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# Excitation of radiative polaritons by polarized broadband infrared radiation in thin oxide films deposited by atomic layer deposition

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This work contributes to the understanding of infrared radiation interaction with matter and its absorption for energy harvesting purposes. By exciting radiative polaritons in thin oxide films with polarized infrared radiation, a further evidence is collected that a link exists between radiative polaritons and the heat recovery mechanism hypothesized in previous research. In the voltage transient occurring when the infrared radiation is turned on, the observed time necessary to reach the maximum voltage and the voltage intensity versus angle of incidence exhibit a mismatch when generated by polarized and nonpolarized infrared radiation. The existence of collective charge oscillation modes in the semiconductor-based elements of the thermoelectric power generators supporting the heat recovery mechanism is suggested as the main source of the discrepancy. © *2013 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4759442]

## I. INTRODUCTION

There is a rising interest in understanding the interaction of the infrared (IR) portion of the electromagnetic spectrum with thin dielectric films[1,2] with the goal of singling out a possible method to harvest IR radiation and transform it into usable electric energy. The ability of radiative polaritons (RPs)[3] to absorb IR radiation in thin planar oxide films deposited by atomic layer deposition (ALD) on a metallic substrate was recently proposed through the heat recovery mechanism (HRM).[1] The HRM is the exploitation of the Seebeck effect in thermoelectric (TEC) power generators to produce an electromotive force (EMF) from the temperature difference $\Delta T$ between the "hot" and the "cold" junctions induced by the excitation of RPs in thin dielectric films.[1] The temperature difference $\Delta T$ is due to the heat produced by the IR radiation absorbed in the thin oxide film and dissipated in the excitation of RPs.[1]

A polariton is a mixed excitation resulting from the strong coupling between the transverse optical (TO) phonons and the IR photon field in dielectric (oxide or semiconductor) layers.[3] Different than nonradiative polaritons,[3] the RPs have a phase velocity such that $(\omega/|\mathbf{k}|)^2 > (c)^2$,[1,3] where $\omega$ is the angular frequency, $|\mathbf{k}|$ the modulus of the wave-vector, and $c$ the speed of light in vacuum. The RPs appear in IR spectra between approximately 100 and 1200 $cm^{-1}$, depending upon oxide chemistry. In a previous work,[1] it was found that the 0TH type-RP plays a crucial role in the HRM. The 0TH type-RP is the solution of the tangent equation (T) in the Fuchs–Kliewer model[3] with frequency closer (0th order) to that of the longitudinal optical (LO) phonon (H, because the $\omega_{LO}$ is the high frequency, whereas $\omega_{TO}$ is the low (L) frequency phonon mode). Specifically, the angular dependence of the EMF due to the excitation of the 0TH type-RP (Ref. 3) suggested the existence of a link between RPs and the HRM. It was found that, concurrently with the increase of the incidence angle $\theta_0$ of the IR radiation, an increase occurs in the intensity of the 0TH type-RP for IR absorptance spectra (Berreman effect[4]) and in the EMF produced by the HRM.[1] In IR absorptance spectra, however, the angular dependence of the RPs is markedly affected by the polarization of the incident IR radiation.[3,5] In particular, the 0TH type-RP is excited with increasing intensity at increasing $\theta_0$ by transverse magnetic (TM) polarized IR radiation, whereas it disappears with transverse electric (TE) polarized IR radiation.[1,3] Here, we show that the polarization of the incident IR radiation imposes a similar trend on the HRM in oxide films. This successful result further links RPs excitation to the HRM and casts away doubts on the ability of RPs to absorb IR radiation. The results, however, unveil some features of the absorbed IR energy which cannot be fully understood through a simple comparison of the RPs excitation behavior in IR spectroscopy and in the HRM.

## II. EXPERIMENT

Amorphous (a) $Al_2O_3$ films on Al foil with thickness below the skin depth and the substrate sensitive thickness (250 nm)[2] are suitable for the proposed investigations because here the 0TH type-RP absorbs up to 40% of the IR radiation,[2] more than any other RP, and exhibits a marked angular and polarization dependence in IR spectra.[1] The substrate sensitive thickness is defined in Ref. 2 as the upper limit thickness where the IR radiation interaction with the thin oxide film significantly

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depends on substrate chemistry and conductivity, and was found to be 250 nm.[2]

