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Research and Development of Palladium/Metal Oxide Based Nanostructures as High-Performance Hydrogen Gas Sensors

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Research and Development of Palladium/Metal Oxide Based Nanostructures as High-Performance
Hydrogen Gas Sensors

by

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An alternative energy source to petroleum is hydrogen fuel-cells, and better hydrogen sensors are needed to detect low hydrogen concentrations to make these fuel-cells safer. Pure palladium hydrogen sensors, based on networks of ultras-small nanowires sputter-deposited on a filtration membrane have shown promising results, especially when alloyed with other metals or when layered with other metals. Unfortunately, even the best palladium-based hydrogen sensors still cannot distinguish hydrogen concentrations below 3% or at high operating temperatures, thus limiting the safety and application of the sensors. This study reports on new resistance based sensors of alternating nanowire network layers of pure palladium and titanium dioxide. These sensors show promise at sensing both low hydrogen concentrations, as low as 0.01%, and at sensing hydrogen at an operating temperature of 150 degrees Celsius; a step in the direction of sensors that work at temperatures approaching 1000 degrees Celsius. Although the titanium dioxide layers are not as sensitive to hydrogen as the palladium, they help to increase the durability and potential operating temperature of the sensor by providing additional adhesion and sensing properties.

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Introduction

Hydrogen gas (H_2) has potential as a future vehicular fuel source; it only produces water as a byproduct, compared to carbon dioxide for internal combustion engines, which enhances the greenhouse effect.¹ Additionally, hydrogen based fuel cells have potential as a short-term or on-site electricity source due to hydrogen's high energy density. Currently, the pharmaceutical, steel, food, and chemical industries use hydrogen in many of their processes, and it is often used as a fuel for space exploration.²

While hydrogen has a large potential as a renewable energy substitute for carbon based fuels such as gasoline, oil, and natural gas, it also has a high potential to be a very dangerous substitute if stored or moved incorrectly or is improperly monitored, due to its flammability and explosive potential in the presence of oxygen.¹ Numerous research teams are studying potential sensing and substrate materials and sensor designs, ranging from mechanical and acoustic based sensors to catalytic and resistance based sensors, the latter of which is this project's focus.⁵ Resistance based sensors come in several forms, including single nanowires, thin films, and nanowire networks. Sensors of all three types are currently under development, with each having distinct advantages and disadvantages. Cost, speed, temperature range, and susceptibility to other gases all need to be taken into account when creating a sensor, as the optimal sensor will be inexpensive, quick, specific to hydrogen, and have a large range of operating temperatures.

Single palladium nanowires are fairly fast, sensitive, and use very little power, but are hard to fabricate and manipulate. Palladium thin films have similar advantages to single nanowires in addition to being much simpler to fabricate, but lack some of the speed and sensitivity of single palladium nanowires. Palladium nanowire networks were chosen for this project because they have a strong blend of speed and sensitivity in addition to their ease of manufacture and low power consumption.²

Palladium (Pd) is the most common sensing material used to create resistance based hydrogen sensors due to several unique attributes.² First, the palladium lattice structure can absorb over 600 times

its own volume in hydrogen.⁹ Second, hydrogen generally induces a resistance increase in palladium due to two different phases that occur when hydrogen is present; the alpha (α) phase, in which palladium and hydrogen form a solid, and the beta (β) phase in which palladium and hydrogen combine to form a hydride (PdH_x); these phases are due to a very specific chemical reaction that causes palladium to have a high selectivity to hydrogen only.² Additionally, palladium hydrogen absorption has shown to be reversible if hysteresis behavior, or deformation, is avoided, allowing multiple uses of resistance based palladium sensors.⁴

While palladium based sensors have many advantages, several disadvantages have also been found. For example, it was found that although the sensors were quicker and more sensitive at smaller thicknesses of palladium, below four nanometers the palladium would begin to become discontinuous; this thickness was deemed the critical thickness. Some of the sensors tested in this project go below this thickness and thus induce a resistance decrease instead of increase.⁹ Lastly, the phase transition from α -phase to β -phase was found to affect the resistance change of palladium above hydrogen concentrations of approximately three percent, an effect which has been avoided through the use of other metals in conjunction with the palladium sensing material.²

This research will examine a new variation of palladium based resistance sensors for sensing hydrogen consisting of combinations of palladium and metal oxide layers of varying thicknesses and numbers on substrates of both silicon and anodized aluminum discs. Using two different substrates will test the effectiveness of this new design as both a thin film and as a nanowire network. It is hoped that the sensors tested will prove to be even quicker, more sensitive at both lower hydrogen concentrations and higher temperatures, and even more durable than previous incarnations of palladium based hydrogen sensors.

Methods

Two different substrates were used for this research; Whatman Company's Anodisc 13 porous

anodic aluminum oxide (AAO) membranes and pure silicon wafers. The experiment's primary focus, nanowire networks, were created using the Anodisc 13 substrates, whereas the thin film controls were made using the pure silicon wafer substrates. Each Anodisc 13 substrate required cleaning and inspection prior to sputter deposition; the silicon substrates were cut from a larger silicon wafer using a diamond cutter prior to sputter deposition.

Each anodized aluminum filter membrane was cleaned in acetone filled beakers set in an ultrasonic bath for fifteen minutes. After the ultrasonic bath, they were submerged in alcohol to dissolve the acetone, and then submerged in de-ionized water to dissolve the alcohol and air dried twenty-four hours on a clean Kimtech brand Kimwipe in a fume hood. A Tescan Model Vega II SBH scanning electron microscope was used to inspect each substrate and determine the side with a 20 nanometer pore diameter, as it was this side that the sputtering of the palladium and metal oxide occurred; the other side of the substrate has 200 nanometer pore diameter which would be too large for the networks.

Both sets of substrates were taken to Argonne National Laboratory to complete the palladium and metal-oxide sputter deposition. Substrates were made using two different working gas sets; one 5 mTorr argon set at 30 sccm, and another 5 mTorr argon and oxygen combination with argon at 30 sccm and oxygen at 10 sccm, both with a 1×10^{-7} Torr vacuum pressure. Samples were made consisting of single, double, and multiple layers of palladium and metal-oxide; the number of layers was mainly a function of palladium and metal-oxide layer thickness.

Using a single edge razor blade, each anodized aluminum oxide substrate was cut into small rectangular pieces approximately 2.5 millimeters wide and 8 millimeters long. These are not precise measurements, but are instead a rough size for how large the substrate needed to be to be viable. As long as the substrate was large enough to connect to the current contacts and still have space for the wires to connect to the voltage contacts without touching it is viable. Next, each substrate was connected to a 2 centimeter square sample holder between the two current contacts, then attached with silver paste. Wires were then placed between the substrate and each voltage contact at a spacing of

approximately 2 millimeters, also attached with silver paste. These sensors were then allowed to dry for twenty-four hours before being subjected to testing using a homemade hydrogen sensor testing system used in previous experiments by Zeng, et. al.^{2,9,11}

Each sensor underwent two tests: one at room temperature (RT) and another at 150 degrees Celsius. Every test assessed sensor performance from 1 percent hydrogen concentration in air down to 0.01 percent at intervals of 1, 0.8, 0.6, 0.5, 0.4, 0.2, 0.1, 0.08, 0.06, 0.05, 0.04, 0.02, and 0.01% in air using a properly calibrated flow controller. These concentrations were chosen because the ignition concentration of hydrogen in air is 4%, and thus if hydrogen can be sensed at these lower concentrations the system where the sensor is can be shut down before the concentration gets high enough to ignite. Every resistance vs. time data set was analyzed by finding the maximum resistance change and the response time is defined for achieving both 90% of maximum resistance change or 50% of maximum resistance change; the first criterion is the lab standard, while the second is a common industry/academic standard.

