Response Kinetics of Doped CuO/ZnO Heterocontacts

Seymen Aygün and David Cann*

Materials Science and Engineering Department, Iowa State University, Ames, Iowa 50011

Received: December 4, 2004; In Final Form: February 4, 2005

In this work, the effects of doping on hydrogen sensitivity and sensor response of CuO/ZnO heterocontacts were examined. Both current−voltage and current−time measurements were utilized in hydrogen/air and hydrogen/nitrogen atmospheres at 400 °C. The addition of Ni to p-type CuO and Ga to n-type ZnO were observed to enhance the sensor properties. Through analysis of the time-dependent current data, it was shown that the sensor response of the heterocontact can be modeled via a two-site Langmuir adsorption model. The response times of the two sites were calculated using this model. While one of the sites showed a significant decrease in response time when the p-side was doped with Ni, the response time of the other site changed only slightly. The highest sensitivity was obtained by doping the n-side with Ga at the expense of the response rate. The fastest response times were achieved when both sides of the heterocontact were doped. This suggests that carrier density may play a significant role in the sensor response.

1. Introduction

Hydrogen gas is used in a number of areas such as aeronautics, nuclear reactors, chemical processing, pharmaceuticals, and fuel cells. It also has many potential applications as a clean, efficient, and renewable energy carrier. It can be used directly for combustion, which produces much more energy than other fuels, or can be used indirectly in fuel cells to produce electricity. Furthermore, it is a nonpolluting energy source with water being its only combustion product. Since it is a flammable and explosive gas, monitoring and leakage detection of hydrogen is critical in these applications. Therefore, sensors that are able to detect hydrogen at low concentrations as well as in the presence of other gases are crucial. This brings the demand for low-cost, reliable, sensitive, and selective hydrogen sensors.

The heterocontact sensor is one such promising candidate for gas sensing with its sensitivity and inherent selectivity characteristics. The sensor is unique in that the selectivity to a specific gaseous species can be tuned by changing the applied bias or the measuring frequency. The bulk heterocontact sensor is formed by clamping a p-type and an n-type ceramic pellet together and operates on the principle of measuring a change in interface impedance due to the adsorption of reducing gases at the interface. The sensor exhibits rectifying current−voltage behavior that is sensitive to reducing gases at positive biases. The most widely studied heterocontact system, CuO/ZnO, shows sensitivity toward many gases, including H_2, CO, water vapor, H_2S, and C_2H_5OH.[1−4] It has also been shown that the frequency and/or bias dependence of the impedance can be used to detect gases and distinguish CO from H_2.[5] In addition to the bulk device, different forms of the heterocontact have been studied, such as thin films and layered structures, which improve the reproducibility and the integrity of the sensor.[6−8] Nonetheless, it is important to note that the bulk sensors made by mechanically contacting the ceramics exhibit clear rectifying characteristics with high sensitivity toward reducing gases.

Semiconductor gas sensors work on the principle of changing their resistance with changing atmospheric composition through the reactions on the sensor surface involving gas molecules. During this change, the sensor switches from one equilibrium state (e.g. resistance in air atmosphere) to another equilibrium state (e.g. resistance in hydrogen atmosphere). Therefore, the sensitivity of a gas sensor, which is the ratio of these resistances in different atmospheres, can be studied either by comparing the sensor response at equilibrium states or analyzing the transition between these states. The former determines the magnitude of the sensor signal, whereas the latter determines the rate of the signal. Both are very important when considering a gas sensor for a particular application. To date, heterocontact research has been focused on equilibrium measurements of the CuO/ZnO system; however, there have only been a few studies that include the current−time behavior of the sensor.[1,9]

The effects of dopants on the I−V characteristics of the heterocontacts have been demonstrated in our previous work.[10] In the present work, the effects of Ni doping in CuO and Ga doping in ZnO on the response kinetics of the heterocontact sensor are reported. The current−time data were fit to a two-site Langmuir adsorption model, and the response and recovery rates of the sites were analyzed for different compositions. The results showed that doping remarkably increased both the overall response time and the sensitivity of the sensor.

