the efficiency of voltage production by NPG devices under the effect of IR radiation. For example, NPG devices with a TE thin film as the active element are interesting because they may enable enhanced control of heat transfer.¹⁴ Moreover, the TE figure of merit $ZT = [\delta^2 \sigma/(\kappa_e + \kappa_{ph})]$, where $\sigma$ is the electrical conductivity, $\kappa_e$ the thermal conductivity due to electrons, and $\kappa_{ph}$ the thermal conductivity due to phonons,¹⁵ can be increased in nanostructured materials such as TE thin film, because $\delta^2 \sigma$ can be increased through electronic band structure engineering, and the total thermal conductivity can be minimized through the increase of phonon scattering while leaving the electron mobility almost unaffected.¹⁵

Thermoelectric thin films fabricated by ALD represent a recent field of research that shows additional great potentials.¹⁶⁻²⁴ The ALD technique was chosen to test IR power generation in a NPG device constructed with a TE thin film as the active element for a number of reasons. First of all, ALD allows for excellent conformal deposition of the TE thin film as the active element for a number of reasons. First of all, ALD allows for precise dose the dopants for TE thin films. In addition, the sequential, self-limiting surface reactions of ALD allow for excellent conformal deposition of the TE thin films on both small and potentially also on large substrates, which is crucial for industrial applications as ALD reactors improve in speed, size, and reduction of precursor temperatures. Then, ALD enables TE thin film growth on nonplanar structures, in complex architectures, and at low temperatures.

II. EXPERIMENT

The nanometric thermoelectric (NTE) element is the core of the NPG device used in the research presented here and is shown in Fig. 1. The NTE element consists of a thin layer of n-type Nb-doped TiO₂ film deposited onto a borosilicate glass substrate. The Nb-doped TiO₂ film was grown from TiCl₄ (Sigma-Aldrich, 99.9%), Nb(OEt)₅ (Alfa Aesar, [http://dx.doi.org/10.1116/1.4901457]

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pplication was conducted at a growth temperature of 210 °C. The composition measured for the Ti0.75Nb0.25O2 film was 68.4 nm, which corresponds to growth rate of 0.034 nm/cycle for the film deposited via 2000 ALD cycles. The Nb/(Ti + Nb) atomic ratio in the films was examined by x-ray reflectivity measurement (XRR). Postdeposition annealing crystallizes the Ti0.75Nb0.25O2 film into the anatase TiO2 structure, a fact that is concluded from the presence of the characteristic 101, 103, 004, 112, 200, 105, and 211 peaks in the GIXRD pattern shown in Fig. 2. As evaluated by XRR analysis, the thickness of the film is 68.4 nm, which corresponds to growth rate of 0.034 nm/cycle for the film deposited via 2000 ALD cycles. The annealed Ti0.75Nb0.25O2 film showed a resistivity of 1.4 mΩ cm, and a Seebeck coefficient of −12 μV/°C at 25 °C.

Figure 3 shows the voltage ΔV(t) and temperature ΔT(t) difference data obtained versus time by radiatively transferring heat to the NPG device using IR radiation in IR power generation,11,31 the voltage ΔV(t) and temperature difference ΔT(t) were measured using Keithley 2000 multimeters, sensitive to direct current voltages from 1 to 1 kV and to temperatures from −270 to 1000 °C. The LABVIEW 2012 software was used to record the measurements as a function of time.11,31 In order to avoid external disturbances from exciting the NPG device, the laboratory was kept at a constant temperature of 20 °C, with device, IR radiation and heat sources housed in a dark, N2 purged isolated sample compartment.11,31 The data were collected for 20 min after starting the illumination with the IR radiation or the heat transfer from the hot plate to the NPG device to allow sufficient time for ΔV(t) and ΔT(t) to approach equilibrium.

