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Polarity Effects on the Surface Morphology, Crystal Orientation and the Electronic Structure of ZnO-based Semiconductor Heterointerfaces

Tatsuru Nakamura

February 2014

Doctoral Thesis at Osaka Prefecture University
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Chapter 1: General Introduction

Research Background

In recent technologies of the semiconductor devices, material surfaces and interfaces grow much importance. Device miniaturization in Si-LSI has already reached the physical limit. It is a stage having the adoption of the three-dimensional stack is considered seriously [1]. These situations lead to the increase in the surface and interface area per unit volume, which enhance a possibility of having a bad influence to an operating characteristic. In high-$\kappa$/metal gate, which is discussed in LSI technology in practice, shift in operating voltage due to unexpected dipole layer at the interface was reported [2]. Further, in the organic electronic devices, since the organic semiconductor layer does not have a normally conductive carrier, it is necessary to externally injected electrons and holes, but the carrier injection is restricted by the relative relationship between the electronic level of the metal and the organic semiconductor [3-5].

Because surface states are different from those in the bulk [6], it is reflected in the electrical characteristics of the device across the surface and interface of the different materials. Metal/semiconductor contact is one of the most controversial issues in the material interface. According to the Mott-Schottky model [3], energy barrier height between the metal and the semiconductor is expressed by work function of the metal and electron affinity of the semiconductor. In practice, however, this model does not generally coincide with the experimental results and the picture of interface states help understanding the formation of Schottky barrier [6]. Therefore, it is very difficult to control the energy level alignment at the interface. Recent study tries to control the
Schottky barrier height using the interfacial dipole layer of the oxides which includes highly ionic chemical bonds [7].

Some dielectrics and semiconductors have spontaneous polarization and this is often avoided characteristic in the practical electronic devices. GaN-based semiconductors, which are blue and ultraviolet light-emitting diode (LED) materials widely used currently, have a spontaneous polarization in the c-axis direction [8]. If quantum wells and superlattices are fabricated along the c-axis direction, the band structure at these heterostructures is inclined and eventually degrades the emission characteristics as LEDs [9]. Due to the reason, some of the GaN-based LEDs are fabricated using nonpolar or semipolar deposition techniques [10-12].

On the other hand, approaches incorporating this feature effectively into the practical devices are also performed. Two-dimensional electron gas (2DEG) is generated even without impurity doping by controlling the polarization of the interfacial polarization positive charge to occur at the interface in GaN-based heterostructures [13]. Recent study enabled effective p-type doping to AlGaN/GaN heterostructure by using polarization grading induced electric field [14].

In this study, the author focused on the characteristic of this polarization, and the goal of the work is to control device characterization by electric polarization. In this work, ZnO is selected as a polar semiconductor with an wurtzite structure like GaN. In addition, ZnO is a semiconductor with piezoelectric and spontaneous polarization. Furthermore, it is expected that it is possible to control the lattice constant and the band gap, the amount of spontaneous and piezoelectric polarization can be intermixed with an oxide such as MgO, MnO and CdO [15-18]. Spontaneous polarization of ZnO is \( P_{sp} \approx 5 \mu\text{C/cm}^2 \) which corresponds to the sheet charge density as high as \( \sigma/e = 2.6 \times 10^{13} \text{ cm}^{-2} \)
Edahiro et al. have reported the formation of 2DEG in ZnO-based heterostructure for the first time [20]. In Zn_{1-x}Mg_{x}O/ZnO systems, polarization-induced 2DEGs were realized [21-23], and its mobility now exceeds 700,000 cm^{2} V^{-1} s^{-1}, which has enabled the observation of fractional quantum Hall effect [24, 25]. Electron spin injection into 2DEG using modulation-doped Zn_{1-x}Mn_{x}O/ZnO heterostructure was reported by Masuko et al. [26].

Furthermore, since high-quality single crystal substrates made by chemical vapor transport or hydrothermal synthesis method are available unlike the III-nitride semiconductors [27, 28], which is a quite important advantage to study the effects of polarity on the electronic structure of the ZnO based heterostructure interfaces. In the thin film growth of ZnO, sapphire has been used as substrate for long years due to its structural similarity to GaN [29, 30]. Polarity of the most of the heteroepitaxial films are reported to be O-polarity and its control was not performed with ease [31, 32]. Since 21st century ZnO single crystal substrate became available and homoepitaxy of ZnO is realized. Polarity-controlled homoepitaxy of ZnO by molecular beam epitaxy [33, 34], pulsed laser deposition [35, 36], and metal-organic chemical vapor deposition [37, 38] were studied. Some of these studies were performed using the Zn-polar face in order to obtain nitrogen-doped p-type ZnO due to its high incorporation efficiency even at high temperature [39, 40]. Kato et al. made the point that O-rich flux condition is important to obtain high-quality Zn-polar ZnO films [33]. In contrast, Takamizu et al. suggested the importance of high-temperature growth above 800 °C [34]. However, there have been few reports on the effects of polarity on the surface and interface electronic structure of polarity-controlled ZnO. In the case of GaN-related materials, single crystal substrates are not available, such effects of single polarity GaN has not been reported.
yet. In this work, ZnO homoepitaxial thin films without any surface defects, pits and hillock that become an origin of the coexistence of each surface polarity were successfully obtained on perfectly polarity controlled ZnO single crystal substrates for the first time. The effect of the surface polarity on the crystallographic growth process and the change in the electronic structure were discussed. Eventually, the interfacial control of organic semiconductor/ZnO and magnetic semiconductor/ZnO interfaces were also discussed in this thesis.

In Chapter 2, surface preparation process of polar ZnO single crystal substrates are discussed. Previous reports have enabled to obtain the atomically-flat O-polar ZnO substrates by wet-chemical etching and thermal annealing in ZnO ambient. In this thesis, therefore, surface pretreatment process for Zn-polar ZnO substrates is studied. Thermal annealing process in air, in vacuum, and in oxygen ambient cannot remove the topmost surface damaged layers. Atomically-flat surface of the Zn-polar ZnO substrates are realized by using wet-chemical etching by HF and UV-ozone cleaning.

In Chapter 3, growth mode of homoepitaxial films on polarity-controlled ZnO substrates by the pulsed laser deposition is discussed. In order to prepare an atomically-flat ZnO homoepitaxial films with polarity-controlled structure, VI/II ratio, growth rate and substrate temperature are controlled. Surface morphology and crystal structure were evaluated by atomic force microscopy (AFM) and X-ray diffraction (XRD). Furthermore, near-surface atomic and electronic structures of ZnO homoepitaxial films are characterized by X-ray photoelectron spectroscopy (XPS), and atomic scattering spectroscopy.

Chapter 4 focused on growth morphology of a ZnO-based diluted magnetic
semiconductor $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($\text{ZnMnO}$, $x \sim 0.12$) on polar ZnO substrates. $\text{ZnMnO}$ is predicted to be a room-temperature ferromagnet by introducing the hole carriers [41]. Furthermore, since spontaneous and piezoelectric polarization is available in their heterointerface, polarization-induced carrier doping into $\text{ZnMnO}$ layer is promising. In this chapter, in order to control the polarization of $\text{ZnMnO}$ films and their interfaces, solution state of Mn ions and strain applied by ZnO substrates were characterized by XRD, and the polarity effects on these properties of $\text{ZnMnO}$ thin films were discussed.

In Chapter 5 and Chapter 6, the author prepared organic semiconductor/polar ZnO heterostructures in order to control the electronic properties of organic semiconductor by polarization of ZnO. In general, organic semiconductor has no free carriers in it and its electrical properties are governed by the interface. Therefore, polarization-induced effects on interface electronic reconstruction at organic/polar ZnO interface is expected [42]. Kim et al. reported the polarity effects of GaN on interface characteristics of copper phthalocyanine/polar GaN heterostructures and the surface electron affinity of each polarity determines the band diagram at the interface [43]. Blumstengel et al. reported the relation between the molecular assembly of $p$-sexiphenyl on polar/nonpolar ZnO and the interface band-offset [44]. However, in this case, different substrate orientation induces the change in molecular orientation, i.e. flat-lying and standing. In this work, similarly-oriented organic ultrathin films were grown on polar ZnO substrates. Thin film growth of pentacene ($\text{C}_{22}\text{H}_{14}$) by ultraslow deposition method on polar ZnO was discussed in Chapter 5. Molecular orientation and packing were evaluated by XRD, which revealed that pentacene molecules are standing upright which coincide with the results of AFM images. Moreover, two-type polymorphs, namely thin-film and bulk phase, coexist in the pentacene crystal.
Thickness dependence of the structural properties revealed the growth morphology of pentacene films on polar ZnO. Electronic structure of pentacene/polar ZnO is discussed in Chapter 6. Kelvin probe force microscopy (KFM) visualized the thickness-dependent surface potential of pentacene on ZnO. XPS study revealed the electronic structures of both pentacene and ZnO and its effect of pentacene coverage.

Chapter 7 summarizes the research results above and proposes the application of polarization of semiconductors to the next-generation optoelectronic devices.

References


Chapter 2: Atomic Control of Polar ZnO Single Crystal Surfaces

2-1 Introduction

In recent years, ZnO and the related materials have attracted much interest because of its potential application to optical and electronic devices, such as ultraviolet light emitters and transparent thin film transistors. [1-3] Therefore, the surface preparation method of the ZnO substrate becomes quite important for the epitaxial growth of the thin films. ZnO is the wurtzite-type crystal, and has crystallographic polarity, Zn-polar (0001) and O-polar (000T) [4, 5]. The difference in the polarity makes the differences in physical and chemical properties of each polar surface. For example, when ZnO single crystals are chemically etched by dilute HCl solution, the surface morphology of the etched substrates is quite different between Zn-polar and O-polar surfaces [6]. This means that polarity dependent surface cleaning methods are needed for preparing the surface of ZnO single crystals. In the epitaxial growth of ZnO and related materials, c-plane sapphire substrates have been used for long years due to its structural similarity with group-III nitride semiconductors such as GaN. In this case, the polarity of epitaxial films of ZnO is normally O-polar due to its surface stability [7]. Some studies are reported about the polarity control of ZnO films grown on sapphire substrate [8, 9]. However, since the single crystal substrates of ZnO have been commercially available after 2000s, control of the polarity of ZnO films are more easily realized by using the ±c-plane ZnO. Furthermore, the use of Zn-polar (0001) ZnO
is effective for nitrogen doping that is important technique for obtaining \( p\)-type ZnO [10]. The surfaces of the other oxide substrates are well engineered by wet-chemical etching [11, 12] or thermal annealing [13] techniques to control the film growth atomically. Regarding the surface treatment methods for ZnO single-crystal substrates, thermal annealing, wet-chemical etching and plasma treatment have also been proposed for each polar surface [14-17]. However, atomically flat substrate of Zn-polar ZnO, which is suitable for the epitaxial growth, has not been obtained yet. In this chapter, therefore, the effect of wet-chemical etching for Zn-polar (0001) ZnO without annealing is discussed.

