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Development of NiO-based thin film structures as efficient H_2 gas sensors operating at room temperatures

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Abstract

P-type NiO thin films have been developed on high resistivity Si and SiO_2 substrates by a pulsed laser deposition technique using an ArF* 193 nm excimer laser at deposition temperature of 300 °C and in 40 Pa partial oxygen pressure. Structures based on such NiO films as host material in the form of Au–NiO Schottky diodes have been subsequently developed under vacuum. In a different procedure, an n-SnO_2 layer has been deposited by a CVD technique on a NiO film to produce a p/n heterojunction. The sensing properties of all above structures have been tested upon exposure to a H_2 flow in air ambient gas at various operating temperature ranging from 30 to 180 °C. For the NiO films, the optimum temperature was about 150 °C exhibiting a sensitivity of 94%. After surface sensitization of NiO by Au the NiO films showed an H_2 response at operating temperature of 30 °C. The sensitivity of p-NiO/n-SnO_2 heterojunction devices was extracted from *I–V* measurements in air and under H_2 flow mixed in air. In this case a dramatic increase of the sensitivity was achieved at operating temperature of 30 °C for a forward bias of 0,2 V.

Keywords: Thin films; Hydrogen sensing; Nickel oxide; P–N hetero-junctions; Tin oxide; Au surface sensitization

1. Introduction

It is well established nowadays that hydrogen is going to be the fuel mainly used for energy generation in the near future due to the fact that fuel cell electricity generators are clean, quiet and more efficient than any other known technology. Additional future widespread uses could include distributed energy supply systems and generally in areas where fossil fuels are mainly used.

It is therefore straightforward that in all these applications safety measures should be of highest concern due to the explosive properties of hydrogen (lower explosion limit of 40×10^3 ppm). To this end, there is an emerging scientific interest in developing solid state hydrogen sensors based on different operation principles [1], as catalytic-type chemi-resistive [2], thermoelectric [3] and micromechanical gas sensors [4], FETs [5], and nano-scale structures [6,7].

Of the catalytic chemi-resistor type, many semi-conducting oxides have been extensively studied as gas-sensing materials so far, like SnO_2, In_2O_3 and ZnO to name the most important [1].

Recent works have shown that NiO is also a promising functional material for applications in resistive-type gas sensors implementing thin NiO films [8,9]. NiO has a wide range of applications due to its chemical stability as well as its optical and electrical properties [10–12]. The gas detection results from conductivity changes of the film, caused by the adsorption of the gas species on the film surface and the subsequent chemical reactions involved [13]. However, no work [8] has been done on NiO film device sensors operating at room temperature.

In this paper, we examine thin NiO films and Au/NiO Schottky diodes, PLD grown, as hydrogen sensing elements operating even

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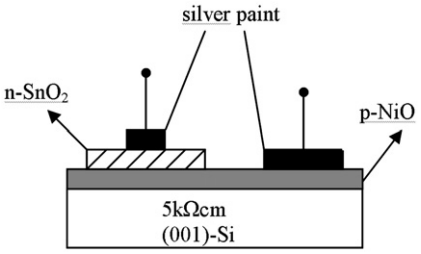

Fig. 1. Schematic drawing of the n-SnO_2/p-NiO heterojunction grown on (001) p-Si substrate.

at room temperature. We also investigate a rather infrequent p–n hetero-junction diode consisting of p-NiO and n-SnO_2 as gas sensing device.

2. Experimental details

2.1. Growth of thin films and Schottky diodes

The depositions of the NiO thin films on Si and SiO_2 were performed inside a stainless steel vacuum chamber. Prior to each irradiation the vacuum chamber was evacuated down to a residual pressure of 7×10^{-4} Pa. We applied the UV laser pulses generated by a Lumonics Mo. TE-861T ArF* excimer laser ($\lambda=193$ nm, $\tau_{FWHM}\sim12$ ns) at a repetition rate of 10 Hz, with the pulse energy ranging from 34 to 40 mJ/pulse. The laser beam was focused on the Ni target (a 99.99% purity metal foil) with an incidence angle of about 45° relative to the normal of the target surface. To avoid fast drilling, the target was placed on a movable vacuum-compatible, computer-controlled XY table. (001) p-Si substrates with specific resistivity of 5 kΩ cm were positioned at 40 mm from the target and were heated during the thin films' growth at 300 °C. The depositions were performed in 40 Pa partial oxygen pressure for 92 min.

For the deposition of Au on the NiO thin films, the reactive gas O_2 was pumped out to the residual pressure and the substrate cooled down to room temperature. Then the Au target, mounted on the same XY table as the Ni target, was placed onto the laser focus. For the Au–NiO Schottky diode, we applied the same UV laser fluence as for NiO. The deposition time for Au was 30 min.

