Microstructural Evidence of Hall Mobility Anisotropy in c-Axis Textured Al-Doped ZnO

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The high electrical conductivity, 1150 S/cm at room temperature, in the ab-plane of c-axis textured Al-doped ZnO is attributed to its high Hall mobility that is almost double the mobility in the c-axis direction. Temperature-independent mobility in the ab-plane below 200 K suggests that ionized impurity dominates the scattering of electron transport, which reasonably agrees with a modified Brooks–Herring–Dingle model taking into account nonparabolic $E$–$k$ dispersion. However, the pronounced anisotropy between ab-plane and c-axis cannot be expected based on the model. Detailed observations of the grain boundary (GB) by means of high-resolution transmission electron microscopy, high-angle annular dark-field scanning transmission electron microscopy, and energy-dispersive X-ray spectroscopy revealed the existence of an Al-enriched, Zn-deficient layer near the GB traversing the c-axis direction. In contrast, the highly conductive direction encompasses a tilt grain boundary, in which coincident sites were observed and Al segregation was barely evident. We conclude that such a preferential segregation in the GB and/or GB structure itself are responsible for the anisotropy of mobility in the textured Al-doped ZnO.

I. Introduction

The well-known zinc oxide is an n-type semiconductor whose conductivity is effectively enhanced by Al or Ga impurity doping, which is promising for practical applications such as thermoelectric materials or transparent conductive oxides. We previously reported that for highly c-axis oriented Al-doped ZnO ceramics, textured by magnetic alignment, the electrical conductivity at room temperature along the ab-plane, i.e., the basal plane of ZnO, increased to $>1000$ S/cm, which was almost twice that along the c-axis. 4–6 This high conductivity along the ab-plane originated from a high mobility of $\sim 90$ cm$^2$/V·s. In addition, the conductivity was found to be a function of the degree of orientation: a higher degree of orientation resulted in a higher level of conductivity. However, an analysis based on a tensor calculation indicated that the orientation of the crystallite was not responsible for the enhancement in conductivity. 4 A study on the Hall mobility of ZnO single crystal without doping reported nearly isotropic properties above room temperature, supporting our analysis. 7

A probable mechanism for the anisotropy of the textured Al–ZnO is the difference in scattering at the grain boundary, which generally originates in the structure and/or the chemical homogeneity at the grain boundary (GB).

In order to solve the uncertainty in the textured Al-doped ZnO system, we performed detailed observations on GBs using high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS). Hall measurement was also carried out to clarify the anisotropy in mobility.

II. Experimental Procedure

C-axis textured Al-doped ceramics were prepared via the magnetic field alignment method. Nominal composition of the ceramics was $\text{Al}_{0.02}\text{Zn}_{0.98}\text{O}$, which was prepared from commercial ZnO powder adding $\gamma$-Al$_2$O$_3$ of 1 mol%. Details of sample preparation can be found elsewhere, 6 but briefly, the procedure was as follows. Because of the anisotropic magnetic susceptibility of ZnO, particles dispersed in liquid start to align within a few seconds in correlation with the magnetic field. These aligned particles were fixed by the gelation of monomer mixed in the liquid. Upon completion of gelation, the samples were dried and sintered via standard ceramic processing. The texture strength of the ceramic was almost 100 multiple of random distribution confirmed by a pole figure of 002 diffraction.

Next, the samples were sliced perpendicular to the c-axis (ab-plane) and parallel to the c-axis (see Fig. 1). Carrier concentration and mobility were analyzed at a temperature range of 80–400 K using a DC Hall measurement system (Resitest8300, Toyo Corporation, Tokyo, Japan). Here, the van der Pauw method was adopted. The current–voltage characteristics of these contacts showed a linear relationship. The applied magnetic field was 0.75 T during the measurement and reverse polarity measurement was carried out to cancel the voltage offset.