Results and Discussion

Multiple thicknesses of palladium and titanium oxide were tested, as were varying numbers of layers, ranging from one to four. Thicknesses for the palladium ranged from 1 nanometers to 3 nanometers; this meant some sensors showed a resistance decrease due to the palladium layers being below the critical thickness while some showed a resistance increase for the opposite reason.^{2,9,11} Titanium dioxide thicknesses ranged from 2 nanometers to 15 nanometers. A typical resistance decrease sensor response is shown in Figure 1. These thicknesses are not measured, but are instead calculated thicknesses using the sputter deposition machine that was used to prepare the sensor substrates.

All samples were tested at hydrogen concentration increments of 1, 0.8, 0.6, 0.5, 0.4, 0.2, 0.1, 0.08, 0.06, 0.05, 0.04, 0.02, and 0.01% in air at both room temperature (Figure 2a and 2b in the Figures and

Tables section) and 150° Celsius (Figure 2c and 2d). The 150° temperature was chosen due to the sensor holder, which can only withstand temperatures up to 200° Celsius. After analyzing the data for each sample, response times and sensitivities were graphed to compare the performance of the samples at both room temperature (RT) and 150° Celsius to determine if the sensor would be adequate for use at higher temperatures.

Figure 2a-d show the sensitivities and response times for all sensors at both room temperature (Figure 2a and 2b) and 150° Celsius (Figure 2c and 2d). Sensitivity is defined as the maximal resistance change divided by the resistance of the sensor when no hydrogen is present. Response time is defined as the time that it takes for 90% of the maximum resistance change to occur ($0.9 \cdot \Delta R_M$).² The reference samples are those that are thin film sensors made using the pure silicon wafers, whereas the non-reference sensors are those made using the anodized aluminum oxide substrates. The first two graphs show that at room temperature the nanowire network sensors generally outperform the thin film reference sensors in terms of both sensitivity and response times, which is the result that was expected. At 150° Celsius, however, the results are mixed, with a nanowire network sensor being the best, followed by thin film reference sensors as the next two best sensors. This was not the expected result, and thus would be a good area for a follow-up study.

Figures 3a and 3b summarize the results of our analysis at a concentration level of 1% for all of the samples tested made with argon as the only working gas during sputtering. Some sensors for this set of tests were made but not tested due to their resistance being greater than 20 mega-Ohms, which is beyond what the sensing setup can handle. These samples are denoted in Figures 3a and 3b by empty spaces where the bar of the bar graph should be. These two figures show that the sample with 15 nanometers of titanium dioxide and 3 nanometers of palladium had both the highest sensitivity and the quickest response time out of all sensors tested regardless of temperature.

Sample graphs of sensitivity vs. concentration and response time vs. concentration are shown in Figures 4a and 4b. The sample used for these graphs, a sample of 15 nanometers of TiO₂ and 3

nanometers of Pd, was the best sample tested at 150° Celsius; it had a quick response time across the concentrations tested in addition to having a high sensitivity of between 40 and 60% across all concentrations tested. As noted above, it is the best sample at 150° Celsius. These figures show that this sample had a quicker response time at 150° Celsius than it did at room temperature and that it was ten times more sensitive at 150° Celsius than at room temperature, which may imply that this sample would be good at temperatures higher than 150° Celsius.

Figures 5a and 5b show a comparison of sensitivity and response time vs. concentration for the 4-layered 2 nm TiO₂/1 nm Pd sample. In both graphs, the oxygen/argon working gas combination nanowire network sample outperforms both the thin film reference samples and the sample made with only argon as the working gas. This provides evidence that the amount of oxygen in the working gas may have an effect on sensor performance because sensors that would otherwise be identical performed differently based on the composition of the working gas; this will likely be a topic of future research with these sensors.

Conclusion

We designed and tested a new type of hydrogen sensor based on multiple layered nanowire networks of titanium dioxide and palladium sputter deposited on anodized aluminum oxide filtration membranes. A sensor that had high sensitivity and fast response times at 150° Celsius was found; the nanowire network sensor made from 15 nanometers of titanium dioxide and 3 nanometers of palladium. This sensor may have the potential to be highly sensitive and have fast response times at temperatures up to 1000° Celsius. Additionally, the presence of oxygen in the working gas during sputter deposition was found to have a positive effect on the response times and sensitivities of the sensors, which could be a topic of future research. Other topics of future research include testing the sensors at higher temperatures between 600 and 1000+ degrees Celsius, which will require heat resistant sensor holders and a stronger heater, and annealing of the samples at 500-1000 degrees Celsius which will change the form of the titanium dioxide and may produce better performance.