The NiO films where almost 200 nm thick, as measured by a Tencor profilometer. The undoped SnO_2 thin films were deposited by atmospheric pressure chemical vapour deposition (APCVD) at 300 °C. The films were grown in a radioactively heated horizontal cold wall quartz chamber by oxidized $SnCl_4$ vapors [14]. An integrated method was applied in order to design the APCVD reactor providing good film uniformity [15]. The resulting SnO_2 films were almost 450 nm thick.

The conduction type (p-type) as well as the concentration and the mobility of the free carriers of the films, were determined from the electrical resistivity and Hall coefficient results, using the Van der Pauw technique.

Dynamic sensor response measurements were performed under a 3% H_2 in air flow at working temperatures between 30 and 210 °C in a stainless steel tube set-up. After introducing the gas into the tube, the resistance of the samples versus time was measured with respect to the working temperature. The sample holder has a copper heater resistance, capable of reaching temperatures up to 400 °C and controlled with an accuracy of ±1 °C. A platinum resistor measures the temperature, and four mechanical point contacts measure film resistance. The gas flow was controlled by two calibrated flowmeters and fed into an injection point located below the sample holder. The electronic circuit for resistance determination consisted of a current source (Keithley Model 225) and a digital multimeter (Agilent 34401A). For the temperature control of the sample, an ITC-502 (Oxford Instruments) controller was used.

2.2. P–N hetero-junction fabrication

For the p–n heterojunction, a NiO thin film grown on (001) Si substrate with thickness of about 200 nm was used. Afterwards, the sample was mounted on the deposition plate of the APCVD reactor, covered by an appropriate golden mask and SnO_2 was deposited on it at 390 °C for 5 minutes in order to obtain a planar p–n hetero-junction. The resulting SnO_2 film was almost 450 nm thick.

Two Ohmic contacts were made using silver paste, on the two discrete areas of the device – namely the SnO_2 and NiO films (Fig. 1). Electrical measurements were carried out in order to obtain the *I–V* characteristics at various ambient temperatures under pure air and 3% H_2 in air gas in the aforementioned sensor-evaluating set-up.

3. Results and discussion

3.1. Electrical properties and gas sensing results

3.1.1. Thin films

The films' deposition parameters and specific electrical resistivity values are shown in Table 1.

Table 1
Deposition parameters and specific electrical resistivity ρ values of thin films implemented as H_2 sensors

Sample	Substrate type	Growth O_2 pressure (Pa)	Growth temperature (°C)	Growth duration (min)	Pulse energy (mJ/pulse)	ρ (Ω. cm)
NiO	Si	40	300	92	34	186
NiO	SiO_2	40	300	92	34	129
n-SnO_2/p-NiO	Si	40	300	92	40	40
Au/NiO (Schottky)	Si	40	300	92 (NiO) 30 (Au)	30	–

The relative response (sensitivity) under gas flow is determined by the formula:

$$S_R = \frac{R_O - R_g}{R_O} \quad (1)$$

where R_O is the film resistance in air atmosphere and R_g is the film resistance in gas atmosphere.

The conduction mechanism in the case of metal oxide thin films depends on two main contributions, namely the intergranular conduction path (the region between the grains) and the intragranular or endocrystallic conductivity. It is rather usual that the former type determines the conduction mechanism, due to the fact that the intragranular regions are quite crystalline and any lattice defects – that appear responsible for the conductivity in wide band-gap semiconductors – are absent. The current transport through the depletion layers at the boundaries between neighbouring grains dominates the film resistance [16].

The H_2 sensing properties of the NiO thin films were strongly dependent on the working temperature (Fig. 2a) as well as the kind of the substrates. As shown in Fig. 2b the R_{gas}/R_{air} ratio of the NiO/Si sensor increases almost 10 times (from 4 to 40) as the working temperature changes from 150 to 210 °C. An enhancement of the response and recovery times is also observed from low to higher working temperatures (Fig. 2a). In particular the response time decreases from 15 to 7 min and the recovery time changes from 2 to 1 min. It seems that the increase of the working temperature accelerates the H_2 adsorption–desorption reactions on the surface of the NiO thin films. A dramatic increase of the H_2 sensitivity is observed at a working temperature of 210 °C in a NiO thin film grown on single Si when compared with that of a film grown on SiO_2 substrate.

