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Design of a gas sensitive transparent heterojunction—The system $SrCu_2O_2$–ZnO

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Abstract

In this study, transparent oxide p–n heterojunction diodes based on $SrCu_2O_2$ (SCO) were fabricated by RF magnetron sputtering. A Zn-terminated polar plane (Zn-face), an O-terminated polar plane (O-face), and a non-polar plane (A-face) of highly orientated polycrystalline ZnO plates were used as substrates to clarify the effect of the surface polarity of ZnO upon the p–n heterojunction characteristics. Highly transparent and very electrically conductive SCO films were obtained by the application of low RF power ($\hat{E} < 0.5\,W/cm^2$) under high deposition pressures (8–10 Pa). Although none of the as-prepared *p*-$SrCu_2O_2$/*n*-ZnO heterojunctions showed a very good rectifying *I*–*V* characteristics, the junction between SCO and the O-terminated ZnO polar surface exhibited clear rectifying *I*–*V* characteristics after post-deposition annealing at 923 K in Ar. The origin of the variation in the *I*–*V* characteristics depending on the crystal axis orientation of the ZnO substrates is assumed to be due to the surface polarity of the ZnO surface. It would appear that not only the gas-sensing characteristics but also the diode properties depend on the crystal axis orientations of ZnO. A transparent pn junction based on zinc oxide (ZnO) is suggested to have the good gas-sensing properties.
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1. Introduction

In 1988, Yanagida proposed the concept of atmosphere-sensitive heterojunction diodes, which had a variety of novel functions.[1] Among these functional junctions, the *p*-CuO/*n*-ZnO heterojunction has been well investigated from the viewpoint of its selective CO gas-sensing properties.[2] It is true that the *p*-CuO/*n*-ZnO heterojunction has the ability of molecular recognition for CO; however, its low sensitivity is a fatal disadvantage. If a p-type semiconductor having much oxidation power is used for the heterojunction, its gas sensitivity would be extremely enhanced. The band diagram of the *p*-CuO/*n*-ZnO heterojunction diode is shown in Fig. 1(A). The narrow band gap and higher energy of its valence band edge suggest that the oxidation power of the electron holes (proportional to the E_h: Energy difference between the valence band and vacuum level) is not very strong. If a p-type semiconductor having a wide band gap with lower valence band energy is applied when making a pn heterojunction (contact), enhanced gas sensitivity would be expected.

Recently, p-type transparent semiconductor films, $CuAlO_2$,[3] $CuGaO_2$,[4] $CuInO_2$[5] delafossites, and $SrCu_2O_2$[6] have been successively developed by Kawazoe and Hosono et al. The materials have a wide band gap with lower valence band energy because their valence band is formed by the hybridization of fully occupied 3d orbitals of copper(I) and 2p orbitals of oxygen ions.[3] The band diagram of the *p*-$CuAlO_2$/*n*-ZnO heterojunction is shown in Fig. 1(B). The E_h of $CuAlO_2$ is far larger than that of CuO, and the strong oxidation power of a hole of $CuAlO_2$ is suggested.

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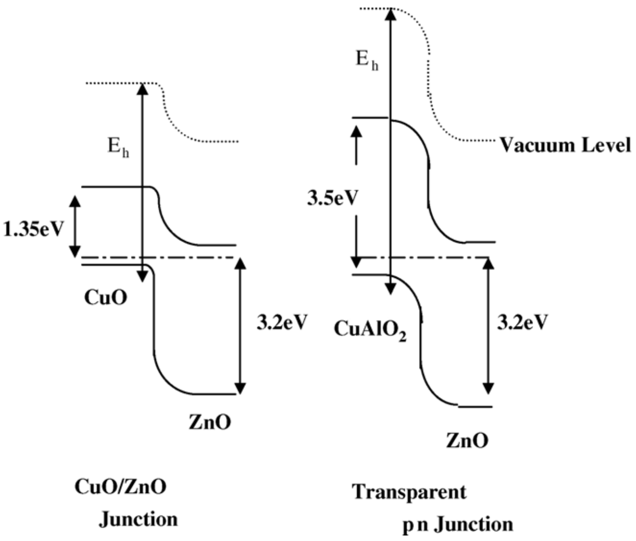

Fig. 1. Schematic band lineup of the CuO/ZnO pn heterojunction and the transparent pn junction ($CuAl_2O_2$/ZnO). E_h means the energy difference between the valence band and the vacuum level, which is proportional to the oxidation power of holes.