The films were deposited using ALD (Ref. 6) with procedure and reactor described elsewhere.[1,7] The corresponding IR spectra acquired with TM and TE polarized IR radiation are also pictured in a previous report.[1] For the HRM measurements, the EMF produced by a 250 nm thick a-$Al_2O_3$ films on a 23 $\mu$m thick Al foil on a TEC power generator [system 1, illustrated in Fig. 1(a)] is compared with that produced by a 23 $\mu$m thick Al foil on a TEC power generator (system 2) in a 30°–70° $\theta_0$ angular range. The bare and lapped TEC power generator (Custom Thermoelectric 07111-9L31-04B) has a nominal 0.14 V/°C Seebeck coefficient, in good agreement with the experimental value of $0.097 \pm 0.011$ V/°C at room temperature.[1] To measure the EMF, the leads of the TEC power generator are connected to a Keithley 2000 multimeter, sensitive to direct current (DC) voltages from $1 \times 10^{-3}$ to $1 \times 10^{6}$ mV. The HRM measurements were acquired by placing systems 1 and 2 on the reflection accessory Veemax II by Pike Technologies in the closed sample compartment of a $N_2$ purged Bruker Vertex 70 IR spectrometer. The IR radiation, produced by a globar (Q301) source, is polarized with a ZnSe middle-IR general purpose polarizer by Pike Technologies prior to illuminating the sample surface, as shown in Fig. 1(a). The polarized IR radiation is inclined at $\theta_0$ angles in the 30°–85° range inside the reflection accessory. Before switching on the illumination with the polarized broadband IR radiation, the EMF of systems 1 and 2 is stabilized at $1 \times 10^{-2}$ mV in the closed sample compartment of the IR spectrometer, which establishes the initial boundary condition of the experiment. The laboratory is kept in the dark and at 20 °C to minimize the contribution of the background radiation.

## III. RESULTS

Upon switching on the broadband polarized IR radiation, the EMF reaches its maximum value, $EMF_{max}$, after 20 s at $\theta_0 = 30°$, 40°, and 70° in TE polarization, and at $\theta_0 = 30°$ and 70° in TM polarization. At the other $\theta_0$ angles in TE and TM polarization, the $EMF_{max}$ values are reached after 30 s, as shown in Fig. 1(b) for system 1. System 2 (data not shown) requires the same amount of time to achieve $EMF_{max}$. Comparing the time versus angle behavior of the two systems, the $EMF_{max}$ value excited with polarized IR radiation (this work) is achieved about 10 s earlier than with nonpolarized IR radiation.[1] Thus, in both systems 1 and 2, the polarized IR radiation increases versus $\theta_0$ the time required to achieve $EMF_{max}$.

The $EMF_{max}$ values increase with $\theta_0$. The larger $EMF_{max}$ value, ~0.04 mV, is obtained for system 1 with TM polarized IR radiation at $\theta_0 = 60°$, as shown in Fig. 2(a). Figure 2(b) indicates that system 1 produces a larger $EMF_{max}$ than system 2 in either TE or TM polarization, and the difference exhibits an angular trend, especially in TM polarization, achieving the maximum value of $9 \times 10^{-3}$ mV at $\theta_0 = 60°$. In TE polarization, on the other hand, the difference in $EMF_{max}$ between systems 1 and 2 exhibits a less pronounced angular trend, being located on average around $4.5 \times 10^{-3}$ mV. This finding is consistent with the expectation, derived from IR spectra

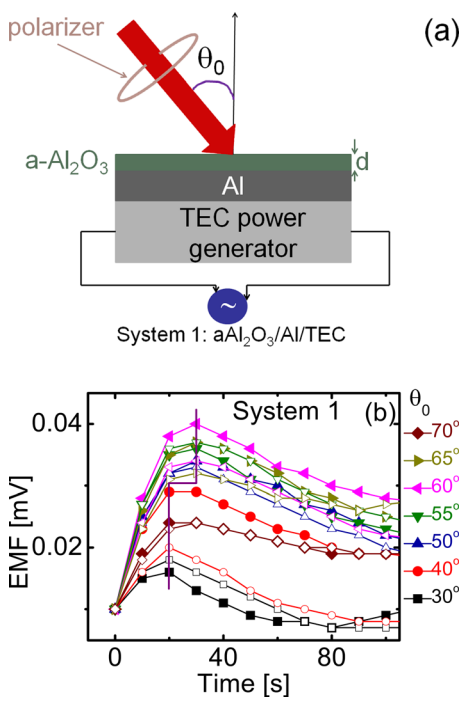


FIG. 1. (Color online) (a) Schematic of system 1 consisting of an a-$Al_2O_3$ film on Al foil on a TEC power generator illuminated at $\theta_0$ by polarized IR radiation. (b) Trends of EMF vs time for system 1 illuminated by TM (filled symbols) and TE (empty symbols) polarized IR radiation at various $\theta_0$ angles. The vertical lines help tracing the $EMF_{max}$ values.