The microstructure of the sintered specimens was observed by transmission electron microscopy (TEM; 3000F, JEOL, Tokyo, Japan). TEM foils were prepared using the standard technique for thin ceramic foils: cutting, grinding, dimpling, and Ar-ion thinning. Energy-dispersive X-ray spectroscopy (EDS; Voyager III, NORAN Instruments Inc., Middleton, WI) was used for elemental analyses of GBs. The spot size was controlled to be $<1$ nm for this EDS analysis. Moreover, HAADF-STEM (JEM2100F equipped with Cs corrector, JEOL) was used to clarify the image contrast of atomic columns. EDS mapping was also carried out using JEM2100F under the conditions of the dwell time of 0.8 ms and the spot size of 0.6 nm. As to the view direction of the GB observations, refer to Fig. 1.

III. Results and Discussion

(1) Anisotropy of Hall Mobility

The results of Hall measurement for the ab-plane and c-axis are shown in Fig. 2. The carrier concentration in each direction

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The mobility of the temperature, indicating degenerate semiconductors of the model and Matthiessen’s rule. Therefore, it is reasonable to assume nonparabolic $E-k$ dispersion, and the BHD model can be modified as Pisarkiewics et al. described:

$$\mu = \frac{3\pi^2 \hbar^2 (4\pi e_0 e_r)^2}{2e^4} \frac{n}{Z^2 N_0 F} m^*$$

where

$$F = \left[ 1 + \frac{4x_1}{x_0} \left( 1 - \frac{x_1}{8} \right) \right] \ln(x_0 + 1) - \frac{x_0}{x_0 + 1} - 2x_1 \left( 1 - \frac{5}{16} x_1 \right)$$

$$x_0 = \frac{4\pi e_0 e_r \hbar^2 (3\pi^2 n)^{1/3}}{e^2 m^*}$$

$$x_1 = 1 - \frac{m_n^0}{m^*}$$

$$m^* = m_n^0 \left[ 1 + 2C \frac{\hbar^2 (3\pi^2 n)^{1/3}}{m_n^0} \right]^{2}$$

From the equations, it can be seen that the mobility is determined by the properties: relative static permittivity ($e_r$), carrier concentration ($n$), DOS effective mass ($m^*$), effective mass at the bottom of conduction band ($m_n^0$), the charge of impurity ($Z$), and its concentration ($N_i$). The symbols $\pi$, $e_0$, $h$, and $e$ have the standard meaning. When $m^*$ is identical with $m_n^0$ above equation reduces to BHD model. Adopting $m^*/m_i$ of 0.31, $C$ of 1.04 eV$^{-1}$ $e_r$ ($c$-axis) of 8.75, $e_r$ ($ab$-plane) of 7.8, $n$ of $9 \times 10^{19}$ cm$^{-3}$, $Z$ of 1, and $N_i = n_i$, $\mu_i$ is estimated as 119 and 102 cm$^2$/V·s for the $c$-axis and $ab$-plane, respectively. Here, higher $\mu_i$ is expected in the $c$-axis direction due to the higher $e_r$ of the $c$-axis. In addition, the anisotropy of $m^*$ is considered to be negligible because of the isotropic Seebeck coefficient, which is a function of $m^*$ and $n$, of this material.$^{5,10}$

In order to estimate total mobility ($\mu$) of the samples, the other scattering mechanisms must be included. To do that, we applied Matthiessen’s rule

$$\frac{1}{\mu} = \frac{1}{\mu_{\text{other}}} + \frac{1}{\mu_i}$$

Here, $\mu_{\text{other}}$ means the mobility scattered by other mechanisms such as scattering by acoustic phonons. For the value of $\mu_{\text{other}}$, we referred to the data on a single crystal with low doping concentration.$^1$ For the mobility of single crystal, it was analyzed that polar optical scattering, deformation potential scattering and piezoelectric scattering were responsible above 50 K;