2. The Model

The barrier height of the heterocontact interface changes with the oxidation of reducing gases adsorbed on either side of the heterocontact. If we consider a simple one-stage kinetic scheme, we can derive a two-site Langmuir model that relates the change in current to the surface coverage of the gas.[11−14] The oxidation reaction of a reducing gaseous species R on the surface of a heterocontact component at high temperatures can be written as

$$O_{ad}^- + R_{ad} \rightarrow RO + e^- \tag{1}$$
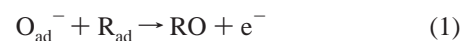
Here, if we assume that the adsorbed oxygen regeneration rate is negligible, the current change across the interface will be proportional to the concentration of the adsorbed reducing gas.[15]

* Corresponding author. Ph: (515)-294-3202. Fax: (515)-294-5444. E-mail: batio3@iastate.edu.
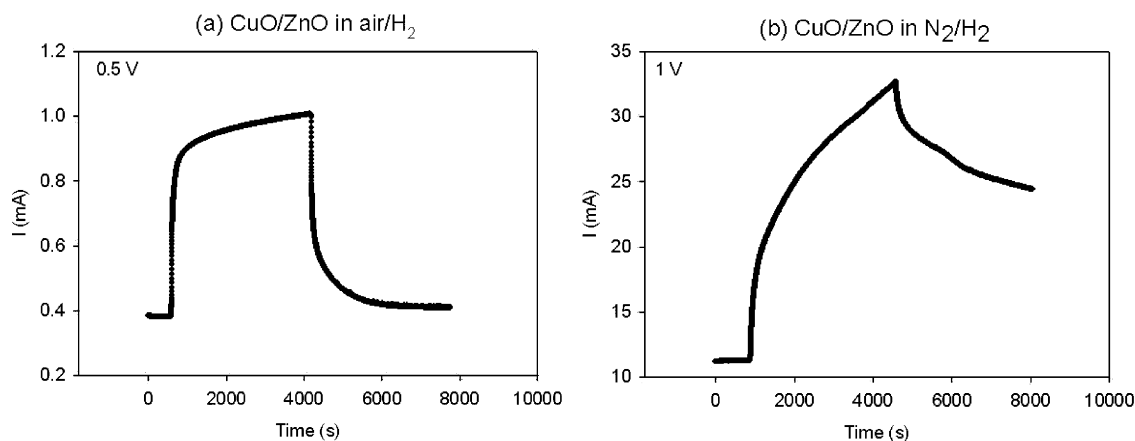
Response Kinetics of Doped CuO/ZnO Heterocontacts

J. Phys. Chem. B, Vol. 109, No. 16, 2005 **7879**

Figure 1. Current−time response of (a) CuO/ZnO in air/H_2 and (b) CuO/ZnO in N_2/H_2 at 400 °C.

Hence, the surface coverage values can be obtained from the normalized current versus time data.

The total number of adsorbed molecules a on a surface can be written as

$$a = n_{total}\theta \quad (2)$$

where n_{total} is the number of sites and θ is the fraction of those surface sites covered. Assuming monolayer coverage, the simple Langmuir rate equation for a single adsorbate on homogeneously active sites is given by[16]

$$\frac{d\theta}{dt} = k_a(1 - \theta)P_{gas} + k_d\theta \quad (3)$$

where P_{gas} is the partial pressure of the gas, and k_a and k_d are the adsorption and desorption constants, respectively. By integrating eq 3, one obtains the relation

$$\theta = \frac{k_a P_{gas}}{k_a P_{gas} + k_d}[1 - \exp(- (k_a P_{gas} + k_d)t)] \quad (4)$$

Substituting $k_1 = k_a P_{gas}$ and $k_2 = k_a P_{gas} + k_d$ gives

$$\theta = \frac{k_1}{k_2}[1 - \exp(-k_2 t)] \quad (5)$$

If there are two types of sites, then the eqs 2 and 5 become

$$a = n_{total}\theta = n_1\theta_1 + n_2\theta_2 \quad (6)$$

$$\theta = \chi_1\theta_1 + \chi_2\theta_2 = \chi_1\frac{k_1}{k_2}[1 - \exp(-k_2 t)] +$$
$$\chi_2\frac{k_3}{k_4}[1 - \exp(-k_4 t)] \quad (7)$$

where $\chi_1 = n_1/n_{total}$, the fraction of sites of type 1, and $\chi_2 = n_2/n_{total}$, the fraction of sites of type 2. Generally, the response time is defined as the time at which the coverage has reached $1/e$ of the final equilibrium current value. Therefore, the reciprocals of the kinetic constants k_2 and k_4 are denoted as the response times for the two sites, τ_1 and τ_2, respectively.