2-2 Experimental

Hydrothermally grown ZnO single-crystal substrates (Tokyo Denpa Co., Ltd.) with 0.5 ° offset-angle toward the \([0\overline{1}0]\) direction were used in all experiments. Zn-polar (0001) face and O-polar (000-1) face of ZnO substrates were used in this study. Substrates were wet-chemically etched or annealed. In some samples, prior to wet-chemical etching, ZnO substrates were treated by UV-ozone exposure to remove the surface contamination and then were rinsed in pure water to eliminate the inorganic particles from the surfaces. The cleaned substrates were etched by NH\(_4\)F-buffered HF (BHF) solution, followed by ultrasonic cleaning in ethanol. The pH value are varied from 5 to 7 under the fixed NH\(_4\)F concentration at 40 wt.%. The pH value of BHF solution was measured by pH test paper. Thermal annealing was carried out in air using the electrical furnace or in the vacuum chamber. The surface morphology of surface-treated ZnO substrates was studied using atomic force microscopy (AFM;
Veeco, Nanoscope) and confocal laser scanning microscopy (CLSM; Olympus, Lext OLS3500). The epitaxial films were deposited by pulsed laser deposition using ArF excimer laser ($\lambda$=193 nm) and ZnO ceramic target.

2-3 Results and Discussion

2-3-1 Surface Treatment of O-polar ZnO Single Crystal Substrates

The surface of as-received ZnO substrates has a lot of scratches and contaminations as shown in Fig. 2-1 due to the process of chemomechanical polishing. The surface does not exhibit atomically flat surface such as step and terrace structure. In order to eliminate the surface scratches and disordered surface layer, the substrates were annealed in the box made of polycrystalline ZnO. By using the ZnO box, the substrates can be located in Zn-rich ambient and can avoid surface roughening such as formation of hexagonal pits [18]. The annealed substrates are shown in Fig. 2-2. The surface of annealed substrates is atomically flat with step and terrace structure. By measuring the height of each atomic step, the height turns out to be 0.26 nm which corresponds to the charge neutral unit cell of ZnO along c-axis.
Fig. 2-1  AFM image of as-received ZnO substrate.

Fig. 2-2  AFM image of annealed O-polar ZnO substrate.
2-3-2 Thermal Annealing of Zn-polar ZnO Single Crystal Substrates

The same investigation was carried out with O polarity for Zn-polar ZnO. The surface treatment of the substrate by a method other than etching is desirable because the etch pits are likely to be due to a dislocation in the crystal when it is chemically etched for Zn-polar ZnO surfaces [6]. After the ultra-pure water cleaning and organic cleaning, thermal annealing treatment was performed in an air atmosphere ZnO ceramic box. Fig. 2-3 shows the annealing temperature dependence of time of 30 minutes in the annealing time. It is confirmed that the appearance of the step structure at 800 °C above, but these steps are the bunching suggesting that the annealing temperature is not optimized for the epitaxy.

Fig. 2-4 shows the surface morphologies of Zn-polar ZnO substrates in case of annealing in vacuum chamber with and without oxygen gas. Annealing temperature in the figure is fixed at 800 °C which is sufficiently high temperature to create atomic steps of Zn-polar ZnO as recognized in Fig. 2-3. With the increase in annealing time, step bunching happens and surface morphology gets rougher. Moreover, by both the cases where annealing time is for 10 minutes and for 30 minutes, it turns out that the substrate surface is ruined, so that oxygen gas pressure is high. Especially in gas pressure of $1 \times 10^3$ Torr or more, the surface roughening appears notably. Especially in the heat treatment in oxygen environment, the segregation of the excess zinc on Zn-polar surface has been reported by the temperature region near 800 °C [19]. It is considered that the same as that of this report has happened in the thermal annealing in a vacuum chamber. Judging from the above results, it is suggested that the surface morphology and the atomic composition of substrate before heat treatment and
composition have a lot of influence on the surface after annealing.

Fig. 2-3  AFM image of Zn-polar ZnO substrate before (a) and after (b-e) annealing.
Annealing temperature: (b) 600, (c) 700, (d) 800, (e) 900 °C
Fig. 2-4 AFM images of annealed Zn-polar ZnO substrates under different oxygen pressure.
2-3-3 Wet-Etching of Zn-polar ZnO Single Crystal Substrates

Since commercially available ZnO substrates are chemomechanically polished, wet-chemical etching is usually carried out to remove the damaged layer. However, the chemical etching often yields etch-pit formation, which is the serious problem for device fabrication. In the case of ZnO single-crystal substrate, since this issue is quite serious, annealing before deposition is normally used for obtaining smooth surface without damaged layer. In the case of Zn-polar (0001) ZnO, moreover, this issue on etch pit formation after chemical etching is more serious compared to that for O-polar (000\(\overline{1}\)) ZnO. Organic cleaning with the polluted substrates surface has enough damage to the surface to form etch pits during wet etching. Therefore, in this work, preliminary cleaning process whose damage to the substrate decreases was considered. The examined surface treatment process is shown below.

1. UV-ozone exposure for 10 minutes
2. Rinsing in pure water for 30 minutes
3. Wet etching by HF+NH\(_4\)F mixture (BHF)
4. Rinsing in pure water for 1 minute
5. Ultrasonication in ethanol for 5 minutes

Fig. 2-5 shows possible changes in the surface during the treatment process above. Before cleaning, the damaged layers due to the chemomechanical polishing lie on the surface of ZnO, and organic and inorganic contamination adsorb on the surface. An
Fig. 2-5  Schematics of cleaning or wet-etching process with UV/ozone treatment.
ultrasonication treatment to the as-received substrate can damage the substrate and can nucleate the etch pits. Thus, instead, we have introduced a UV-ozone treatment before wet cleaning. It is expected that almost of the organic contamination is decomposed by UV-ozone treatment. Furthermore, since this treatment makes the surface hydrophilic, it is also expected that the effect of rinsing in pure water is enhanced and which make us to begin wet etching with less damage preliminary treatment.

To clarify the etching process during the wet-chemical etching by BHF, etching time dependence of (0001) ZnO single crystal was investigated. Fig. 2-6 shows AFM images of BHF-treated ZnO substrates. The pH value of BHF for these samples was fixed at 6.5 for moderate etching rate. NH₄F concentration of 40 wt.% was used. The sample etched for 10 seconds (Fig. 2-6 (a)) does not exhibit the step structure. The step structure appears after more than thirty seconds. However, the shape and the area of the terraces for 30-second-etched sample are inhomogeneous as shown in Fig. 2-6 (b). The shape of the steps gradually get straight with increasing the etching time from 1 minutes to 5 minutes (Fig. 2-6 (c) and (d)), and become almost straight and homogeneous when the surface is etched for more than 10 minutes (Fig. 2-6 (e)). The step-height shown in Fig. 2-6 (e) measures 0.52 nm, which corresponds to unit cell of wurtzite ZnO along c-axis. As the etching progresses, however, the formation of the etch-pit begins. It probably starts near the dislocation existing at the surface because of a higher etching rate normal to the surface near the dislocation. The surface of the sample after etching for 20 minutes (Fig. 2-6 (f)) shows numbers of hexagonal pyramid-shaped etch-pits. Fig. 2-7 represents an etching time dependence of the root-mean-square (RMS) roughness of BHF etched ZnO substrates shown in Fig. 2-6. At first 30 seconds, RMS increases
Fig. 2-6 Surface morphology of Zn-polar ZnO substrates treated by BHF (pH~6.5) solution.
slightly suggesting that the surface damaged layer is removed. RMS values show almost no changes the samples etched for 1-10 minutes, however, begin to increase again above 10 minutes. It is because surface roughening including formation of etch pits occurs above 10 minutes. Therefore, alternative method to obtain uniform atomic step structure was considered. Based on these experimental results, the BHF etching process for Zn-polar ZnO single crystal can be explained as the similar mechanism as described in Ref. 20. Before BHF treatment, the surface of Zn-polar ZnO is flat having the amorphous-like damaged layer at the topmost layer. At the first stage of BHF etching, the topmost amorphous layer is etched (upper figure Fig. 2-8 (a)), and then the nuclei of the pits form at the dislocation edge. These nuclei grow as faceted etch-pits during etching process (lower figure of Fig. 2-8 (a)). Moreover, the etched region in amorphous layer gets together during further etching process. After removal of amorphous layer, the step-edges get linear and resulting in the formation of uniform step structure all over the substrate surface. During the etching process, however, the nuclei of faceted etch pits also grow. The surface asperity originated in the etch pits is unfavorable for atomically-controlled epitaxial growth. However, at the beginning of the wet-chemical etching that removes the damaged layer at the surface of the untreated substrates and further etching introduces the etch-pit formation that yields inhomogeneous step structures. Therefore, the lower pH of BHF solution was used so as to reduce the etching time and enhance the uniform etching of the amorphous layer without growing the faceted etch-pits as shown in Fig. 2-8 (b). The AFM image of the sample etched in the BHF with the pH of around 5 is shown in Fig. 2-9. Other etching conditions are the same as the sample shown in Fig. 2-6. Reducing the etching time by decreasing the pH values of BHF, the flat and uniformly-etched ZnO surface can be obtained. The
Fig. 2-7 Change in RMS roughness of BHF (pH=6.5) treated Zn-polar ZnO substrates as a function of etching time.
Fig. 2-8 Schematics of Zn-polar ZnO surfaces during wet-etching treated by BHF. (a) pH~6.5, (b) pH~5.5.
dominant step-height of the sample shown in Fig. 2-9 is measured as 0.52 nm. Although the step height corresponds to double monolayer, we succeeded in obtaining uniform step and terrace structure with straight step edge without etch-pit formation. These experimental results reveal that lowering the pH reduces the etching time of damaged layer that leads to the reduction of pit formation. Note that this etching process does not need the high-temperature annealing process.

In order to observe the effect of thermal annealing on the surface morphologies of newfound surface treated substrate, the substrates were annealed at 800 °C in vacuum chamber. The AFM images of annealed Zn-polar ZnO substrates are shown in Fig. 2-10. There are no surface segregations or step bunching as shown in Fig. 2-3 or Fig. 2-4. These results make the point that a new surface treatment method by UV-ozone cleaning and wet chemical etching has an effect on preparing thermally-stable and atomically-flat Zn-polar ZnO surfaces.
Fig. 2-9  Surface morphology of Zn-polar ZnO substrates treated by BHF (pH~5.5) solution.
Fig. 2-10 Surface morphology of annealed Zn-polar ZnO substrates after the treatment by BHF with the pH of 6.5 under vacuum (a) and oxygen ambient (b).
2-4 Conclusion

The surface treatment method of Zn-polar ZnO single-crystal substrates was investigated. The wet-chemical etching by BHF leads to the formation of not only the step and terrace structure and but also etch-pits at the surface. Lowering the pH of BHF solution enhances the etching rate of damaged layer leading the reduction of pit formation due to the shortening the etching time. Atomically-flat substrates without etch pits were successfully obtained by optimizing the pH of the BHF solution. Homoepitaxial ZnO thin films grown on the ZnO substrates after chemical etching using optimized BHF solution exhibit the atomically-flat surface without etch pit. This newly developed novel chemical etching process is quite impressive for epitaxial growth because it does not need any high temperature-annealing process for obtaining step and terrace structure.