Figures and Tables

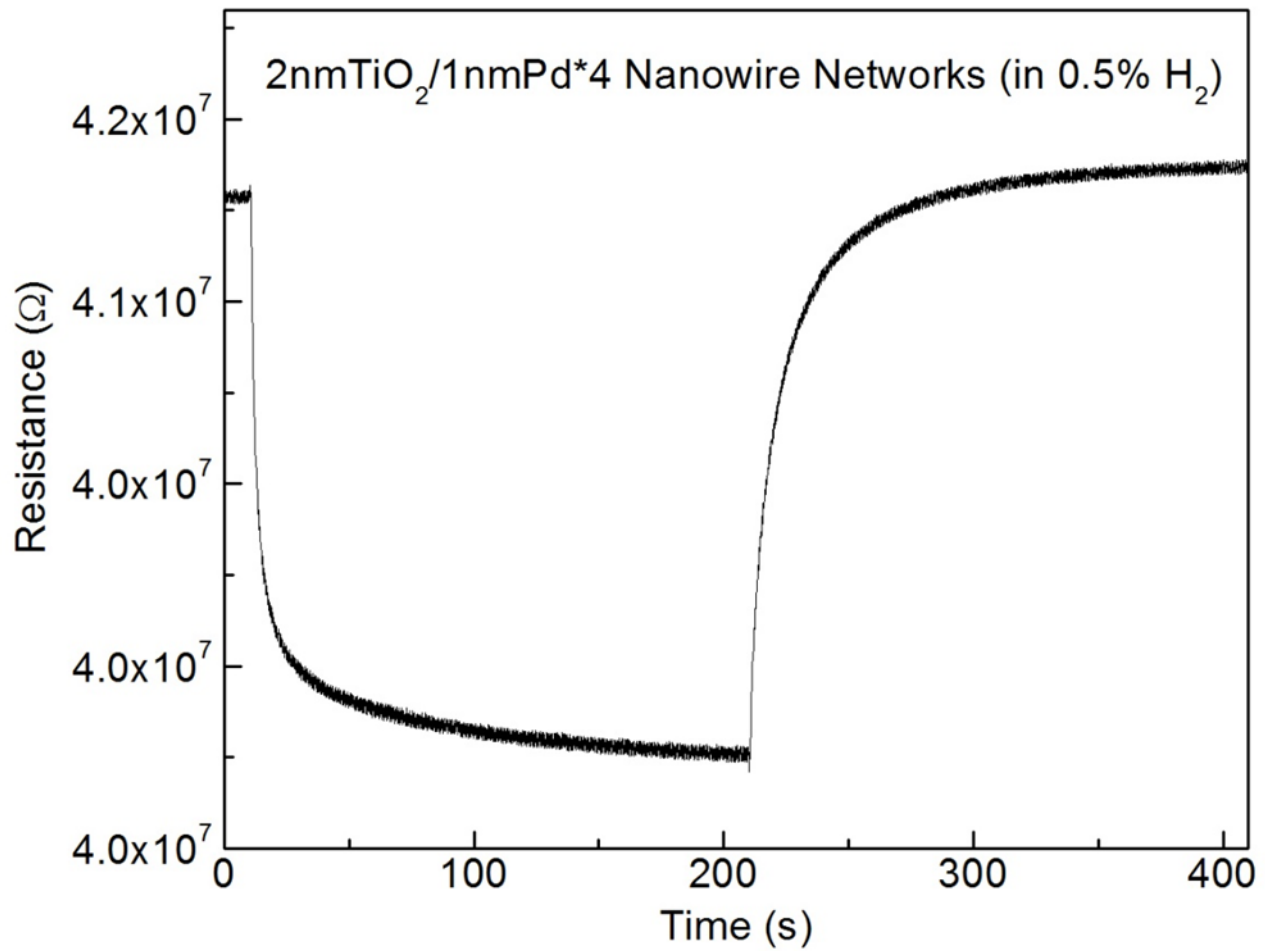


Fig. 1. Resistance vs. Time graph for an alternative deposition sample (2nm TiO₂/1 nm Pd/2nm TiO₂/1 nm Pd/2nm TiO₂/1 nm Pd/2nm TiO₂/1 nm Pd) at 0.5% H₂. This sample represents a typical response for a sensor based on a resistance decrease.

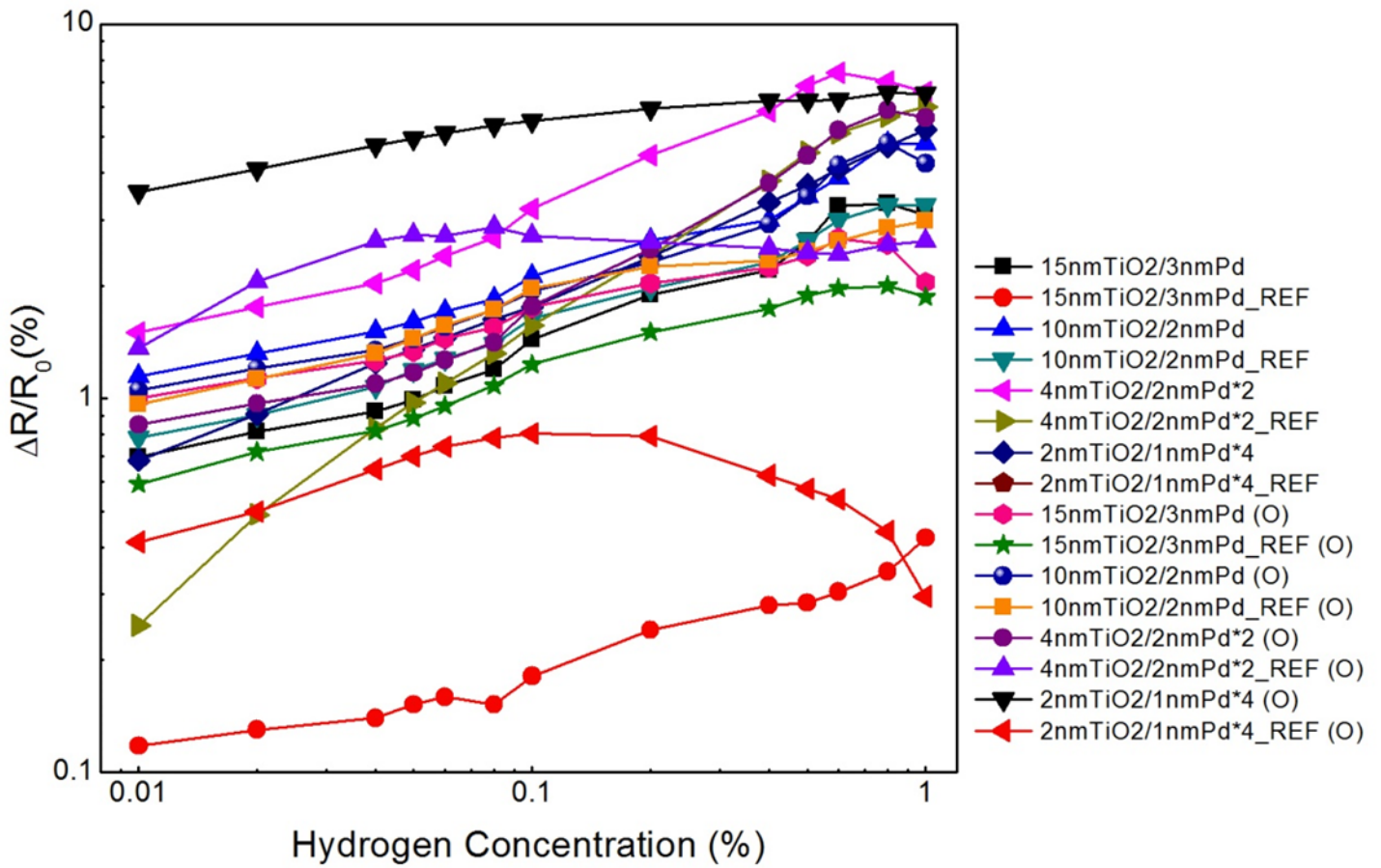


Fig. 2a. Sensitivity vs. Hydrogen Concentration graph for all samples at room temperature. As a key, REF indicates a thin film reference sample sputter-deposited on to a silicon substrate, and (O) indicates a sample produced with oxygen as a portion of the working gas during sputter deposition. If REF is not present, the sample is a nanowire network on the AAO substrates.

