Design of a Gas Sensitive Transparent Heterojunction -the System $SrCu_2O_2$-ZnO-

Yoshinobu Nakamura[1*], Yasuhiro Yoshida[2],Yumiko Honaga[2] and Satoru Fujitsu[2]

[1]Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[2]Department of Materials Science and Ceramic Technology, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa, 251-8511, Japan

Abstract

Transparent nt pn junction based on zinc oxide (ZnO) will have an ability of highly sensitive gas sensor material. We fabricate transparent oxide *p-n* heterojunction diodes based on $SrCu_2O_2$(SCO) by RF magnetron sputtering. Zn-terminated polar plane (Zn-face), O-terminated polar plane (O-face), and non-polar plane (A-face) of polycrystalline ZnO plates were used as substrate to clarify the effect of surface polarity of ZnO upon the *p-n* heterojunction characteristics. Highly transparent and well electrically conductive SCO films were obtained by the application of low RF power (Ê < $0.5W/cm^2$) under highly deposition pressures (8 ~ 10 Pa). Although all the as-prepared *p*-$SrCu_2O_2$ / *n*-ZnO heterojunctions showed not so good rectifying I-V characteristic, however, the junction between SCO and O-terminated ZnO polar surface exhibited clear rectifying I-V characteristics after post-deposition annealing at 923K in Ar. The origin of the variation in the I-V characteristics depending on the crystal axis orientation of the ZnO substrates is guessed to be due to the surface polarity of the ZnO surface. It is appeared that not only gas sensing characteristics but their diode properties also depend on their crystal axis orientations of ZnO.

Key Words: Sputtering, Heterojunction, Rectifying character, ZnO, Sensor

1.Introduction

In 1988, Yanagida had proposed the concept of atmosphere sensitive heterojunction diodes, which had a variety of novel functions[1]. Among these functional junctions, CuO/ZnO heterjunction has been well investigated from the view point of its selective CO gas sensing properties[2]. It is indeed that the CuO/ZnO heterojunction has an ability of molecular recognition for CO, but it has a fatal disadvantage of its low sensitivity. If a p-type semiconductor having much oxidation power is use for the heterojunction, I believe its gas sensitivity would extremely be enhanced. The band diagram of CuO/ZnO heterojunction diode is shown in Figure 1(A). Because of a narrow band gap and higher energy of its valence band edge, the oxidation power of electron holes (be proportional to E_h:Energy difference between valence band and vacuum level) suggested to be not so strong. If a p-type semiconductor having a wide band gap with lower valence band energy is applied for the making a pn heterocontact, 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] are developed one after another by Kawazoe and Hosono et.al. These materials have wide band gap with lower valence band energy, because their valence band is formed by hybridization of fully occupied 3d orbitals of copper(I) and 2p orbitals of oxygen ions[3]. The band diagram of $CuAlO_2$/ZnO heterojunction is shown in Figure 1 (B). $E_h$of $CuAlO_2$ is far larger that that of CuO and strong oxidation power of a hole of $CuAlO_2$ is suggested. Figure 2 shows current-voltage (I-V) responses of $CuAlO_2$/ZnO heterojunction having different crystal axis orientation relationships and their variation by CO and H_2 introduction. As our expects, it shows excrement gas sensitivity comparing with CuO/ZnO heterojunction. To be much more interesting, its gas sensitivity strongly depend on crystal axis orientation of ZnO and the junction between $CuAlO_2$ and ZnO (Zn-terminated surface) have excellent gas sensing characteristics.

Aiming at practical use, Ushio et.al. had fabricated atmosphere sensitive CuO/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 ZnO based pn junction diode, the crystal axis orientation relationship between p-type semiconductor and ZnO is determined uniquely [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 try to deposit transparent p-type semiconductor film on highly oriented ZnO polycrystalline substrates having a variety of c-axis orientations by the RF magnetron sputtering technique. p-

SrCu2O2/n-ZnO heterojunction diodes are fabricated and the effect of crystal axis orientation of ZnO on their junction properties will be discussed.

