

An oxygen sensitive ZnO–SiO₂–Au device using photodesorption of oxygen

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A significant breakdown of the rectification characteristic of the ZnO–SiO₂–Au device occurs with UV irradiation and is enhanced with increasing light intensity and a reverse bias voltage at which the device is kept under UV irradiation. Complex impedance plots of the device reveal that an increase in leakage current observed after UV irradiation is mainly due to a decrease in the barrier height. The magnitude of breakdown and recovery of the rectification characteristic is dependent on the ambient partial pressure of oxygen. The variation of the barrier height is explained by oxygen desorption under UV illumination and by oxygen adsorption in the dark.

1. Introduction

The oxygen adsorption on the surface of a n-type semiconductor is attained by capturing electrons of a semiconductor [1] and then chemisorptive states of oxygen are formed at a few eV below the bottom of the conduction band of a n-type semiconductor, e.g. 0.8 to 1.0 eV for O₂⁻ on the ZnO surface [2]. Oxygen adsorbed on the semiconductor surface can be removed by emitting electrons of chemisorption states into the conduction band or by injecting holes into chemisorption states. The energy levels of oxygen chemisorption states are fairly high, so that a high temperature is required to thermally excite electrons from chemisorptive states into the conduction band. For a semiconductor with high carrier density and a low effective mass, electrons in chemisorption states can be released even at low temperature by tunnelling through the space charge layer. We call this process field assisted desorption. The field assisted desorption of oxygen was recently confirmed in a α -Fe₂O₃–Au diode [3]. The desorption by hole injection was found in photodesorption of oxygen at the ZnO surface [4]. However, the oxygen desorption by the hole injection has not been studied in detail. The purpose of this work is to elucidate oxygen desorption by hole injection, and to develop an oxygen sensor with high sensitivity even at room temperature. For this purpose, a ZnO–SiO₂–Au device is fabricated to generate effectively holes at the ZnO surface by band gap illumination, and the adsorption and desorption of oxygen is intensively investigated by analysing the change in electronic properties of the device.

2. Experimental

ZnO film was deposited on a glass substrate (Corning 7059) using a RF magnetron sputtering apparatus.

The sputtering was performed at 50 W RF power at 1 Pa (95% Ar + 5% O₂) for 135 min. SiO₂ was subsequently deposited on the sputtered ZnO surface. Sputtering conditions were the same as those for the ZnO sputtering. Gold was deposited on the SiO₂ surface by vacuum evaporation. There are two peaks of (002) and (004) in X-ray diffraction patterns of the sputtered ZnO film. Thus, the sputtered ZnO film had a *c*-axis orientation perpendicular to the film surface. Observation with a scanning electron microscope of the sputtered ZnO film indicated that the ZnO film has a porous and columnar structure. The thickness of the sputtered ZnO film and the SiO₂ was evaluated to be about 900 and 100 nm, respectively. The electric resistivity of the ZnO film was measured by the four-probe technique and was found to be 22 Ω cm. The carrier density of the sputtered ZnO film was found to be $1.5 \times 10^{15} \text{ cm}^{-3}$ by using the obtained resistivity and the drift mobility of $200 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ [5]. A high pressure 500 W mercury lamp was used as a light source for UV illumination. The action spectrum of the photocurrent was measured to confirm hole generation at the ZnO surface. The action spectrum of the photocurrent was measured using a 500 W xenon lamp, a monochromator, a light chopper (80 Hz), and a lock-in amplifier. Impedance measurements of the ZnO–SiO₂–Au device were carried out for the assignment of the resistance change before and after UV illumination.

3. Results

The current–voltage (*I*–*V*) characteristics of the ZnO–SiO₂–Au device are shown in Fig. 1. Curve A shows a slight leakage current in spite of metal–insulator–semiconductor structure. This leakage current may arise from partial ZnO–Au contact