Fig. 1. Geometrical setup of mobility measurement and transmission electron microscopic (TEM) observation. ZnO crystals are schematically represented as hexagon with $a$, $b$, and $c$ axes. The Hall mobility of $ab$-plane and $c$-axis was measured in the setup (a) and (b), respectively. Here, $E$ and $B$ fields indicate the direction of electric and magnetic fields during the measurement. Because of the $c$-axis texturing of the sample, grain boundaries (GBs) in $ab$-plane possess tilt GB (setup a) and those along $c$-axis resemble twist GB (setup b). TEM observations of each GB were performed in the direction orthogonal to the sheet.

was an identical value of $9 \times 10^{19}$ cm$^{-3}$ and independent of temperature, indicating degenerate semiconductors of the sample. The mobility of the $ab$-plane was almost double that of the $c$-axis for the entire temperature range. Below 200 K, the mobility was almost constant, which suggests scattering by ionized impurity. The influence of ionized scattering in degenerate semiconductors can be expressed by the Brooks–Herring–Dingle (BHD), model.$^9$ In addition, Minami et al.,$^9$ reported that a high carrier concentration leads to increase in density-of-states, DOS, effective mass that estimated from plasma frequency. Young et al.,$^{10}$ also reported the increase of DOS effective mass based on Seebeck and Nernst coefficients measurements. Their estimated DOS effective mass showed quantitative agreement. Therefore, it is reasonable to assume nonparabolic $E-k$ dispersion, and the BHD model can be modified as Pisarkiewics

Fig. 2. Hall measurement of $c$-axis textured ZnO. (a) Temperature ($T$) dependence of mobility ($\mu$) along the $c$-axis and on the $ab$-plane. (b) Carrier concentration ($n$) and anisotropy of mobility ($\mu_{ab}/\mu_c$). Lines in (a) indicate a semi-theoretical prediction based on the modified Brooks–Herring–Dingle model and Matthiessen’s rule.
below that temperature, ionized scattering dominated the mobility confirmed by the $T^{3/2}$ dependence on nondegenerate semiconductors.\(^7\)

The lines in Fig. 2 show the mobility based on Eq. (2). The estimated mobility shows less temperature dependence at low temperature, and decreases with temperature. As to the difference between $c$-axis and $ab$-plane, the anisotropy at low temperature is not expected so large compared with the observed mobility. Especially, deviation of the observation from the modified BHD model was unreasonably large for $c$-axis, indicating pronounced GB influence for $c$-axis which was not taken into account in the above calculation. In addition, the mobility of $c$-axis resembled with that of randomly oriented one,\(^5\) which also implicates GB influence on the mobility.

(2) Origin of the Anisotropy

In a previous report,\(^4\) we noted that periodic structure was often observed on the $ab$-plane. The typical structure of these grain boundaries is shown in Fig. 3. The edge on HRTEM image depicts the absence of an intergranular phase\(^4\) which was identified neither Al$_2$O$_3$ nor ZnAl$_2$O$_4$. It is rational that at a coherent grain boundary, the structure is energetically stable, so that a lower level of impurity segregation is tolerated compared with that in a random grain boundary.\(^13\) In contrast, Al segregation was found to be pronounced at boundaries crossing the $c$-axis direction as shown in Fig. 4. In addition, Al was barely detected in the grain interior, suggesting that the solid solution of Al in the Zn site was less than the detection limit of 0.5 at\% which agrees reasonably well with an SIMS analysis.\(^14\)

The detailed structure of grain boundaries on the $ab$-plane was further observed by HAADF-STEM. Figure 5 shows images at a GB on the $ab$-plane. In the HAADF-STEM image, the positions of the atomic columns are directly imaged as bright spots. In this case, the Zn-O columns are imaged as bright spots. It is surprising that the coincident sites were observed as seen in the inset in Fig. 5. It is also noted that the regular arrangement disappears near the neighbor shown by the arrow. Zn defects and/or Al atoms would exist in that area, which may be induced by the mismatch in atomic positions caused by the tilt angle of the grains.\(^13\)
Slight Al segregation is observed, while Zn deficiency is not significant. The mapping images of Al (b), oxygen (c), and Zn (d). Al segregation and Zn deficiency are pronounced at the GB. In contrast, the mapping image, a clear contrast at the GB is observed, indicating dopant segregation along the GB. In addition, a GB with a relatively high tilt angle between adjacent grains showed a weak Al contrast, as seen in Fig. 7, even in the ab-plane direction. However, the Zn contrast at the GB was not significant.