2.Materials Selection and Preparation

In conformity with our view, suitable candidates for p-type semiconductor for a gas sensitive transparent pn heterojunction are $SrCu_2O_2$ (Band gap:3.3eV) and $CuAlO_2$(Band gap: 3.5eV). From the viewpoint of the oxidation power of holes in valence band, $CuAlO_2$ is judge to be appropriate rather than $SrCu_2O_2$, however, as is shown in Figure 2. $CuAlO_2$/ZnO heterojunction(contact) shows only poor rectifying character. On the other hand, it had already reported that $SrCu_2O_2$ film can epitaxially grow on ZnO substrate at lower temperature and it shows good rectifying character[9]. Then we select $SrCu_2O_2$ for a candidate for p-type semiconductor for the heterojunction. In the present paper, $SrCu_2O_2$ is named SCO.

(1) Preparation of ZnO substarte

Highly oriented ZnO polycrystalline substrate was prepared by the vapor transport method reported previously [10]. In this method, obtained ZnO crystal was assembly of numerous fine needle-like crystals, which was oriented in the [0001] direction. ZnO substrates having different crystal axis orientation were prepared. Their surfaces were Zn-terminated polar surface, O-terminated polar surface and non-polar surface and they were named Zn-face, O-face and A-face, respectively. Zinc oxide (ZnO) substrates were polished by an automatic ultrasonic polisher using #8000 abrasive paper and finally finished by using 0.5μm diamond paste. The polished ZnO substrates were annealed at 1173K in O_2 for obtaining a flat and defects free surface [11]. Surface finish of the ZnO substrates was checked by AFM observation and their surface roughness were evaluated to no more than 50nm.

(2) SCO film preparation on ZnO Substrates and Evaluation of Junction Properties

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

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

3.Results and Discussion The nature of the prepared SCO film strongly depends on the sputtering conditions under the film growth process. For obtaining transparent and electrically conducting SCO film, lower sputtering power (less than $0.5W/cm^2$) and lower oxygen partial pressure are found out to be required. Without post-deposition annealing, the prepared films are amorphous. We checked the polarity of Hall voltage of as-deposited SCO film and confirm its p-type conduction. The deposition parameters for preparing transparent and well conductive films are summarized in Table 1.By using these deposition parameters, we prepare SCO films on highly oriented polycrystalline ZnO substrates having different crystal axis orientations. Three types of SCO/ZnO heterojunctions(SCO/ZnO(Zn-face), SCO/ZnO(O-face) and SCO/ZnO(A-face) having the same carrier densities are prepared. We checked the I-V characteristics of these three junctions, however all of the as-deposited heterojunction never show nonlinear I-V characteristics.

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

Figure 3 shows the I-V characteristics of the SCO/ZnO heterojunction prepared on Zn-, O- and A-face of ZnO substrates. All the junctions show nonlinear I-V characteristics and forward currents expornentially increase with an increase in applied voltage. Depending on the crystal axis orientation of ZnO substarte, variation in the I-V characteristics is observed and difference in the onset potential is quite obvious between these three specimens. The onset potential for the forward current is summarized in Table 2 and they are SCO/ZnO(Zn-face)> SCO/ZnO(A-face)> SCO/ZnO(O-face). The surface work function of ZnO (i.e., energy difference between conduction band and vacuum level) had evaluated to Zn-face (4.25eV) < A-face (4.64eV) < O-face (4.95eV)[12]. Guessing from the value of the work functions, surface barrier height lineup is Zn-face> A-face > O-face and difference in the onset potential between the SCO/ZnO (Zn-face) and the SCO/ZnO (O-face) presumed to be 0.7eV. However, the result of Table 2 is quite different from our speculation. Comparing with the I-V curves of the SCO-ZnO epitaxial junctions [9], larger reverse current are observed for all our samples and that would be due to poor crystallinity of the SCO films. The heterojunction prepared on ZnO(O-face) shows higher apparent resistance and the degree of rectifying character is far larger those of SCO/ZnO(Zn-face) and SCO/ZnO(A-face). These results have consensus of the result of the CuO/ZnO pn heterojunction system, which is made by depositing CuO films on ZnO single crystal substrates by RF magnetron sputtering technique[13]. Considering the atomic arrangement of polar surface of ZnO, 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 electrical properties of heterojunctions based on ZnO. Probably, for charge compensation of ZnO surface, lattice defect having opposite charge would produce in the SCO film and would modify carrier transport through the junction.