3. Experimental Section

Ceramics of doped CuO and ZnO were prepared via solid-state processing routes. The batches were prepared using appropriate stoichiometric amounts of powders of ZnO (Aldrich, 99+%), CuO (Alfa Aesar, ACS), Ga_2O_3 (All-Chemie, 99.999%),

and NiO (Alfa Aesar 99%). After that, the powders were milled in zirconia media for 6 h and then dried overnight. Doped CuO powders were calcined at 800 °C, and doped ZnO powders were calcined at 900 °C for 12 h in air. After the addition of approximately 1 wt % PVA (poly vinyl alcohol) binder, the powders were pressed into pellets by cold uniaxial pressing. The pressures for CuO and ZnO compositions were 100 and 20 MPa, respectively. The pellets of CuO were sintered at 900 °C for 24 h in air, and the pellets of ZnO were sintered at 1000 °C for 3 h in air. The sintered pellets were ground down to a thickness of 1 mm, and Heraeus (C1000) silver electrodes were painted on one side of the pellets. They were then fired at 550 °C for 30 min. To ensure reproducible electrical properties, the surfaces at the heterocontact interface were ground with 600-grit SiC-based paper. The electrical measurements of the heterocontacts were performed in a NorECs Probostat conductivity cell. A Keithley 237 high voltage source measure unit was used for dc current−voltage and dc current−time measurements in various atmospheres. Dry air (N_2:O_2 = 4:1) or high-purity N_2 was used as the carrier gas for H_2 to dilute the hydrogen to 4000 ppm. The flow rate of the gases was fixed at 200 mL/min using mass flow controllers.

4. Results and Discussion

Sensor Response of CuO/ZnO Heterocontact and the Constituent Oxides. The current−time plots of an undoped CuO/ZnO heterocontact in air/H_2 and in N_2/H_2 atmospheres at 400 °C are shown in Figure 1. When hydrogen gas was introduced into the atmosphere, the potential barrier at the heterocontact interface decreased, and therefore, the current passing through the heterocontact sensor increased (Figure 1a). The increased current corresponded to a sensitivity ($I_{hydrogen}/I_{air}$) of ~2.6, which is close to the value obtained from I−V measurements.[10] When the hydrogen gas was turned off, the current reverted to its original value, indicating that the process is reversible. The steep initial slope of the curve obtained after shut off shows that the recovery was also quite fast. The importance of the presence of oxygen is clearly seen in Figure 1b. In the absence of oxygen, the sensor response was much slower and most importantly there was no full recovery, indicating a possible reduction of the sensor.

The responses of the constituent oxides were also investigated (Figure 2). As expected from eq 1, when the oxides were exposed to hydrogen, the conductivity of p-type CuO was decreased and that of n-type ZnO was increased. The response of CuO was much faster than that of ZnO, which can be attributed to the lower density of CuO. A quantitative compari-
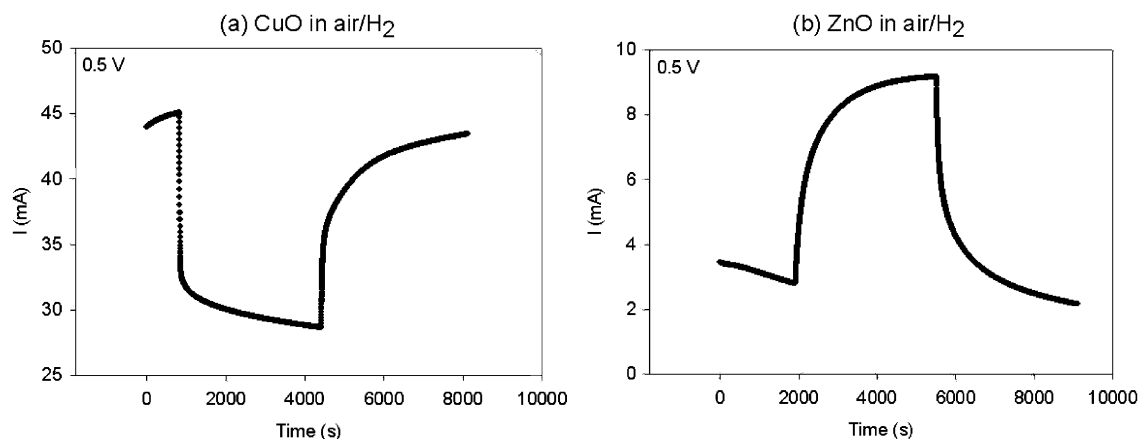
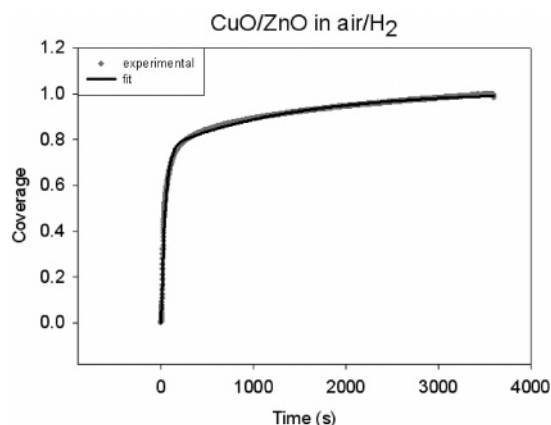**Figure 2.** Current−time response of (a) CuO in air/H_2 and (b) ZnO in air/H_2.