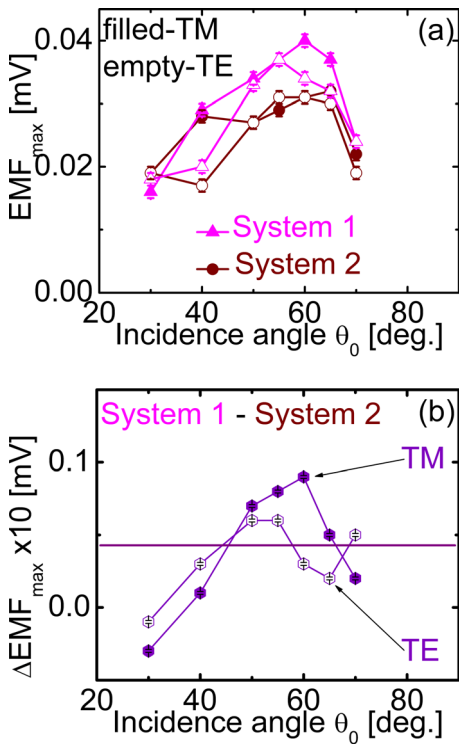


FIG. 2. (Color online) (a)Values of $EMF_{max}$ vs $\theta_0$ and (b) difference between the $EMF_{max}$ vs $\theta_0$ for systems 1 and 2 illuminated by TM (filled symbols) and TE (empty symbols) polarized IR radiation. In panel (b), the original values are multiplied by 10, and the horizontal line marks the average difference in TE polarization.

and from literature,[1,3–5] that the 0TH type-RP is excited with increasing absorption of TM polarized IR radiation at increasing $\theta_0$ and responds with weaker absorption to TE polarized IR radiation.

Analysis of the data in Fig. 3 indicates that the $EMF_{max}$ values obtained with TE and TM polarized IR radiation are $5.5 \pm 1.2$ times smaller than those obtained with nonpolarized IR radiation in Ref. 1. This result can be ascribed to the presence of the polarizer in the IR radiation path before reaching system 1 or 2. However, absorption area analysis of the 0TH type-RP in IR spectra in Figs. 4(a) and 4(b) indicates that the IR radiation reaching the oxide film after traveling through the polarizer is $3.2 \pm 0.4$ times smaller than that not passing through it. Thus, some additional factor prevents the IR radiation from reaching systems 1 and 2 with polarized IR radiation. In addition, Fig. 3 shows that the largest $EMF_{max}$ value occurs at $\theta_0 = 60°$ for systems 1 and 2 illuminated by polarized IR radiation and at $\theta_0 = 70°$ for the systems illuminated by nonpolarized IR radiation. This observation diverges from peak area analysis obtained from IR spectroscopy data showing that the 0TH type-RP in a 250 nm thick a-$Al_2O_3$ film on Al foil achieves its maximum absorption peak at $\theta_0 = 70°$ (92.7 a.u.) and $\theta_0 = 60°$ (25.6 a.u.) when excited with TM, Fig. 4(a), and nonpolarized, Fig. 4(b), IR radiation, respectively.

## IV. DISCUSSION

To understand the shorter amount of time to achieve $EMF_{max}$ in Fig. 1(b) and the lower $EMF_{max}$ of the HRM excited in systems 1 and 2 by polarized versus nonpolarized IR radiation (Fig. 3), we hypothesize that collective charge oscillation modes exist in the semiconductor-based elements of the TEC power generator. These collective charge could be at the origin of the observed slow relaxing[8] EMF. In system 1, the IR radiation excites such collective charge oscillation modes concurrently to the RPs, and the two excitations are entwined. When polarized IR radiation illuminates systems 1 and 2, less intense radiation is involved than with nonpolarized radiation. A number $N_p$ and $N_{np}$ of collective charge oscillation modes are generated with polarized and nonpolarized IR radiations,

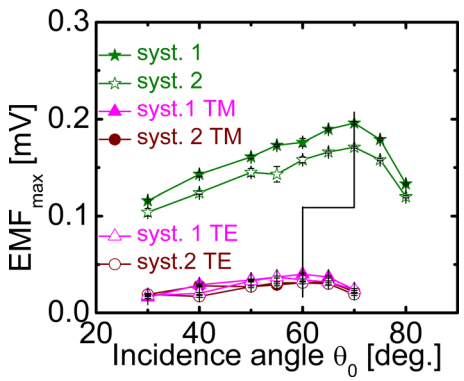


FIG. 3. (Color online) Values of $EMF_{max}$ vs $\theta_0$ for systems 1 (triangles) and 2 (circles) illuminated by TM (filled symbols) and TE (empty symbols) polarized and by nonpolarized IR radiation (filled stars for system 1 and empty stars for system 2, from Ref. 1). The vertical lines help tracing the $EMF_{max}$ values.

