

UV irradiation effects on hydrogen sensors based on SnO₂ thin films fabricated by the photochemical deposition

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Abstract

We fabricated highly sensitive room temperature hydrogen sensors based on SnO₂ films. The films were deposited by the photochemical deposition. The deposition solution containing 10mmol/L of SnSO₄ was dropped on the substrate and irradiated with light of an Hg arc lamp. The sample annealed at 200°C showed resistance decrease by a factor $>10^3$ for a 0.05% H₂+Ar mixed gas (0.1atm) at room temperature. The sensitivity and response speed were further improved by UV irradiation using a low-pressure Hg lamp both in vacuum and in air.

Keywords photochemical deposition (PCD), SnO₂, hydrogen gas sensor, UV irradiation

1. Introduction

Detection of hydrogen is very important for fuel cell applications for reasons of safety. Resistive gas sensors based on semiconductor oxides such as SnO_2 are widely used because of their high stability and sensitivity, but usual resistive gas sensors need to be heated up to 300°C or above to obtain high sensitivity and high rapidity. As a result, power consumption is large, and they are not compatible with silicon electronic circuits.

Several research groups have reported on resistive gas sensors based on SnO_2 with sensitivity to hydrogen at room temperature [1-3]. The gas sensing results from the adsorption of gas molecules on the surface and subsequent carrier trapping and de-trapping. Therefore, the sensing is expected to strongly depend on the surface condition of the sensor. In this study, to improve the gas sensor properties further, we attempt to modify the surface condition by irradiating the sensor surface with the UV light. It has been reported that the light irradiation enhances the sensitivity of the gas sensor [4-6]. In all of such researches, the sensor was continuously irradiated while the sensor response was measured, and the irradiation is thought to promote the adsorption and desorption of gas molecules, resulting in enhancement of the gas sensors sensitivity. However, for continuous irradiation during the sensing, the power consumption needs to be large and the system cannot be compact. In our study, UV light is once irradiated for one hour before the measurement of the gas sensor. Thus UV light need not be irradiated during the gas sensing; accordingly it is possible to reduce the power consumption and simplify the gas sensor device.

2. Experimental detail

The SnO_2 films were deposited by the photochemical deposition (PCD) [7-10]. A small amount of the solution was dropped on the glass substrate and irradiated with the UV light, as shown in Fig.1(a). When an aqueous solution containing Sn^{2+} ions is irradiated with UV light, SnO_2 particles synthesized in the solution precipitate onto the substrate, to form a film [10]. Thus the film is constituted of small particles and its surface/volume ratio is large. Hence the film has a large number of the surface reaction sites and thus is advantageous for sensor devices. The pH was adjusted with HNO_3 to 1.4, and the solution contained 10 mmol/L of

SnSO₄. The light source was an ultrahigh-pressure mercury arc lamp of 500 W, and the substrate area of about 1 cm ϕ was irradiated through a spherical lens. The one irradiation time was 5min, and the substrate was washed with water and dried before the new solution was dropped on it. We repeated this process 10 times and obtained SnO₂ thin films with a thickness of around 0.15 μ m. The sensitivity strongly depends on the thickness (repetition time), and the above condition was found to be optimum in the previous work [9]. After the film deposition, Au electrodes, shown in Fig.1(b), were formed by vacuum evaporation. To enhance the sensitivity for hydrogen, Pd is doped by a similar photochemical technique. A 2 mmol/L PdCl₂ solution is dropped on the SnO₂ film surface and then irradiated with the mercury arc lamp for 5 min. The samples were annealed in nitrogen ambient at 200°C and fully stabilized by being stored in air for more than one week.

After the sensor fabrication described above, we performed another UV irradiation for further improvement of the sensitivity of gas sensors. The UV irradiation by a low-pressure mercury lamp was carried out in air or in vacuum for one hour. The dominant irradiation line is at 254 nm, and the total irradiation power is about 10 mW/cm².