More recent studies enabled the surface control of Zn-polar ZnO substrates by wet chemical etching and it suggests that the defect density of the epitaxial films are reduced by adopting the etching [21]

References


Chapter 3: Growth Mode of ZnO Thin Films by Pulsed Laser Deposition

3-1 Introduction

In the thin film growth of ZnO and its related materials, a feature of polarity sometimes becomes problems. To obtain the \( p \)-type ZnO, for example, doping of nitrogen should become the key technology [1]. Sumiya \textit{et al.} reported that high-temperature nitrogen incorporation into the Zn-polar ZnO surface is superior to that into the O-polar ZnO surface [2]. Look \textit{et al.} succeeded to obtain nitrogen doped ZnO films with \( p \)-type conduction on Zn-polar ZnO single crystals [3]. Therefore, to understand the growth mechanism of ZnO films on Zn-polar ZnO becomes important. In contrast, reproducible fabrication of \( p \)-type ZnO with O-polarity by repeated temperature modulation method with Pulsed laser deposition (PLD) was reported by Tsukazaki \textit{et al.} [4], however, the quite high activation energy of acceptor (~100 meV) and its high compensation ratio (\(N_D/N_A \sim 0.8\)) are still far-out technology. Recent studies demonstrate current-induced light emission in Zn-polar Mg\(_x\)Zn\(_{1-x}\)O/ZnO-based ultraviolet LED by nitrogen-doping suggesting the availability of Zn-polar ZnO growth [5, 6].

Regarding the homoepitaxial growth of Zn-polar ZnO, there are several reports using molecular beam epitaxy (MBE) [7, 8], pulsed laser deposition [9], and metalorganic vapor phase epitaxy [10]. Kato \textit{et al.} reported that Zn-polar ZnO films with smooth surface and high crystallinity were obtained by plasma assisted MBE under
the oxygen-rich flux conditions [7]. ZnO films with atomically flat surface were achieved at the growth temperature above 700 °C. In the case of PLD, on the other hand, there is no report on the Zn-polar ZnO films with atomically flat surface because it is very hard to control the amount of supplied zinc and active oxygen independently.

To study the behavior of Zn and O atoms on ZnO single crystal substrate and the effect of their stoichiometry for the surface morphology and the crystallinity, optical emission spectroscopy of the plume during PLD was carried out to estimate O/Zn flux ratio under the various deposition conditions such as oxygen pressure, laser fluence, and the distance between target and substrate. The effect of the surface polarity of the substrate on the growth process is also discussed.

3-2 Experimental

ZnO films were prepared on Zn-polar or O-polar ZnO single crystal substrate by using PLD technique. Schematic of PLD system in this study is illustrated in Fig. 3-1. Zn-polar ZnO substrates (Tokyo Denpa Co., Ltd.) whose (0001) and (000-1) surfaces have offset angles of 0.5° toward \( m \)-direction are cleaned by acetone, ethanol and pure water, followed by annealing at 800 °C for 30 minutes in the atmosphere. ZnO ceramic was used as the target made from ZnO powder (99.999 %). ZnO powder is pressed, and sintered at 1000 °C for 10 hours into the ceramic. ArF excimer laser (193 nm) (Lambda Physik, Compex) was used for PLD in all experiments. Optical emission spectroscopy (OES) of the plume was carried out in the wavelength range of 200-950 nm. Optical emission from the plume was detected by multichannel photo-analyzer (Hamamatsu Photonics, PMA-12) through the viewing port of the vacuum chamber. The position of
the photo-detector can be moved so as to make the optical emission mapping of the plume and it was set at the position of near the substrate as shown in Fig. 3-2. The OES measurements were carried out at room temperature at the different oxygen pressures, distances from the target to substrate, and laser fluence. 

ZnO thin films were deposited on O-polar and Zn-polar ZnO substrate, which was mounted on Si (100) substrate using silver paste. Depositions were carried out at the growth temperatures of 700 and 800 °C, at the oxygen pressures from $1 \times 10^{-5}$ to $1 \times 10^{-3}$ Torr, and at the laser fluence of 190 or 270 mJ/cm$^2$. Pulse repetition rate of excimer laser was fixed at 5 Hz for all depositions. Prior to the deposition, O-polar ZnO substrates were cleaned and etched by acetone and diluted HF solution, and annealed at 930 °C for 10 hours. 

Surface morphologies of ZnO films were characterized by atomic force microscopy (AFM) (NanoScope, NanoScope III). The AFM measurements were performed on the contact mode, and non-conductive silicon nitride was used as a probe material. Atomic arrangement at the near-surface of ZnO was characterized by neutral atom scattering spectroscopy (Pascal Co., Ltd., TOFLAS-3000). The measurement was performed under a pressure of $5 \times 10^{-6}$ Torr using 3 keV He$^0$ source. Fundamental principles of this technique are similar to those of coaxial impact-collision ion scattering spectroscopy [11]. In order to understand the surface electronic structure of the samples, X-ray photoelectron spectroscopy (XPS) study was performed at room temperature by using Al$K\alpha$ radiation ($h\nu$=1486.6 eV). The surface of ZnO films and single crystal substrates were pretreated before XPS measurement by an ex-situ UV-ozone cleaning for ten minutes. Calibration of the electron kinetic energy was performed using C 1$s$ peak (285 eV) due to the surface contamination and Au 4$f_{7/2}$ signal from gold film
evaporated on the sample surfaces. A total energy resolution of the XPS system is 0.7 eV.

3-3 Results and Discussion

3-3-1 Optical Emission Study of Plume in the Pulsed Laser Deposition of ZnO

OES measurement was carried out to estimate the number of excited species of zinc and oxygen atoms in the vapor phase. O/Zn flux ratio is calculated from emission intensity of Zn* and O* peak lines. Fig. 3-3 shows the OE spectrum of plume measured at the oxygen pressure ($P_{O2}$) of $1 \times 10^{-3}$ Torr, target-substrate distance ($d_{T-S}$) of 30 mm, and laser fluence ($E$) of 190 mJ/cm$^2$. The emission peaks indicated with open circle corresponds to atomic zinc (Zn*), open squares to zinc ion (Zn$^{+*}$), and open triangle to atomic oxygen (O*), respectively [12, 13]. In this paper, optical emission lines at 333.5 nm (Zn*) and 777.2 nm (O*) are used for discussion.

Fig. 3-4 (a) shows the oxygen pressure dependences of OE intensities at 333.5 nm and 777.2 nm corresponding to Zn* and O* respectively. Above the $P_{O2}$ of $1 \times 10^{-3}$ Torr, the OE intensity of Zn* moderately increases as the oxygen pressure increases. Emission intensity of O* drastically increases at $1 \times 10^{-3}$ Torr, and decreases at above $5 \times 10^{-2}$ Torr. Fig. 3-4 (b) shows emission intensity ratio of O* and Zn*. $I_{O*}/I_{Zn*}$ value is constant at the $P_{O2}$ less than $1 \times 10^{-4}$ Torr, and drastically increases at the $1 \times 10^{-3}$ Torr with increasing the oxygen pressure, and decreases at $5 \times 10^{-2}$ Torr that corresponds to the change of O*. This also suggests that the oxygen gas pressure does not affect for the flux at the $P_{O2}$ below $1 \times 10^{-4}$ Torr. However, the $P_{O2}$ around $1 \times 10^{-3}$ Torr, high $I_{O*}/I_{Zn*}$
Fig. 3-1 Schematic of pulsed laser deposition system in this study.

Fig. 3-2 Photograph of plumes emitted from ZnO under various oxygen pressure.
Fig. 3-3 Optical emission spectrum of ZnO. Square, circle and triangle symbols denote the signals of Zn**, Zn*, and O*, respectively.
value is observed. In this $P_{O2}$ range, the ambient oxygen gas is partially activated by laser fluence, and these activated species seems to reach the substrate. The collision and the scattering would be responsible for the exponential decreases of $I_{O^*}/I_{Zn^*}$ at the $P_{O2}$ above $1 \times 10^{-2}$ Torr.

Fig. 3-5 shows intensity ratio $I_{O^*}/I_{Zn^*}$ versus laser fluence, $E$. $I_{O^*}/I_{Zn^*}$ ratio gradually increases with increasing the $E$. It is known that high laser fluence activate much more oxygen molecules near the target, and the activated oxygen radicals are supplied to the substrate [12]. In this experiment, the laser fluence above 250 mJ/cm$^2$, the $I_{O^*}/I_{Zn^*}$ ratio saturates. However, high $I_{O^*}/I_{Zn^*}$ ratios are obtained under the wide $d_{T-S}$ condition. These results imply that O/Zn flux ratio strongly depends on $E$, $d_{T-S}$, and $P_{O2}$.

3-3-2 Growth Mode Control of Zn-polar ZnO Homoepitaxial Films

After above OES measurements, homoepitaxial ZnO thin films were deposited to discuss the effects of O/Zn ratio on the film growth process. AFM images of ZnO thin films grown on Zn-polar ZnO substrates with different $E$ and $T_g$ are shown in Fig. 3-6. $P_{O2}$ and $d_{T-S}$ were fixed at $1 \times 10^{-5}$ Torr and 30 mm, respectively. The three-dimensional growth with the large grains and pits is confirmed in the film grown at 600 °C. Shift of growth mode from three-dimensional to two-dimensional growth is recognized with a rise in growth temperature, and the surface flatness characteristics improve. All the samples grown at 750 °C exhibit highly-flat surface morphologies and no pits are observed as seen in the samples grown at lower temperature. In the film growth of ZnO, a pit is formed when surplus Zn adatoms hop to other terrace tops on
Fig. 3-4 (a) Optical emission intensity and (b) intensity ratio $I_{O^*}/I_{Zn^*}$ of plume at different oxygen pressure.
Fig. 3-5 Optical emission intensity and its intensity ratio $I_{O^*}/I_{Zn^*}$ of plume with different laser fluence and oxygen pressure (a) $P_{O2}=1\times10^{-5}$ Torr, and (b) $P_{O2}=1\times10^{-3}$ Torr.
the O-terminated ZnO surface [14]. It is in particular thought that it is easy to form a pit on Zn-polar ZnO than on O-polar ZnO surfaces because topmost O atoms on Zn-polar ZnO have three dangling bonds (and one dangling bond on O-polar ZnO), which lead to the need of higher energy for desorption of excess Zn adatoms than on O-polar ZnO surfaces. However, increasing the growth temperature can suppress the hopping and can enhance the desorption of excess Zn adatoms. This results in the suppression of pit formation at higher growth temperature (750 °C). These results simultaneously suggest that the growth of Zn-polar ZnO needs higher growth temperature than on O-polar ZnO in order to obtain atomically-flat surfaces of homoepitaxial films. Some reports describe that high-temperature growth at above 800 °C enables atomically-flat two-dimensional growth without pits in Zn-polar ZnO growth [8, 15]. In addition, when we focus on the change in the surface morphology against those in laser fluence, higher laser fluence, in other words O-rich condition does not always contribute to flat surface morphology. When laser fluence increases, the emission intensity of both O* and Zn* in plume increases together as shown in Fig. 3-5. In addition, it is expected that the O/Zn ratio also increases under that condition. The above-mentioned result suggests that not only the temperature (thermal energy) but also the O/Zn flux ratio and growth rate have a big influence on a film growth mode of ZnO.

