PRF 56642-ND10: A New Ability to Study Ultrafast Spectroscopy in Natural Oxides

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The primary objective of this research is to understand the linear and nonlinear optical properties of oxide films; here we have focused mostly on $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films. While we continue work on our second harmonic generation studies and natural oxide growth, our most significant advancements have been with our pump-probe setup to study carrier dynamics and relaxation mechanisms. On the pump-probe project alone, one paper is near submission (planned submission to *ACS Applied Materials and Interfaces*), and another two are in planning stages. This is in addition to the already reported paper in *Topics in Catalysis,* another one or two planned for the second harmonic angular work, and more to follow based on ongoing natural oxide efforts. This grant has supported the dissertation work of two graduate students, Guerau Cabrera and Saeed Yousefi.

A spin dependent pump-probe setup has been developed to study whether the observed dynamics are due to the majority or minority spins. Understanding the spin dynamics can play an important role in the dynamics of ferromagnetic system. **Figure 1** provides the results of our experiment on free carrier dynamics of 43.1nm of LSMO on top of the STO substrate (which is almost ready to submit) indicating a negative rise due to electron-electron scattering followed by a decaying signal. After the negative rise, the electrons (which are now in the conduction band) will couple with the phonons and relax back to the bottom of the conduction band in a sub-picosecond time scale. The ultra-fast decay time constant ($\tau_{e\text{-}p}$) of ~0.2 ps is also independent of pump power and is consistent with electron-phonon relaxation in LSMO and other systems. The medium time constant ($\tau_{p\text{-}s}$) which is on the order of tens of picoseconds due to phonon-assist spin relaxation, increases slightly with the excitation power. The long time constant ($\tau_{h/r}$) which is on the order of nanoseconds and is beyond the measurement range of the setup, indicates an increase with increasing the laser power, due to heat diffusion or slow radiative recombination.

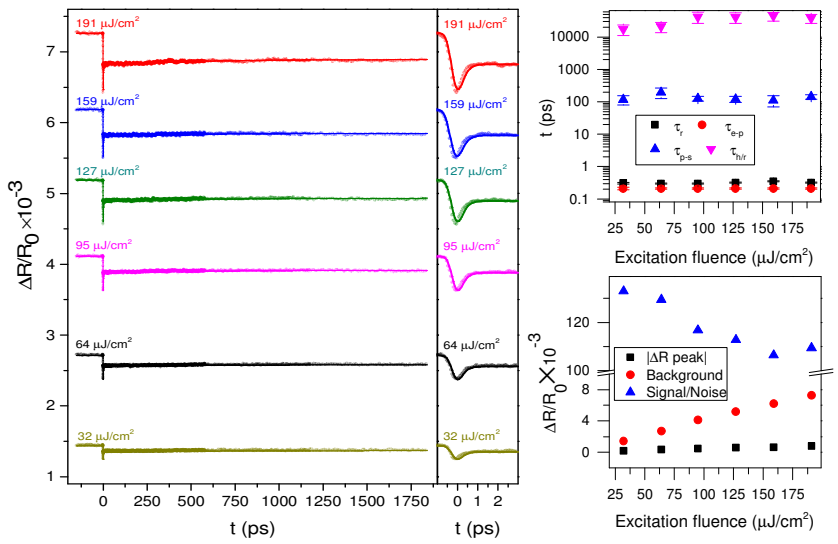

Figure 1. *(a) Reflectivity measurements for 43.1 nm of LSMO thin film on STO substrate with different excitation power. (b) TR measurements zoomed in to the first 3ps to show the ultra-fast decay due to the electron-phonon interaction. (c) Decay time constants for different decay components as a function of excitation power (d) Absolute value of ΔR/R0, and background plateau due to heating as a function of excitation power.*

After understanding the true origin of the dynamics in the system we turned our attention to the ultra-thin film systems which can be important for the next generation devices. By decreasing the film thickness, surface to bulk ratio increases and surface electrons dominate the features from the bulk electrons. Subsequently, we found additional energy states (midgap surface states or Tamm levels) emerge between the valence band and conduction band extrema, providing extra relaxation channels. A thorough study of the surface states is critical for device application point of view, since recombination due to these states drastically affects the efficiency of optoelectronic devices. **Figure 2** shows the result of reflectivity measurements on LSMO samples with different thicknesses. While films with thickness above ~ 20 nm have the same type of dynamics, thinner films show an extra relaxation mechanism emerging as the LSMO film become thinner (surface recombination, τ_s).