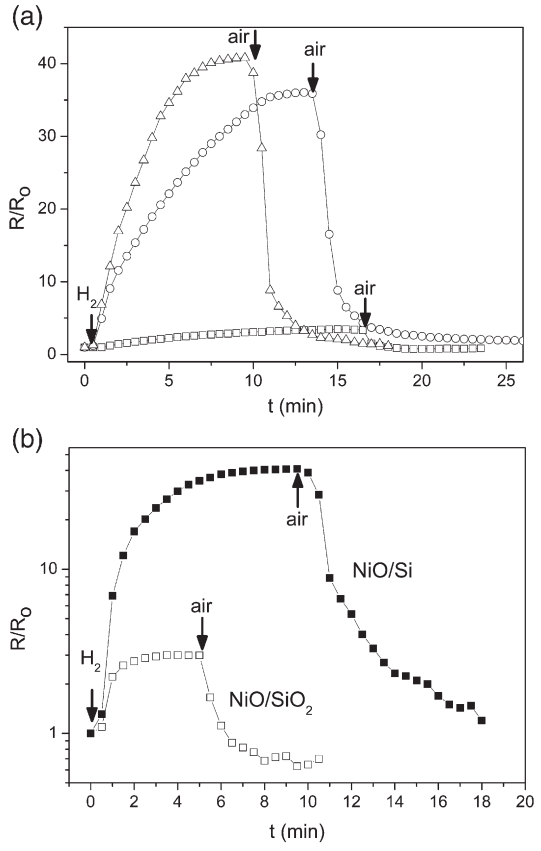

Fig. 2. Dynamic response characteristics of NiO thin films exposed in 3% H_2 in air mixture: (a) films deposited on (001) Si at working temperatures of 150 °C (□), 180 °C (○) and 210 °C (△); (b) comparison of dynamic response characteristics for films deposited on (001) Si and SiO_2 substrates at 210 °C. H_2 mixture application started at 0 min and ceased at each curve's maximum.

NiO films when exposed in reducing environment as in our case exhibit a rather large increase in their resistivity as opposed to the behaviour observed in the case of n-type oxides (SnO_2, ZnO), which exhibit decrease of their resistivity under H_2 exposure. An explanation of the above difference is probably related to the influence of the film porosity (high active area per volume ratio) on the recombination or not between the injected carriers after the adsorption reactions into the film surface and the existent majority carriers of the film. It is well-known that the as-grown NiO films show a p-type electrical conductivity [8,17] due to the non stoichiometric matrix of the grown samples. The vacancies are produced by the metal (Ni^{2+}) deficiency at cation sites [18].

The ambient O_2, adsorbed and incorporated on the surface oxide is considered as $O^-_{2,ads}$ or O^-_{ads} negative charged chemical species. Under H_2 exposure the gas-sensing mechanisms can be described by the following reactions:

$$2H_{2,gas} + O^-_{2,ads} \leftrightarrow 2H_2O_{vap} + e^- \quad (2)$$

$$H_{2,gas} + O^-_{ads} \leftrightarrow H_2O_{vap} + e^- \quad (3)$$

The produced electrons injecting in the p-NiO result in an increase of electrical resistivity of the film due to the recombination with the majority carriers (holes).

3.1.2. Au–NiO Schottky diodes

In the case of the Schottky or p–n type sensing elements, the relative response (sensitivity) can be defined as:

$$S_I = \frac{I_O - I_g}{I_O} \quad (4)$$

where I_o is the forward current at a specific bias value in air while I_g the forward current in the gas flow at the same bias value.

The H_2-sensing mechanism of Au–NiO Schottky diodes can be explained by using the basic properties of a metal–semiconductor rectifying contact biased in the presence of H_2 flow [19,20]. When the Fermi level of the metal is lower than that of the semiconductor, a potential barrier Φ_b builds up [21]. This corresponds to a depletion region due to carrier transport from the semiconductor to the metal, followed by the ionization of the impurities under the semiconductor surface, for zero bias. Under non-zero bias conditions, the width of the depletion region decreases or increases depending on the applied bias – forward or reverse, respectively. For a forward bias onto the