Structural properties of Zn-polar ZnO homoepitaxial films shown in Fig. 3-6 were evaluated by XRD. The results are shown in Fig. 3-7. The samples grown at 600 °C exhibit peak shift to lower 2θ angle from the substrate peak. In this case, since the growth conditions are Zn-rich and low temperature without re-evaporation of zinc adatoms, defects such as excess zinc and oxygen vacancy induced lattice expansion in the films. On the other hand, extremely high laser fluence can also make defects. The
Fig. 3-6 AFM images of homoepitaxial ZnO thin films grown on Zn-polar ZnO substrates.
Fig. 3-7 X-ray Diffraction patterns of 0002 reflection for ZnO thin films grown on Zn-polar ZnO substrates.
samples grown by the laser fluence at 210 mJ/cm² show peak shifts toward higher diffraction angle at about 20–36°. At higher E condition, not only O/Zn ratio but also the growth rate increase. Supply rate of source material exceeds the migration rate of adatoms, which can be an origin of oxygen-rich type defect formation.

In order to investigate the origins of defects in homoepitaxial films revealed by XRD, ultraviolet/visible light region transmittance were measured. Fig. 3-8 shows the results of transmittance measurement. For comparison, the transmittance of ZnO single crystal substrate was also evaluated (Fig. 3-8 (a)). In the transmittance values of film samples, contribution of the substrates was eliminated. ZnO single crystal substrate has enough high quality not to exhibit any defect absorption. On the other hand, in homoepitaxial film samples, as shown in Fig. 3-8 (b), there are roughly two types of absorption peaks recognized. At lower substrate temperature (600 °C), strong absorption at wavelength of 400-500 nm is observed. According to the discussion above, this originates from Zn-rich type defects such as oxygen vacancy. As this absorption occurs near the absorption edge of ZnO, it is possible that shallow levels are formed in the ZnO films. The samples grown with high laser fluence, on the other hand, light absorption occurs in the wide wavelength region. Note that higher laser fluence leads the film thicker, which is one possible reason for the wide-range absorption. However, because a similar tendency is observed in XRD profiles, O-rich type defects are reflected in the absorption spectra.
Fig. 3-8 UV/VIS optical transmission spectra of (a) substrate and (b) ZnO thin films grown on Zn-polar ZnO substrates.
3-3-3 Comparison of Thin Film Growth Morphology between Zn- and O-polar ZnO

The results of foregoing section indicate the possibility of different growth morphologies between Zn- and O-polar ZnO. In order to discuss the effect of polarity on the growth morphology of homoepitaxial films, homoepitaxial films with each polarity were prepared at the same time. AFM images of Zn- and O-polar homoepitaxial films against substrate temperature are shown in Fig. 3-9. In the case of Zn-polar ZnO, the sample grown at 600 °C exhibits small grains, which implies the lack of surface migration of adatoms for two-dimensional growth. By elevating the growth temperature, two-dimensional growth is realized at 800 °C. In these samples, optimized surface pretreatment is not applied; therefore, step-and-terrace structure and pits can coexist in the same samples. In the case of O-polar ZnO, on the other hand, two-dimensional growth with step-and-terrace structure is observed at 700 °C which is much lower than that of Zn-polar ZnO.

Fig. 3-10 shows XRD 2θ-ω profiles of these homoepitaxial films around 0002 reflection of ZnO. Laue oscillations are clearly recognized in some samples, which gives the thickness values of the epitaxial films. Layer thickness $d$ is estimated by following relationship,

$$d = \frac{\lambda}{2(\sin \theta_1 - \sin \theta_2)} ,$$

where $\theta_1$ and $\theta_2$ represent the peak position of each fringe, and $\lambda$ represents the wavelength of X-ray (CuKα). At the growth temperature of 700 °C, thickness values of Zn- and O-polar ZnO are deduced to be 95 nm and 77 nm, respectively. That is, the growth rate of Zn-polar films is 1.2 times higher than that of O-polar ZnO films. This is
because the surface of ZnO is terminated by oxygen atoms regardless of polarity [16], and the number of dangling bonds of topmost O on Zn- and O-polar ZnO is 3 and 1, respectively. Therefore, Zn-polar ZnO surface can stabilize Zn adatoms more easily than O-polar ZnO, resulting in higher growth rate of homoepitaxial films. Above discussion does not conflict with polarity-dependent growth mode transition between two- and three-dimensional growth modes.
Fig. 3-9 AFM images of homoepitaxial ZnO thin films grown on Zn- and O-polar ZnO substrates.
Fig. 3-10 X-ray Diffraction patterns of 0002 reflection for ZnO thin films grown on Zn- and O-polar ZnO substrates.
In order to realize the ZnO-based spintronic devices, the polarity is one of the most important properties to control the electronic structure at the interface. ZnO has a crystallographic polarity along the c-axis direction, which can induce charge carriers at the heterointerface and the surface, and should affect the incorporation of adatoms during the film growth. Previous works in Chapter 3-3-2 have revealed the effect of O/Zn ratio on the surface morphology and the growth mode of homoepitaxial ZnO films grown on Zn-polar ZnO substrates. In order to discuss the correlation between the polarity and the growth process of ZnO, however, topmost surface atomic arrangements of polar ZnO surfaces should become important.

In this study, therefore, near-surface atomic structure and electronic structure at the surfaces of ZnO single crystal and homoepitaxial film with each polar surface were characterized using surface-sensitive methods, and the effects of polarity on the surface structure of ZnO were discussed using ZnO substrates and epitaxial films with O- or Zn-polar surface.

The existence of polarization at the interface should cause the interfacial potential distribution to accommodate the charge at the interface [17]. However, if the polarization exists at the surface, adsorption of the molecules and/or atomic relaxation will occur. Therefore, atom scattering spectroscopy and XPS were carried out using single crystal substrates and homoepitaxial films with step and terrace structure. Each polar surface of ZnO substrate was treated by organic solution and hydrofluoric acid, followed by thermal annealing at 950 °C in a ZnO ceramic box to construct a flat surface without desorption of zinc atoms [18]. As a result, atomically-flat steps and
terraces are clearly observed in the pretreated substrates as shown in Fig. 3-11 (a) and 3-11 (b). AFM images for homoepitaxial films grown on these substrates are shown in Fig. 3-11 (c) and 3-11 (d). Atomically-flat step and terrace structures are also recognized. X-ray diffraction $2\theta-\omega$ scans for these epitaxial films exhibit no apparent peak splitting.

Two-dimensional growth of homoepitaxial films is realized on each polar surface of ZnO by tuning the O/Zn ratio and the growth temperature, as reported before [19, 20]. The results of Hall effect are listed in Table 3-1. The carrier density of the films are almost 1 order of magnitude higher than that of substrate, because the surface treatment conditions were determined so as not to increase the carrier density but to keep the surface structure without forming the surface defect structure such as step bunching, pits, hillocks and dislocations.

Atom scattering spectroscopy was carried out to obtain information on the surface atomic structure of the polar ZnO substrates and the epitaxial films as shown in Fig. 3-11. Schematic of measurement system and simulation patterns of atomic scattering spectroscopy of ZnO are illustrated in Fig. 3-12. The polar and the azimuthal angle dependences of Zn signals are plotted. As can be seen in Fig. 3-13 (a)-(f), the patterns for the epitaxial films ((c) and (d)) are identical to those from the single crystal substrate ((a) and (b)) and simulation patterns of 2-nm-thick unstrained Zn-polar (0001) and O-polar ($\langle 0001 \rangle$) surfaces ((e) and (f)) suggesting that the near-surface structures of polar ZnO substrate maintains after ZnO deposition including adsorption or atomic relaxation. Polar angle dependences of Zn signal intensity are also shown in Fig. 3-13 (g). The scattering profiles corresponding to each surface polarity are recognized.

Photoemission spectra in the valence band region of ZnO single crystal substrates and homoepitaxial films are shown in Fig. 3-14. Valence band of ZnO is
Table 3-1 Carrier concentrations and mobilities of the samples used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polarity</th>
<th>Carrier concentration (cm⁻³)</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Zn-polar</td>
<td>1.8 × 10¹⁵</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>O-polar</td>
<td>3.1 × 10¹⁵</td>
<td>136</td>
</tr>
<tr>
<td>Film</td>
<td>Zn-polar</td>
<td>1.7 × 10¹⁶</td>
<td>169</td>
</tr>
<tr>
<td></td>
<td>O-polar</td>
<td>7.5 × 10¹⁷</td>
<td>125</td>
</tr>
</tbody>
</table>

Fig. 3-11 AFM images for (a) Zn-polar, and (b) O-polar single-crystalline ZnO substrates, and (c) Zn-polar and (d) O-polar homoepitaxial films.
Fig. 3-12 (a) Experimental setup of He atom scattering spectroscopy. (b) Simulated scattering patterns are also shown for Zn-polar and O-polar ZnO surfaces.
Fig. 3-13 Atom scattering patterns for ZnO substrates and homoepitaxial films. Polar and azimuthal angle dependence of the Zn signal intensity for a (a) Zn- and (b) O-polar ZnO substrates, and those of homoepitaxial films ((c) and (d)), respectively. (e) Polar angle dependence of the Zn signal intensity. Polar angles of ±90 ° correspond to the directions of <10-10>. Closed and open symbols mean substrates and homoepitaxial films. Circular and square symbols mean Zn- and O-polar samples, respectively.
mainly composed of O 2p and Zn 3d states which correspond to the photoemissions at 3-8 eV and ~10 eV, respectively [21]. The photoemission intensity of Zn-polar ZnO at around 4 eV is higher than that of O-polar ZnO, whatever the film or substrate. Such phenomenon has been reported using hard and soft X-ray photoemission spectroscopy [22, 23]. Although it is still in controversy, the adequacy has been confirmed by using other techniques such as coaxial impact-collision ion scattering spectroscopy and convergent beam electron diffraction [24] and the use of the XPS spectra corresponding to O 2p state at around 4eV is now recognized as a powerful tool for determining the polarity of wurtzite crystal such as ZnO and InN [25, 26]. If the polarity influences on the O 2p photoemission spectra, these results support those of atom scattering spectroscopy.