The gas sensing properties were measured using a static test system which included a test chamber (about 18 L in volume) and an electrical-characterization workstation system. To examine the gas sensitivity of the sample, current at an applied voltage of 2 V was measured at room temperature (about 300 K), first in vacuum (about 50 Pa), and then in an Ar+H₂ mixed gas ambient. The H₂ content in the mixed gas was 5% and 0.05%, and the gas pressure was 0.1 atm. X-ray photoelectron spectrum (XPS) measurement was performed using XPS PHI-5000 (ULVAC-PHI) with the Al K α line used as an X-ray source.

3. Results and discussion

Figure 2 shows the response to 5%H₂+Ar(0.1atm) before and after the UV irradiation in air. The resistance decrease rate within initial three minutes after introduction of hydrogen is 5.4×10^2 before the UV irradiation, and 4.1×10^3 after the UV irradiation. i.e, the resistance decrease rate grew by almost one order of magnitude. This results show that the response was quickened by the UV irradiation in air.

The recovery characteristics are also important for a gas sensor. The sensor resistance which is decreased with introduction of hydrogen should increase when hydrogen is removed. Figure 3 shows the recovery characteristics of the sensor which was UV-irradiated in air. The resistance first decreased upon exposure to 5% H_2 +Ar(0.1atm). The resistance increased by a factor of 2-3 when the chamber was vacuumed. Then, at the exposure to air, the resistance increased by more than three orders of magnitude, and the initial resistance was reached within about 3 min. The quick recovery in air could be due to H_2O molecules[9].

Figure 4 shows the response before and after the UV irradiation in vacuum. The resistance decrease rate within the initial three minutes after introduction of the hydrogen is 6.4×10^2 before the UV irradiation, and 1.3×10^3 after the UV irradiation for 5% H_2 +Ar(0.1atm). To see the effects of the UV irradiation more obviously, the response was measured with 0.05% H_2 +Ar(0.1atm). For 0.05% H_2 +Ar(0.1atm), there is almost one order of magnitude difference in the resistance decrease rate within the initial ten minutes between before and after UV irradiation in vacuum, as shown in Fig.4. Thus, the UV irradiation in vacuum improved the sensitivity of the gas sensor as did the UV irradiation in air.

It is necessary to confirm the stability of the sensor after the UV irradiation. We examined the sensing properties at intervals of two weeks, and-six months after the UV irradiation in air. The results are shown in Fig. 2. The sensors were kept in the air atmosphere during those intervals. They showed almost the same response as just after the UV irradiation within the experimental uncertainty, and thus we concluded that the response was steady. The stability was also confirmed for the sample UV irradiated in vacuum.

The sensitivity of our sensors is strongly influenced by the Pd doping. Without Pd doping, the current increased only by a factor of 2-3 with introduction of 5% H_2 +Ar(0.1atm). Therefore, one could suppose that the annealing and the UV irradiation affected the chemical state of Pd. Thus we performed the XPS measurement for the samples annealed in nitrogen, and UV irradiated in air and in vacuum, before and after a surface cleaning by the Ar^+ ion sputtering for 6 seconds. For all the sample surfaces, the main peak of metal Pd (3d $_{5/2}$) is located at 335.3 eV. By fitting the observed spectra with Gaussian curves, we obtained relative intensities of the metal Pd peak and the two satellite peaks of Pd located at around 336.3 eV (PdO) and 338.1 eV (PdO $_2$). The results are shown in Fig. 5. Before the sputtering,

the percentage of metal Pd is almost the same for all the samples. For the sample UV-irradiated in air, the signal of PdO was not observed, and the signal of PdO₂ was observed more strongly than for the others. After the Ar sputtering, the percentages of metal Pd, PdO and PdO₂ were almost the same for the all samples, and Pd was dominantly in the metallic or elemental state. Thus we did not find clear correlation between the chemical state of Pd and the sensor sensitivity.