Figure 3. Coverage vs time plot for CuO/ZnO in air/H_2 and the two-site fit.

Figure 4. Current−time response of 1.5 mol % Ni−CuO/ZnO in air/H_2.

son of Figures 1a and 2 shows that the resistance of the heterocontact was much larger than the sum of the resistances of the bulk constituent oxides. This indicates that the interfacial resistance was dominant over the bulk resistances. This agrees well with the ac impedance data and the proposed equivalent circuit in which the bulk resistance values were found to be much smaller than the interface resistance.[17]

The coverage vs time plot was derived by normalizing the current vs time data. The electrical response of the sensor is a dynamic process, and when hydrogen gas is introduced, the adsorption and desorption of the gas occurs simultaneously until the gas is shut off. During this process, when the number of adsorbed molecules becomes equal to the number of desorbed molecules, equilibrium, and hence monolayer coverage, is achieved. The coverage vs time plot for a CuO/ZnO hetero-contact is shown in Figure 3. Attempts were made to fit the data to a simple single site Langmuir isotherm; however, the fit was poor, with an R^2 value of 0.7852. The curves were fit to the two-site model with satisfactory results, with an R^2 value of 0.9930. The data suggest that there should be two energeti-cally different adsorption sites, which is consistent with our system formed by two different materials. The single pellet measurements showed that both materials were affected by hydrogen adsorption, and hence, they or their interactions may stabilize two different adsorption sites at the interface. The response times of the sites, τ_1 and τ_2, were calculated using this model, and the values of 45 and 1400 s were obtained, respectively. These response times show no obvious relationship to the response times derived from the data for the constituent oxides in Figure 2, CuO ($\tau_1 = 19$ s, $\tau_2 = 1535$ s) and ZnO ($\tau_1 = 130$ s, $\tau_2 = 852$ s). This is consistent with the idea that
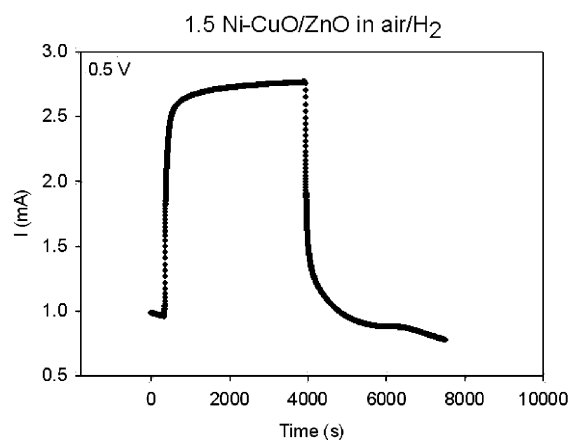
the sensor response is dominated by interfacial effects rather than bulk effects.[10] The response rate of the second site is significantly slower than the first site, affecting the overall sensor response, especially at coverage above ∼0.5. The heterocontacts were doped in an attempt to increase the response rate of the second site and hence the overall response and to increase the sensitivity of the sensor.