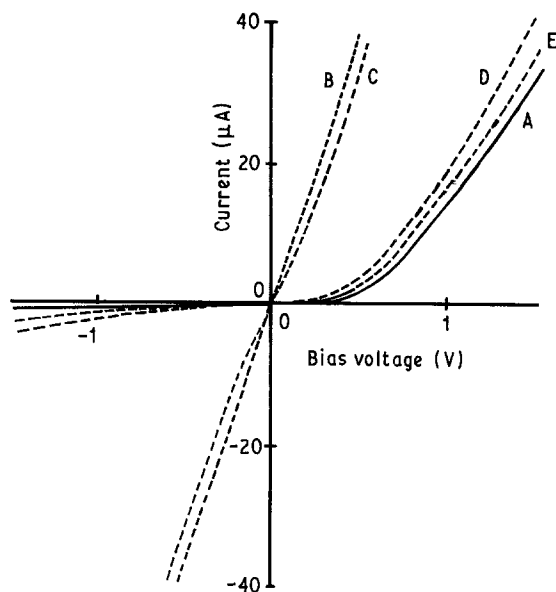


Figure 1 Current-voltage characteristics of a ZnO-SiO₂-Au device. Full curve A: before UV illumination; broken curve B: under UV illumination; broken curve C: immediately after UV illumination has been turned off; broken curve D: kept in the dark for 10 h in oxygen after UV illumination; broken curve E: kept in the dark for 30 h in oxygen after UV illumination.

formed in vacuum evaporation of gold, because of the porous structure of the SiO₂ film. The current density of curve A is about 100 times less than that of a ZnO-Au diode. Under this condition, the spatial variation of the quasi-Fermi level in the space charge layer of ZnO [6] can be ignored. This allows that holes are effectively generated at the ZnO surface in the depletion region by UV irradiation. In the dark, I - V curves are unchanged when a bias voltage is swept from -2.0 to 1.5 V in either nitrogen or oxygen, while UV irradiation in nitrogen results in a drastic change in the I - V curve. In Fig. 1, the curve B is a I - V curve in the nitrogen ambient gas containing 200 p.p.m. oxygen under UV illumination, and curve C is a I - V curve measured immediately after the UV irradiation has been turned off. It should be noted that UV irradiation of the ZnO-SiO₂-Au device results in breakdown of the rectification characteristic. Curves D and E are I - V curves of the device kept in the dark for 10 and 30 h in oxygen respectively. As is evident from the curves D and E, recovery of the rectification characteristic is accelerated by exposing the device to an oxygen atmosphere in the dark.

Fig. 2 shows the current variation at 0.5 V as a function of time. Where UV irradiation is turned on, the forward current is increased up to about $15 \mu\text{A}$ within 1 sec, and then is gradually increased with a relaxation time of a few hours. After the UV irradiation has been turned off, a small fraction of the current quickly decreases and subsequently a large portion of the current decays with a long response time. The rate of the current decay in the dark is accelerated by changing the ambient gas from nitrogen containing 200 p.p.m. oxygen to oxygen. In photocurrent measurements using a lock-in amplifier, the photocurrent of 5 pA flowed in the reverse direction when the irradiation was turned on. The frequency of chopping light is 80 Hz , so that the response time of the photocurrent

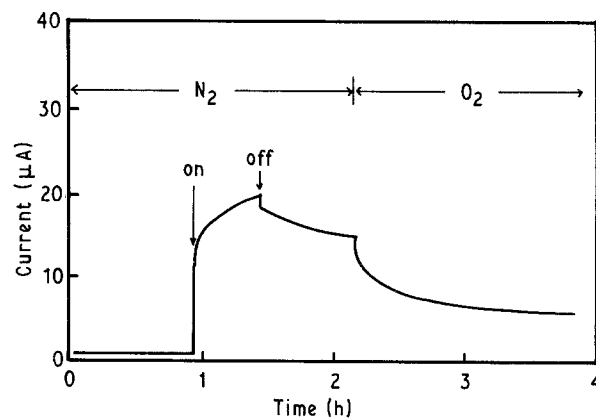


Figure 2 Current variation at 0.5 V as a function of time. "On" and "off" denote that UV illumination is turned on and turned off, respectively.

due to the electron transfer from gold to the valence band of ZnO would be shorter than 2 msec. As seen in Fig. 2, the response time of about 1 sec is obtained for the rapid rise just after UV irradiation has been turned on. Thus, this rapid rise of current does not depict the photocurrent due to the charge transfer.

In Fig. 3, the ratio of I_p/I_d is plotted as a function of a bias voltage at which the device is kept under UV illumination, where I_d and I_p denote the current values at ± 0.2 before and after UV illumination. A value of I/I_0 larger than unity means breakdown of the rectification characteristic. The current ratio I_p/I_d is enhanced with a reverse bias voltage. The current ratio at -0.2 V exhibits strong bias dependence compared with that at $+0.2 \text{ V}$. As is well known, hole generation at a MIS device is more effective at a larger reverse bias voltage, because electron-hole recombination is depressed with a decrease in the surface electron density which depends exponentially on a bias voltage. Thus, the results in Fig. 3 suggest that the breakdown of rectification characteristic results from hole generation at the ZnO surface.