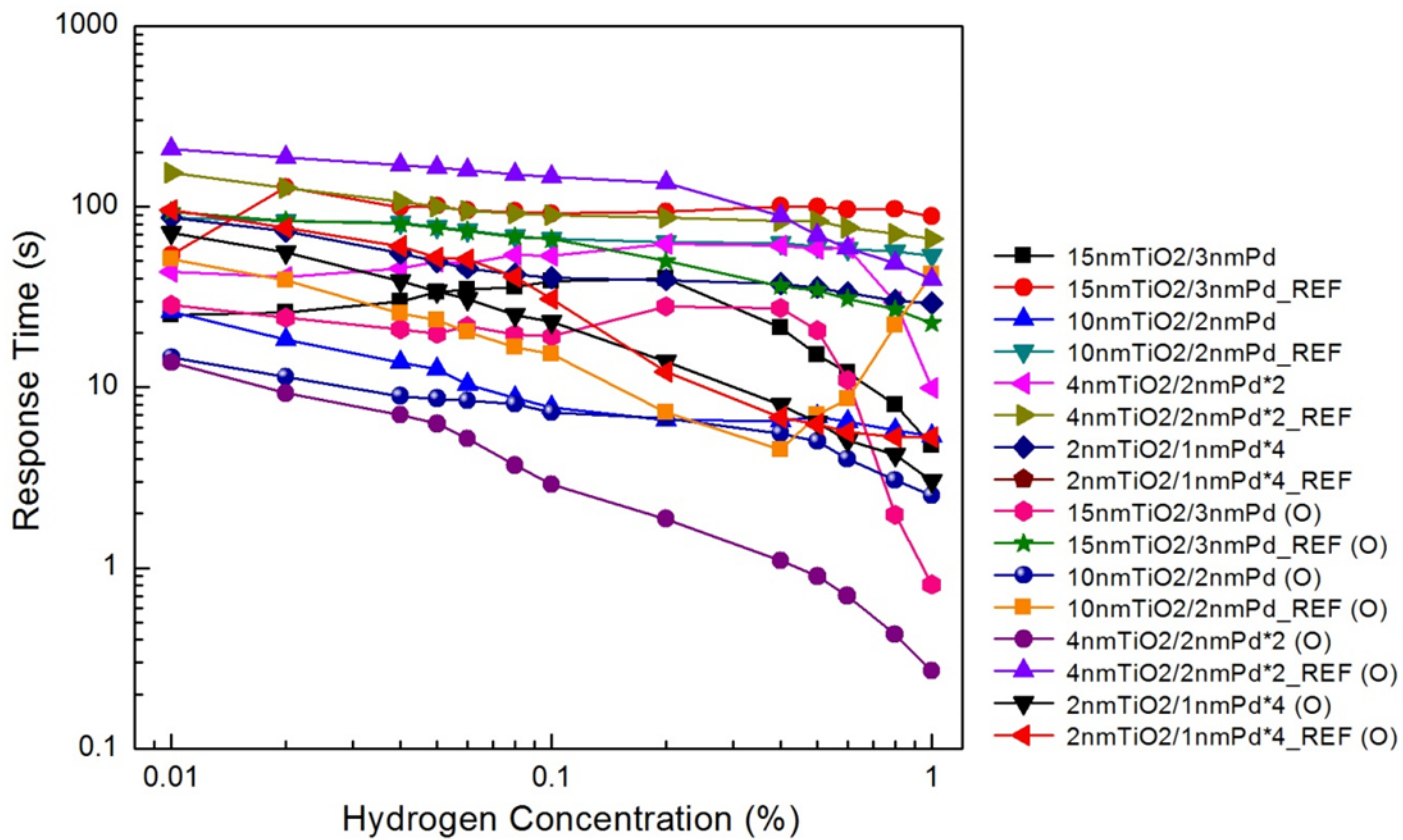


Fig. 2b. Response Time vs. Hydrogen Concentration graph for all samples at room temperature. Note that the thin film reference samples are on average slower than their nanowire network counterparts.

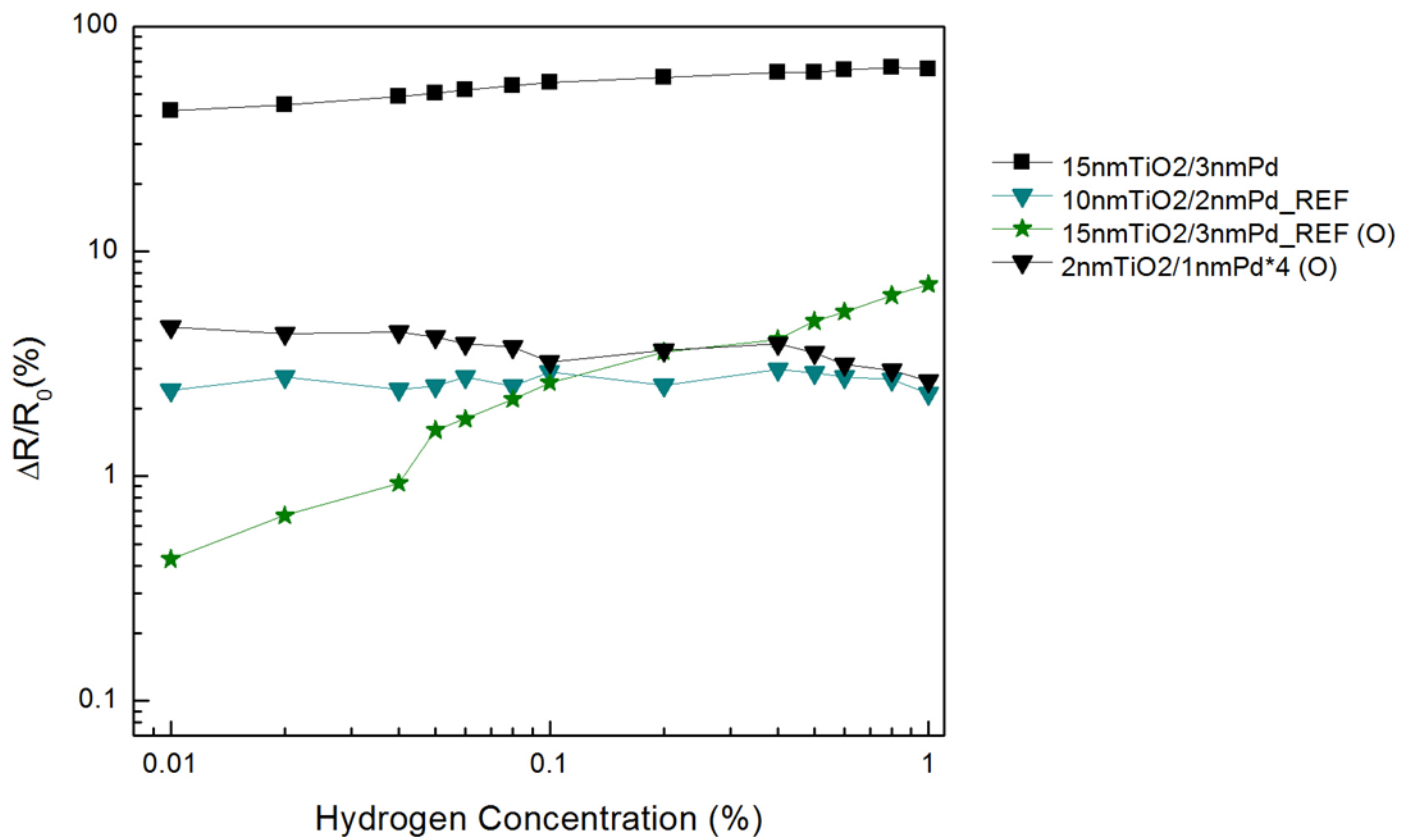


Fig. 2c. Sensitivity vs. Hydrogen Concentration graph for all samples at 150° Celsius. Note that data is only available for 4 of the samples; the rest either had too low of a sensitivity or could not be tested due to high sensor resistance beyond what our testing system could handle.

