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Anita J. Vincent-Johnson
James Madison University

Kyle A. Vasquez
James Madison University

John E. Bridstrup
James Madison University

Andrew E. Masters
Custom Thermoelectric

Xiaofeng Hu
James Madison University

See next page for additional authors

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Authors
Anita J. Vincent-Johnson, Kyle A. Vasquez, John E. Bridstrup, Andrew E. Masters, Xiaofeng Hu, and Giovanna Scarel

Heat recovery mechanism in the excitation of radiative polaritons by broadband infrared radiation in thin oxide films

Anita J. Vincent-Johnson,[1] Kyle A. Vasquez,[2] John E. Bridstrup,[1] Andrew E. Masters,[3] Xiaofeng Hu,[2] and Giovanna Scarel[1,a)]
[1]*Department of Physics and Astronomy, James Madison University, Harrisonburg, Virginia 22807, USA*
[2]*Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, Virginia 22807, USA*
[3]*Custom Thermoelectric, Bishopville, Maryland 21813, USA*

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This work probes radiative polaritons in thin oxide layers as a mean to capture and absorb broadband infrared radiation and transform it into heat. A heat recovery mechanism, based on the Seebeck effect, is used as the tool of the investigation. Heat production challenges the current understanding which views the excitation of radiative polaritons as only accompanied by the emission of electromagnetic radiation. The heat recovery mechanism presented here can inspire the design of infrared energy harvesting devices, similar to photovoltaic cells, and other devices to convert energy from a wide range of the electromagnetic radiation spectrum using thermoelectric power generators. © *2011 American Institute of Physics*. [doi:10.1063/1.3643464]

The objective of this work is to prove that (a) short lifetime ($\sim$ ps) radiative polaritons (RPs)[1] excited by the coupling between transverse optical (TO) phonons in a thin oxide film and infrared (IR) photons produce heat and that (b) this heat can be transferred to a thermoelectric (TEC) power generator which, through a heat recovery mechanism based on the Seebeck effect, converts it into electricity. The theory by Kliewer *et al*. based on conservation of momentum[1,2] and on retardation[1,2] predicts that the excitation of RPs is only followed by field radiation. For radiative plasmons in relatively ideal metal films, Ferrell proposed that radiation competes favorably with electronic damping and that the decay of the radiative plasmons manifests itself almost entirely as radiation.[2] For RPs in dielectric layers, no phenomenon competing with radiation was predicted by Kliewer *et al*.[1] This work indicates instead that heat production competes with radiation in the process of RP excitation, and that the produced heat is released within the thin oxide film.

A polariton is a mixed excitation resulting from the strong coupling between the TO phonons and the IR photon field in dielectric (oxide or semiconductor) layers.[1] Differently than non-radiative polaritons,[3] the RPs have a phase velocity such that $(\frac{\omega}{|\mathbf{k}|})^2 > (c)^2$,[1] where ω is the angular frequency, $|\mathbf{k}|$ is the modulus of the wave-vector, and c is the speed of light. Radiative polaritons respond to this unphysical situation by giving off energy.[1] Generally, theory[1] assumes that this energy is the radiation emitted at frequencies depending upon IR radiation incidence angle θ_0 and oxide layer thickness. Therefore, the polaritons are named "radiative" and are held responsible of the optical properties in the IR region of the dielectric layers.[4] Dissipation and damping phenomena, thus heat production, are not included in the theory of Kliewer *et al*.,[1,4] which only considers the boundary conditions between dielectric layers and perfect conductors or insulators. We thus hypothesizes that in thin oxide films on substrates with finite conductivity, heat is produced. We indirectly reveal the produced heat by the heat recovery mechanism as follows. Once produced in the excitation of RPs, heat can be transferred from the dielectric film to a TEC power generator. On the "hot" junction, the heat gives rise to a temperature difference ΔT with the "cold" junction. We experimentally estimated that the TEC power generator used in this work is sensitive down to $\Delta T \cong 2 * 10^{-3}$°C for $2 * 10^{-4}$V. This ΔT is transformed into an electromotive force (EMF), i.e., electricity, via the Seebeck effect: $EMF = S \cdot \Delta T$, where S is the Seebeck coefficient. The IR radiation absorption by RPs has a marked dependence on the IR radiation incidence angle θ_0 and polarization (transverse electric—TE or transverse magnetic—TM).[1,4] Thus, to prove that the heat recovery mechanism is linked to RP excitation, here, we compare the dependence of the EMF versus θ_0 with the dependence of the absorption of the RPs in the IR spectra versus θ_0. The study with TE and TM polarized IR radiation will be pursued in a future experiment.