References

1. H.Yanagida, Intelligent Materials – A New Frontier-. Angew.Chem., 1988, **27**, 1389-1392.

2. Y. Nakamura, H.Yoshioka, M.Miyayama, H.Yanagida, T.Tsurutani and Y.Nakamura, Selective CO gas sensing mechanisms with CuO/ZnO Heterocontact, J. Electrochem. Soc., 1990, **137**, 940-943.

3. H.Kawazoe, M.Yasukawa, H.Hyodo, M.Kurita, H.Yanagi, and H.Hosono,P-type electron conduction in transparent thin films of $CuAlO_2$, Nature(London), 1997, **389** , 939-942.

4. H.Yanagi, H.Kawazoe, A.Kudo, M.Yasukawa, and H.Hosono, Chemical Design and Thin Film Preparation of p-type conductive transparent oxides, J. Electroceramics, 2000, **4**, 407-414.

5. H.Yanagi, T.Hase, S.Ibuki, K.Ueda, and H.Hosono, Bipolarigy in electrical conduction of transparent oxide semiconductor $CuInO_2$ with delafossite structure ;Appl. Phys. Lett., 2001, **78**, 1583-1585.

6. A.Kudo, H.Yanagi, H.Hosono, and H.Kawazoe, $SrCu_2O_2$: A p-type conductive oxide with wide band gap. Appl. Phys. Lett., 1998, **73**, 220-222.

7. Y.Ushio Y, M.Miyayama, H.Yanagida , Fabrication of thin-film CuO/ZnO jeterojunction and its humidity sensing properties, Sensor and Actuator B, 1993, **12**,135-139.

8. H.Ohta, K.Kawamura, M.Orita, N.Sarukura, M.Hirano, and H.Hosono, UV-emitting diode composed of transparent oxide semiconductor p-$SrCu_2O_2$/n-ZnO. Electronics Lett. 2000, **36,** 1.-2.

9. H.Ohta, M.Orita, M.Hirano, and H.Hosono, Fabrication and characterization of ultraviolet-emitting diodes composed of transperernt p-n junction , p-$SrCu_2O_2$ and n-ZnO.J. Appl. Phys.2001, **89,**5720-5725.

10. F.Noritake, N.Yamamoto, Y.Horiguchi, S.Fujitsu, K.Koumoto, and H.Yanagida, Vapor-phase growth of transparent zinc oxide ceramics with c-axis orientation, J. Am. Ceram. Soc., 1991,**74** .232-233.

11.H.Maki, N.Ichinose, S.Sekiguchi, N.Ohashi,T.Nishihara, H.Haneda, and J.Tanaka, Surface structure of ZnO single crystals analyzed by ion scattering spectroscopy, Jpn. J. Appl. Phys. Part 1, 1999 **38,** 2741-2743.

12. H.MOORMANN, D.KOHL, and G.HEILAND, Work function and band bending on clean cleaved zinc oxide surfaces, Surface Science, 1979, **80** ,.261-264.

13. S.Suzuki, Y.Nakamura, M.Miyayama, and T.Kudo, Abstract of the Annual Meeting of the Ceramic Society, Jpn., Electrical and gas sensing properties of CuO/ZnO heterojunction(contact) based on ZnO single crystal. Paper No. 1E-18, 2000, pp.201.

Table 1 Summary of deposition parameters

Electrode distance	7cm
RF Power	$0.5W/cm^2$
Sputtering gas	Ar (Purity: 5N)
Deposition Pressure	9Pa
Substrate Temperature	673K
Deposition Time	4h x 2
Post-deposition Annealing	3h x2 at 923K

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(Ref.8) □3.0 (Ref.9)