For n-type oxide semiconductors, an oxygen atom adsorbed on the surface traps a carrier to become a negative ion at the grain boundary. These adsorbed oxygen ions generate a potential barrier between grains, which must disturb the free conduction of the electrons. Under the hydrogen ambient, the oxygen ions are removed by reactions with hydrogen atoms, which leads to decrease in the barrier height and increase in the current. The UV irradiation in air may enhance the oxygen adsorption, while some oxygen ions may be removed by the irradiation in vacuum [11]. Since both the irradiations in air and in vacuum have similar effects in our experiment, the effects of the UV irradiation cannot be explained by change of the amount of adsorbed oxygen. In addition, as noted above, we did not find any clear correlation between the chemical state of Pd and the sensitivity. Thus, the improvement by the UV irradiation is not only due to change in the chemical states of surface atoms but also other factors. One possible cause of the improvement observed in this work is the increase in number of reaction sites on the SnO₂ surface owing to rearrangement of Sn-O bonding induced by the UV irradiation.

Our hydrogen sensor can be fabricated by the simple fabrication process. Moreover, it can be integrated to silicon circuits since it is thin-film type and needs no heating. For the actual application, the sensor resistance may need to be tuned by donor doping for matching with the sensing circuit.

4. Conclusions

We fabricated highly sensitive room temperature hydrogen sensors based on SnO₂ films deposited by the photochemical deposition. The sensor showed resistance decrease by a factor $>10^3$ for 5%H₂+Ar(0.1atm) at room temperature. We observed significant enhancement in the

sensitivity of the gas sensors by UV light irradiation by the low-pressure mercury lamp both in air and in vacuum.

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Figure

Figure 1 (a): schematic of the photochemical deposition apparatus. (b): pattern of the inter-digit electrode formed on the film.

Figure 2 Response to 5% H_2 +Ar(0.1atm) for the sample before and after UV irradiation in air. The responses two weeks and six months after the irradiation are also shown.

Figure 3 The response-recovery characteristics of the sample UV-irradiated in air for 5% H_2 +Ar(0.1atm).

Figure 4 Response to 5% and 0.05% H_2 +Ar(0.1atm) for the sample before and after UV irradiation in vacuum.

Figure 5 Ratios of Pd species (metal Pd, PdO, and PdO₂) in the various samples. “0 sec” means the data taken without Ar sputtering, and “6 sec” after 6 seconds Ar sputtering.

