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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.¹ 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.²–⁴ Commercially available bulk TE devices produce a voltage Δ𝑉(𝑡) when a temperature difference Δ𝑇(𝑡) is established between its “hot” and “cold” junctions. This phenomenon is TE power generation, which obeys the Seebeck effect,⁴–¹⁰ where Δ𝑉(𝑡) = −𝑆 ∗ Δ𝑇(𝑡) and 𝑆 is the Seebeck coefficient. According to recent studies, Δ𝑉(𝑡) and Δ𝑇(𝑡) are not linearly related when heat is transferred radiatively from the IR radiation to a bulk TE device.¹¹ More specifically, Δ𝑉(𝑡) raises at least one order of magnitude faster than Δ𝑇(𝑡). In addition, in certain circumstances Δ𝑉(𝑡) decays while Δ𝑇(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

\[ ZT = \frac{S^2 \sigma}{C_1 + C_2 + \frac{C}{T}} \]

where \( \sigma \) is the electrical conductivity, \( C_2 \) the thermal conductivity due to electrons, and \( C_1 \) the thermal conductivity due to phonons,¹⁵ can be increased in nanostructured materials such as TE thin film, because \( S^2 \sigma \) 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.¹⁶–²⁹ 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 enables to precisely 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, 99.99%), Nb(OEt)₃ (Alfa Aesar, 99.9%), and other precursors as shown in Table I. The nanometric thermoelectric (NTE) element is the core of the NPG device used in the research presented here and is shown in Fig. 1.
To construct the NPG device, the NTE element was secured to two copper strips, as shown in Fig. 1. The two contact points between the copper strips and the NTE element served as the “hot” and “cold” junctions of the NPG device. Determining which junction is the “hot” or “cold” one is arbitrary, but, once specified, the junctions remained the same for all experiments. The NTE element was 12 × 10 mm² in size. The contact area of the film with each copper block was roughly 42 mm². The copper strips were 19.8 × 33.1 × 1.0 mm³ in size. To test the effectiveness of the TE thin film, measurements were conducted with the NPG device without TE thin film in the NTE element so that just the borosilicate glass acted as effective element.

The commercially available bulk TE power generator device referred to in this research is a 07111–9L31–04B device by Custom Thermoelectrics Inc.11,31 in which the active TE element is doped Bi₁₃Te₃₀-based alloy.

As in previously published reports on IR and TE power generation,11,31 the voltage ΔV(t) and the 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.”11 In 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, shown in Fig. 1, was removed such that the NPG device was in contact with the sample holder. The two configurations were chosen to replicate those applied to a bulk TE device in Refs. 11 and 31.

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 Scholar 170 hot plate was used to supply heat to be conductively and convectively transferred to the NPG device31 for TE power generation. The hot plate was kept to a fixed surface temperature of 37.5 °C across all measurements.

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 a 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/K at 25 °C.24

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...
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.[11]

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:

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

where $\Delta V_0$ and $\Delta V_f$ are the initial and final voltages, respectively, and $\tau$ is the time constant.[11] 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 generation.
Infrared and thermoelectric power generation in thin ALDTiO.75Nb0.25O2 films

Fig. 4. (Color online) For an NPG device with a 600 °C annealed TiO.75Nb0.25O2 film originally deposited via ALD as the active element and excited by conductively and convectively transferring heat from a hot plate, panels (a) and (b) show the experimental trends (empty circles) and fitting (solid lines) of the voltage ∆V(t) and the temperature ∆T(t) differences, respectively, in the “away” configuration. On the other hand, panels (c) and (d) display the experimental trends (empty circles) and fitting (solid lines) of the voltage ∆V(t) and the temperature ∆T(t) differences, respectively, in the “toward” configuration. The time tinc in (a) and (c) indicates the amount of time since the beginning of the heat transfer to the NPG device after which the voltage ∆V(t) starts increasing. Such incubation time was not observed in TE power generation with a bulk TE device (Ref. 31).

TABLE I. Fitting parameters used for Eq. (1) applied to the voltage ∆V(t) produced in time by illuminating with IR radiation a NPG device with a TE 600 °C annealed TiO.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 tinc in (a) and (c) indicates the amount of time since the beginning of the heat transfer to the NPG device after which the voltage ∆V(t) starts increasing. Such incubation time was not observed in TE power generation with a bulk TE device (Ref. 31).

<table>
<thead>
<tr>
<th>Configuration</th>
<th>∆V0,1 (µV)</th>
<th>t1 (s)</th>
<th>∆Vf,1 (µV)</th>
<th>tf (s)</th>
<th>∆V0,2 (µV)</th>
<th>t2 (s)</th>
<th>∆Vf,2 (µV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;away&quot;</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>&quot;toward&quot;</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>

For comparison, in the “away” configuration, the bulk TE device yields t1, t2, and ∆Vf,2 of 8.1 s, 63.7 s, and 720 µV, respectively (Ref. 11).
Table II. 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 Ti$_{0.75}$Nb$_{0.25}$O$_2$ film originally deposited via ALD as the active element. The results obtained in the “away” and “toward” configurations are summarized. The coefficients $\alpha$ 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, $\alpha$, is on average 30 $\mu$V/s, whereas the rate of increase of temperature difference, $\beta$, is on average 0.02 °C/s (Ref. 31). The $\Delta V_0$ values are similar to those found in this research, while the $\Delta V_0$ values are 1140 and $-620 \mu$V in the “away” and “toward” configurations, respectively (Ref. 31).

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

\[
\Delta V(t) = \Delta V_0 + \alpha \times t \tag{2}
\]

and

\[
\Delta T(t) = \Delta T_0 + \beta \times t, \tag{3}
\]

in both the “away” and “toward” configurations. The $\alpha$ 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 rates of increase $\alpha$ 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, 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 about one order of magnitude lower than those obtained using a bulk TE device. All the relevant values are reported in Table II. Differently than in the case of the bulk TE device, 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. It is significant that in TE power generation, $S$ for the NPG device with the thin Nb-doped TiO$_2$ film as active TE element is estimated as $-10.0$ and $-21.0 \mu$V/°C in the “away” and “toward” configurations, in good agreement with the value of $-12 \mu$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 TiO$_2$ 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 $0.61 \mu$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 TiO$_2$ 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 Ti$_{0.75}$Nb$_{0.25}$O$_2$ film was measured as $S = \frac{\Delta V(t)}{\Delta T(t)}$ 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 $-21.0$ $\mu$V/°C in the “away” and “toward” configurations, respectively. These last two values are of the same order of magnitude as that of $-12 \mu$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. 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. 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 TiO$_2$ 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.

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