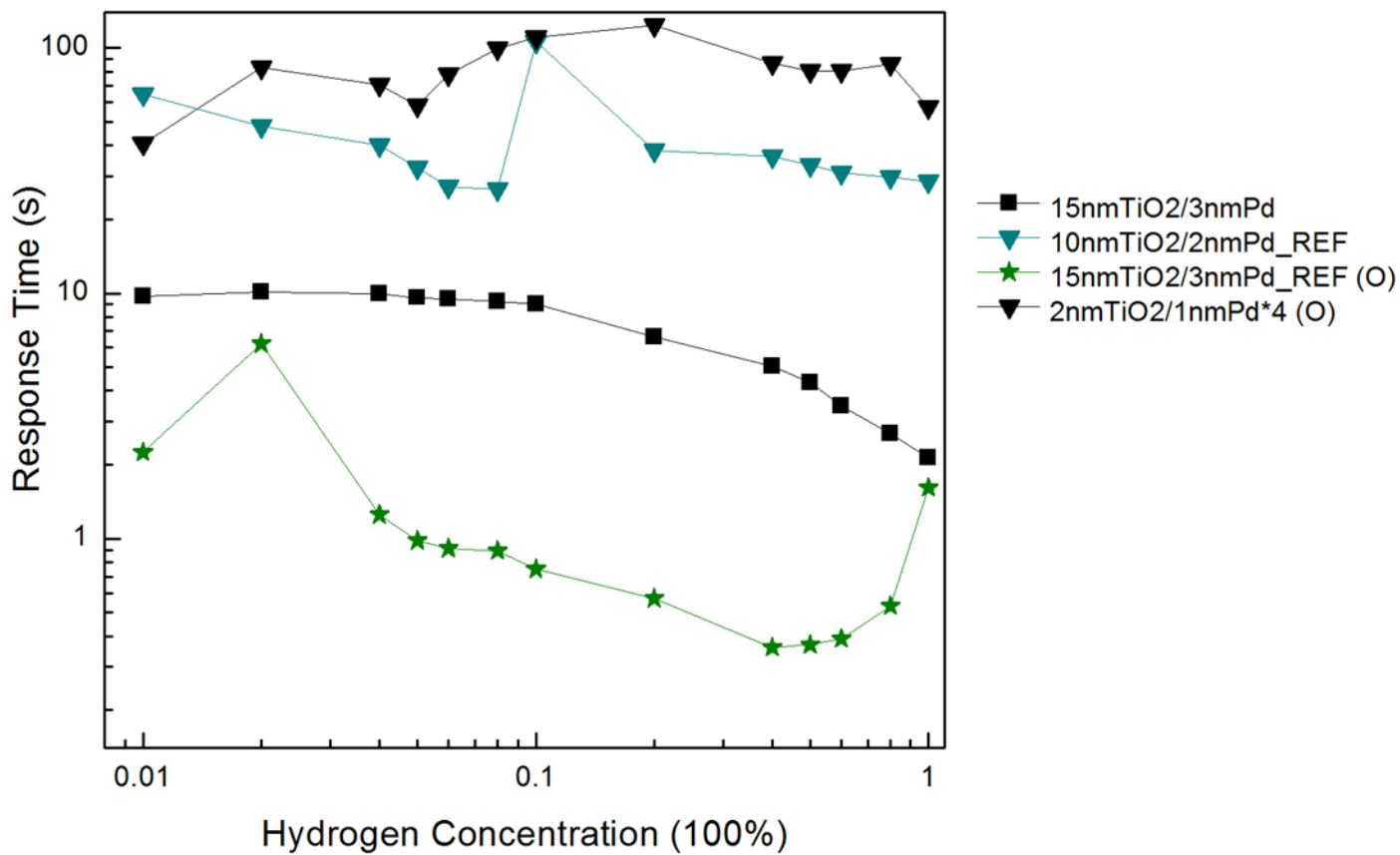


Fig. 2d. Response Time vs. Hydrogen Concentration graph for all samples at 150° Celsius. Note that data is only available for 4 of the samples; the rest either had too long of response times or could not be tested due to high sensor resistance beyond what our testing system could handle.