Fig. 4 shows the relation of the ratio I_p/I_d to light intensity of UV irradiation. The ratio I_p/I_d increases with the light intensity, so that the breakdown of the rectification characteristic is also enhanced with

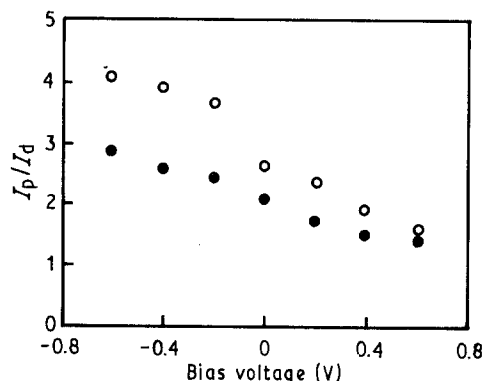


Figure 3 Dependence of breakdown of rectification characteristic on a bias voltage at which the device is kept in nitrogen under UV illumination. I_d is the dark current before UV irradiation, and I_p the dark current after UV irradiation has been carried out for 5 sec. Open circles and full circles are the current ratio I_p/I_d detected at -0.2 V and that at 0.2 V , respectively. The light intensity is 1 mW cm^{-2} .

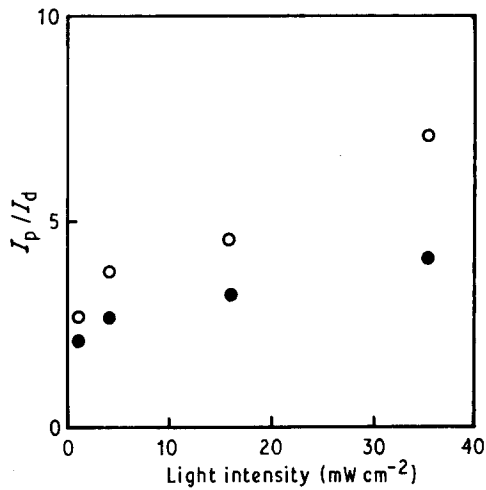


Figure 4 Dependence of breakdown of rectification characteristic on light intensity. I_d is the dark current at ± 0.2 V before UV irradiation, and I_p is the dark current at ± 0.2 V after the device kept at 0 V has been irradiated for 5 sec with UV light. Open circles and full circles denote the current ratio I_p/I_d at -0.2 and 0.2 V, respectively.

light intensity. It is noteworthy that there is no linear relationship between I_p/I_d and light intensity. In general, hole concentration at the ZnO surface is proportional to the light intensity. If the hole generation is the rate-determining step for oxygen desorption, a linear relationship will be observed between I_p/I_d and light intensity. This non-linear relationship, therefore, implies that the hole injection is not a rate-determining step under UV irradiation with light intensity larger than 4 mW cm^{-2} .

Fig. 5 shows the dependence of I_o/I_n on a bias voltage at which the device is kept in the dark, where I_o and I_n are the dark currents of the device to which a given bias voltage is applied for 20 min in oxygen and in nitrogen, respectively. The current ratio I_o/I_n is slightly decreased at a forward bias voltage, that is, the recovery rate of the rectification characteristic is slightly accelerated at a forward bias voltage.

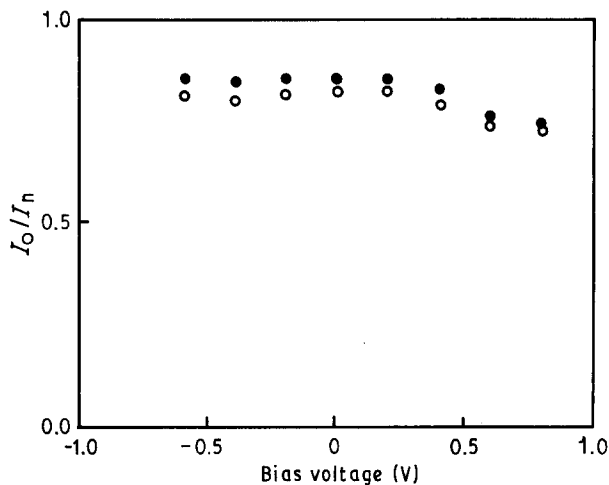


Figure 5 Dependence of recovery of rectification characteristic on a bias voltage at which the device is kept in dark. I_o is the dark current at ± 0.2 measured after the device in oxygen has been kept at a given bias voltage for 20 min. I_n is the dark current at ± 0.2 measured after the device in nitrogen has been kept at a given bias voltage for 20 min. Open circles are the current ratio at -0.2 V and full circles are that at 0.2 V.

