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VO_2 thin films synthesis for collaborators and various applications

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Abstract

Vanadium dioxide (VO_2) is an attractive material for a variety of applications due to its metal-to-insulator transition (MIT) observed at modest temperatures. This transition takes VO_2 from its low temperature insulating monoclinic phase to a high temperature (above 68°C) metallic rutile phase. This transition gives rise to a change in resistivity up to 5 orders of magnitude and a change in complex refractive index (especially at IR wavelengths), which is of interest for radar circuit protection and tunable control of infrared signature. Recently, collaborations have been initiated between CINT scientists and external university programs. The Enhanced Surveillance funds help fund this work which enabled synthesis of VO_2 films for several collaborations with internal and external researchers.

Introduction

Vanadium dioxide (VO_2) is an attractive material for a number of applications stated above. Sandia has several years of experience working with VO_2 thin films thanks to work led by Paul Clem. Through his numerous publications on the topic, internal and external researchers have asked to set up collaborations based on this material. The work shown here funded by Enhanced Surveillance describes several of these collaborations.

One such collaboration is with Ting (Willie) Luk at CINT and Qiaoqiang Gan at the University of Buffalo. The goal of this program is to incorporate ultrathin (10-50 nm) VO_2 films on metasurface substrates for thermally tunable optical devices. With the VO_2 film on a visible super absorbing metasurface substrate, coupling between the phase transition of the MIT and meta-structure can enable devices that are thermally and optically tunable. The primary fabrication challenge is to produce homogeneous ultrathin VO_2 films. Whereas typical sol-gel deposition is used for films of >100nm, optimal device performance requires films that are approximately 10 nm thick.

A second collaboration is with Igal Brener and his post-doc Qiang Liu at CINT. The goal of this collaboration is to incorporate the excellent phase transition properties of VO_2 onto various metamaterials. This work will investigate the potential effects of coupling metamaterials to VO_2 with the ultimate goal of understanding if metamaterials can influence the VO_2 phase transition properties. For this study, VO_2 films will be deposited on standard and metamaterial substrates by our group and the optical and electrical properties studied by our collaborators at CINT.

The final collaboration is with Prof. Bryan Huey at University of Connecticut. Prof. Huey specializes in various flavors of atomic force microscopy (AFM) and is world-renowned in conductive AFM (c-AFM) techniques. Through these studies, we will be able to provide a fundamental understanding of the conduction mechanisms in VO_2 on the micrometer scale to support more reliable radar circuit protection and optical property control. Prof. Huey has performed initial c-AFM studies on VO_2 films using previously deposited samples provided by Paul Clem. The work is nearing publication stage, however, additional samples are needed to aid in their measurements. These additional samples require a conductive layer (such as platinum) under the VO_2 to serve as a bottom electrode. Initial attempts have shown that the vanadium may interact with the Pt preventing the formation of pure VO_2. Therefore, a systematic optimization process is required to ensure high quality films are deposited for this project.

Unfortunately, this project was cut short due to the fact that the PI moved to a different organization a mere couple months after the funding became available. While a number of films were synthesized and sent to collaborators, several of the goals were not attained because of the move. In addition, we are awaiting results from several of the groups as their measurements/processing/analysis can take significant time to complete.

Approach

VO_2 films were deposited using a chemical solution technique. For this process, vanadium ethoxide and tungsten ethoxide were dissolved in a mixture of IPA/acetic acid. A small amount (0.25-2%) of tungsten was used to help aid in the crystallization of the correct VO_2 phase. After mixing at room temperature, the solution was spin-coated onto glass, SiO_2/Si or sapphire substrates at 3000rpm for 30sec. The film was then heat treated at 300°C for 5 min on a hotplate. Films were crystallized at 700°C for 1 hour in a tube furnace under flowing H_2/N_2 that had passed through an ice bubbler prior to entering the furnace. X-ray diffraction was used to characterize the phase of the films. VO_x can adopt a large number of phases and it can often be challenging to make a film with the correct phase (VO_2). Once it was determined that the films were of good crystalline quality, they were sent to various collaborators.

Results and Impacts

Goal Deliverables:
1. Optimize ultrathin (10-50nm) VO_2 films and study optical properties at CINT (Willie Luk - CINT)
2. Integrate ultrathin VO_2 films on metasurface samples (substrates provided by University of Buffalo)
3. Provide VO_2 films on various substrates for metamaterials studies (Igal Brener – CINT)
4. Provide VO_2 films on glass and determine optimal deposition conditions for films on conducting substrates. Provide samples for c-AFM (Bryan Huey – University of Connecticut)

Actual Deliverables:
1. In collaboration with Willie Luk at CINT, we optimized film deposition conditions to produce good quality films on glass and sapphire substrates. One outcome of this work was to learn that the lowest W

doping possible (0.25%) lead to film properties that were ideal for W.Luk and his collaborators at University of Buffalo. Unfortunately, we did not have enough time to try thinner films.

