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Structural and Optical Properties of Perovskite Thin Films

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Abstract

This work describes a study of the structural and optical properties of a thin film, Sr_2CrReO_6 (SCRO), grown on $SrTiO_3$ (STO) substrate via ellipsometry and Raman scattering. Ellipsometry was used to measure the dielectric function (DF) and Raman scattering was used to directly measure the vibrational modes. The vibrational features manifested in the DF were modeled using an oscillator which allowed us to find the frequencies of the transverse and longitudinal optical phonons. The combination of a double perovskite crystalline structure and tetragonal structure (a = 5.52 Å, c = 7.80 Å) of SCRO provides a complicated dielectric function. Transmission spectra indicate that the film is a small band gap semiconductor (~0.24 eV). We successfully created a model of the substrate that is consistent with prior work, giving our technique merit. Portions of the DF of the SCRO have been successfully modeled but the entire model is a work in progress.

Background

Perovskite Thin Films

- Perovskites are interesting materials that exhibit interesting magnetic and electric properties (i.e., magnetoresistance, ferroelectricity, and superconductivity).
- Perovskites have a crystal form of ABX_3 (i.e., A, B and X are different atoms such as in $SrTiO_3$) and double perovskites have a crystal form of $A_2BB'O_6$ (i.e., A, B and B' are different atoms such as in Sr_2CrReO_6)
- Because perovskites contain multiple atoms, they have complex vibrational modes and electronic structure.

Dielectric Function

- Each material has a unique dielectric function (DF) and ellipsometry is an experimental technique that can determine the DF.
- The DF describes the electrical, optical and vibrational properties of a material.

Vibrational Modes

- A phonon is discrete quanta of vibrational energy. Depending on the mode of vibration, longitudinal and transverse phonons can be produced in a material by exciting them with a laser beam.
- Certain modes are only found via Raman spectroscopy, some only through ellipsometry, and some cannot be found through either method.

Band Gap

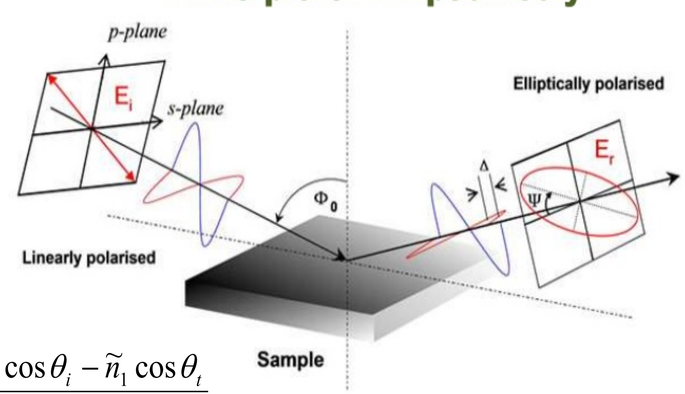
- The band gap of a semiconductor is the minimum energy needed for an electron to be excited into a higher state.
- Electrons can be excited by light; If the energy of light is equal to the band gap energy, the light will be completely absorbed.

Purpose

- The purpose of this project was to explore the vibrational modes and electronic transitions of both Sr_2CrReO_6 (SCRO) and $SrTiO_3$ (STO) .
- This was done using ellipsometric, Raman, and transmission spectroscopy.

Ellipsometry

Principle Of Ellipsometry[1]



$$r_p = \frac{\tilde{n}_2 \cos\theta_i - \tilde{n}_1 \cos\theta_t}{\tilde{n}_1 \cos\theta_t + \tilde{n}_2 \cos\theta_i}$$

$$r_s = \frac{\tilde{n}_1 \cos\theta_i - \tilde{n}_2 \cos\theta_t}{\tilde{n}_1 \cos\theta_i + \tilde{n}_2 \cos\theta_t}$$

$$\frac{r_p}{r_s} = Tan(\Psi)e^{i\Delta}$$

Samples & Modeling Techniques

Samples

- We studied two samples; a $SrTiO_3$ (STO) bulk sample and a thin film of Sr_2CrReO_6 (SCRO) grown on a STO substrate.
- The thickness of the SCRO sample was reported, by Aidan Lee, as 226 nm, measured using x-ray reflectivity.