Amorphous (a) aluminium oxide (Al_2O_3) films were deposited at 150 °C on a 23 μm thick Al foil via atomic layer deposition (ALD)[5] in a custom-made horizontal hot wall viscous flow reactor described elsewhere.[6] The Al foil was cleaned by immersion in a 10% HF solution for 60 s. In each ALD cycle, the samples were exposed to $AlCH_3$ and de-ionized H_2O for 1 s. Metal organic and water precursor pulses were followed by 8 s long purges in Ar. The aAl_2O_3 film thickness on H terminated Si(100) was measured to be on average 250 ± 30 nm using a variable-angle spectroscopic ellipsometer (J. A. Woollam Co.). The reflectance (R) of the aAl_2O_3 film on Al foil (aAl_2O_3/Al) was studied using a N_2 purged Bruker Vertex 70 Fourier transform IR spectrometer in the 30-80° θ_0 range. The broadband IR radiation is generated in the IR spectrometer by a globar (Q301) source. For the variable angle reflectance measurements, a Veemax II by Pike Technologies accessory was used. The IR radiation was polarized in the TE and TM states with a ZnSe middle-IR general purpose polarizer (Pike Technologies). The absorptance (A) spectra are plotted as 100%-R versus frequency in cm^{-1} (Fig. 1).

a)Author to whom correspondence should be addressed. Electronic mail: scarelgx@jmu.edu.

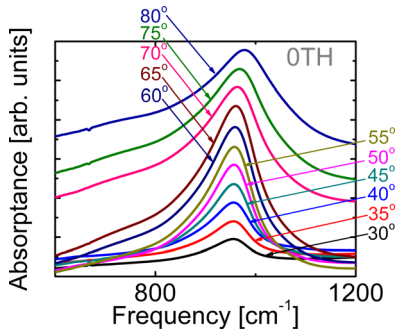

FIG. 1. (Color online) Absorptance of the 0TH type of RP in a 250 nm thick aAl_2O_3 film on Al foil illuminated by TM polarized broadband IR radiation at various values of θ_0.

For the measurements involving the heat recovery mechanism, a bare and lapped TEC power generator with alumina-ceramic surface (Custom Thermoelectric 07111-9L31-04B) was used. The TEC power generator has a nominal 0.14 V/°C Seebeck coefficient, which is in good agreement with the experimental value of 0.097 V/°C. System 1 consists of a 250 nm thick aAl_2O_3 film on Al foil placed on a TEC power generator. System 2 consists of Al foil placed on a TEC power generator. The size of the Al and aAl_2O_3/Al foils was slightly smaller than the surface area of the "hot" junction of the TEC power generator. The Al and aAl_2O_3/Al foils were mounted on top of the "hot" junction of the TEC power generator and placed on the variable angle reflection accessory inside the sample compartment of the IR spectrometer with the IR source off. After connecting the leads of the TEC power generator with a Keithley 2000 multi-meter, sensitive to direct current (DC) voltages from 1 μV to 1 kV, the sample compartment was closed and left in the dark laboratory room at 20 °C. A reading of 0.01 mV on the multi-meter indicated that the systems had achieved a stable initial condition for the experiment. Systems 1 and 2, illustrated in the inset of Fig. 2, were then exposed to the broadband non-polarized IR radiation in the middle IR region (350–4000 cm^{-1}) generated by the Q301globar source in the IR spectrometer. As soon as the systems were illuminated by the IR radiation at a certain angle θ_0 from 30° to 80°, an EMF was generated. The relaxation of the EMF was then observed for 6 min and 40 s after turning on the broadband IR radiation. In that time interval, the EMF values were collected every 10 s during the first minute and 40 s, and then, in the following 5 min, every 20 s.