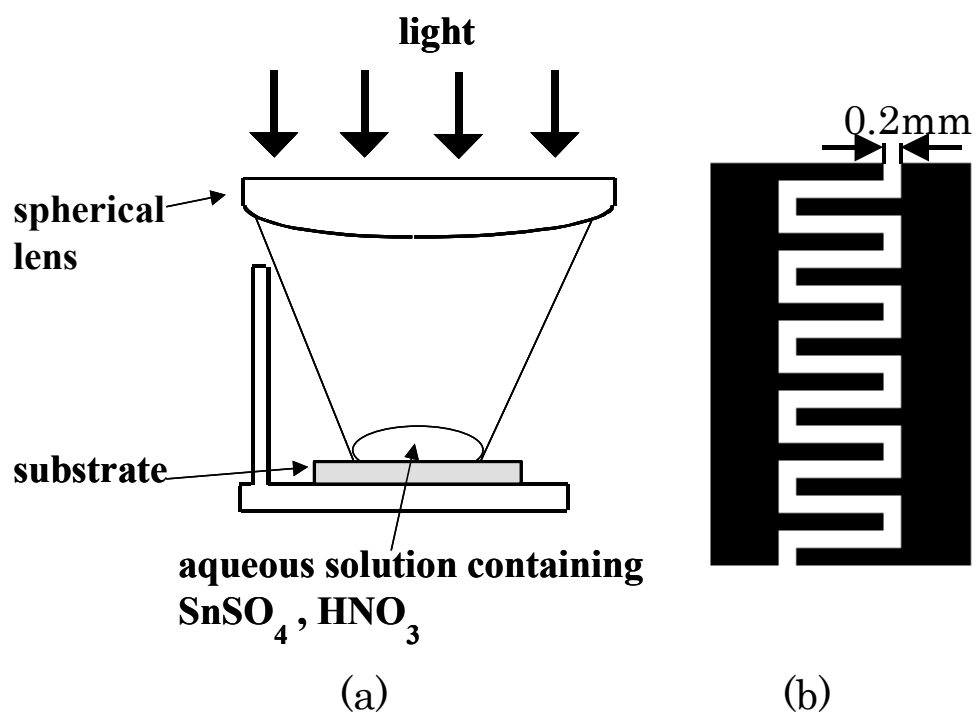


Figure 1

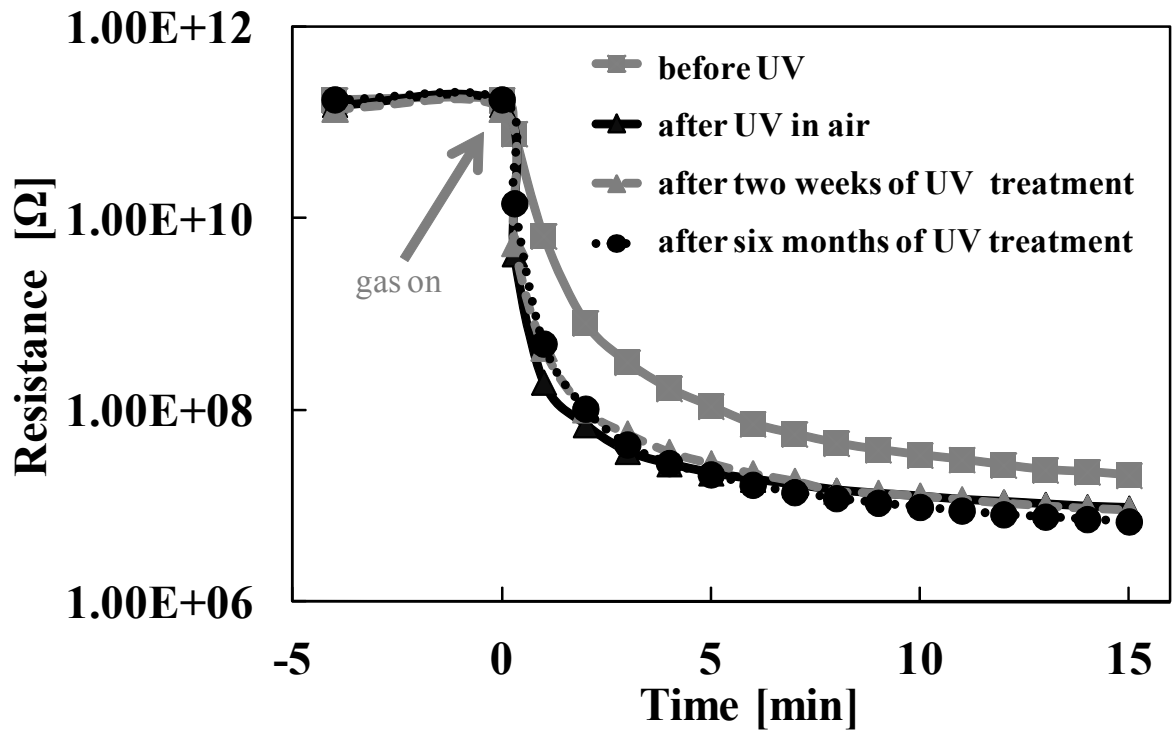