Fig. 2 shows the current–voltage (*I*–*V*) responses of the $CuAlO_2$/ZnO heterojunction, which has different crystal axis orientation relationships, and their variation by the introduction of CO and H_2. As our expects, it shows excrement gas sensitivity comparing with *p*-CuO/*n*-ZnO heterojunction. As expected, excellent gas sensitivity is obtained in comparison with the *p*-CuO/*n*-ZnO heterojunction. It is noteworthy that its gas sensitivity strongly depends on the crystal axis orientation of ZnO and that the junction between $CuAlO_2$ and ZnO (Zn-terminated surface) has excellent gas-sensing characteristics.

Aiming at practical use, Ushio et al. fabricated atmosphere-sensitive *p*-CuO/*n*-ZnO heterojunctions in array patterns by continuous thin solid film deposition using a photolithographic process.[7] However, during the successive film deposition process for making a ZnO-based pn junction diode, the crystal axis orientation relationship between the p-type semiconductor and ZnO is uniquely determined.[8,9] First of all, the effect of the crystal axis orientation relationship on the basic properties of the transparent pn heterojunction must be discussed for the materials design of the gas-sensing transparent pn junction diode.

In the present study, we attempted to deposit transparent p-type semiconductor film on highly oriented ZnO polycrystalline substrates having a variety of *c*-axis orientations using the RF magnetron sputtering technique. *p*-$SrCu_2O_2$/*n*-ZnO heterojunction diodes were fabricated, and the effect of the crystal axis orientation of the ZnO on their junction properties was examined.

2. Materials selection and preparation

Suitable candidate p-type semiconductors for a gas-sensitive transparent pn heterojunction are $SrCu_2O_2$ (band gap: 3.3 eV) and $CuAlO_2$ (band gap: 3.5 eV). From the viewpoint of the oxidation power of holes in the valence band, $CuAlO_2$ is judged to be more appropriate than $SrCu_2O_2$, however, as shown in Fig. 2, the *p*-$CuAlO_2$/*n*-ZnO heterojunction (contact) shows a poor rectifying character. On the other hand, it has already been reported that the $SrCu_2O_2$ film can epitaxially grow on a ZnO substrate at lower temperature and shows a good rectifying character.[9] Therefore, $SrCu_2O_2$ was selected as the candidate p-type semiconductor for the

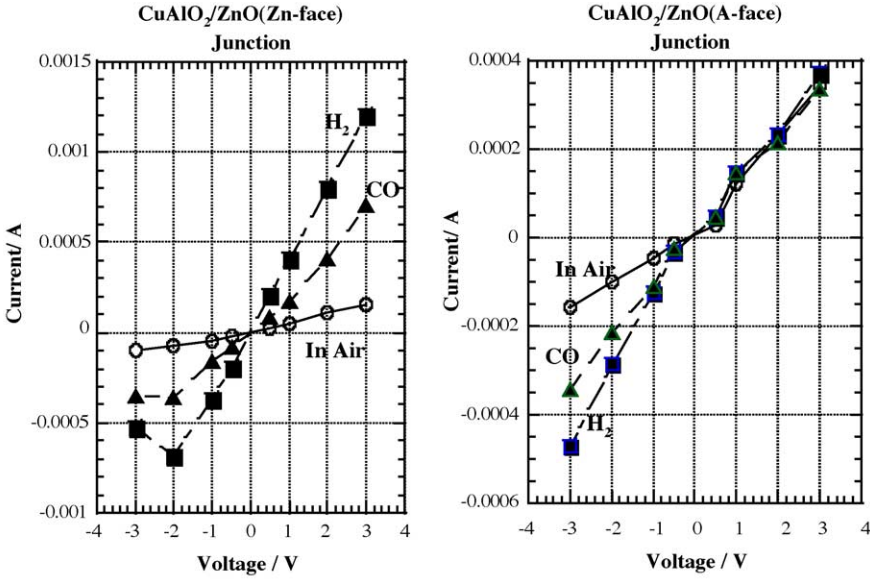

Fig. 2. The effect of H_2 and CO gas introduction (1000 ppm) on the *I*–*V* characteristics of the $CuAlO_2$/ZnO (Zn-face) and the $CuAlO_2$/ZnO (A-face) heterojunction. The gas sensitivity strongly depend on the crystal axis orientation of the ZnO and the $CuAlO_2$/ZnO (Zn-face) shows better gas sensitivity. The $CuAlO_2$/ZnO (A-face) heterojunction does not show gas-sensing properties when it is forward biased.

heterojunction. In the present paper, $SrCu_2O_2$ is referred to as SCO.