For more detailed study about the surface electronic structure for polarity controlled ZnO, the amplitude of surface band bending at polar ZnO is estimated using photoemission spectra in the valence band region. The energy difference of surface band bending $E_{bb}$ in non-degenerated semiconductor is expressed as [27]

$$E_{bb} = E_g - (E_F - E_V) - (E_C - E_F)$$

$$= E_g - (E_V - E_F) - \frac{kT}{e} \ln \left( \frac{2(2\pi m^*kT/h^2)^{3/2}}{n} \right),$$

where $E_g$ is the band gap energy of ZnO with $E_g = 3.37$ eV [28], and the term $(E_F - E_V)$ is the energy difference between the Fermi level and the valence band maximum, and the term $(E_C - E_F)$ is the energy difference between the conduction band maximum and the Fermi level, $k$ is the Boltzmann’s constant, $T$ is the absolute temperature ($T = 300$ K), $e$ is the elementary charge, $m^*$ is the electron effective mass ($m^* = 0.32m_0$), $h$ is the Planck’s constant, $n$ is the electron concentration, respectively. The term $(E_F - E_V)$ can
Fig. 3-14 X-ray photoemission spectra in the valence band region of ZnO substrates and homoepitaxial films. Blue and red lines correspond to Zn- and O-polar ZnO, and solid and dashed lines to single crystal substrates and homoepitaxial films, respectively.
be estimated by valence band photoemission spectra. The energy difference \( (E_C - E_F) \) was calculated with using the carrier concentration, \( n \), determined by Hall-effect measurement. Note that the calculated energy of the valence band maximum (VBM) determined by XPS corresponds to that at ZnO surface and not in the bulk. On the other hand, the Fermi level should be constant even at the surface. Thus, the surface band bending can be calculated with using the VBM position \( (E_F - E_V) \) at the surface and the Fermi level position \( (E_C - E_F) \) in the bulk. As a result of the calculation, \( E_{bb} \) values for single crystal substrates and homoepitaxial films turned out to be positive as listed in Table 3-2. Based on these calculations, the surface energy bands of Zn- and O-polar ZnO single crystals and those of homoepitaxial films are upwardly bended. The sign of band-bending energy are identical.

Several surface electronic structures including band bending in ZnO and related materials are proposed theoretically and experimentally. A theoretical work by Meyer et al. proposed a charge rearrangement mechanism that the surface electrons at O-polar surface move to Zn-polar surface to cancel the internal electric field [29]. Several experimental reports that the presence of surface states [30], upward band bending with polarity dependence [31] and downward band bending or even surface electron accumulation [32, 33]. However, present study does not agree with any reports and only our work show the near surface structure of the epitaxial films. Near-surface structures of our epitaxial films with Zn- and O-polar surfaces are identical to those of the substrate with Zn- and O-polar surface including surface adsorption and/or atomic relaxation. This kind of experimental conditions, i.e. sample quality leads to our experimental results.
Table 3-2 Calculation results of the band-bending energy for ZnO. Here, the values of $E_{C_{BM}}-E_F$ are calculated using the carrier concentration of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polarity</th>
<th>$E_F-E_{V_{BM}}$ (eV)</th>
<th>$E_{C_{BM}}-E_F$ (eV)</th>
<th>$E_{bb}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Zn-polar</td>
<td>2.9</td>
<td>0.20</td>
<td>+0.3</td>
</tr>
<tr>
<td></td>
<td>O-polar</td>
<td>2.9</td>
<td>0.19</td>
<td>+0.3</td>
</tr>
<tr>
<td>Film</td>
<td>Zn-polar</td>
<td>2.9</td>
<td>0.15</td>
<td>+0.3</td>
</tr>
<tr>
<td></td>
<td>O-polar</td>
<td>2.6</td>
<td>0.05</td>
<td>+0.7</td>
</tr>
</tbody>
</table>
3-4 Conclusion

Optical emission from the plume during the homoepitaxial growth of ZnO thin films using PLD method was investigated and the relationships between the O/Zn flux ratio in the vapor phase and the film growth process were discussed. It is revealed that the O/Zn flux ratio could be controlled by laser fluence, oxygen pressure, and target-substrate distance. Surface morphology of ZnO thin films on Zn-polar ZnO substrates is improved through high temperature growth technique. Zn-rich flux promotes pit formation and O-rich flux yields the three-dimensional growth. The difference of the growth processes on Zn-polar and O-polar substrates was also discussed. The difference should be due to the difference in the number of surface dangling bond of oxygen adatoms, i.e. three dangling bonds for Zn-polar ZnO and one for O-polar ZnO. This difference results in the difference in the growth rate of films, minimum temperature for two-dimensional growth and more between Zn- and O-polar ZnO. These results indicates that in order to obtain atomically-flat Zn-polar ZnO films, approaches such as low-speed growth, high-temperature growth or oxygen-rich flux condition compared with O-polar ZnO is important.

Near-surface atomic structure and electronic structure of polar ZnO were studied using the ZnO single crystal substrates and the homoepitaxial films with atomically-flat step and terrace structure. Atom scattering spectroscopy revealed that near-surface structure of homoepitaxial ZnO films is identical to those of the single crystal substrate and simulated pattern using unstrained 2-nm-thick ZnO surface suggesting that the surface quality including the defect density and surface strains also equivalent. The surfaces of these samples show upward band bending regardless of the
polarity of ZnO, as revealed by X-ray photoelectron spectroscopy. We can conclude that the surface energy bands of all the samples (Zn- and O-polar ZnO single crystals and those of homoepitaxial films) are upwardly bended probably originated that the defect density of the epitaxial films at near-surface is as low as the single crystal substrates.
Fig. 3-15 Possible growth mode maps against growth temperature and laser fluence in the growth of ZnO by PLD
References


6886 (2002).


Chapter 4: Effect of Polarity on Mn Incorporation in the Epitaxial Growth of ZnO

4-1 Introduction

ZnO films, which are developing for conductive transparent oxide, are also expected for spintronic devices. Our group has succeeded in growth of ZnO-based diluted magnetic semiconductor (DMS)/semiconductor heterostructures that contain magnetic impurities in the barrier layer on sapphire (0001) and the ZnO (0001) single-crystal substrates [1-3]. Furthermore, spin-dependent transport in ZnO layer underneath of the ZnMnO barrier layer is also reported [4]. However, this magnetic interaction from ZnMnO DMS to ZnO is quite small because these ZnMnO films are n-type and exhibit paramagnetic nature. To increase the magnetic interaction, ferromagnetic ZnO is strongly desired. For that purpose, p-type ZnMnO would be required because ZnMnO with p-type conduction is theoretically predicted as a room-temperature ferromagnet [5]. In order to fabricate p-type ZnMnO, effective nitrogen doping is necessary. However, as described in Chapter 3, nitrogen accepter is quite deep (~100 meV) and strong self-compensation effect should happen. In this work, therefore, effective p-type doping using polarization of ZnO and ZnMnO is proposed. Simon et al. reported the effectively p-type doped AlGaN:Mg using the GaN-AlN composition grading toward the c-axis direction [6]. Discontinuity of spontaneous and piezoelectric polarization generates polarization charges at the surface and interface. Continuous polarization discontinuity can activate the bulk electrons and holes whose carrier density does not affected by
thermal energy [7, 8]. Ye et al. reported the formation of three-dimensional electron slabs base on graded-MgZnO/ZnO heterostructures [9]. However, polarity-induced $p$-type doping into ZnO and related materials has not been reported before.

Therefore, in this Chapter, thin film growth of ZnMnO and structural analysis for estimation of spontaneous and piezoelectric polarization were discussed in order to realize the polarity-induced p-type doping to ZnMnO.

4-2 Experimental

All the samples in this study were prepared by pulsed laser deposition (PLD). Undoped and 10 at.% Mn-doped ZnO ceramic target was used. Incorporated Mn concentration of O-polar ZnMnO films was determined to be 12 at.% by energy-dispersive X-ray spectroscopy. Surface morphologies of ZnMnO films were characterized by AFM (Veeco, NanoScope III / SII Nanotechnology, NanoNavi Real with S-image). Crystal structure and the lattice constant were evaluated by XRD (Philips, X’Pert MRD). Electrical properties were measured by Hall-effect measurement (Toyo Corporation, ResiTest 8300) using van der Pauw geometry. Indium solder was used for Ohmic electrode.

4-3 Results and Discussion

4-3-1 Optical Emission Analysis of ZnMnO Target in Pulsed Laser Deposition
At first, in order to understand the effects of laser ablation, optical emission from ZnMnO target was analyzed. Fig. 4-1 represents the emission spectrum measured under the conditions of $1 \times 10^{-5}$ Torr oxygen ambient and 96 mJ/cm$^2$ laser fluence. Emissions due to Zn*, O* and Mn* are clearly observed. Laser fluence dependence of emission intensity of each active species was evaluated. Fig 4-2 (a) shows laser fluence dependence of emission intensity Zn* (334 nm), O* (777 nm) and Mn* (403 nm), and their intensity ratios are shown in Fig. 4-2 (b). As described in Chapter 3, higher laser fluence leads to oxygen rich flux condition. Furthermore, At higher laser fluence condition, much more Zn* is supplied to the substrates than Mn*. 
Fig. 4-1 Optical emission spectrum of ZnMnO.

Fig. 4-2 Laser fluence dependent Optical emission intensity (a) and its ratio (b).
4-3-2 Surface Morphology of Zn-polar ZnMnO Thin Films

In the thin film growth of Mn-related DMS such as (In,Mn)As, low temperature growth (as low as ~200 °C) is often performed. In this work, at first, growth temperature was widely changed from 500 °C to 900 °C. Surface morphologies and XRD patterns of ZnMnO films grown on Zn-polar ZnO substrates are shown in Fig. 4-3. The sample grown at 500 °C exhibits very smooth surface with 0.21 nm RMS roughness (cf. ~0.15 nm for O-polar ZnO substrates), however, Mn-related secondary phase Mn$_2$O$_3$ 222 reflection is observed in XRD 20-ω profile. By increasing the substrate temperature, such secondary phases disappear in the XRD profiles. More detailed temperature dependent surface morphologies are shown in Fig. 4-4. At higher temperature two-dimensional growth of ZnMnO films are obtained as the same analogy of the growth on undoped ZnO. Thus, growth mode modulation of ZnMnO films was tried using knowledge of the case of ZnO. According to Ref. 10, growth mode transition is expressed as Fig. 4-5 against the growth rate and temperature. Discussion in Chapter 3 implies that adatoms on Zn-polar ZnO surface needs much higher energy for enough migration than O-polar ZnO, which corresponds to the shift of the boundary to higher growth temperature (shift to the right in Fig. 4-5). At enough high temperature as high as 800 °C, growth mode evolution between the two- and three-dimensional growth modes should be observed. Therefore, growth rate was tuned by changing the pulse repetition rate of excimer laser. Pulse repetition rate dependence of surface morphologies of ZnMnO films are shown in Fig. 4-6. The sample deposited at 1 Hz shows three-dimensional grains and the surface morphology is quite rough. By increasing the repetition rate, formation of these grains are suppressed and
Fig. 4-3 Growth temperature dependent AFM images and XRD $2\theta-\omega$ profiles of Zn-polar ZnMnO films.
Fig. 4-4 Growth temperature dependent AFM images of Zn-polar ZnMnO films
Fig. 4-5 Growth phase diagram of undoped ZnO thin films as a function of growth rate and temperature [10].
substrate-induced step edges are clearly observed in the samples grown at 5 and 8 Hz. Behavior of growth morphology evolution is also confirmed in the RMS value as shown in Fig. 4-7. Monotonous decrease in RMS roughness is confirmed as the repetition rate increases and the values almost saturates above 5 Hz.

