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**RE: “Semiconductor-to-Metal Transition in Rutile TiO2 Induced by Tensile Strain” (cm-2016-04881e)**

Dear Dr. Choi:

Please find as part of this resubmission the revised manuscript entitled: “Semiconductor-to-Metal Transition in Rutile TiO2 Induced by Tensile Strain” (cm-2016-04881e) by Eric Benson, Elisa Miller, Sanjini Nanayakkara, Drazenka Svedruzic, Suzanne Ferrere, Nathan Neale, Jao van de Lagemaat, and Brian Gregg. We have addressed these reviewer’s concerns through revisions in the text as well as additional XRD and Raman data has been added to the supporting information. References pertaining to defect induced semiconductor-to-metal transitions were also added to the main text. The additions do not change the interpretation or presentation of our results but offer more clarification for the readers. Specific responses to the reviewers are detailed below in red.

*Reviewer 1*

**I can agree that the strain changes physical or chemical properties of TiO2, and it also causes the increase of the carrier concentration. However, I am not convinced that the phase of TiO2 under the strain is a metal as authors claim.**

To be consistent with the literature, we use the “semiconductor to metal” terminology. Semiconductor to metal transitions (insulator/metal) have been previously attributed an increase in carrier concentration and formation of degenerate bands due to doping as described by Mott. To help guide the reader, we have added clarifying sentences in the abstract and the introduction with additional references (ref 40-41). We are not claiming that the strained material is a new phase of TiO2 or a ‘metal’ in the formal definition, but rather ‘metal-like’ wherein the strained material behaves more like a metal than a semiconductor.

**First of all, it is correct that as the carrier density increases, the depletion width becomes narrower so that the tunneling takes place more easily. However, if the bulk is a metal, there would be no Schottky barrier existed.**

See previous comment. As the carrier density increases, we do not believe we are seeing a metal phase of rutile TiO2, but rather what can be attributed to an apparent degenerative doping of TiO2, which still contains a Schottky barrier.

**Besides, the ohmic behavior in current-voltage curves (Figure 6) does not always mean that the bulk is a metal. It can occur when the tunneling is large as a result of a doping effect by the strain.**

See previous two comments; additionally this is discussed in the manuscript (page 10, eq 2).

**Second, XPS data (Figure 5) does not seem convincing that it is real.**

XPS has been repeated on multiple samples and a consistent measurable intensity near the Fermi level is observed. While we agree that the effect is small in the XPS, we believe that the additional experiments (CAFM, electrochemistry) support this conclusion.

**Overall, in this article, it seems important to prove that TiO2 is a metallic state under 5% strain but none of data for the evidences of metalic phase seems convincing. I would suggest authors to do the temperature dependent conductivity measurements.**

Unfortunately, due to sample configuration and the temperature for the Martensite-Austenite transition of the nitinol substrate, we are precluded from taking detailed temperature dependent conductivity measurements.

**Additional question: In table 1, why is the SS capacitance not recovered to the unstrained value after being relaxed?**

We believe that the SS capacitance does not recover to the unstrained value due to the reactivity of the surface OVs. Under experimental (ambient/aqueous) conditions surface OVs should react to form pairs of surface OH groups that remain once the strain is relieved.

*Reviewer 2*

**1. The authors proposed a mechanism underlying the strain-induced increasing carrier density that the ionization energy of oxygen vacancy decreases with increasing tensile strain. However, a theoretical paper by another group in the same NREL (Yin et al, APL 99, 142109 (2011)) concluded that the ionization energy of OV in TiO2 is very shallow relative to the CBM and is little dependent on the strain. The reason is because the chemical natures of CBM and the defect level are differently originated. Maybe the authors did not pay attention to the story because this highly relevant paper was not cited.**

We thank the reviewer for bringing this paper to our attention; however, there is no mention of systematic uniaxial strain on the entire lattice, only the local strain around a single vacancy. Additionally it pertains to anatase rather than rutile TiO2. However, generally the paper concludes that if the CBM is a non-bonding d state than the OV should be shallow and near the CBM, which is consistent with our results. Additionally, the SS potentials only changes by ~50 mV with respect to the *Ufb* under strain, and brief discussion of this has been added to the manuscript with this citation (page 11).