2.1. Preparation of the ZnO substrate

A highly oriented ZnO polycrystalline substrate was prepared by the vapor transport method reported previously.[10] In this method, the obtained ZnO crystal was an assembly of numerous fine needle-like crystals oriented in the [0 0 0 1] direction. Zinc oxide (ZnO) substrates having a different crystal axis orientation were prepared. Their surfaces were a Zn-terminated polar surface, an O-terminated polar surface, and a non-polar surface, and they are referred to as Zn-face, O-face, and A-face, respectively. The zinc oxide (ZnO) substrates were polished with an automatic ultrasonic polisher using #8000 abrasive paper and finished using 0.5 μm diamond paste. The polished ZnO substrates were annealed at 1173 K in O_2 to obtain a flat and defect-free surface.[11] The surface finish of the ZnO substrates was checked by AFM observation, and their surface roughness was evaluated to no more than 50 nm.

2.2. SCO film preparation on ZnO substrates and evaluation of junction properties

Surface-finished ZnO substrates were annealed at 923 K under 10^{-5} Pa in the sputtering chamber to remove surface-adsorbed oxygen or OH groups. The SCO film was deposited on the ZnO substrate by the RF magnetron sputtering technique using the sputtering target of $SrCu_2O_2$ doped with 3% of a potassium sintered compact. The target was prepared by the traditional bulk ceramic preparation method.[4] After the film deposition, post-deposition annealing was conducted at 923 K for the crystallization of as-deposited films.

An Ohmic electrode for *p*-SCO, nickel metal was soon deposited on the as-prepared SCO film to avoid the collusion of SCO as a result of the moisture. An indium–gallium (In–Ga) alloy was attached at the back surface of the ZnO substrate for Ohmic contact. Finally, 200 μm-square mesa-type gold electrodes were deposited, and lead wire was contacted using a micro-probe system. The voltage–current (*V–I*) characteristics of the junction specimen were evaluated using a curve-tracer (KIKUSI Model 5802) with a voltage scan rate of 500 V/s (50 Hz).

3. Results and discussion

The nature of the prepared SCO film strongly depends on the sputtering conditions under the film growth process. To obtain transparent and electrically conducting SCO film, lower sputtering power (less than 0.5 W/cm^2) and lower oxygen partial pressure are required. Without post-deposition annealing, the prepared films are amorphous. We checked the polarity of the Hall voltage of as-deposited SCO film and confirmed its p-type conduction. The deposition parameters for preparing transparent and well conductive films are summarized in Table 1. Using these deposition parameters, we prepared SCO films on highly oriented polycrystalline ZnO substrates having different crystal axis orientations. Three types of *p*-SCO/*n*-ZnO heterojunctions (SCO/ZnO (Zn-face), SCO/ZnO (O-face), and SCO/ZnO (A-face), which have the same carrier densities, were prepared. We checked the *I–V* characteristics of these three junctions; however, none of the as-deposited heterojunctions showed nonlinear *I–V* characteristics.

Table 1
Summary of the deposition parameters

Electrode distance (cm)	7
RF power (W/cm^2)	0.5
Sputtering gas	Ar (Purity: 5N)
Deposition pressure (Pa)	9
Substrate temperature (K)	673
Deposition time	4 h × 2
Post-deposition annealing	3 h × 2 at 923 K

By post-deposition annealing, the films showed better transparency than as-deposited films. By XRD analysis, the crystallization of the SCO films was confirmed. Judging from the XRD analysis, SCO films deposited by the sputtering technique were polycrystalline with random crystal axis orientations. All the XRD peaks were very weak, suggesting that either the film was not well crystallized or its large part was still in the amorphous phase. The XRD diffraction signals of SCO on ZnO (O-face) were rather weak comparing with those on ZnO (Zn-face). As for the SCO film deposited on the A-face, no XRD peaks were observed, and the film was either poor in crystallinity or still amorphous. All the sputtered SCO films, however, showed good transparency and p-type electric conduction after post-deposition annealing.