Figure 2

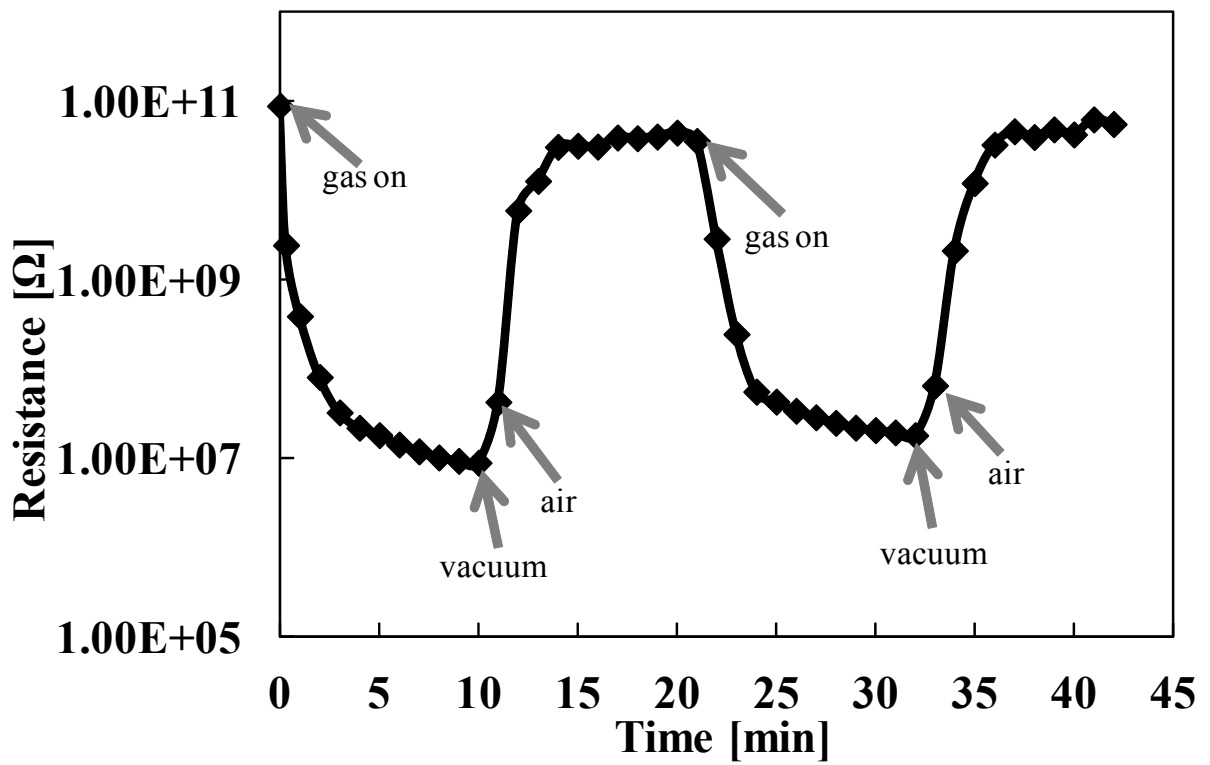


Figure 3