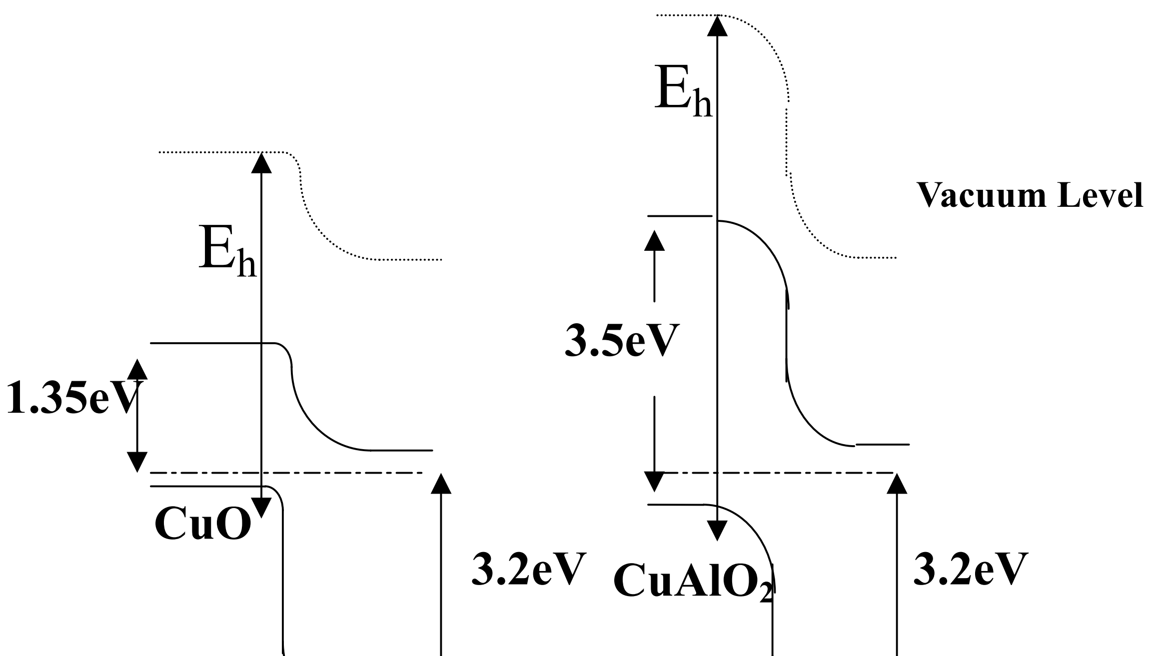
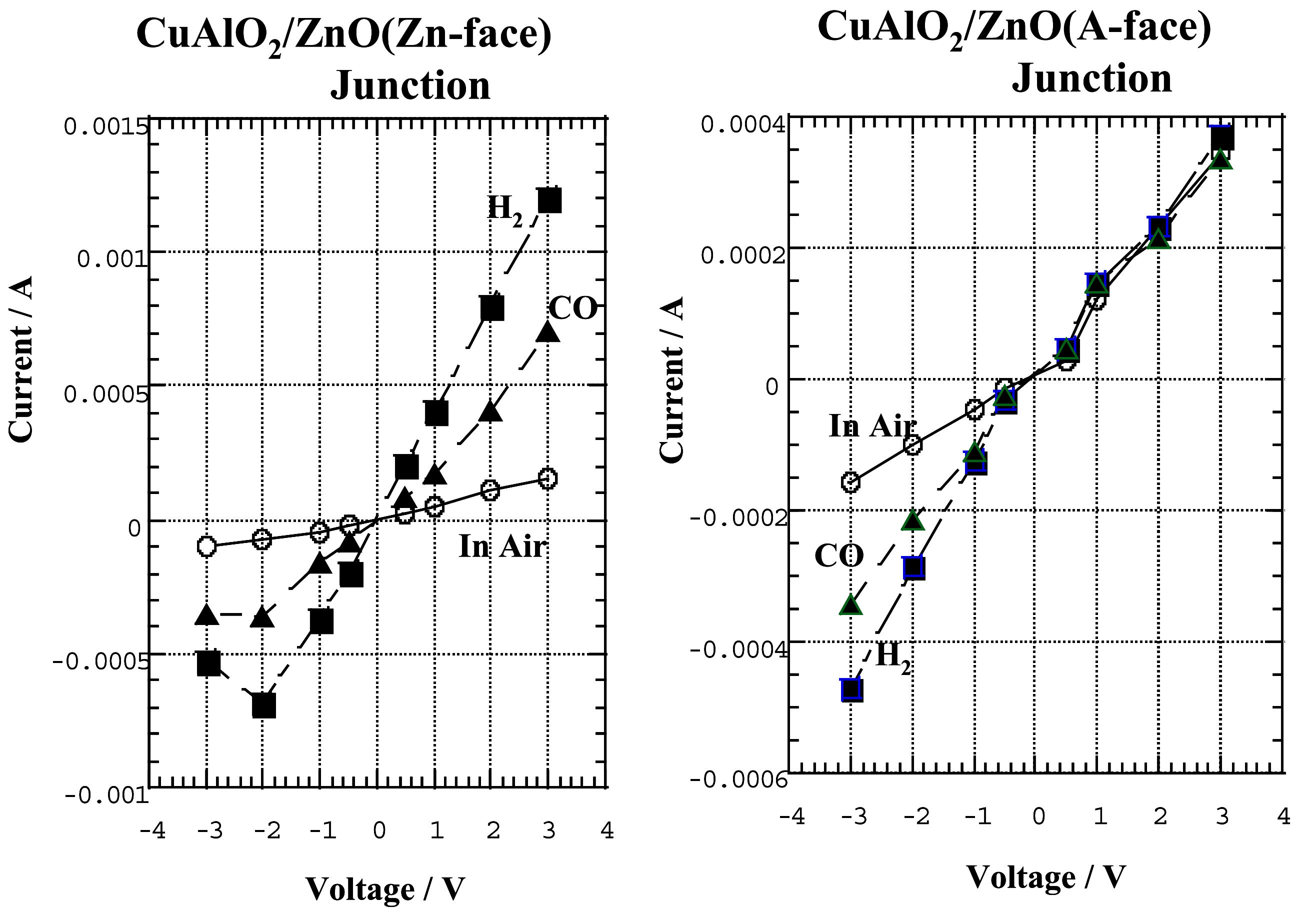