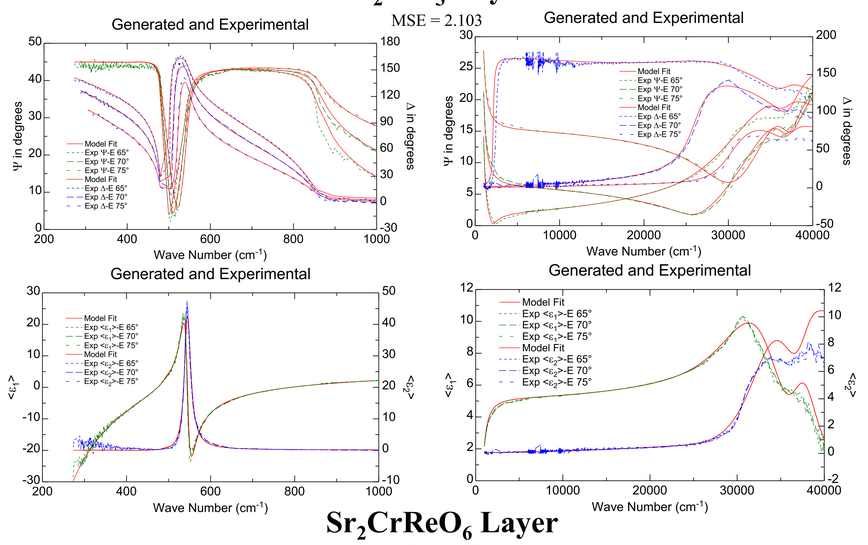
Models

- In order to fit the experimental ellipsometry spectra, the samples had to be modeled as a layered-structure. The electronic and vibrational transitions of each layer were modeled as a collection of oscillators.
- Specifically, samples were modeled using a TO-LO oscillator to represent the phonons, Rho-Tau-Drude oscillator to represent the free electron absorption, and another oscillator to represent the band-electron absorption.
- The TO-LO oscillator has the physical parameters for the location of longitudinal and transverse optical modes.
- The Rho-Tau Drude oscillator models metallic properties and is important if the samples are doped, which might be the case in SCRO. [2] It also determines the physical parameters such as the reduced mass, carrier mobility, and number of carriers.