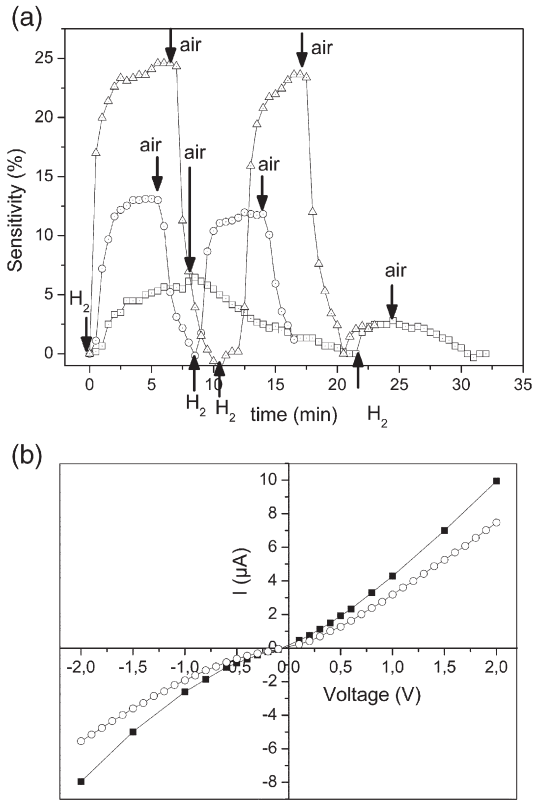

Fig. 3. (a) Dynamic response characteristics of Au/NiO/Si Schottky diode exposed in 3% H_2 in air mixture at working temperatures of 70 °C (△), 50 °C (○) and RT (29 °C) (□) and at forward bias of 2.4 V. (b) *I–V* characteristic at 29 °C of the Schottky diode in air flow (■) and in the presence of 3% H_2 in air mixture flow (○).

Au–NiO Schottky diode under H_2 flow, the current decreases due to the increase of the effective barrier height (Fig. 3b). The effective barrier height increases due to the aforementioned recombination of injected electrons with the majority carriers (holes). This is attributed to the time dependent diffusion of the atomic hydrogen, created by catalytic decomposition of adsorbed H_2 molecules on the Au–Schottky contact. The enhanced oxidation of adsorbed hydrogen due to Au effect can be seen in Fig. 3a where the response time of the Schottky diode working at 70 °C is identical to the response time of the NiO thin film working at 210 °C. The action of Au could be attributed to the formation of strongly reactive species according to the reaction equation used in a similar case regarding Pd catalysts [8]. In our case the reaction equation becomes:

$$H_2 + 2Au^+ \leftrightarrow 2H(Au^+)$$

and then the hydrogen species are oxidized according to Eqs. (2) and (3).

These reactions describe the exchange of charges between the absorbed species and the metal oxide surface. According to this exchange a charge depletion or accumulation is formed on the film surface having Au clusters or between the grains of the film. The formation of the strongly reactive species $H(Au)^+$ accelerates the charge exchange thus improving the sensing properties of the film.

3.1.3. P–N diodes

Electrical measurements using the Van der Pauw technique were conducted on the NiO thin film prior to SnO_2 deposition. The NiO film was of high specific resistance (40 Ω cm) and low carrier concentration values (10^{16} cm^{-3}), while electrical resistivity, carrier concentration (n-type) and Hall mobility values of 0.06 Ω cm, 2×10^{19} e/cm^3 and 6 cm^2/V s, respectively, were measured for the deposited SnO_2 film. Mobility value for NiO was almost negligible. The NiO thin film's thickness was found to be ~200 nm.

Clear rectifying *I–V* characteristics were exhibited with a forward threshold voltage of about 0.6 V. The ideality factor *n* of the diode was found to be ~12, with negligible variation as the working temperature increased later. Fig. 4a shows the *I–V* characteristics obtained at three different temperatures (28, 60 and