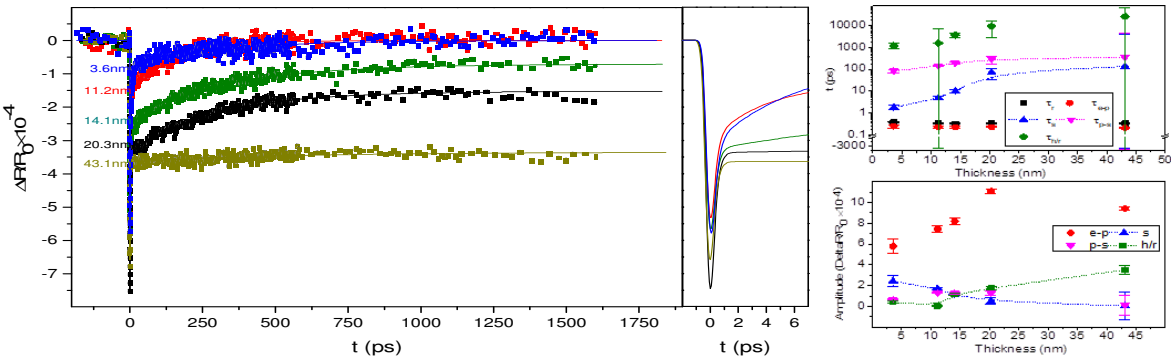

Figure 2. (a) Reflectivity measurements for LSMO thin films with different thicknesses (b) Decay time constants for different films showing the surface recombination time constant (blue dots) increases with the thickness. (c) Amplitudes of decay components showing the energy dissipated by the surface recombination decay component is comparable to the energy due to recombination.

Our results show while the rise, ultra-fast and medium decay time constants are almost independent of the film thickness, the fast and slow decay time constants increase with film thickness. The amplitude plot (**Figure 2 (c)**) shows the electrons lose most of their energy via interaction with phonons, since the magnitude of the amplitudes for the electron-phonon decay components (red) are almost an order of magnitude higher than the other components. The other three decay components almost have the same contribution in electrons energy relaxation. The general increase in the electron-phonon relaxation amplitude with thickness shows that the bandgap decreases with thickness and the interaction with phonons becomes less effective in higher bandgaps which is consistent with quantum size effect for strongly correlated LSMO semi-metal system. **Figure 2 (b)** indicates a separate mechanism as the thickness of the film decreases, however this mechanism becomes undistinguishable from the electron-hole recombination as the film thickness reaches its bulk value. We attribute this separate mechanism to surface recombination since it happens when the surface to bulk ratio increases. The increase of the surface recombination time constant (τ_s) with thickness indicates the electrons reach the surface faster as the film becomes thinner. **Figure 2 (c)** shows the strong effect of surface recombination in thinner films (less than ~20 nm thick) and in these films, electrons lose most of their energy without any radiative or thermal recombination. On the other hand, as the thickness increases, the surface recombination appears to be negligible with respect to the other decay components. In the thicker films (above ~20 nm thick) strong radiative or thermal recombination are responsible for the energy loss in the electrons.

As a result of averaging many scans we were able to reveal different vibrational modes (**Figure 3**). Understanding vibrational modes, such as plasmons, magnons and phonons can initiate new applications for thin films. Moreover, understanding and controlling phonon interaction with spin and electrons (which is a major reason for heat diffusion in devices) can help companies increase the efficiency and lifetime of their devices by controlling the dissipated heat energy in the computer chipsets and other devices. Our fitting results indicate distinct vibrational modes in different regions. We performed wavelet analysis to understand more about the vibrational modes. More data have been taken on the films with different thicknesses and oxygen vacancies and are currently under analysis. Wavelet analysis is a unique approach to study pump-probe data and offers many advantages for understanding changes with time, as is typical when different relaxation mechanisms are at play; we plan to write a methods paper. We also plan to do these measurements on natural oxides called olivines, which are commonly found in the Earth's crust. After optimization, we have been able to achieve less than one unit cell roughness, comparable to other state of the art oxide growth.

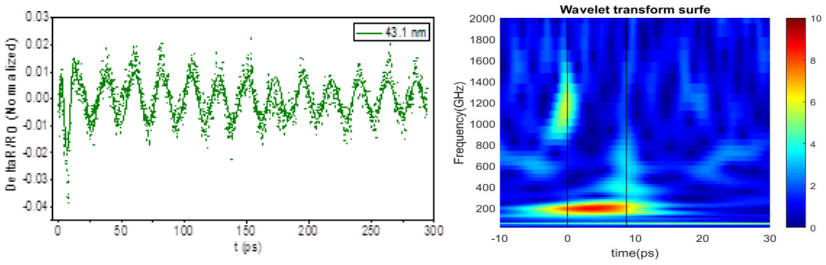

***Figure 3.** Vibrational modes with wavelet analysis to extract more information about the vibrational modes*