Two physical configurations of the NPG device were tested: the “away” and the “toward.” The “away” configuration, the NPG device was insulated from the sample holder, as shown in Fig. 1. In contrast, in the “toward” configuration, the insulating medium is removed such that the copper strip chosen as the “hot” junction is directly attached to the anodized aluminum sample holder.

III. RESULTS AND DISCUSSION

The composition measured for the Ti0.75Nb0.25O2 film corresponds well to the nominal film composition, as XRF studies yielded a value 0.244 for the Nb/(Ti + Nb) cation ratio. Postdeposition annealing crystallizes the Ti0.75Nb0.25O2 film into the anatase TiO2 structure, a fact that is concluded from the presence of the characteristic 101, 103, 004, 112, 200, 105, and 211 peaks in the GIXRD pattern shown in Fig. 2. As evaluated by XRR analysis, the thickness of the film is 68.4 nm, which corresponds to growth rate of 0.034 nm/cycle for the film deposited via 2000 ALD cycles. The annealed Ti0.75Nb0.25O2 film showed a resistivity of 1.4 mΩ cm, and a Seebeck coefficient of −12 μV/°C at 25 °C.24

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A Globar (Q301) lamp was utilized to provide broadband IR radiation in the middle IR region (350 – 7500 cm−1, or between 20 and 2.2 μm of wavelength) for IR power generation. On the other hand, a Corning Scholiar 170 hot plate was used to supply heat to be conductively and convectively transferred to the NPG device11,31 for TE power generation. The hot plate was kept to a fixed surface temperature of 37.5 °C across all measurements.

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These data point out a lack of correlation between the trends in time of $\Delta V(t)$ and $\Delta T(t)$, as shown in Fig. 3, thus violating the Seebeck effect. On the other hand, Fig. 4 displays the $\Delta V(t)$ and $\Delta T(t)$ data obtained versus time by conductively and convectively transferring heat to the NPG device using heat from the hot plate in TE power generation. Figures 3 and 4 display the trends of $\Delta V(t)$ and $\Delta T(t)$ collected in the “away” and “toward” configurations. All the data presented were acquired in the first 20 min (1200 s) following the start of the excitation of the NPG device. The values of $\Delta V(t)$ in IR power generation in Fig. 3 are in the microvolt range, and are about three orders of magnitude lower than those revealed in IR power generation using a bulk TE device and reported in Table I. The values of $\Delta V(t)$ in TE power generation in Fig. 4, found in the microvolt range, are about three orders of magnitude lower than those reported in Table II for TE power generation using a bulk TE device. The lower voltages obtained with the NPG device are ascribed to the fact that the NPG device consists of only one couple of TE junctions, whereas the bulk TE device consists of 142 couples of TE junctions.

It is noticeable that in IR power generation the voltage $\Delta V(t)$ in the “away” configuration after the exponential transient at the end of the 20 min measurement is about four times larger than that in the “toward” configuration. This characteristic is in agreement with the differences found in IR power generation with the bulk TE power generator device.

The $\Delta V(t)$ data for IR power generation in Figs. 3(a) and 3(c) were each fitted with an exponential function as follows:

$$\Delta V(t) = \Delta V_0 e^{-\frac{t}{\tau}} + \Delta V_f,$$

where $\Delta V_0$ and $\Delta V_f$ are the initial and final voltages, respectively, and $\tau$ is the time constant. In the “away” configuration, the fitting of the voltage $\Delta V(t)$, shown in Fig. 3(a), required two sets of parameters for Eq. (1), in agreement with the fittings of the $\Delta V(t)$ obtained using a bulk TE power device.
generator device. These parameters are summarized in Table I. One set was used to fit the experimental data from the start of the excitation with IR radiation up to a time \( t_s \) of about 200 s named the separation time. The second set of parameter was used to fit the experimental data after \( t_s \). The existence of a separation time is in agreement with the findings in IR power generation using a bulk TE power generator device. However, the value of \( t_s \) obtained in IR power generation using the NPG device is about two orders of magnitude larger than that obtained using a bulk TE power generator device. In the “toward” configuration, the fitting of the voltage \( \Delta V(t) \) data in Fig. 3(c) required only one set of parameters for Eq. (1), as summarized in Table I. Accordingly, no separation time was found. This finding is in contrast with the behavior of IR power generation obtained using a bulk TE device. However, the time constant \( \tau \) is large and comparable to that found after \( t_s \) in the “away” configuration. The absence of a separation time and the large value of the time constant in the trends for \( \Delta V(t) \) in the “toward” configuration suggest that the voltage is unable to rapidly rise under the effect of the IR radiation, in contrast with the behavior revealed in IR power generation with a bulk TE device. In summary, the values of the time constants and separation time reported in Table I suggest that the dynamics of \( \Delta V(t) \) in IR power generation with a NPG device is slower than with a bulk TE power generator device, as will be further discussed below.

Significant trends are absent in the \( \Delta T(t) \) data in Figs. 3(b) and 3(d) in the case of IR power generation obtained using a NPG device, but the \( \Delta T(t) \) values vary in the range of a fraction of a degree which is comparable to that revealed in IR power generation for a bulk TE device.

For TE power generation, where heat is convectively and conductively transferred from a hot plate to activate either the NPG device, the \( \Delta V(t) \) and \( \Delta T(t) \) data in Fig. 4 were fitted using the linear functions:

![Figure 4](image_url)

**Table I.** Fitting parameters used for Eq. (1) applied to the voltage \( \Delta V(t) \) produced in time by illuminating with IR radiation a NPG device with a TE 600 °C annealed Ti0.75Nb0.25O2 film originally deposited via ALD as the active element. The results obtained in both the “away” and “toward” configurations are summarized. The separation time \( t_s \) indicates the amount of time since the beginning of the illumination with IR radiation after which the voltage \( \Delta V(t) \) switches the value of the parameters in Eq. (1). For comparison, in the “away” configuration, the bulk TE device yields \( t_1, t_2, \) and \( \Delta V_{1-2} \) of 8.1 s, 63.7 s, and 720 µV, respectively (Ref. 11).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \Delta V_{0-1} ) (µV)</th>
<th>( t_1 ) (s)</th>
<th>( \Delta V_{f-1} ) (µV)</th>
<th>( t_s ) (s)</th>
<th>( \Delta V_{0-2} ) (µV)</th>
<th>( t_2 ) (s)</th>
<th>( \Delta V_{f-2} ) (µV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“away”</td>
<td>−4.0±0.1</td>
<td>87±2</td>
<td>4.1±0.1</td>
<td>200</td>
<td>−2.5±0.1</td>
<td>175±5</td>
<td>4.5±0.3</td>
</tr>
<tr>
<td>“toward”</td>
<td>−1.3±0.1</td>
<td>150±10</td>
<td>1.4±0.2</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>
II. On the other hand, the rates of increase of the offsets. The values of these parameters are summarized in Table II. Deviations from the linear behavior in Figs. 4(b) and 4(d) are related to the existence of a super-cycle in the cycle or to the influence on the super-cycle of the “away” or “toward” configurations.31 The parameters used to fit with a linear function the voltage \( \Delta V(t) \) and the temperature \( \Delta T(t) \) differences when heat is conductively and convectively transferred from a hot plate to the NPG device with a TE 600 °C annealed Ti0.75Nb0.25O2 film originally deposited via ALD as the active element. The results obtained in the “away” and “toward” configurations are summarized. The coefficients \( x \) and \( \beta \) are the rates of increase of \( \Delta V(t) \) and \( \Delta T(t) \) with time, respectively, whereas \( \Delta V_0 \) and \( \Delta T_0 \) are the initial offsets. For comparison, in all configurations examined using a bulk TE device, the rate of increase of the voltage, \( x \), is on average 30 \( \mu \text{V/s} \), whereas the rate of increase of temperature difference, \( \beta \), is on average 0.02 °C/s (Ref. 31). The \( \Delta T_0 \) values are similar to those found in this research, while the \( \Delta V_0 \) values are 1140 and –620 \( \mu \text{V} \) in the “away” and “toward” configurations, respectively (Ref. 31).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>( \Delta V_0 ) (( \mu \text{V} ))</th>
<th>( x ) (( \mu \text{V/s} ))</th>
<th>( \Delta T_0 ) (°C)</th>
<th>( \beta ) (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“away”</td>
<td>–1.5 ± 0.1</td>
<td>0.06 ± 0.01</td>
<td>0.75 ± 0.02</td>
<td>0.005 ± 0.004</td>
</tr>
<tr>
<td>“toward”</td>
<td>–5.5 ± 0.3</td>
<td>0.16 ± 0.01</td>
<td>–0.42 ± 0.01</td>
<td>0.006 ± 0.001</td>
</tr>
</tbody>
</table>