Effects of Dopants on the Sensor Response. In our previous study, Ni doped-CuO/ZnO heterocontacts were observed to show the highest sensitivity to hydrogen among all the mono-valent and isovalent dopants, such as Li, Na, Sr, and Ca, using current voltage measurements.[10] Therefore, Ni was selected as the dopant for CuO in this work. The current vs time plot of a 1.5 mol % Ni−CuO/ZnO heterocontact is shown in Figure 4. As can be seen, the current values were higher than that of the pure heterocontact with a slightly higher sensitivity of ∼2.8. The data were again fit to the two-site Langmuir isotherm, and the response times, τ_1 and τ_2, were obtained as 50 and 822 s, respectively. When compared to the pure heterocontact, τ_1 changed slightly, whereas there was a dramatic decrease in τ_2. This resulted in attaining higher coverage values at smaller response times.

Doping of the n-type ZnO constituent was also examined. Both acceptor (Li) and donor (Ga) dopants were used. Figure 5a shows the I−V characteristics of a CuO/1.5 mol % Li-doped ZnO heterocontact. The heterocontact did not show rectifying characteristics and the current values were on the order of microamperes. The loss of rectifying behavior suggests that the p−n junction was degraded. The large reverse bias (saturation) currents suggest that a large minority carrier concentration was
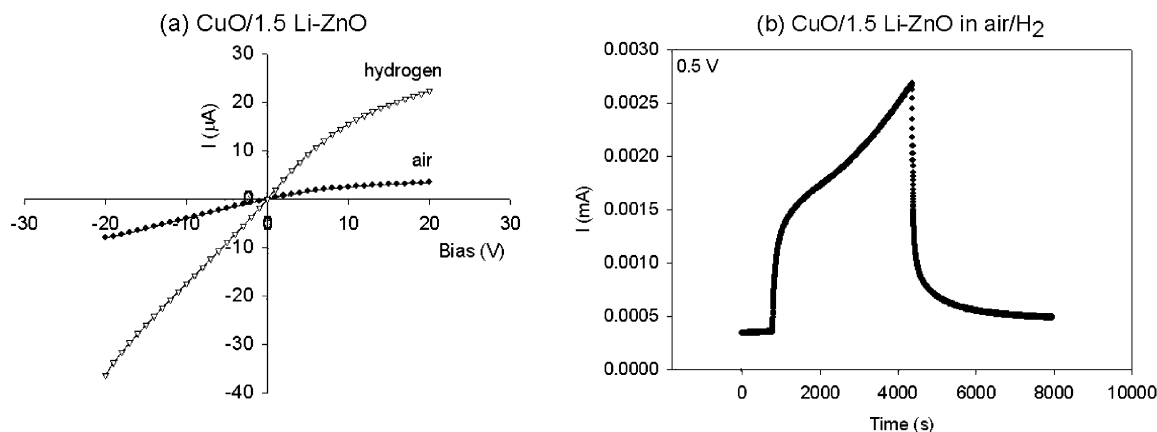
Response Kinetics of Doped CuO/ZnO Heterocontacts

J. Phys. Chem. B, Vol. 109, No. 16, 2005 **7881**

Figure 5. (a) Current–voltage plot for CuO/1.5 mol % Li–ZnO and (b) current–time response of CuO/1.5 mol % Li–ZnO in air/H$_2$.
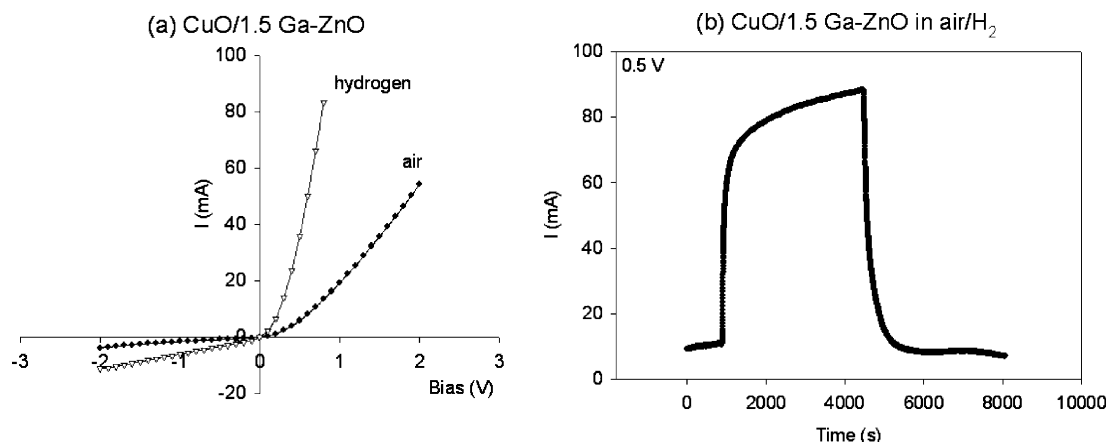

Figure 6. (a) Current–voltage plot for CuO/1.5 mol % Ga–ZnO and (b) current–time response of CuO/1.5 mol % Ga–ZnO in air/H$_2$.

present in ZnO, which can be attributed to the holes provided by the acceptor Li. The current vs time response of the heterocontact was also different than the other samples (Figure 5b). The overall response was very slow and the slowly increasing part of the response curve might be an indication of bulk effects in addition to surface adsorption.