2. Once the correct W concentration was determined (see Actual Deliverable #1), we attempted to deposit films on substrates provided by the University of Buffalo. Unfortunately, the vanadium in the VO_2 reacted very strongly with the layers in their substrates and, due to time constraints, we were not able to determine a reasonable method to overcome this problem.

3. A number of different W doped VO_2 films were provided to Qiang Liu (post doc working for Igal Brenner at CINT). Through this work, the objective was to investigate whether realizing strong coupling between the VO_2 optical phonons and the resonance of metallic metamaterials/resonators would influence the phase transition characteristics, such as the transition temperature and/or the transition amplitude, of VO_2 thin films and/or VO_2 nanostructures. From the VO_2 films we provided, Qiang Liu used the fabrication facility to create nano-ribbons out of the blanket films. He then measured phase transition behavior of an as-received film and a film that was fabricated into nano-ribbons. The data is shown in Figure 1. These samples have been sent to an external collaborator for spectroscopic characterization. Further testing needs to be performed in order to determine if there is a correlation between optical phonons and metamaterial structure/resonance.

VO_2 thin film **VO_2 Nanoribbon**

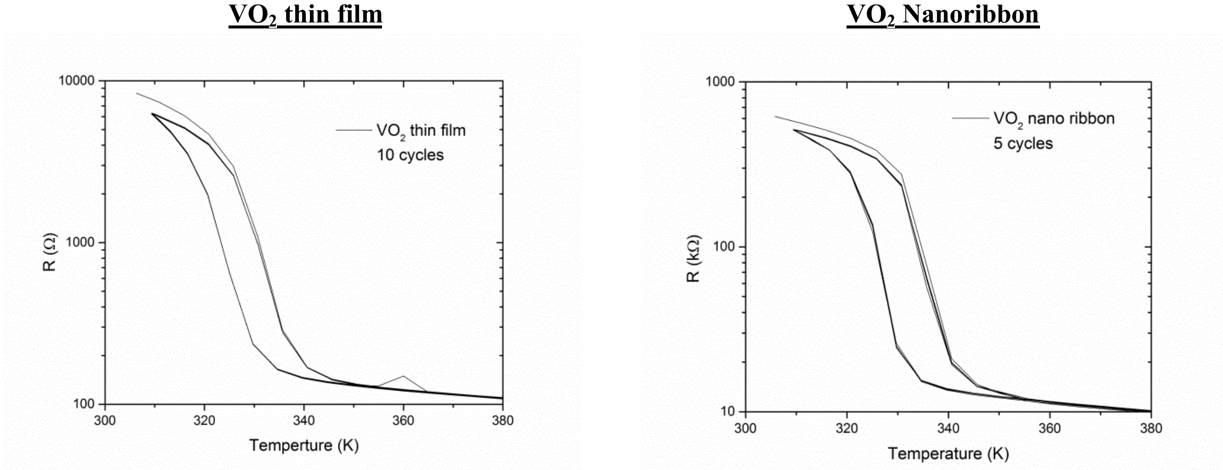

Figure 1 Phase transition behavior of VO_2 film and VO_2 nanoribbon. These devices were fabricated in an effort to study whether strong coupling between optical phonons and the nanoribbon resonance would affect phase transition behavior. Work is on-going to determine if a correlation exists.

4. VO_2 films with different W doping concentrations were deposited on glass substrates and provided to the collaborators at University of Connecticut. We are still awaiting data from that group. In addition, some time was spent trying to deposit VO_2 on conductive substrates for this collaboration. Unfortunately, the vanadium tended to react with the metallic electrode creating an unwanted V-metallic layer. Several attempts were made to made to use a conductive oxide as the electrode, however, due to time constraints, the optimum deposition conditions were not determined. We are currently awaiting c-AFM results on the films deposited on glass substrates.

Conclusions and Future Work

Given the short time allotted to this effort (primarily due to the fact that the PI moved to a new organization), several of the goals were met. Of the VO_2 films provided to various collaborators, it was determined that the films behaved as desired and we are awaiting more in-depth results from the collaborators on their specified projects. One challenge we discovered was the difficulty in depositing VO_2 on metallic surfaces or substrates. This is one area that could use some investment in the future.

Milestone Status:

(see results section above)