\[
\Delta V(t) = \Delta V_0 + x \cdot t
\]
and
\[
\Delta T(t) = \Delta T_0 + \beta \cdot t,
\]
in both the “away” and “toward” configurations.31 The \( x \) and \( \beta \) coefficients are the rate of increase of \( \Delta V(t) \) and \( \Delta T(t) \) with time, respectively, whereas \( \Delta V_0 \) and \( \Delta T_0 \) are the initial offsets. The values of these parameters are summarized in Table II. Deviations from the linear behavior in Figs. 4(b) and 4(d) are related to the existence of a super-cycle in the heating procedure of the hot plate. The different effects in Figs. 4(b) and 4(d) relate to a different phase of the super-cycle or to the influence on the super-cycle of the “away” or “toward” configuration of the NPG device. The rates of increase \( x \) of \( \Delta V(t) \), reported in Table II, are two orders of magnitude lower than those obtained in the case of TE power generation using a bulk TE device,31 also reported in Table II. On the other hand, the rates of increase \( \beta \) of \( \Delta T(t) \) in TE power generation using the NPG device are on one order of magnitude lower than those obtained using a bulk TE device.31 All the relevant values are reported in Table II. Differently than in the case of the bulk TE device,31 the voltages \( \Delta V(t) \) obtained with the NPG device in the “away” and “toward” configurations start increasing with a delay of about 200–400 s after beginning the heat transfer from the hot plate. The existence of this incubation time, labeled \( t_{inc} \) in Figs. 4(a) and 4(c), is in accord with the overall slow dynamics occurring with the NPG device. This issue will be further discussed below.

The differences found between IR and TE power generation point out the lack of equivalence between heat transferred radiatively from IR radiation, and heat transferred conductively and convectively from a hot plate, in agreement with earlier findings.11 It is significant that in TE power generation, \( S \) for the NPG device with the thin Nb-doped TiO2 film as active TE element is estimated as −10.0 and −21.0 \( \mu \text{V/°C} \) in the “away” and “toward” configurations, in good agreement with the value of −12 \( \mu \text{V/°C} \) reported in Ref. 24 for the cation ratio \( x = 0.25 \). The differences found between IR and TE power generation are not expected to change with, e.g., larger \( S \) value for the thin TE film, because of the radically different physical mechanisms taking place in the two cases, as verified in bulk TE devices with different characteristics (data not published).

Figure 5 shows the \( \Delta V(t) \) data obtained with the NPG device without the layer of thin TE Nb-doped TiO2 film on the borosilicate glass substrate. Both IR and TE power generation data are examined in the “away” and “toward” configurations. The \( \Delta V(t) \) values sporadically fluctuate between −1.12 and 0.61 V in all examined cases. The data can simply be described as overflow values given by the Keithley 2000 multimeter used to collect the \( \Delta V(t) \) data. The absence of significant trends in the voltage difference \( \Delta V(t) \) data in the case of IR power generation for a NPG device without the thin Nb-doped TiO2 film as active TE element suggests that the thin TE film grown using ALD is truly effective (see Fig. 5). Thus, further research should clarify what unique capability of the ALD technique could improve the effectiveness of the TE thin films in IR power generation. For example, one question to be addressed is whether precisely controlling the doping or the film thickness could affect and improve the voltage output of the NPG device.