Dielectric Functions

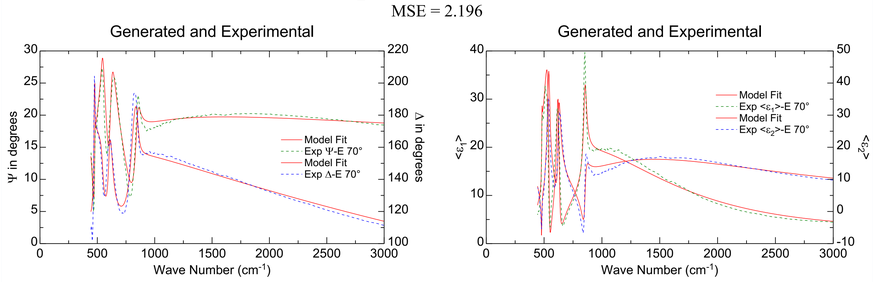
Sr_2TiO_3 Layer

MSE = 2.103



Sr_2CrReO_6 Layer

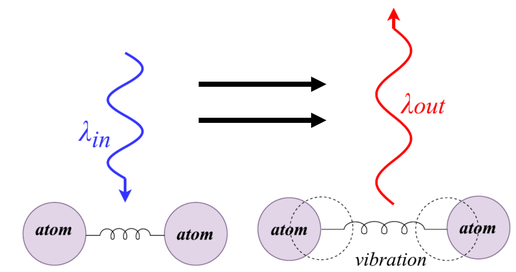
MSE = 2.196



	E_{TO} Ellips.	E_{LO} Ellips.	E_{gap}	E_{gap}
SCRO	624 ± 1 cm^{-1}	780 ± 20 cm^{-1}	N/A	N/A
SCRO	77.4 ± 1 meV	96.7 ± 2.5 meV	N/A	N/A
STO	544.9 ± .2 cm^{-1}	757 ± 2 cm^{-1}	33600 ± 800 cm^{-1}	37700 ± 300 cm^{-1}
STO	67.6 ± 0.1 meV	93.9 ± 0.3 eV	4.1659 ± 0.0992 eV	4.6742 ± 0.0372 eV

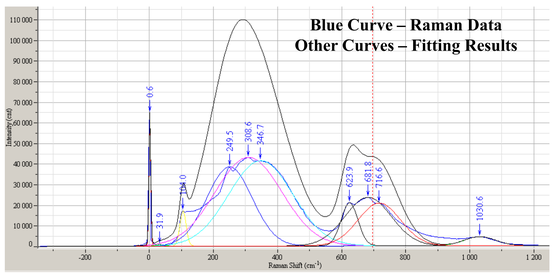
- We have captured the TO and LO phonon of STO located at 544.9 ± 0.2 cm^{-1} and 757 ± 2 cm^{-1}, respectively.
- For the SCRO sample, we found a TO and LO phonon at 624 ± 1 cm^{-1} and 780 ± 20 cm^{-1} respectively.
- The electronic transitions found for STO are in agreement with published results. [3]
- The TO and LO energies of STO also agree with the predicted theoretical phonon dispersion results. [4]
- Because our model for STO agrees with previous results, we are confident that the model for SCRO is also accurate.
- We strangely do not see any feature around the band gap (~1693 cm^{-1})

Raman Scattering



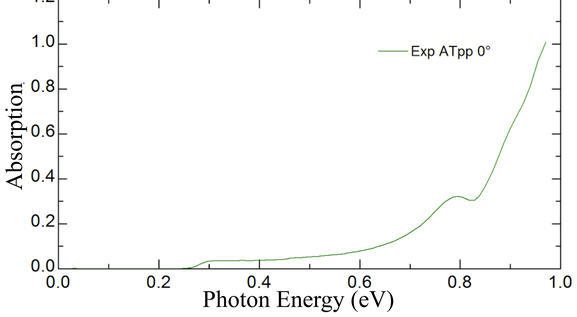
$$E_{photon\ in} = E_{phonon} + E_{photon\ out}$$

- Raman spectroscopy excites vibrational modes in the solid using light.
- Light scatters back with a change in energy equivalent to the vibrational energy.



- The original Raman spectrum (blue curve) was fitted with several Gaussian fits, each representing a phonon mode.
- Eight phonon modes were detected at 104.0, 249.5, 308.6, 346.7, 623.9, 681.8, 716.6, and 1030.6 cm^{-1}.
- Gosh et al. predicted there to be a large number of modes in double perovskites. [5]

Transmission Spectrum



- We successfully recovered the band gap of ~0.24eV (~1936cm^{-1}), which was originally found by Hauser et al.. [2]
- The bump ~0.8eV or 6452cm^{1} is likely to be a higher order transition.

Conclusion

- The STO model is complete and the model for SCRO is a work in progress.
- Multiple phonon modes were detected in the sample in ellipsometry and Raman scattering.
- We only see a single vibrational mode in both Raman and ellipsometry.
- We captured the band gap of SCRO in the transmission spectrum and possibly the band gap of STO in the ellipsometry data.
- We do not see a band feature in the ellipsometry data for SCRO

References

1. Adapted from https://www.slideshare.net/foolishcrack/ellipsometry
2. Hauser et al., Physical Review B 85, 161201(R) (2012)
3. Zollner et al., J. Vac. Sci. Technol. B 18(4), Jul/Aug 2000
4. Feng et al., Applied Physics Express 8, 071501 (2015)
5. Gosh et al., J.A.C. S. p7[8] 2014 2564-2572

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