Figure 1 depicts the absorptance spectra of the 250 ± 30 nm thick aAl_2O_3 film on the Al foil. The spectra were collected with TM polarized broadband IR radiation in the 30–80° θ_0 range. The only peak appears around 950 cm^{-1}, slightly blue shifting with increasing θ_0. The peak corresponds to the 0TH type of RP excited near the longitudinal optical (LO) phonon LO4 frequency of aAl_2O_3.[1,7] Its absorptance increases with θ_0, a phenomenon known as the Berreman effect.[8] For the same sample, RPs are absent in spectra collected with TE polarized broadband IR radiation in the middle IR region.

Figure 2 shows the time relaxation of the EMF in a TEC power generator after the excitation of RPs in system 1 with broadband middle-IR radiation at selected values of θ_0. It can be observed that (1) the maxima of the EMF values (EMF_{max}) depend on θ_0 and (2) the EMF_{max} values are achieved with a 40 s delay for $\theta_0 > 70°$ and with a 30 s delay for $\theta_0 < 70°$. Similar delays were found for system 2. This response is constrained by the intrinsic time constant of the TEC power generator. After exciting the RPs and reaching the EMF_{max} value, systems 1 and 2 relax quasi-exponentially for a certain time interval, while the IR radiation keeps illuminating them. We believe that, in accordance with our hypothesis, the quasi-exponential relaxation is linked to the limited lifetime (few ps) of the RPs and retarded by the intrinsic time constant of the TEC power generator. To formulate a theoretical model, the results of further experimental studies are needed, in particular those performed with TE and TM polarized IR radiation.

Figure 3(a) displays the EMF_{max} values versus θ_0 for systems 1 (filled triangles) and 2 (filled circles). The error is the standard deviation obtained from two measurements for each point. The EMF_{max} values of system 1 are always higher than those of system 2. The actual difference is reported versus θ_0 in Fig. 3(b), where, at each angle, the system providing the

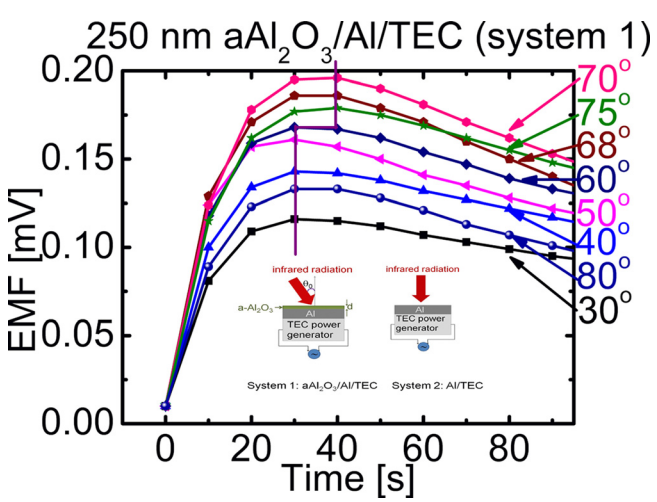

FIG. 2. (Color online). Time evolution of the EMF generated upon illuminating system 1 at selected values of θ_0. The vertical lines mark the EMF_{max} values. Inset: Schematics of systems 1 and 2.

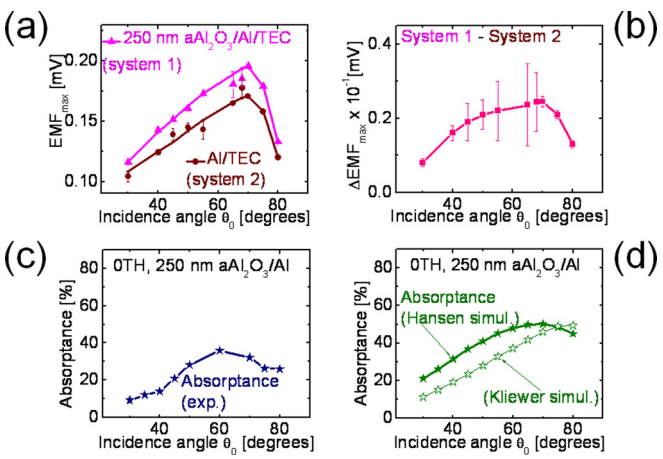

FIG. 3. (Color online) (a) EMF_{max} versus θ_0 for system 1 (filled triangles) and system 2 (filled circles). (b) Difference between EMF_{max} versus θ_0 for systems 1 and 2. Experimental (c) and simulated (d) absorptance versus θ_0 of the 0TH type of RP from IR spectra. The simulations were obtained from the Hansen (Ref. 9) and Kliewer (Ref. 4) methods.