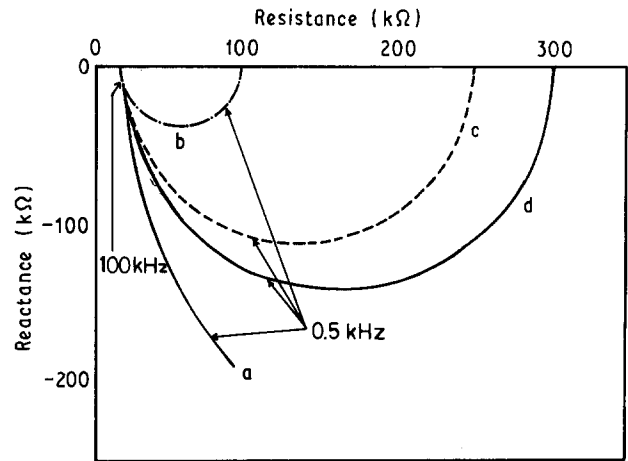


Figure 6 Complex impedance plots of the ZnO-SiO₂-Au device. Plots (a) and (b) are complex impedance plots at 0 and 0.3 V before UV irradiation, respectively. Plot (c) is the complex impedance plot at 0 V after the device at 0 V has been irradiated for 5 sec with light intensity of 1 mW cm^{-2} . Plot (d) is the complex impedance plot at 0 V for the device which is kept at 0 V for 20 min in an oxygen atmosphere.

Nevertheless, the bias dependence of the recovery rate is not so noticeable compared with that in the breakdown of the rectification characteristic shown in Fig. 3.

Complex impedance plots of the ZnO-SiO₂-Au in the dark are shown in Fig. 6. Plots (a) and (b) are the complex impedance plots at 0 and 0.3 V before UV irradiation, respectively. It is seen from plots (a) and (b) that the diameter of semicircles in the range of 100 kHz to 5 Hz is dependent on a bias voltage. Accordingly, these semicircles are due to the impedance of the ZnO-SiO₂-Au interface, and thus the intercepts of these plots at higher frequencies with the resistance axis give the ZnO bulk resistance. The ZnO bulk resistance of 20 kΩ is estimated from plots (a) and (b). Plot (c) is the complex impedance plot in the dark after UV irradiation has been carried out for 2 min. The ZnO bulk resistance of 20 kΩ and the interface resistance of 260 kΩ were estimated from plot (c). The ZnO bulk resistance after UV irradiation is just the same as that before UV irradiation, but the interface resistance is significantly reduced by UV irradiation. Plot (d) is the complex impedance plot of the device kept for 20 min in oxygen after UV irradiation. The resistance of the ZnO-SiO₂-Au interface is estimated to be about 300 kΩ from plot (d). This value is larger than that after UV irradiation, but is far smaller than the initial value of 650 kΩ before UV irradiation.

Fig. 7 shows the action spectrum of photocurrent at 0.5 V. The photocurrent spectrum has a maximum at 380 nm corresponding to the wavelength of exciton absorption. The decrease in photocurrent at a wavelength shorter than 380 nm results from the reduction of light intensity of the xenon lamp. The photocurrent at a wavelength longer than 400 nm is associated with levels of oxygen vacancies [6]. The action spectrum supports the view that holes are sufficiently generated at the ZnO surface by UV irradiation of the device kept at 0.5 V.

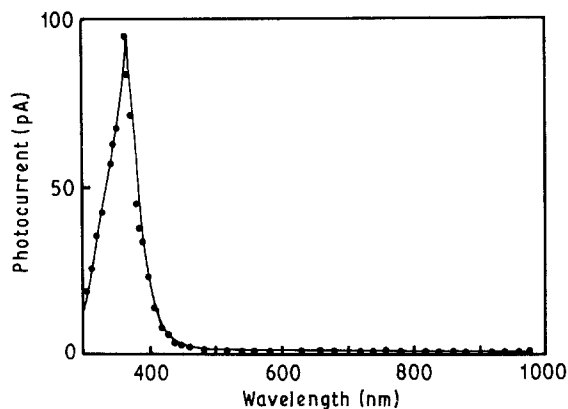


Figure 7 Photocurrent spectrum of the ZnO-SiO₂-Au device kept at 0.5 V in air.