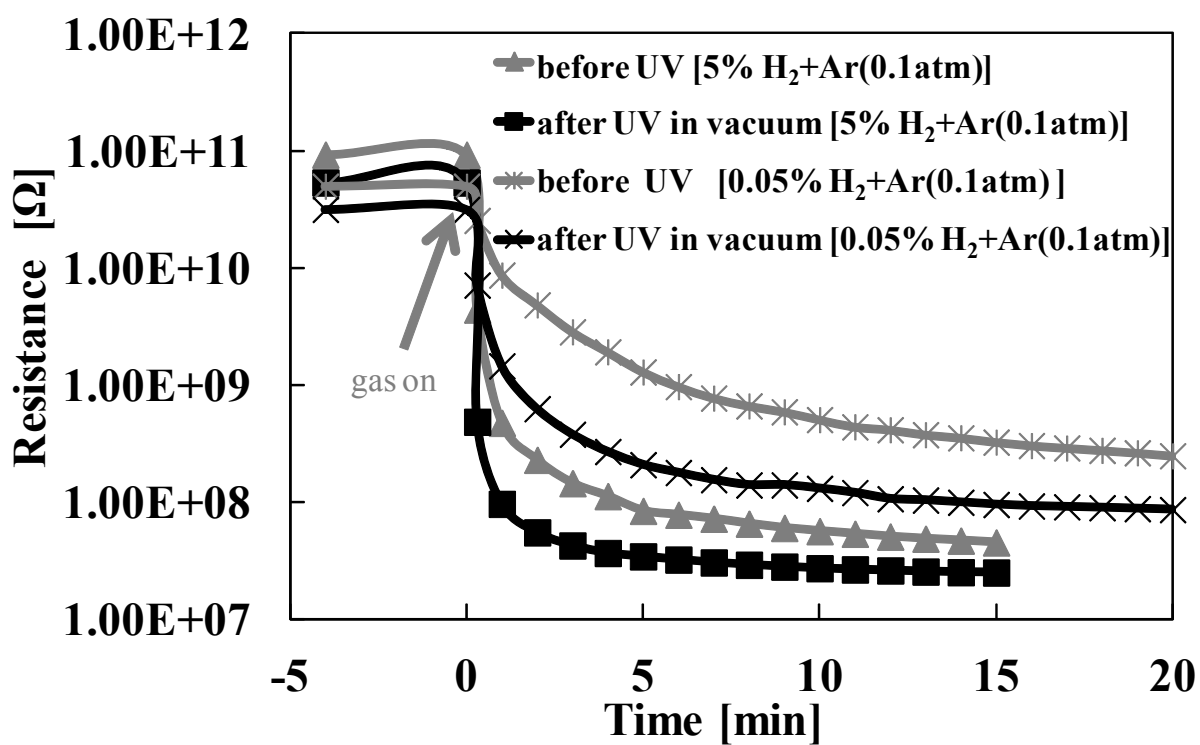


Figure 4

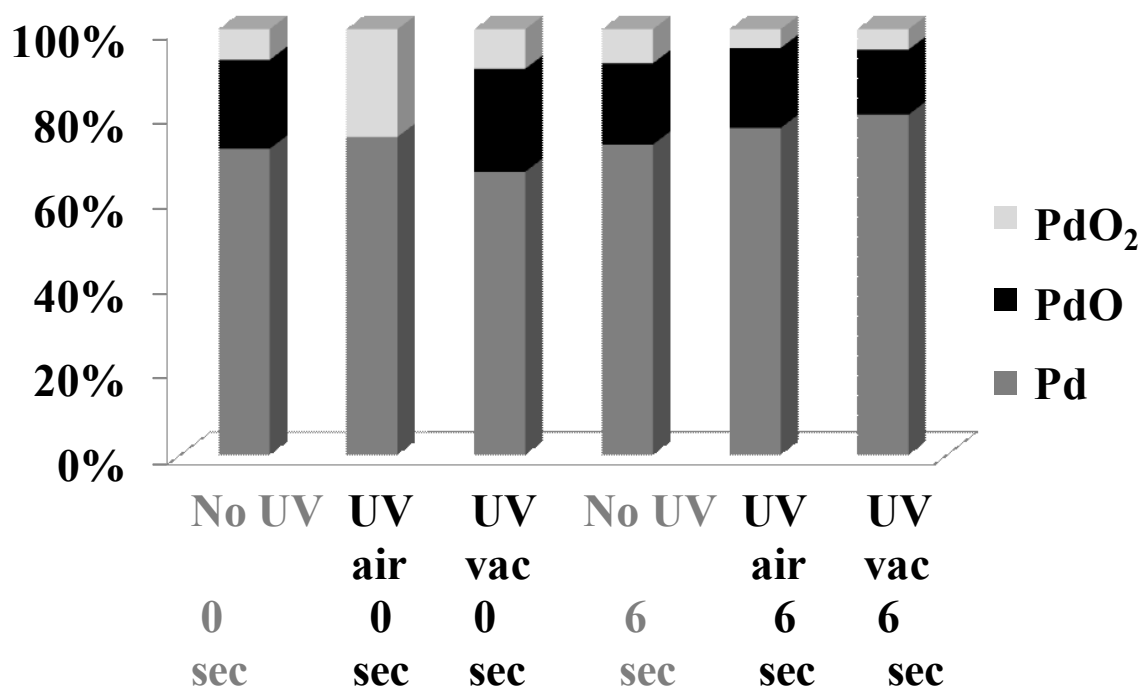


Figure 5