**2. The other possible mechanism, i.e., the reported transition correlates with the strain-induced increasing formation and diffusion of OV, is abandoned by the authors without additional experiments. Actually, this mechanism is consistent with many theoretical predictions (ref. 30, 49, 50). Therefore, I suggest the authors conduct more experiments to explore the possible mechanism, for instance, by changing the temperature to activate or suppress the kinetics in formation or diffusion of OV.**

The increased formation and diffusion of OVs throughout the thickness of the entire film would require oxygen diffusion through 50-100 nm of material, which we believe is not feasible at these temperatures. In order for oxygen diffusion to take place during sample preparation, the sample had to be heated at 500 C for 30 minutes to form 50 nm of oxide. Additionally from the solid-oxide fuel cell community, O2 diffusion typically requires temperatures around 800 C. Unfortunately due to sample configuration and the temperature for the Martensite-Austenite transition of the nitinol substrate, this precludes detailed temperature dependent studies.

**3. Although the authors claimed that the TiO2 film is rutile. But I didn't find any proof in the context. It is necessary to prove the TiO2 film is in rutile or anatase phase because the two phases are different in responding to the strain.**

Additional grazing angle XRD and Raman spectra, consistent with the literature and rutile TiO2, have been added to the supplemental information (Figure S8).

**4. The captions are difficult to read because there lack of necessary punctuation signs.**

Additional punctuation was added in order to improve the readability of the manuscript captions.

*Reviewer 3*

**1) Is there any direct image about the thin film structure? Maybe X-ray diffraction measurement and Raman spectroscopy can help elucidate the detailed structure. Though aerobic oxidation of NiTi is documented in literature, the structure of the TiO2 thin film in this experiment may not be exactly the same and needs further elucidations. Under strain the originally thought rutile (110) surface may undergoes structure reconstructions or other orientations of surface can become important.**

Additional grazing angle XRD and Raman spectra, consistent with the literature and rutile TiO2, have been added to the supplemental information (Figure S8). Additionally no Magnéli or sub-oxide phases were detected in the XRD measurements under strain.

**2) What is the main metallic area in the thin film? At the surface or in the bulk? XPS and UPS spectra suggest the density of states near Fermi level come from the sub-surface area. But usually the surface will provide in-gap states, will that affect the metallic behavior?**

The XPS and UPS results show that the sub surface (~2-10nm) of the thin film is metallic in behavior. These are surface sensitive measurements and typically measure the top ~10 nm. However, we believe that this subsurface composition should be representative of the bulk of the film. UPS results suggest that there is no metallic character within the top ~2nm presumably from surface re-organization. We do not expect the in-gap surface states to affect the metallic nature of the bulk under strain.

**3) Is the conductance anisotropy present? The in-plane and cross-film conductance may be different if the surface area is more conductive? Also what if the film become much more thicker or even the bulk rutile TiO2? Will the semiconductor-metal transition still survive?**

While investigating the conductance anisotropy of the films would be interesting, due to the metallic nature of the nitinol substrate the conductance will be dominated by the cross-film conductance in both cases. As noted in the manuscript, the semiconductor-to-metal transition is present in both 50 nm and 100 nm thick films, thicker films were not thoroughly investigated due to the propensity of thicker films to fissure under experimental conditions.

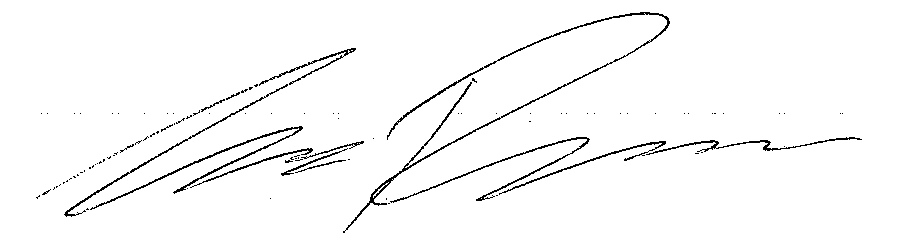
**4) In the paper it is assumed unlikely that strain influences the formation of new oxygen vacancies with oxygen diffusion into and out of the film. Why is this unlikely? Is there any experimental proof? Maybe during the strain procedure and measurements, vary the partial pressure of oxygen in the environment can affect the conductance.**

The increased formation of OVs and diffusion of oxygen throughout the thickness of the entire film would require oxygen diffusion through 50-100 nm of material which we believe is not feasible at these temperatures. To get oxygen diffusion during sample preparation to create the ~50 and ~100 nm of TiO2 required heating (500 C) under aerobic conditions for 30 min and 120 min respectively.

All other minor issues were addressed within the text, figures and references.

We believe that our manuscript has been strengthened by the review process and that it is now suitable for publication in *Chem. Matter.* Please advise us if any additional materials or information are necessary for publication.

Sincerely,



Eric E. Benson, Ph. D.