Figure 1 Schematic band lineup of CuO/ZnO pn heterojunction and transparent pn junction ($CuAl_2O_2$/ZnO). Eh means the energy difference between valence band and vacuum level, which is proportional to the oxidation power of holes.



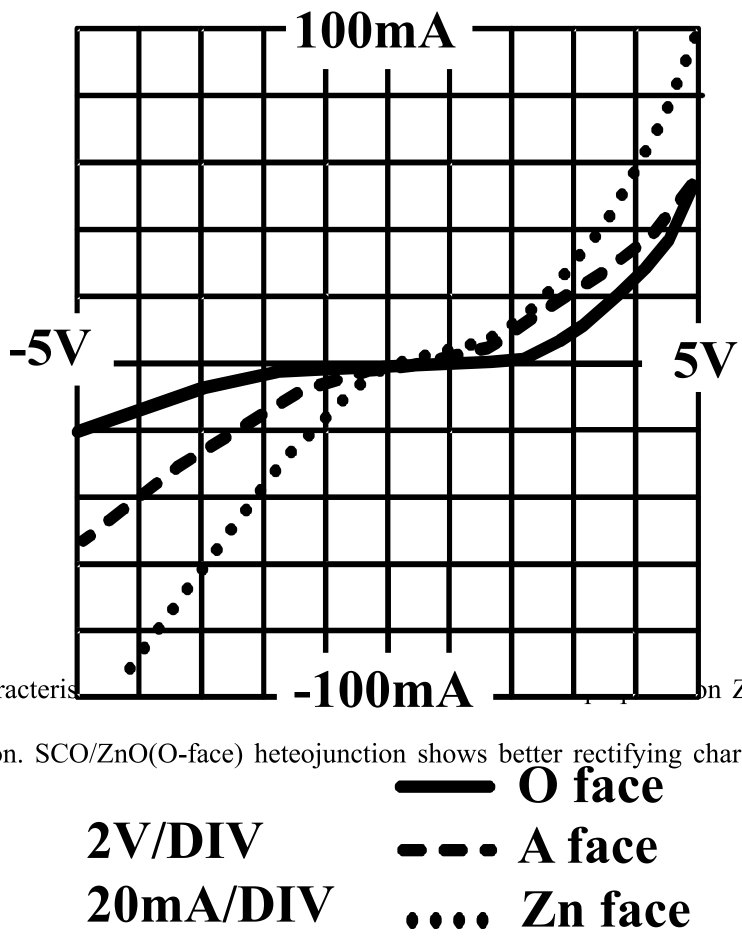


Figure 3 Variation in I-V characteris ... on ZnO substrates having different crystal axis orientation. SCO/ZnO(O-face) heteojunction shows better rectifying character with the current onset potential of 2.2V.

X