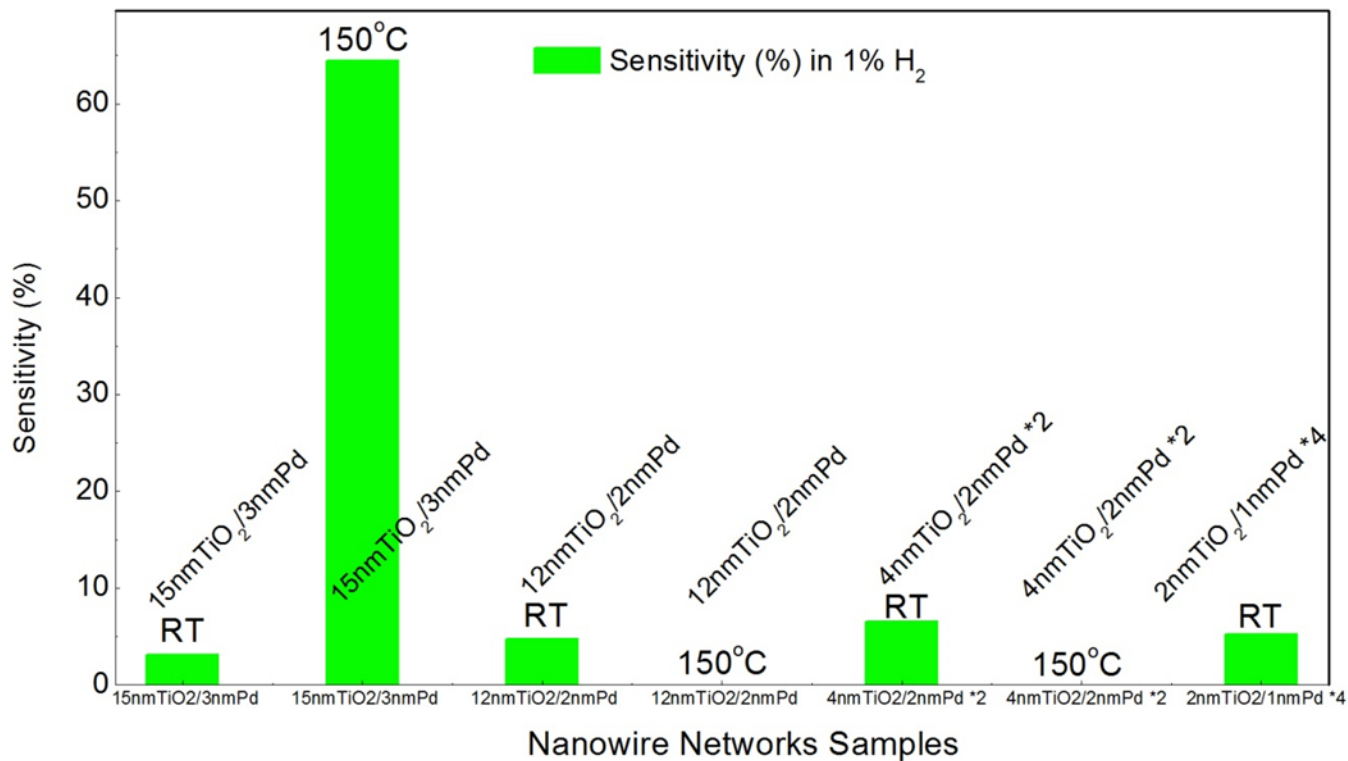


Fig. 3a. Bar graph of sensitivities of selected sensors at a hydrogen concentration of 1%. The 15 nm TiO₂/3 nm Pd sample is much more sensitive than any other sample.

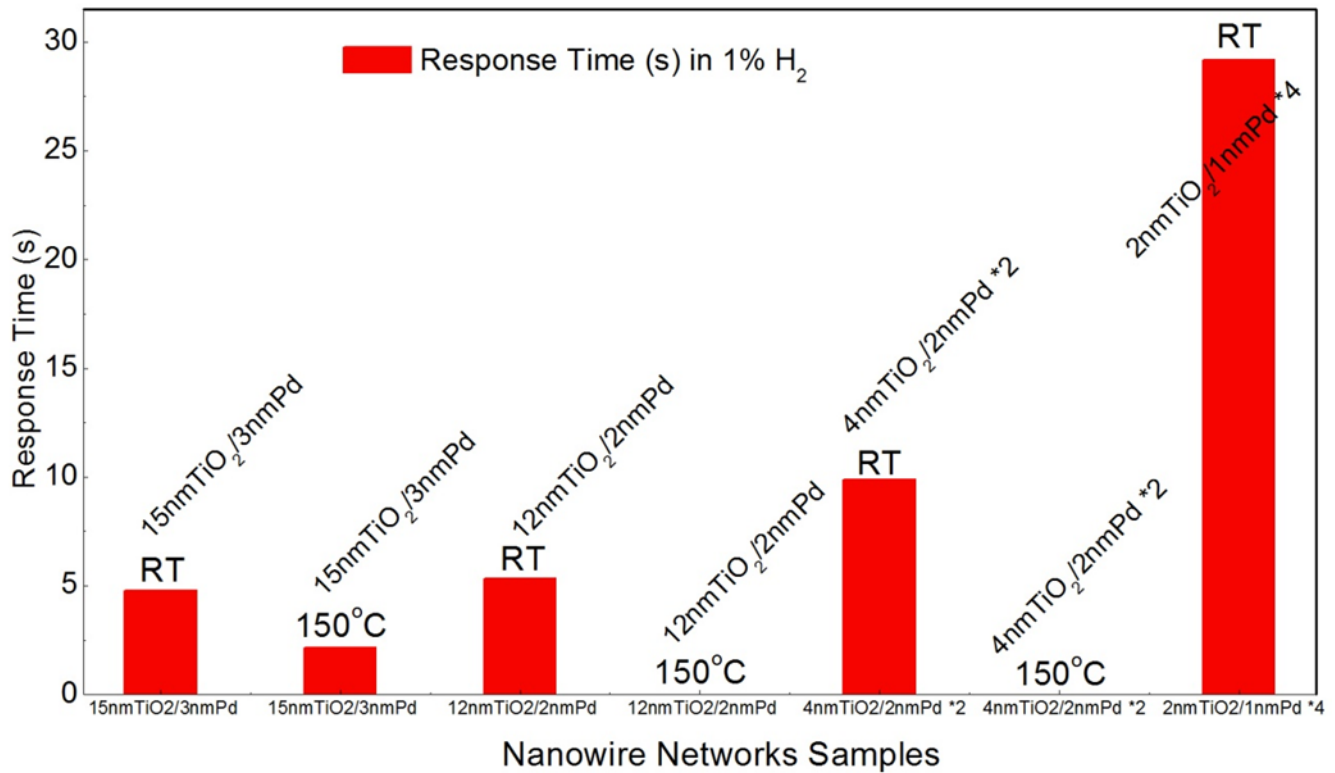


Fig. 3b. Bar graph of response times of selected sensors at a hydrogen concentration of 1%. The 15 nm TiO₂/3 nm Pd sample is several seconds quicker than any other sample.