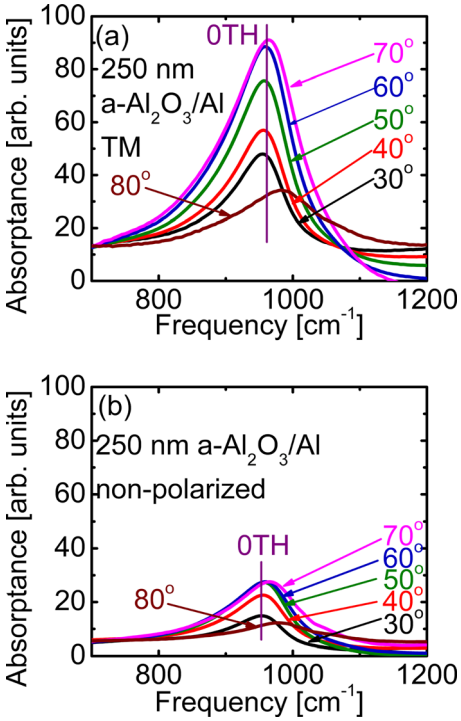


FIG. 4. (Color online) IR absorptance spectra for a 250 nm thick a-$Al_2O_3$ film on Al foil at various $\theta_0$ illuminated by (a) TM and (b) nonpolarized IR radiation. The peak corresponding to the 0TH type-RP is clearly marked. For spectra in panel (a), the polarizer is placed in the IR radiation path before its interaction with the oxide film.

respectively. Our data suggest that $N_p < N_{np}$. As proof of concept, we note that when $\theta_0$ and, concurrently, the normal component, $E_\perp$, of the TM polarized electric field on the oxide film surface increase, also the time necessary to achieve $EMF_{max}$ increases, as observed in Fig. 1(b). The response of the RPs to polarized IR radiation develops concurrently to the $N_p$ collective charge oscillation modes. The RPs further absorb part of the polarized IR radiation. Inefficiencies in the heat transfer process to the TEC power generator might contribute to the $EMF_{max}$ ratio obtained with polarized and nonpolarized broadband IR radiation and to the mismatch of the $\theta_0$ angles where the maxima in EMF and spectroscopic absorption occur upon the excitation of the 0TH type-RPs by polarized and nonpolarized IR radiation (Fig. 3). The specific characteristics of the collective charge oscillation modes excitation might change with different boundary conditions, e.g., if systems 1 and 2 were stabilized outside the spectrometer.[9,10] The effect of the boundary conditions and time, and the exact nonlinear mechanism of the collective charge oscillation modes in the HRM needs further understanding.

The decay of the EMF in Fig. 1(b) is an unusual voltage transient, which is nonlinear with respect to the IR radiation illumination. It is not yet fully understood. However, the authors hypothesize that collective charge motion in the TEC power generator becomes chaotic because of the nonlinearity between collective charge motion and the momentum imparted to them by the continuous broadband IR radiation. The chaotic motion could explain the EMF decay. A model describing the phenomenon is in preparation.

The $EMF_{max}$ values obtained with TE and TM polarized IR radiation being $5.5 \pm 1.2$ times smaller than those obtained with nonpolarized IR radiation in Ref. 1 refer to the unusual voltage transient which is nonlinear with respect to the IR radiation illumination and which is detected upon turning on the continuous broadband IR radiation in an insulated compartment. The considered $EMF_{max}$ values are very small, and their evolution with time decreases the EMF further due to the hypothesized chaotic phenomena. For applications and fundamental understanding, it is more useful to understand what happens beyond the transient voltage point, after the interaction between the broadband IR radiation and the TEC power generator has stabilized. Preliminary data indicate that the EMF raises some time after the chaotic phenomena have relaxed. The investigation is currently under way.

## V. SUMMARY AND CONCLUSIONS

To summarize, we show that the angular response of the heat recovery mechanism is different with transverse electrically or magnetically polarized infrared radiation, as expected from the behavior of radiative polaritons in infrared spectroscopy. However, the time necessary to reach the maximum voltage and the voltage intensity in the heat recovery mechanism are, respectively, faster and lower with polarized than with nonpolarized infrared radiation. These findings can be explained by viewing the excitation of the heat recovery mechanism by infrared radiation to occur concurrently with the excitation of N collective charge oscillation modes in the semiconducting elements of the thermoelectric power generator. The number N increases with infrared radiation intensity. This excitation of the collective charge oscillation modes is faster with smaller N. The characteristics of the collective charge oscillation modes involved in the heat recovery mechanism needs further studies.

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