Fig. 3 shows the *I–V* characteristics of the *p*-SCO/*n*-ZnO heterojunction prepared on the Zn-, O-, and A-faces of ZnO substrates. All the junctions show nonlinear *I–V* characteristics, and the forward currents exponentially increase with an increase in the applied voltage. Depending on the crystal axis orientation of the ZnO substrate, variation in the *I–V* characteristics is observed, and the difference in the onset potential is quite obvious among these three specimens. The onset potentials for the forward current is summarized in Table 2; they are SCO/ZnO (Zn-face) < SCO/ZnO (A-face) < SCO/ZnO (O-face). The surface work function of ZnO (i.e., the energy difference between the conduction band and vacuum level) was evaluated as Zn-face (4.25 eV) < A-face (4.64 eV) < O-face (4.95 eV).[12] Estimating from the value of the work

Table 2
Onset potential of the *I–V* response of the SCO/ZnO heterojunction

Materials	Onset potential (V)
SCO/ZnO (Zn-face)	0.7
SCO/ZnO (A-face)	0.9
SCO/ZnO (O-face)	2.2
SCO/ZnO (O-face) (by PLD)	1.05[8]–3.0[9]

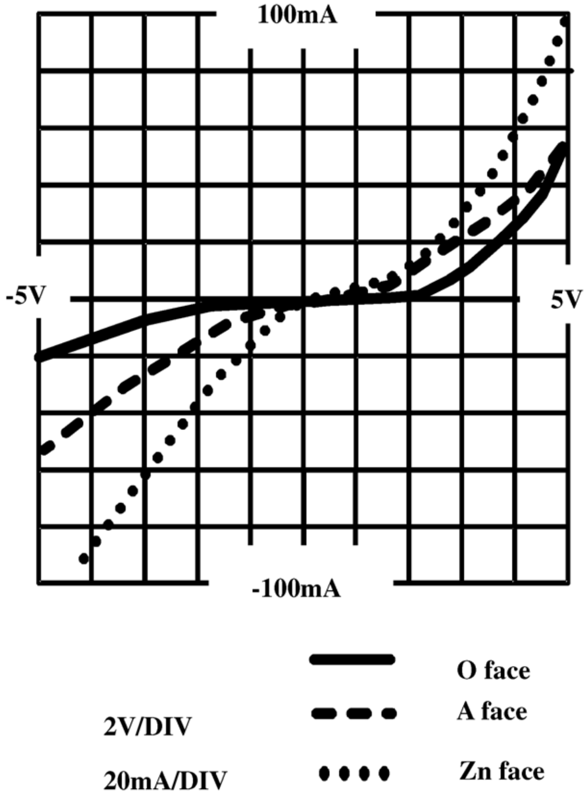

Fig. 3. Variation in *I*–*V* characteristics of the SCO/ZnO heterojunctions, which is prepared on ZnO substrates having different crystal axis orientation. The SCO/ZnO (O-face) heteojunction shows better rectifying character with the current onset potential of 2.2 V.

functions, the surface barrier height lineup was Zn-face > A-face > O-face, and the difference in the onset potential between the SCO/ZnO (Zn-face) and the SCO/ZnO (O-face) was presumed to be 0.7 eV. However, the result of Table 2 is quite different from our speculation. Comparing with the *I*–*V* curves of the *p*-SCO–*n*-ZnO epitaxial junctions,[9] larger reverse currents are observed in all our samples, possibly to be due to the poor crystallinity of the SCO films. The heterojunction prepared on ZnO (O-face) shows higher apparent resistance, and the degree of the rectifying character is far larger than those of SCO/ZnO (Zn-face) and SCO/ZnO (A-face). These results agree with the result of the CuO/ZnO pn heterojunction system, which is made by depositing CuO films on ZnO single-crystal substrates by the RF magnetron sputtering technique.[13] Considering the atomic arrangement of the polar surface of ZnO, the surface charge of ZnO (O-face) is negative, and that of ZnO (Zn-face) is positive. The polarity of the interface charge between SCO and ZnO would be the origin of the variation in the electrical properties of heterojunctions based on ZnO. Probably, for the charge compensation of the ZnO surface, a lattice defect having opposite charge would be produced in the SCO film and would modify the carrier transport through the junction. Tuning up in the gas-sensing characteristics of the *p*-SCO/*n*-ZnO heterojunction will be possible by selecting of the ZnO surface appropriate for gas sensing.

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