The Seebeck coefficient \( S \) provided by the 600 °C annealed Ti0.75Nb0.25O2 film was measured as \( S = -[\Delta V(t)/\Delta T(0)] \) from the voltage and temperature difference several hours after starting the excitation of the NPG device. In TE power generation, \( S \) is estimated as −10.0 and −21.0 \( \mu \text{V/°C} \) in the “away” and “toward” configurations, respectively. These last two values are of the same order of magnitude as that of −12 \( \mu \text{V/°C} \) reported in Ref. 24 for the cation ratio \( x = 0.25 \).

Finally, as inferred from the data in Table I, the time constants and the separation time \( t_e \) used for the fittings of the \( \Delta V(t) \) data in Fig. 3 are one to two orders of magnitude larger than those used for fitting the \( \Delta V(t) \) data from IR power generation obtained using a bulk TE device.11 In addition, in TE power generation using the NPG device there is an incubation time \( t_{inc} \) of about 200 to 400 s before the voltage \( \Delta V(t) \) starts increasing after initiating the conductive and convective transfer of heat from the hot plate, as shown in Fig. 4. The slow dynamics could be ascribed to the fact that the NPG device consists of only one couple of TE junctions, whereas the bulk TE device consists of 142 couples of TE junctions. Arranging several NPG devices in series or in parallel could allow solving not only the problem of the slow dynamics, but also that of the low voltages found in Figs. 3 and 4, and in Tables I and II. The slow dynamics could also be ascribed to the fact that thermal conductivity decreases with thickness in thin films.33 Possibly electric resistance increases with decreasing film thickness due to the scattering induced by the interfaces between film and surrounding.

IV. SUMMARY AND CONCLUSIONS

This research studies the interaction between IR radiation and a NPG device. The NPG device consists of a nanometric
TE element made of a thin Nb-doped TiO₂ film deposited via ALD onto a borosilicate glass substrate. The results suggest an overall agreement of the trends in IR power generation of a bulk TE device, examined in a previous study, and of a NPG device. Namely, the produced voltage cannot be ascribed to the Seebeck effect. On the other hand, both the NPG and bulk TE devices behave in agreement with the Seebeck effect in TE power generation, where heat is convectively and conductively transferred from a hot plate to the devices. These results point out the lack of equivalence between heat transferred radiatively on one hand, and heat transferred conductively and convectively on the other, in agreement with earlier findings using a bulk device. The reason explaining the difference between the behavior of IR power generation in the “away” and the “toward” configurations is still missing. An explanation would aid in understanding what ALD film engineering could do to improve voltage production. However, the present results suggest that the violation of the Seebeck effect takes place even in the NPG device. This finding is very promising since, without the limitations imposed by the Seebeck coefficient in voltage production, and by exploiting the possibility to improve the efficiency through thin film engineering via ALD, the NPG device could be applied to efficiently harvest IR radiation.

The violation of the Seebeck effect in IR power generation using the NPG device constructed using a thin TE thin film suggests that, through thin film engineering, it could be possible to develop new ways to efficiently harvest radiation with NPG devices. In particular, the use of ALD deposited TE films is of great interest to reach this goal because of, e.g., the ability of ALD to dose the dopants and to provide sequential, self-limiting surface reactions, which enables excellent conformal and controllable deposition on both small and large substrates at an industrial scale. In addition, device engineering can develop strategies to solve the problems related to the slow dynamics and the low voltage values revealed in this research in a NPG device with only one junction.

**ACKNOWLEDGMENTS**

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