4-3-3 Structural Analysis of ZnMnO Thin Films by X-ray Diffraction

In order to evaluate the lattice constant of ZnMnO films, XRD reciprocal space mapping around 20-25 reflection was carried out. The results are shown in Fig. 4-8. Dashed lines in Fig 4-8 (b) and (c) represent the lattice constants of fully-compressive strained O-polar $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{O}$ films which were grown using the same target ($\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$). As the repetition rate increases, in-plane lattice constant $a$ approaches that of compressive strained O-polar $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{O}$. In contrast, out-of-plane lattice constant $c$ is not influenced by growth rate. There are two possible reasons; one is the change in strain state of ZnMnO films depends on the growth rate, the other is change in the Mn incorporation efficiency. Here, unit cell volume of the ZnMnO films are compared with those of relaxed and strained ZnMnO films with O-polarity. Unit cell volume of ZnMnO films by assuming the wurtzite crystal structure ($= (3\sqrt{3}/2)a^2c$) is shown in Fig. 4-9 (a). Lattice constants of relaxed and compressively strained ZnMnO are expressed as [11],

\[
\begin{align*}
    a_0(x) &= 0.13x + 3.248 \\
    c_0(x) &= 0.13x + 5.205
\end{align*}
\]
Compressively strained:

\[ a(x) = 3.248 \]

\[ c(x) = 0.50x + 5.205 \quad \text{(in Å unit)} \]

where \( x \) indicates the molar fraction of Mn. Fig. 4-9 (b) represents the results of calculation. By increasing the repetition rate, the unit cell volume decreases by about 0.6 %. Volume of the sample grown at 1 Hz is almost the same as that of O-polar \( \text{Zn}_{0.88}\text{Mn}_{0.12}\text{O} \), which is apparently recognized by comparing Fig. 4-9 (a) and (b). Above results implies that solid solubility limit of Mn on Zn-polar ZnO is less than 12 at.%. As the growth rate increases, incorporated Mn concentration decreases due to the selective growth of ZnO. At 8 Hz, Mn concentration is low enough to incorporate Mn ions almost completely. In this case, \( \text{ZnMnO} \) film is able to be grown pseudomorphically. According to Fig. 4-8, solid solubility limit of Mn on Zn-polar ZnO surfaces is roughly obtained to be 8 at.% which is much lower than that on O-polar ZnO (>15 at.%). These results strongly suggest the difference in the Mn incorporation efficiency between on Zn-polar and on O-polar ZnO surfaces. This is not competing with the other cation-substitution type solid solution system such as \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) [12].
Fig. 4-6 Pulse repetition rate dependence of AFM images of Zn-polar ZnMnO films
Fig. 4-7 Pulse repetition rate dependence of RMS roughness of the samples in Fig. 4-6.
Fig. 4-8 Pulse repetition rate dependence of XRD-RMSs of Zn-polar ZnMnO films.
(a) Reciprocal space maps around 20-25 reflection.
(b) and (c) lattice constants deduced from RSMs.
Fig. 4-9 Unit cell volume of ZnMnO films. (a) repetition rate dependence of the volume of ZnMnO films on Zn-polar ZnO. (b) Calculated unit cell volume according to Ref. 11.
4-4 Conclusion

In this chapter, effects of Mn-doping on growth morphologies of polar-ZnO are discussed. Extremely low temperature growth induces the secondary phase of Mn$_2$O$_3$ revealed by X-ray diffraction. At high-temperature growth at 800 °C, ZnMnO films with flat surface morphology were obtained at higher growth rate contrary to our expectations. X-ray diffraction measurements revealed this is because Mn ions were not incorporated completely due to its solid soluble limit. By increasing the growth rate, preferential formation of ZnO becomes dominant and the surface roughness improved. These results suggest the difference in the Mn incorporation efficiency between on Zn-polar (~8 at.%) and on O-polar ZnO (>15 at.%) surfaces.

References


Chapter 5: Ultraslow Deposition of Pentacene Molecular Thin Films Grown on Polarity-Controlled ZnO Substrates

5-1 Introduction

Organic/inorganic heterostructures have become much important in the field of organic electronics [1-3]. Most of the organic optoelectronic devices are composed of organic and inorganic materials that act as the active layer, charge transport and injection layer, and their performance strongly depends on the interface of each material. These interfaces often cause troubles in charge injection into organic semiconductors [4], however, it can make us to produce the new and noble functionalities in organic electronics. For example, a threshold voltage tuning in the organic field-effect transistors was realized by inserting self-assembled monolayers between the gate dielectric and the organic semiconductor channel [5]. Metallic electrical conduction was performed in organic semiconducting heterointerface [6].

In this study, an attention is focused on zinc oxide (ZnO) as an inorganic semiconductor, because it is well known as a surface-sensitive material. For example, the surface of ZnO is metallized by hydrogen adsorption [7, 8]. Furthermore, ZnO with wurtzite structure has large crystallographic anisotropy in surface energy and spontaneous polarization [9] along the c-axis which produces the formation of two-dimensional electron gas (2DEG) at the ZnO-based heterointerface induced by polarity discontinuity [10, 11], though 2DEG is normally formed by using band-offset. Moreover, ZnO is an important candidate material in organic electronics because of the potential application to transparent electrodes and n-type semiconducting layers [12-14].
Electronic coupling between Wannier and Frenkel excitons in an organic material/ZnO systems have been experimentally observed. Electronic excitation energy can be transferred with an efficiency of up to 50% from an inorganic ZnO quantum well to an organic overlayer mediated via dipole-dipole interaction [15].

In order to discuss the properties of organic/ZnO interface, sufficient understandings about the formation process of molecular assembly and the interfacial energy-level alignment are required. The orientation of organic thin film is governed by the surface electronic structure including surface energy of substrate material [16]. For example, a change in adsorption state of organic molecules depending on the polarity of ZnO was reported [17, 18]. The surface termination or reconstruction, and electronic structure changes depending on the polarity of the ZnO substrate [19-21], the orientation of molecular thin films is affected by the polarity. However, there are few reports about the relationship between the growth morphology of organic thin films and the polarity of atomically flat ZnO substrate because it is very difficult to obtain the perfectly polarity-controlled ZnO for both faces even for using ZnO single crystal substrates. Especially for the O-polar ZnO substrates, very few researchers have succeeded in obtaining the atomically flat surface. However, we have successfully obtained atomically flat Zn-polar and O-polar ZnO surfaces without step bunching, surface defects and pits [22] that is quite important to examine the effect of polarity using perfectly polarity-controlled ZnO surface.

In this work, therefore, thin film of pentacene, which is one of the most popular small-molecule organic semiconductors, is grown on perfectly polarity-controlled ZnO surface by the ultraslow deposition method and the effects of the polarity on the growth process are discussed.
In this study, hydrothermally grown ZnO single-crystal substrates were used [23]. The Zn-polar (0001) and the O-polar (000-1) surfaces of ZnO substrates were cleaned and annealed to prepare atomically-flat surfaces that should be real polarity-controlled ZnO substrate [22], because the existence of damaged layer, pits, hillock and bunched step at the substrate surface indicates that the surface is no longer single polarity. Pentacene ultrathin films were grown on ZnO substrates by ultraslow molecular-beam deposition method [24] with a background pressure of \(5 \times 10^{-7}\) Pa. Thermally-oxidized silicon dioxide (SiO\(_2\)) was also used as a reference material for the substrate in this work. The growth rate was fixed to \(\sim 1\) molecular layer (ML) per hour. As for the growth of pentacene films on ZnO, the relation between polarity and morphology, orientation and thermal desorption behavior has been discussed before [25]. Compared to the report, the conditions are about 1/10 times much lower growth rate and about 30 °C higher substrate temperature in this work, in other words, near equilibrium growth conditions. Therefore, it is expected that growth morphology of pentacene films reflects molecule-substrate interaction effectively. Molecular orientation and film thickness of pentacene were determined by X-ray diffraction (XRD) using Cu \(K\alpha\) radiation (Bruker AXS, D8 Discover). Surface morphology was characterized by tapping-mode atomic force microscopy (AFM; SII NanoTechnology, SPI4000 with E-sweep).
5-3 Results and Discussion

5-3-1 Substrate and Temperature Dependent Surface Morphology of Pentacene/ZnO

To study the effect of the substrate-polarity on the film growth process of the pentacene, atomically flat surface with single-step and terrace structure without damaged layer, pits and hillocks should be required to obtain perfectly polarity-controlled ZnO substrate surface. Fig. 5-1 shows AFM images of the Zn-polar, (a) and O-polar, (b) ZnO substrates. The atomically flat surfaces with single-step and terrace structure without any defects [22] are recognized indicating that perfectly polarity-controlled ZnO substrates are obtained. The thickness dependence of the surface morphology of pentacene films grown on polarity controlled ZnO substrates and SiO$_2$ surface are shown in Fig. 5-2. All the samples shown in this figure are grown at 52 °C. On Zn-polar ZnO, three-dimensional nucleation of molecules is recognized in an only 1 ML deposited sample. And as the thickness increase, large grains with a few μm in diameter are formed in 9 ML pentacene on Zn-polar ZnO. On O-polar ZnO, large pentacene grains are also observed in the samples of 9 ML pentacene deposited ZnO. However, in the initial stage of growth, pentacene film on O-polar ZnO exhibits monolayer grains, which is a clear difference as compared with that on Zn-polar ZnO. It is revealed that the height of the pentacene monolayers is ~1.5 nm that roughly corresponds to the long axis of pentacene. This indicates the pentacene molecules stand on polar ZnO surfaces as well as on SiO$_2$ surfaces as confirmed in many other studies.
Fig. 5-3 shows the summary of RMS values with different substrate temperature and thickness. The RMS value of pentacene films grown on Zn-polar ZnO monotonously increases from the initial stage, which corresponds to the Volmer-Weber growth mode. Meanwhile, pentacene films on the O-polar ZnO exhibit the layer-by-layer mode at the first few MLs even at low substrate temperature, and then show a significant increase in the RMS. Therefore, in other words, a critical thickness
Fig. 5-1  AFM images of (a) Zn-polar and (b) O-polar ZnO substrates after surface treatment.