Contrary to Li doping, Ga doping had a substantial impact on the sensitivity and on the sensor response, and the CuO/1.5 mol % Ga–ZnO heterocontact showed the highest sensitivity among all the samples in this work. The I–V plot shows well-defined rectifying characteristics, as shown in Figure 6a, with very high forward currents, especially in the presence of hydrogen. In fact, the response in hydrogen exceeded the current range of our instrumentation above a bias of 0.8 V. The energy-band diagram that was proposed by Baek et al.[7] suggests that the potential barrier that electrons must overcome is much smaller than that of holes. Therefore, the current through the heterocontact will be dominated by electrons. This can explain the large increase in the forward currents by donor doping the n-type ZnO. The sensitivity obtained from current–time measurements (Figure 6b) was also the highest with a value of ~8.2. The response times, τ_1 and τ_2, were calculated as 58 and 1372 s. When we compare these values with the ones obtained from the pure CuO/ZnO heterocontact, it was noted that the response times of both sites were similar ($\tau_{1pure} \sim \tau_{1doped}$ and $\tau_{2pure} \sim \tau_{2doped}$). Yet the sensitivity increased significantly.

Finally, to investigate a possible synergistic effect of doping both p- and n-type materials, the current–time measurements for a 1.5 mol % Ni–CuO/1.5 mol % Ga–ZnO heterocontact were performed (Figure 7). The current values were observed to be between that of the 1.5 mol % Ni–CuO/ZnO and CuO/
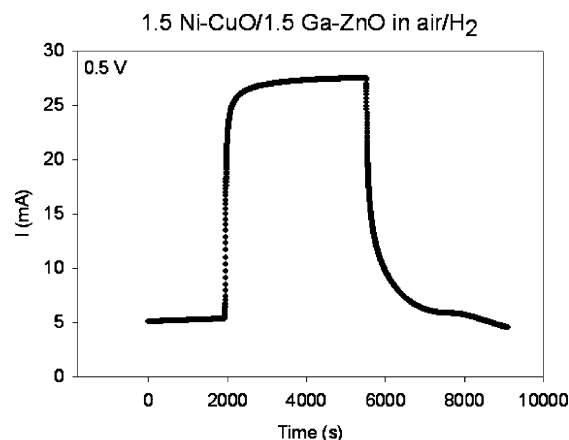

Figure 7. Current–time response of 1.5 mol % Ni–CuO/1.5 mol % Ga–ZnO in air/H$_2$.

TABLE 1: Sensitivity, Response Times of the Sites, and Overall Response Times for Various Compositions

	sensitivity	τ_1 (s)	τ_2 (s)	$t_{0.7}$ (s)	$t_{0.8}$ (s)	$t_{0.9}$ (s)
CuO/ZnO	2.6	45	1400	100	216	818
1.5 Ni–CuO/ZnO	2.8	50	822	81	121	308
CuO/1.5 Ga–ZnO	8.2	58	1372	171	524	1384
1.5 Ni–CuO/1.5 Ga–ZnO	5.1	44	693	67	98	203

1.5 mol % Ga–ZnO samples. The sensitivity of the heterocontact was also between with a value of ~5.1. The synergistic effect was clearly observed in the rate of the sensor response with τ_1 and τ_2 of 44 and 693 s showing the quickest responses for both site 1 and site 2.
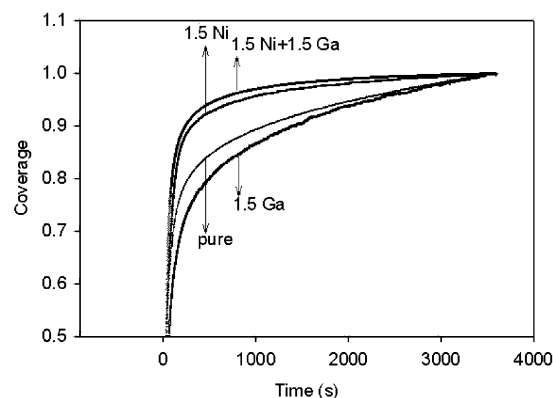
Figure 8. Coverage vs time plots of the pure and the doped heterocontacts.