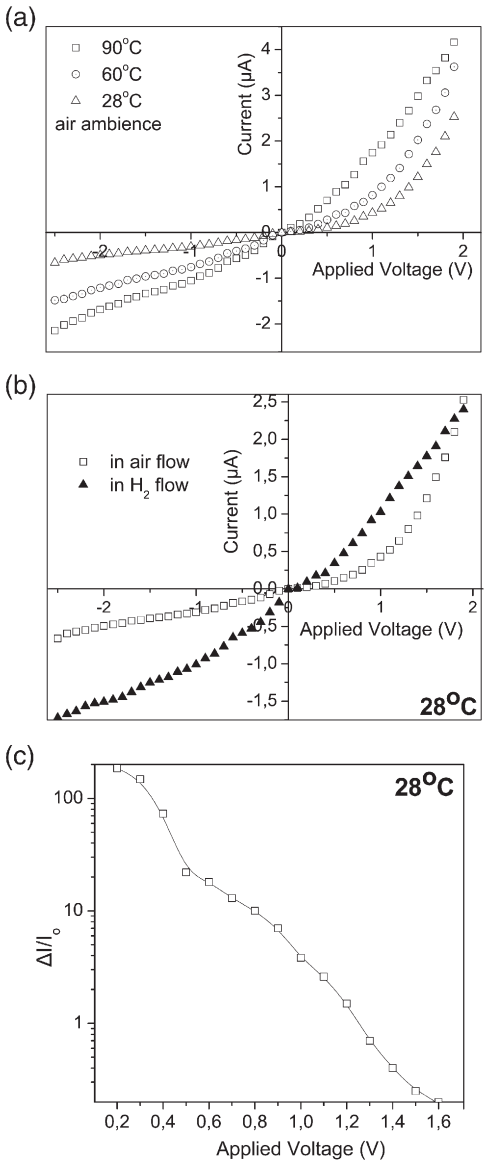

Fig. 4. (a) *I–V* characteristics of n-SnO_2/p-NiO on (001) Si hetero-structure at 28 °C, 60 °C, 90 °C, in air ambience, (b) modification of the *I–V* characteristic at 28 °C and (c) sensitivity ($S_I = \Delta I/I_0$) of the p–n junction vs. forward voltage at 28 °C, in the presence of 3% H_2 in air mixture flow.

90 °C) with the contact region exposed to air ambience. The increase in the current is strongly dependent on the applied forward bias of the diode. When the contact region was exposed to 3% H_2 in air flow, a significant modification of the *I–V* curve took place (Fig. 4b). The current values correspond to the steady sensitized state of the diode, meaning that we biased the diode at 1 V forward, exposed it at the H_2 mixture flow until the current stabilized at a higher value; afterwards we took out measurements. The same procedure was followed at each temperature. The p–n diode in forward bias showed sensitivity values over 380% (28 °C at +1 V bias) with a tendency to decrease as the bias voltage and temperature increase and reaction times of ~12 min.

All three *I–V* characteristics at temperatures of 30, 60 and 90 °C showed a decreasing rectifying behavior, as the working temperature was increased. This is a typical semiconductor behavior in general, usually taking place though at higher temperatures. In our case, where a hetero-junction between a highly conductive and carrier-rich material (n-SnO_2) and a relatively insulating material is formed, it is obvious that the contact region in the side of NiO will be depleted from free carriers, even at relatively high forward biases. Due to band bending in this area, electrons would tunnel through the barrier in order to reach the opposite side [22]. The p–n hetero-junctions so formed between a non-degenerate semiconductor (NiO) and a degenerate semiconductor (SnO_2) will have apparently similar characteristics like metal–insulator–semiconductor (MIS) tunnel diodes, provided the non-degenerate oxide is quite thin. In this study, the thickness of the NiO thin film is almost 200 nm, more than half of the thickness of tin oxide film (450 nm). The current in the forward bias is then controlled mainly by the generation current due to temperature change, turning the forward bias part of the *I–V* characteristic from exponential to linear (Fig. 4a). It is attributed to the extraction of additional carriers from deeper states in the gap, leading to an increase of the diode ideality factor. The current in the reverse bias is also dependent on temperature despite the large contact barrier that promotes leak currents.

Exposure of the diode in the hydrogen in air mixture also turns the diode's *I–V* characteristic into almost linear, even at room temperature (Fig. 4b). This behavior is generally attributed to a lowering of the inherent electronic barrier height, probably due to an interfacial dipole layer formation. This collapse effect is common in conventional semi-conductor gas sensors [23]. This assumption is also justified due to the relatively high hydrogen concentration used in our experiments (3% in air) as compared to some hundreds of ppm or less commonly used in gas sensing experiments. It is generally expected that this behavior is easily reversible and fast, thus requiring little energy to return the sensor to its initial pre-sensing state in a short time-frame limited mainly by the gas mass transport properties inside the test chamber. The fact that the sensing reactions are reversible even at room temperature as mentioned earlier additionally supports this assumption.

4. Conclusions

PLD grown NiO thin films have been examined as potential H_2 sensors at temperatures between 150 and 210 °C with best results at working temperature of 210 °C on (001) Si substrate. NiO films deposited on SiO_2 showed poor sensing properties even at elevated temperatures. The implementation of a Schottky Au/NiO/Si diode as sensing element lowered remarkably the required working temperature even at RT with 8% sensitivity and response times of 7–8 min. Further optimization of the Au film structure of the device might lower the reaction time, as seen in other researchers' works.

A CVD grown n-SnO_2 thin film deposited by CVD on PLD grown p-NiO films has also been evaluated as gas sensing device. This device has exhibited higher sensitivity compared to that of a sensor based on pure NiO as well as a room temperature operation. Its sensitivity was found to be strongly dependent on the applied forward bias of the diode and its *I–V* characteristic exhibited typical metal oxide dependence on the working temperature. The conversion of the *I–V* characteristics from exponential to linear in the presence of the hydrogen mixture is attributed to the lowering of the diode effective barrier height due to the formation of interfacial dipole layer.

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