Fig. 5-2  Film thickness dependence of the AFM images of pentacene grown on Zn- and O-polar ZnO and thermally oxidized SiO$_2$. The substrate temperature is fixed at 52 °C.
Fig. 5-3  Thickness dependent root-mean-square surface roughness of pentacene/Zn-polar ZnO, pentacene/O-polar ZnO, pentacene/SiO$_2$. 
for three-dimensional growth of pentacene on the O-polar ZnO surface is thicker than that on Zn-polar ZnO. On the other hand, pentacene films grown on SiO₂ surfaces have comparatively small RMS values about 10 nm or less in all samples, which is similar to those on O-polar ZnO. These differences are probably due to the adversity of the surface diffusion of pentacene molecules originated from the larger number of dangling bonds at the oxygen-terminated Zn-polar ZnO surface.

In order to enhance the surface diffusion of pentacene molecule on ZnO, thin film deposition under higher substrate temperature condition was performed. Change in the surface morphology of pentacene films on Zn-polar ZnO, O-polar ZnO and the SiO₂ substrates are summarized in Fig. 5-4. The substrate temperature is elevated from 52 °C to 64 °C compared with that in Fig. 5-2. In pentacene films grown on SiO₂ surfaces, there are no significant changes against the thickness and the growth temperature as compared to Fig. 5-2. In the films on ZnO, pentacene molecules form monolayer grains at the initial stage of the growth (1~2 ML). These films are atomically flat and monolayer-height steps of ZnO (0.26 nm) are recognized in the AFM images. However, it is obvious that, as the growth goes on, the surface morphologies of the films on Zn- and O-polar ZnO get rough at the thickness above 6 ML and aggregation begins to occur. After 9-ML-thick deposition, eventually, very flat region and aggregated regions coexist in the same surface and maximum difference in height exceeds 50 nm as shown in Fig. 5-5. Such aggregation is not recognized in pentacene/SiO₂ suggesting that the interface between polar ZnO and pentacene are energetically unstable. As described above, two-dimensional growth at the initial stage are realized even on Zn-polar ZnO by elevating the substrates temperature by 12 °C, however, molecular aggregation on Zn- and O-polar ZnO is induced.
Fig. 5-4  Surface morphologies of pentacene films grown on ZnO and SiO$_2$ substrates grown at 64 °C as a function of layer thickness.

Fig. 5-5  Surface morphologies of 9-ML-thick pentacene on Zn-polar ZnO grown at 64°C.
Fig. 5-6 (a)-(c) shows change in root-mean-square (RMS) values of the surface roughness of the pentacene on Zn-polar (open circle) and O-polar ZnO (open square), SiO$_2$ (open diamond) substrates. Although the RMS of the pentacene on SiO$_2$ does not change at the thickness below 9 ML, those of ZnO drastically increase above 6 ML. There are little differences in the surface morphologies between the both polarities of ZnO. Fig. 5-7 is the schematic of the growth process of the pentacene on ZnO substrate. At the thickness below 4.5 ML, pentacene grows with layered structure. However, molecules near the substrate become unstable and move to the upper terrace at the thickness above 6 ML. This mechanism is considered from the AFM images of the aggregated grain i.e. periphery of the aggregated grain is higher compared to other regions. This growth and aggregation processes are almost identical to that on each ZnO surface. Moreover, the surface roughness values of pentacene/SiO$_2$ samples exhibit no substrate temperature dependences. They also originated from the diffusibility of pentacene molecule on SiO$_2$ surface. These results indicate that the aggregation of pentacene molecules as shown in Fig. 5-4 are thermally activated and it originated from the energetic balance among surface energies of ZnO and pentacene, and cohesion energy at the pentacene/ZnO interface, and aggregation energy of pentacene molecule. At a high substrate temperature (64 °C), pentacene molecules have enough migration energy resulting in a layer-by-layer like growth mode at the initial stage (1~2 ML). However, at a thickness region of 9 MLs, excess thermal energy enhanced desorption of the molecule moving to upward terrace of the surface so as to minimize the total interface energy which is schematically illustrated in Fig. 5-7. Eventually, molecular aggregation occurs as shown in Fig. 5-4.
Fig. 5-6  Film thickness dependences of RMS roughness of pentacene grown on (a) Zn- and (b) O-polar ZnO and (c) thermally oxidized SiO$_2$. The samples with different substrate temperature are shown by solid circles (64 °C), and solid squares (58 °C), respectively. (d) Schematics of the speculated mechanism for molecular aggregation.

Fig. 5-7  Schematics of the speculated mechanism for molecular aggregation on ZnO.
5-3-2 Molecular Orientation of Pentacene/ZnO Studied by X-ray Diffraction

At low temperature (52 °C), clear differences in growth process could be observed between Zn-polar and O-polar ZnO substrates. However, there is little difference in the surface morphology of pentacene at 64 °C. Therefore, X-ray diffraction measurements were performed in order to evaluate the molecular orientation and the polymorph of the pentacene films. Typical XRD patterns of the pentacene thin films with 9 ML grown on Zn- and O-polar ZnO and thermally oxidized SiO$_2$ substrate are shown in Fig. 5-8. All the samples in this study exhibit 00$l$ Bragg reflections ($l = 1, 2, 3$) of pentacene indicating that the pentacene molecules grow with upright orientation on polar ZnO surfaces. Moreover, diffractions with different $d$-spacing values are observed in the XRD patterns. They can be assigned to the thin-film phase ($d_{001}=1.54$ nm) and the bulk phase ($d_{001}=1.45$ nm) based on previous reports [29, 30]. It is different from the report by El Helou et al. which obtained only the thin-film phase of pentacene up to the thickness of 35 nm [25]. The formation of these polymorphs can result from the competition of substrate-molecule interaction and intermolecular interaction during the crystal growth. The thickness dependence of the fraction of the thin-film and the bulk phases $I_{TF}/(I_{TF} + I_B)$ was plotted in Fig. 5-9 (a) and (b) so as to evaluate change in polymorph ratio during the growth. 002 reflections were used in this analysis. The Polymorph ratio for the samples with the thickness below 4 MLs cannot be evaluated due to the thin thickness. In the samples grown at 64 °C (Fig. 5-9 (a)), the thin-film phase is dominant at the initial stage of thin film growth of pentacene in the same as previous reports [30, 31]. Intensity ratio $I_{TF}/(I_{TF} + I_B)$ at the initial stage (< 6 ML) is near 1 indicating that pentacene consist of only thin-film phase. In thicker region, though the
growth continues, the ratios for pentacene/O-polar ZnO and pentacene/SiO$_2$ do not show significant changes at the thickness up to 9 MLs. However, the fraction of the thin-film phase for pentacene/Zn-polar ZnO drastically decreases at the thickness above 8 MLs. On the other hand, as shown in Fig. 5-9 (b), the samples grown at 52 °C which does not show any molecular aggregation, the changes in $I_{TF}/(I_{TF} + I_B)$ is quite moderate as compared with Fig. 5-9 (a). Consideration with the results of the surface morphology and molecular orientation discussed above, quite a little difference in the interaction between the molecules and the substrates causes different growth morphologies such as layer-by-layer growth and three-dimensional growth including aggregation. Furthermore, the thin-film phase is a dominant polymorph in pentacene/ZnO and the formation of bulk phase is correlated with the molecular aggregation during the growth.
Fig. 5-8  XRD patterns of pentacene films grown on Zn- and O-polar ZnO substrates at 64 °C.
Fig. 5-9  Composition ratio of thin-film ($I_{TF}$) and bulk ($I_B$) phase pentacene molecules in pentacene/ZnO grown at 64 °C (a) and 52 °C (b), respectively.
5-4 Conclusion

By using the ultraslow deposition method, two-dimensional growth of pentacene ultrathin films was observed on SiO₂, but the aggregation of pentacene molecules was recognized on ZnO substrate regardless of its polarity. At a substrate temperature as high as 64 °C, the surface morphology of the pentacene on O-polar ZnO is identical to that on Zn-polar ZnO. However, the ratio between the bulk phase and film phase of pentacene apparently increases during the aggregation in pentacene/Zn-polar ZnO samples, which was not observed in pentacene/O-polar ZnO. At a lower substrate temperature, on the other hand, surface morphology exhibits a clear difference between the both polarities; pentacene films on the Zn-polar ZnO show three-dimensional growth from the early stage of the deposition originating from the surface diffusibility of pentacene molecules on the ZnO surfaces. These results give an important implication for developing high-quality organic/ZnO heterostructures with a well-aligned molecular crystal.

References


Chapter 6: Polarity-Dependent Interface Formation in Pentacene/ZnO Heterostructures

6-1 Introduction

Recently, organic/inorganic hybrid heterostructures have attracted much attention for its excellent optical and electrical properties achieved by combining the organic and the inorganic semiconductors. For example, enhanced photoresponses such as photovoltaic effects at the organic/inorganic interface has been interesting [1].

ZnO is a semiconductor with a wide band-gap (3.37 eV) that exhibits optoelectronic properties in the ultraviolet region [2, 3]. Excitons related to charge transfer across the interface in organic/ZnO systems have been observed [4]. A good Schottky contact to $n$-type ZnO was reported using a conducting polymer, and this enabled the electric field tuning of two-dimensional electrons in Mg$_x$Zn$_{1-x}$O/ZnO heterostructures [5, 6]. ZnO has crystallographic anisotropy within its wurtzite structure, and therefore exhibits crystallographic polarity along its $c$-axis. The polarity of ZnO affects its surface dangling-bond configuration and spontaneous polarization, and eventually leads to differences in crystal growth morphology, impurity incorporation and surface/interface electronic structure [7-10]. When an organic/ZnO heterointerface is formed, the growth morphology of the organic material and the resulting interface electronic structure can be modulated by ZnO [11-13]. Kim et al. reported the electronic properties of interfaces between copper phthalocyanine films and polar GaN surfaces [14]. Ozawa et al. reported the effects of polarity of ZnO on molecular assembly and
decomposition, and interface energy-level alignment in tetrathiafulvalene/ZnO heterostructures [15]. However, there have been no reports about the relationship between the polarity and interface electronic structure, using the change in electronic states during a few monolayers’ growth of organic materials on polar inorganic semiconductors.

In Chapter 5, the growth morphologies of small-molecule organic semiconductor pentacene on polar and nonpolar ZnO surfaces were discussed and the author has been successful in layer-by-layer assembly of pentacene molecules on polar ZnO. In this chapter, therefore, electronic structure of organic/ZnO hetero-interface was discussed. Local potential measurement by scanning Kelvin probe force microscopy and X-ray photoelectron spectroscopy were carried out. The effect of polarity on the interface electronic structure in layer-by-layer pentacene ultrathin films on polar ZnO surfaces is investigated.