larger error determines the uncertainty. The difference in EMF_{max} values between systems 1 and 2 increases with θ_0 from 30° to ~70° and decreases from ~70° to 80°. This trend resembles that of the absorptance versus θ_0 of the 0TH type of RP in a 250 nm thick aAl_2O_3 film on Al foil derived in Fig. 3(c) from the experimental data in Fig. 1 and in Fig. 3(d) from simulations obtained with the Hansen method.[9]

Figure 3(d) also compares the absorptance versus θ_0 of the 0TH type of RP in a 250 nm thick aAl_2O_3 film on Al foil derived from the Hansen[9] and Kliewer[4] methods. The two methods differ in that the former assumes a metal layer with the finite conductivity of Al, while the latter assumes infinite conductivity. The absorptance derived from the Kliewer method[4] is solely due to the 0TH type of RP, is lower than that obtained with the Hansen method, and does not exhibit a sharp maximum at 70°.

The correlation found here between the difference in EMF_{max} of systems 1 and 2 in Fig. 3(b), and the absorptance versus θ_0 of the 0TH type of RP in a 250 nm thick aAl_2O_3 film on Al foil in Figs. 3(c) and 3(d), supports the hypothesis that heat (i) is produced in the excitation of the 0TH type of RPs and (ii) can be revealed through the recovery mechanism. As shown in Fig. 3(d), this phenomenon was not predicted in the RPs theory of Kliewer *et al.*,[1] where all energy was confined by laws of conservation of momentum and retardation in the radiated fields. Considering that a substrate with finite conductivity was used in the Hansen method, and that chemistry and conductivity of the substrate profoundly influence the IR radiation absorption by RP excitation, as inferred from Fig. 3(d), we argue that dissipation phenomena take place, and that the energy from the incident broadband IR radiation can be converted in the thin oxide films into something other than radiative energy.

The large uncertainties in Fig. 3(b) are attributed to the continuous illumination of systems 1 and 2 by IR radiation during the EMF relaxation. These uncertainties blur the response to the RP excitation of the TEC power generator constrained by its time constant. Exploring the heat recovery mechanism by exciting the RPs with stable ultra-fast and high repetition rate photon pulses of the order of magnitude of the RP lifetime, or even less, should lower the uncertainties in the determination of the EMF_{max} values. This experiment is planned in the near future and is expected to unambiguously link the excitation of RPs in IR radiation absorption to the EMF_{max} values.

In summary, a correlation is found between the angular dependence of the heat recovery mechanism and the absorptance of the 0TH type of RPs excited in thin alumina films. This result indicates that heat is produced in the excitation of RPs. To unambiguously prove this correlation, stable, ultrafast, and high repetition rate photon pulses of the order of magnitude of the RP lifetime should be used. These results are expected to impact the exploitation of RPs to convert IR radiation into usable energy, and could inspire the future exploration, for energy conversion purposes, of the interaction between TEC power generators and radiation in a broad spectrum of frequencies including the visible, ultraviolet, and x-ray regions.

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[1]K. L. Kliewer and R. Fuchs, Phys. Rev. **150**, 573 (1966).
[2]R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).
[3]K. L. Kliewer and R. Fuchs, Phys. Rev. **144**, 495 (1966).
[4]R. Fuchs, K. L. Kliewer, and W. J. Pardee, Phys. Rev. **150**, 589 (1966).
[5]M. Ritala and M. Leskelä, in *Handbook of thin film materials*, edited by H. S. Nalwa (Academic, San Diego, CA, 2002), Vol. 1, pp. 103–159.
[6]K. A. Vasquez, A. J. Vincent-Johnson, W. C. Hughes, B. H. Augustine, K. Lee, G. N. Parsons, and G. Scarel, "*Wetting properties induced in nano-composite POSS-MA polymer films by atomic layer deposited oxides*," J. Vac. Sci. Technol. A (to be published).
[7]Y. T. Chu, J. B. Bates, C. W. White, and G. C. Farlow, J. Appl. Phys. **64**, 3727 (1988).
[8]D. W. Berreman, Phys. Rev. **130**, 2193 (1963).
[9]W. N. Hansen, J. Opt. Soc. Am. **58**, 380 (1968).