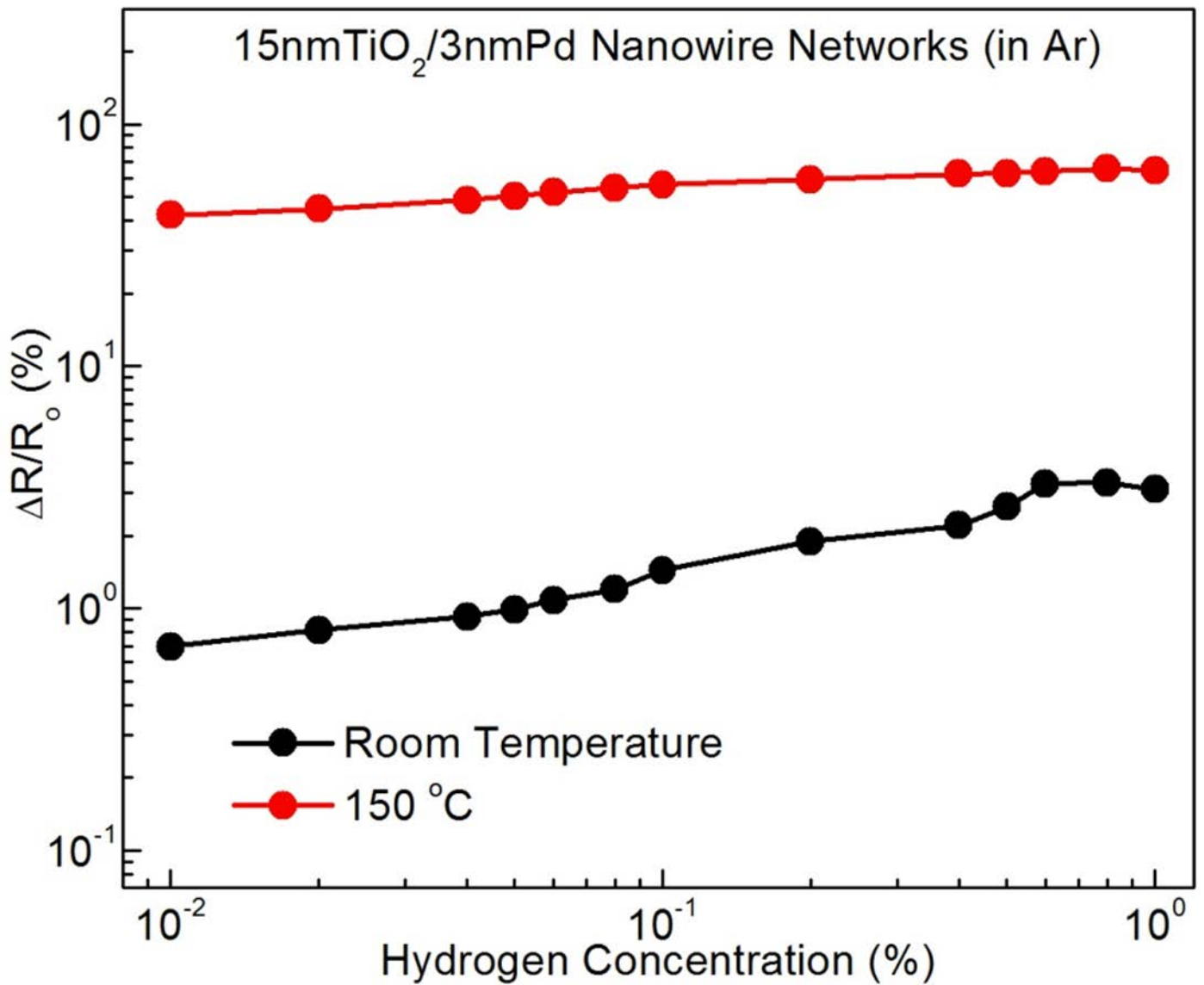


Fig. 4a. Sensitivity vs. Concentration graph for the 15 nm TiO₂/3 nm Pd sample. The graph shows that this sensor was over 10 times more sensitive at 150° Celsius than at room temperature.

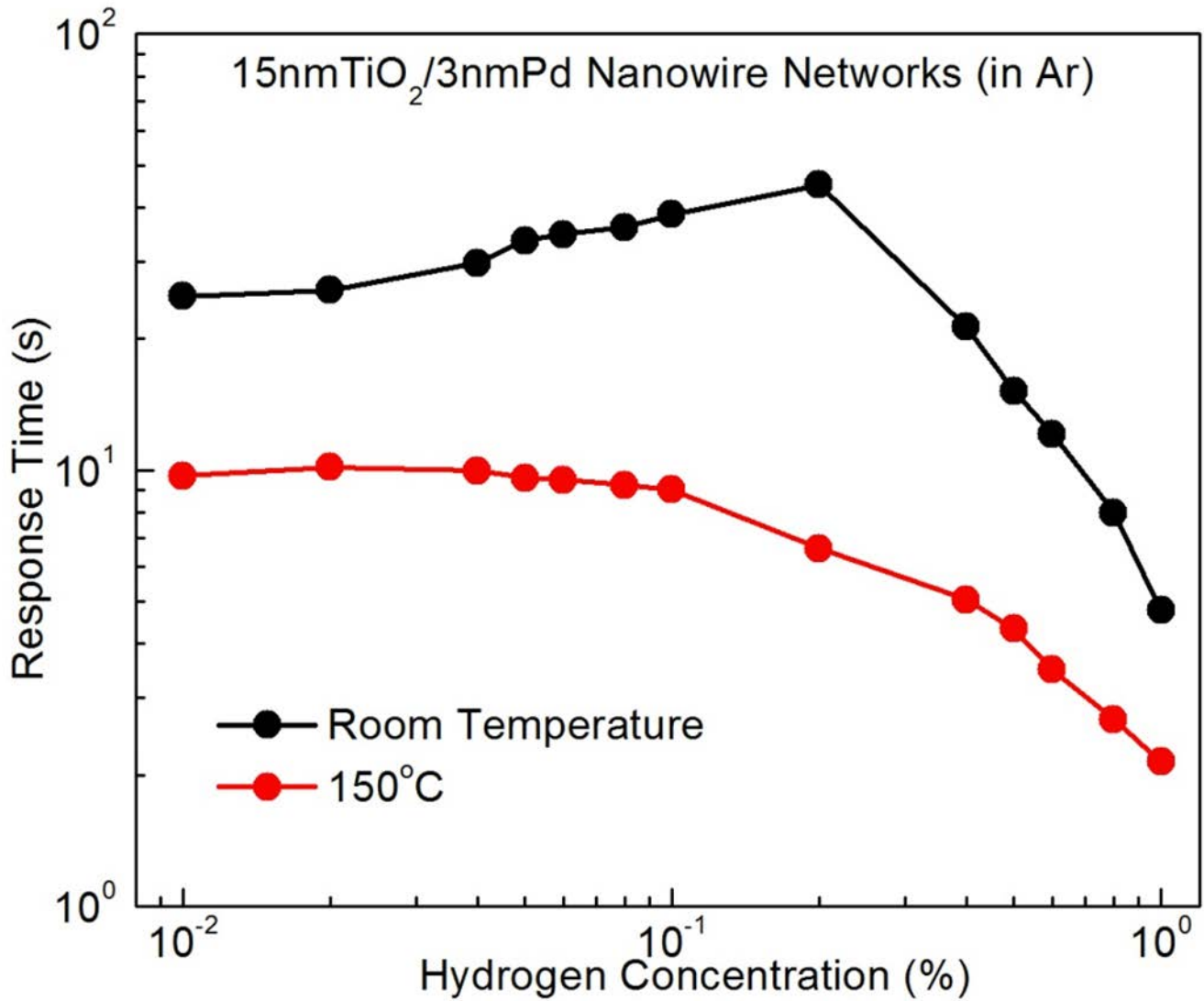


Fig. 4b. Response time vs. Concentration graph for the 15 nm TiO₂/3 nm Pd sample. The graph shows that this sensor was much quicker at 150° Celsius than at room temperature.