4. Discussion

As seen in Fig. 3, the leakage current is increased after UV irradiation of the device in nitrogen. The complex impedance plots in Fig. 7 reveal that this increase in the current originates from the reduction of the interface resistance. The interface resistance is affected by various factors, e.g. the barrier height, the contact area, ion mobility in SiO₂ [8]. Among these factors, the change in the barrier height accounts for the effect of UV irradiation, because UV irradiation not only reduced the interface resistance but also destroyed the rectification characteristic arising from the presence of the barrier. The barrier height is varied by the change in the work function of the metal, by the change in the charge of interface states, and by the formation and disappearance of charged interface states. Since the work function of gold was reported to be independent of the ambient partial pressure of oxygen [9], the change in the barrier height for the ZnO-SiO₂-Au device is attributable to interface states. In addition, the recovery rate of the rectification characteristic is affected by the ambient oxygen partial pressure (Fig. 2). Thus, the barrier height change seems to in connection with adsorption and desorption of oxygen. That is, the variation of the barrier height results from the formation and disappearance of charged interface states, rather than the change in charge of interface states [10-11]. These interface states may originate from species such as O₂⁻, O⁻, and O²⁻ [12]. The action spectrum of the photocurrent in Fig. 5 certifies that holes are sufficiently generated at the ZnO surface. Hence, the reduction of the barrier height after UV irradiation is referred to the desorption of oxygen by the hole injection into chemisorption states of oxygen.

As seen in Fig. 2, the rapid increase in current is followed by the slow increase in current when UV irradiation is turned on. This implies the presence of two types of desorption process, i.e. fast and slow desorption. The rate of the hole injection into the chemisorption states of O₂⁻, O⁻, and O²⁻ is expected to be fairly large because of the large exothermic process. This speculation is also supported from the conclusion that the hole injection is not the rate-determining step for oxygen desorption. Since the oxygen desorption of O₂⁻ + h⁺ → O₂ includes no successive reaction, the rate for this desorption process is expected to be large. On the other hand, the

oxygen desorption of either 2O⁻ + 2h⁺ → O₂ or 2O²⁻ + 4h⁺ → O₂ is followed by the recombination reaction of O + O → O₂. This successive reaction may lower the rate of oxygen desorption. Consequently, the rapid increase observed just after UV irradiation is associated with the oxygen desorption of O₂⁻ + h⁺ → O₂, while the slow increase in current reflects the reaction of 2O⁻ + 2h⁺ → O₂ or 2O²⁻ + 4h⁺ → O₂.

As mentioned above, the change in interface resistance was ascribed to the change in the barrier height. Under these circumstances, the ratio of the interface resistance can be expressed approximately in the form $\exp(q\Delta\Phi/kT)$, where $\Delta\Phi$ is the barrier height change. The reduction of the barrier height by 0.023 eV is evaluated by using values of 650 and 260 kΩ for the interface resistance before and after UV irradiation (see Fig. 6). This reduction of the barrier height results from the decrease in charge of the electric double layer across SiO₂. The removed chemisorption states by UV irradiation is estimated to be of $5 \times 10^{11} \text{ cm}^{-2}$ by assuming a capacitance value of $3.3 \mu\text{F cm}^{-2}$ for SiO₂ film with a thickness of 100 nm. This estimated value for interface states is about thousand times less than the number of zinc atoms at the 001 plane of ZnO surface.

The bias dependence of the breakdown of the rectification characteristic is in agreement with the theoretical prediction that the breakdown of the rectification characteristic is enhanced as hole density is increased with a reverse bias and with light intensity [3]. On the other hand, the recovery of the rectification characteristic is not so remarkable at a forward bias voltage, as seen in Fig. 5. Such weak bias dependence of the recovery of the rectification characteristic can be explained by the dependence of the electron density on a bias voltage. That is, the capacitance of the space charge layer of ZnO is increased with a forward bias voltage, and approaches the capacitance of SiO₂ film. Under the accumulation condition, the potential drop in the ZnO space charge layer is almost unchanged even by applying a bias to the device and thus the surface electron density is fixed to a value which is determined by carrier density of ZnO and a thickness of SiO₂ [12]. As seen in Fig. 2, the response time for the oxygen adsorption is too slow to be used as an oxygen sensor. The reason for this slow response arises from the thick SiO₂ film (100 nm) and low carrier density of ZnO ($1.5 \times 10^{15} \text{ cm}^{-3}$). The improvement of the response time seems to be achieved by increasing the carrier density of ZnO and by employing the device with thin SiO₂.

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