Summary and Conclusions. The sensitivities, the response times of sites 1 and 2, and the overall response of the sensors are summarized in Table 1. The overall responses of the heterocontacts are designated by $t_{0.7}$, $t_{0.8}$, and $t_{0.9}$, which are defined as the time required for the sensor to reach a surface coverage of 0.7, 0.8, and 0.9, respectively. As can be seen from the data, doping the p-side resulted in significant decrease in the response time of site 2, while site 1 changed only slightly. Doping the n-side decreased the response rate of the sensor; however, the sensitivity was substantially increased. The coverage vs time plots of the heterocontacts are compared in Figure 8. The overall response of the sensor at 90% coverage, $t_{0.9}$, was lowered by a factor of 4 with the synergistic effects of doping both sides of the heterocontact. Even though the response kinetics of the Ga-doped heterocontact was the slowest, it is important to keep in mind that the sensor reaches very high sensitivity values within that time.

In conclusion, hydrogen sensors based on CuO/ZnO heterocontacts were successfully produced, and both the sensitivity and the response kinetics of the sensor were enhanced by doping.

The kinetics data were fit to a two-site Langmuir adsorption isotherm indicating that the adsorption process takes place on two energetically different sites. Doping the p-type side was observed to modify the response rate of one of the sites while changing the other site only slightly. Doping the n-side resulted in the highest sensitivity with a value of ∼8.2. The synergistic effect of doping both p- and n-sides resulted in reaching surface coverage of 70% in slightly more than a minute.

References and Notes

(1) Nakamura, Y.; Ando, A.; Tsurutani, T.; Okada, O.; Miyayama, M.; Koumoto, K.; Yanagida, H. *Chem. Lett.* **1986**, 413.

(2) Nakamura, Y.; Yoshioka, H.; Miyayama, M.; Yanagida, H. *J. Electrochem. Soc.* **1990**, *137*, 940.

(3) Toyoshima, Y.; Miyayama, M.; Yanagida, H.; Koumoto, K. *Jpn. J. Appl. Phys.* **1983**, *22*, 1933.

(4) Hu, Y.; Zhou, X.; Han, Q.; Cao, Q.; Huang, Y. *Mater. Sci. Eng. B* **2003**, *99*, 41.

(5) Hikita, K.; Miyayama, M.; Yanagida, H. *J. Am. Ceram. Soc.* **1995**, *78*, 865.

(6) Ushio, Y.; Miyayama, M.; Yanagida, H. *Sens. Actuators B* **1994**, *17*, 221.

(7) Baek, K. K.; Tuller, H. L. *Solid State Ionics* **1995**, *75*, 179.

(8) Nakamura, Y.; Watanabe, K.; Jung, S. J.; Osawa, H.; Yoshioka, H.; Yanagida, H. *J. Catal.* **1995**, *153*, 350.

(9) Jung, S. J.; Yanagida, H. *Sens. Actuators B* **1996**, *37*, 55.

(10) Aygun, S.; Cann, D. *Sens. Actuators B* (in press), DOI 10.1016/j.snb.2004.10.004.

(11) Liu, C. J.; Hsieh, J. C.; Ju, Y. H. *J. Vac. Sci. Technol. A* **1996**, *14*, 753.

(12) Manno, D.; Micocci, G.; Serra, A.; Giulio, M. D.; Tepore, A. *J. Appl. Phys.* **2000**, *88*, 6571.

(13) Chaudhary, V. A.; Mulla, I. S.; Vijayamohanan, K.; Hegde, S. G.; Srivinas, D. *J. Phys. Chem. B* **2001**, *105*, 2565.

(14) Ho, K. C.; Tsou, Y. H. *Sens. Actuators B* **2001**, *77*, 253.

(15) Wlodek, S.; Colbow, K.; Consadori, F. *Sens. Actuators B* **1991**, *3*, 123.

(16) Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*; John Wiley & Sons: New York, 1996.

(17) Miyayama, M.; Hikita, K.; Uozumi, G.; Yanagida, H. *Sens. Actuators B* **1995**, *24−25*, 383.