Based on the aforementioned microstructural observations, GB structures and resultant dopant segregation along with defect formation are considered as possible causes for the anisotropy of mobility. In addition to the GB characters, the other geometrical factors such as the number as well as the width of GB may also influence to the anisotropy.

As with the ab-plane direction, our textured ceramics showed elongation of grain size.4 Hence the number of GB was lower in the ab-plane, which agrees the trend of anisotropy. Besides, randomly oriented ceramics having similar grain size with that of the ab-plane stayed at half of the mobility of the ab-plane, showing the GB density does not solely explain the high mobility along the ab-plane. Furthermore, the mobility along the ab-plane is mostly identical to that of a heavily doped single crystal as estimated in the previous section, which implies the electrons are mainly scattered by ionized impurity, in other words ionized dopant in the grain, and the scattering at GB is thus considered as minor effect. The atomically ordered GB along the ab-plane, Fig. 5, supports this argument.

In contrast to the ab-plane, the scattering at GB along the c-axis is thought to be significant. Accumulated defects as observed by STEM, segregated GB layer shown in Fig. 3, and potential barrier near GB are the possible causes for the lowering in mobility along the c-axis. Among them, the influence of scattering by potential barrier is considered to be limited, although the Arrhenius plot of conductivity above the room temperature suggests formation of the potential barrier along the c-axis.16 This is clear from the mobility <200 K. In the temperature region, the temperature-independent lower mobility was observed in this direction, indicating that thermally activated scattering is responsible for the low mobility. Hence, we can discard the scattering via potential barrier. However, to distinguish other factors is not straightforward. The correlation between accumulation of defects and formation of GB layer makes it difficult further.

Generally speaking, the GB observed along the c-axis resembles to that of randomly oriented ceramics showing dopant segregation similarly. Considering the situation in the randomly oriented ceramics as well, plausible mechanism for the low mobility is summarized as follows. As we demonstrated by EDS mapping images, the dopant segregation occurs profoundly at the GB with low-coherency, possibly to reduce GB energy. Along with the segregation, Zn vacancy also accumulates near the vicinity to ensure the charge neutrality. Hence concentration of defects, i.e., dopant and zinc vacancy, near GB tends to be higher compared with that of grain interior. Such accumulated defects sure to shorten the mean free path of electron, resulting in low mobility. Other geometrical influence modifies mobility in some extent. Consequently, the difference in defect concentrations resulting from the crystallographic orientation of grains at GBs causes the anisotropy.

### III. Conclusions

Zinc oxide essentially possesses high electron mobility, and shows anisotropy at low temperature, which was reported for a single crystal with low carrier concentration.1 In degenerate semiconductors, however, the high mobility and anisotropy...
should be reduced by ionized scattering as a result of doping, which we predicted based upon modified BHD model. Unexpectedly, significant anisotropy was experimentally observed in c-axis textured ceramic. Detailed observations of the grain boundaries were performed by means of HRTEM, HAADF-STEM, and EDS mapping, and the following conclusions were reached.

1. On the ab-plane, tilt GB with periodic structure was frequently confirmed. Furthermore, coincident sites were directly observed by means of HAADF-STEM. On the contrary, there was no such specific arrangement at GB crossing the c-axis direction.

2. An aluminum layer was observed at the GB along c-axis. On the other hand, such segregation was seldom found at GB on the ab-plane.

3. EDS mapping revealed that Al segregation led to a deficiency in Zn.

These findings clarified that the anisotropy of c-axis textured ZnO originates in the GB structure. That is, there is a disordered GB itself as well as dopant segregation along with vacancy formation in the vicinity, resulting in low mobility along the c-axis in Al-doped ZnO. This structure resembles the GB of randomly oriented ZnO, which causes the low mobility.

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