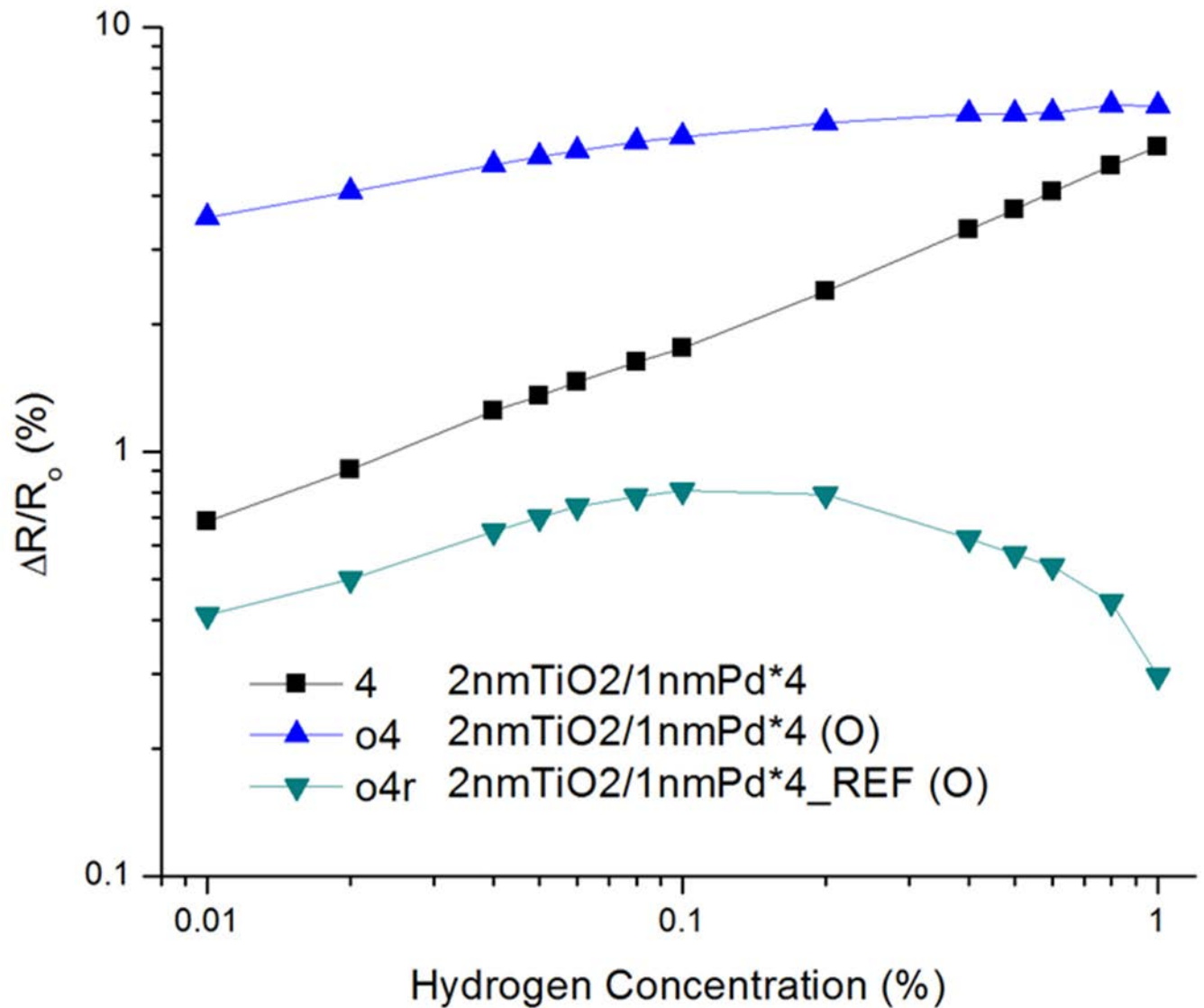


Fig. 5a. Sensitivity vs. Concentration graph for the 4-layered 2 nm TiO₂/1 nm Pd sample. The graph shows that the sample made with oxygen as part of the working gas had a sensitivity approximately 5 times greater than that made without oxygen, and almost 10 times greater than the thin film reference sample.

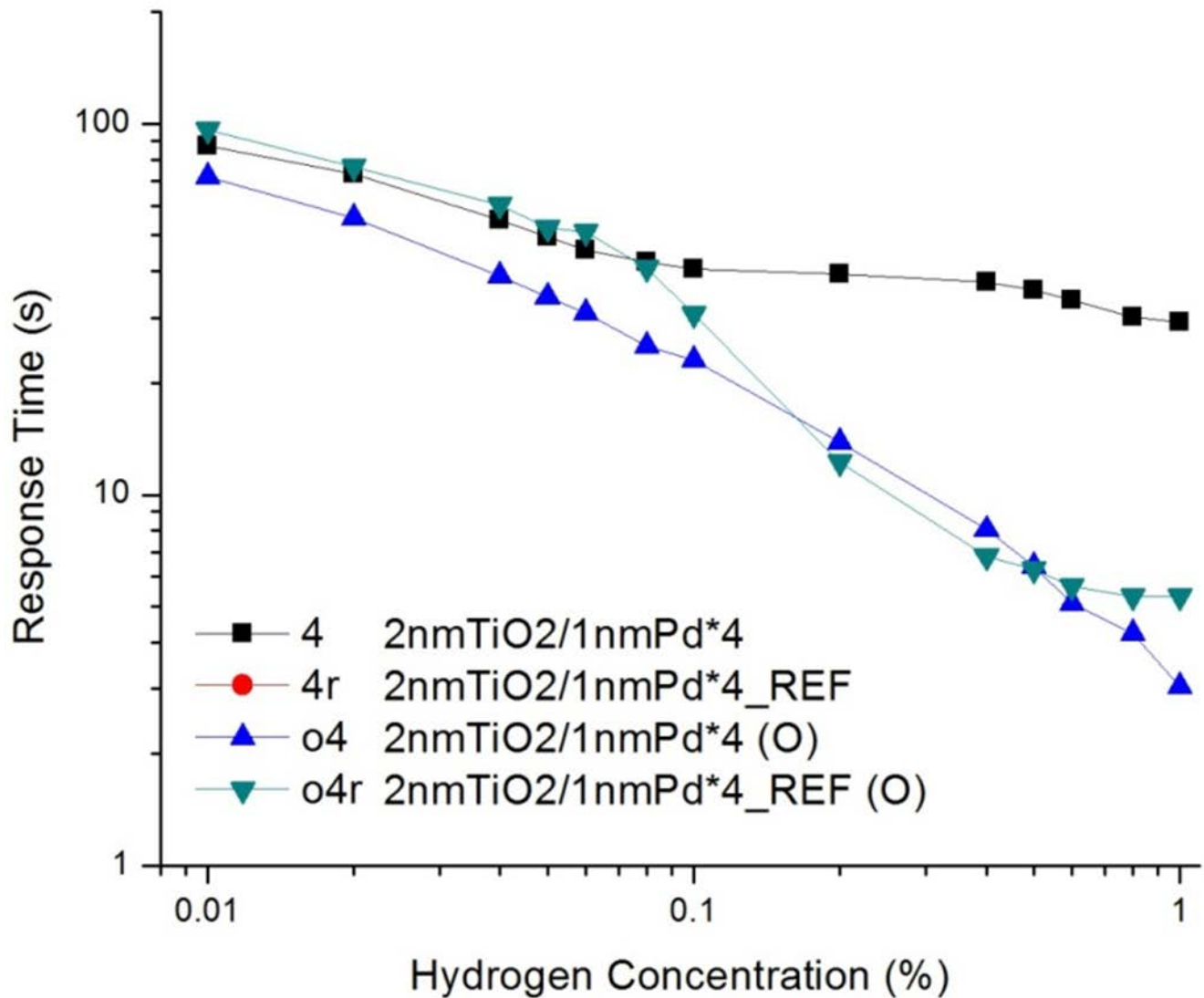


Fig. 5b. Response time vs. Concentration graph for the 4-layered 2 nm TiO₂/1 nm Pd sample. Similar to Figure 5a, the sample made with oxygen as part of the working gas generally has a shorter response time than either of the reference samples or the sample made with only argon in the working gas.

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