6-2 Experimental

Hydrothermally grown ZnO single crystals (Tokyo Denpa) were used as substrates [16]. ZnO surfaces containing Zn- and O-polar faces were chemically etched, and annealed to prepare atomically flat surfaces with 0.26-nm-high atomic steps. This corresponded to a charge-neutral molecular layer, with no defects such as pits, hillocks and bunched steps [17]. Pentacene ultrathin films were grown on substrates by ultraslow deposition [18]. The growth rate and substrate temperature were fixed to ~1 molecular layer (ML) per hour and 64 °C, respectively. The molecular orientation and thickness of pentacene films were determined by X-ray diffraction (XRD), using Cu $K_a$ radiation
(Bruker AXS, D8 Discover). Surface morphologies of pentacene films were characterized by atomic force microscopy (AFM; SII NanoTechnology, SPI4000), the details of which are available elsewhere [19]. Local surface potential measurements by scanning Kelvin probe force microscopy (KFM) were simultaneously performed by the AFM instrument. An Au-coated cantilever was used in surface potential measurements. The chemical bonding states of pentacene and ZnO were characterized by X-ray photoelectron spectroscopy (XPS; Thermo Scientific, Theta Probe). Al $K_{\alpha}$ radiation ($h\nu=1486.6$ eV) was used as the excitation source, with a total energy resolution of 700 meV. Binding energies were calibrated from the Au 4$f_{7/2}$ photoemission peak at 84.0 eV.

6-3 Results and Discussion

6-3-1 Surface Potential Measurement of Pentacene/ZnO Heterostructures by Scanning Kelvin Probe Force Microscopy

Interfacial electronic structures in organic-coated inorganic surfaces are affected by the organic materials’ molecular orientation. The ionization potentials of pentacene layers on metals and insulators vary with pentacene orientation because of the existence of an intramolecular dipole [20, 21]. XRD measurements of pentacene/ZnO heterostructures have been reported, which aid our understanding of the pentacene orientation on ZnO surfaces [19]. Typical XRD patterns of the pentacene thin-film phase ($d_{001}=1.54$ nm) have been reported from samples containing one
pentacene ML [22, 23]. Below 3 MLs thickness, only the thin-film phase with upright (00/I) orientation was observed. Above 4.5 MLs, the thin-film phase and bulk phase ($d_{001}=1.45$ nm) coexists. This indicated that some interaction between pentacene and ZnO exists at thicknesses <3 MLs.

Pentacene ultrathin films exhibit upright orientations on Zn- and O-polar ZnO surfaces. KFM surface potential measurements were recorded on substrate surfaces before and after deposition of 1, 2, 3 and 9 pentacene MLs, to evaluate the electronic state of pentacene during deposition. The surface morphologies of pentacene grown on Zn- and O-polar ZnO surfaces are shown in the left side of Fig. 6-1 (a) and (b), respectively. The nominal thicknesses of these samples are 1–3 MLs. An atomically flat region with trace monolayer growth over a wide range is observed, indicating that the pentacene thin film grows in a layer-by-layer mode during the initial growth. Surface potential images taken in the same areas are shown in the right side of Fig. 6-1 (c) and (d), respectively. While the surface topographic images appear comparable, a difference in surface potential of the substrate and first and second layers of the pentacene islands is apparent. The potential for the Zn-polar ZnO surface is larger than that for the O-polar ZnO surface. However, the surface potential of pentacene decreases at thicknesses >3 MLs, and the difference in potential with pentacene growth cannot be distinguished. This suggests that the electronic state of pentacene ultrathin films of thicknesses <2 MLs is modified by the ZnO surface. Similar phenomena have been observed in other organic semiconductor/metal systems [24, 25] and in organic/inorganic semiconductor heterostructures [26].

The dependence of pentacene/ZnO surface potential on pentacene film thickness is shown in Fig. 6-2. The surface potential varies with pentacene thickness at
Fig. 6-1  Surface potential of pentacene/ (a) Zn-polar and (b) O-polar ZnO by KFM.
Fig. 6-2  Surface potential of pentacene/ZnO against the thickness of pentacene. Values of absolute thickness is adopted for those below 2 MLs, and average thickness above 3 MLs.
<2 MLs. The change in monolayer step potential becomes unclear at pentacene thicknesses >3 MLs. Therefore, absolute potential values are used below 2 MLs, and average potential values are used above 3 MLs. The surface potential of 0 meV corresponds to the work function of the Au-coated probe, which is ~5.1 eV. For both Zn- and O-polar ZnO, the surface potential increases within the first 2 MLs, and then decreases to reach its original surface potential of bulk pentacene (~5 eV) [27, 28] on both Zn- and O-polar ZnO. This potential increase at thicknesses <2 MLs corresponds to the depletion of pentacene on Zn-polar ZnO. It is more predominant than that on O-polar ZnO, suggesting that the electronic interaction at the pentacene/Zn-polar ZnO interface is stronger.

6-3-2 Polarity-dependent Interface Formation in Pentacene/ZnO Heterostructures

XPS was used to study the changes in electronic state of the pentacene/ZnO interface. The binding energies of Zn $2p_{3/2}$ and Zn $3d$ which correspond to core-level electron shift to positive side by pentacene deposition for both Zn-polar and O-polar ZnO surfaces. Fig. 6-3 (a) and (b) show the photoemission spectra of valence band regions from Zn-polar (a) and O-polar (b) ZnO substrate surfaces and 1 ML pentacene deposited substrates. Peaks at around 10.2 eV correspond to Zn $3d$, and shift to higher binding energy by 0.4–0.5 eV after the deposition of 1 ML of pentacene. Zn $2p$ and O $1s$ core spectra of the Zn- and O-polar ZnO substrates exhibit similar tendencies (not shown), suggesting that the pentacene layer moves the Fermi level of ZnO toward
The HOMO state of pentacene exhibits polarity dependence. Angle-resolved XPS was used to investigate changes in the electronic states of pentacene/ZnO interfaces. Fig. 6-4 shows the change in Zn 2p\textsubscript{3/2} photoemission peak against photoelectron escape depth. The photoelectron escape depth is proportional to the inelastic mean free path (IMFP) × cos(take-off-angle), according to the Tanuma-Powell-Penn (TPP-2M) equation [29, 30] for Zn- and O-polar ZnO with and without pentacene layers. As the photoelectron escape depth decreases, the surface sensitivity decreases, and the emission of O- and Zn-polar ZnO substrate peaks shift to higher binding energies. This suggests that the electronic band structures of both ZnO surfaces bend downward before pentacene deposition. The binding energy and degree of downward band bending differ between the two polarity surfaces, with a larger band bending observed for O-polar ZnO. After the deposition of 1 ML of pentacene, the samples exhibit downward band bending at ZnO surfaces regardless of polarity. The
Fig. 6-3  Valence region photoemission spectra of pentacene/ZnO heterostructures and ZnO single crystals. The left side shows (a) 9ML, and (b) 1ML-pentacene covered Zn-polar ZnO, and (c) Zn-polar ZnO bare surface. Corresponding plots for O-polar samples are shown in the right side ((d), (e) and (f)).
Fig. 6-4  Zn 2p\textsubscript{3/2} photoemission spectra for pentacene/ZnO heterostructures. (a) Angle-resolved spectra for 1ML-pentacene/Zn-polar ZnO. (b) Take-off angle dependence of the Zn 2p\textsubscript{3/2} peak positions for pentacene/Zn-polar ZnO (open and closed circles) and for pentacene/O-polar ZnO (open and closed squares). Plots for 1ML-pentacene samples denote open symbols and dashed lines and 9ML-pentacene samples denote closed symbols and solid lines.
band bending of the Zn-polar ZnO surface increases with pentacene deposition. That of the Zn-polar ZnO surface does not change within the experimental uncertainty. A shift to higher binding energy implies greater carrier accumulation at the ZnO surface.

The above results indicate a change in the electronic state of pentacene/ZnO interfaces with pentacene deposition, which are shown in Fig. 6-5. The electronic band structures of both ZnO surfaces bend downward. The binding energies and degree of downward band bending increase upon approaching the pentacene/ZnO interface, and these values for the O-polar ZnO surface are larger than those for the Zn-polar ZnO surface. The energy shift of 0.2–0.3 eV is sufficient for the accumulation of surface electrons, taking into account typical donor levels of ZnO [31]. This suggests that greater carrier accumulation occurs at the pentacene/O-polar ZnO interface, which provides a screening effect to inhibit the interaction between pentacene and ZnO. The electronic state of pentacene ultrathin films increases with increasing pentacene thickness at <2 MLs. This increase is larger for pentacene/Zn-polar ZnO than for pentacene/O-polar ZnO indicating that the interaction of pentacene and O-polar ZnO is suppressed by charge accumulation. Therefore, the shoulder corresponding to the HOMO state of pentacene is observed at the VBM of ZnO. Electronic orbital hybridization should occur at the pentacene/Zn-polar ZnO interface, so the surface band bending of Zn-polar ZnO increases upon pentacene deposition. A quantum structure such as a two-dimensional electron gas may be obtained for the pentacene/O-polar ZnO surface, because of carrier accumulation. However, the electronic structure of the Zn-polar ZnO surface is more easily modulated than that of the O-polar ZnO surface. These results demonstrate the potential of the use of polarization for organic/polar material interfaces in innovative molecular electronics.
Finally, the Hall-effect measurement for 1 ML pentacene/Zn-polar ZnO was carried out. Temperature dependent electron transport properties are shown in Fig. 6-6. In this measurement, silver paste was used for forming Ohmic contact. It was confirmed that Hall voltage of the samples was negative, which indicates the samples are \( n \)-type semiconductor. For comparison, data of ZnO substrate are also shown. Temperature dependence of sheet resistance (a) and sheet carrier concentration (b) of pentacene/ZnO exhibit semiconductor-like behavior, i.e., suppressed electron activation and insulating at low temperature. Compared with those of ZnO substrate, sheet electron density is enhanced \( \sim 10 \) times higher than that of ZnO, which implies that electrons are injected from pentacene into ZnO. Electron mobility of pentacene/ZnO shows monotonous decrease by lowering temperature (Fig. 6-6 (c)), indicating that suppressed electron scattering is not observed in this system. However, electron concentration of pristine ZnO substrates used in this study is about \( 3 \times 10^{16} \) cm\(^{-3} \) which includes enough defects and impurities to disturb the formation of 2DEG. Higher quality ZnO with electron density \(< 10^{16} \) cm\(^{-3} \) will be able to reveal the interface formation mechanisms in detail.
Fig. 6-5 Schematic illustration of energy-level alignment of polar ZnO/pentacene heterostructures speculated in this study. The words $E_{\text{vac}}$, $E_C$, $E_V$, and $E_F$ in this figure denote the energy levels of the vacuum, the conduction band minimum, the valence band maximum, and the Fermi level, respectively.
Fig. 6-6 Electron transport properties of 1ML pentacene/Zn-polar ZnO (closed circles) and ZnO substrate (closed square).
6-4 Conclusion

In conclusion, KFM and angle-resolved XPS analyses of pentacene/polar ZnO heterostructures were carried out, using atomically flat ZnO single crystal surfaces. The electronic band structures of both ZnO surfaces bend downward. The binding energies and degree of downward band bending increase upon approaching the pentacene/ZnO interface. These values for the O-polar ZnO surface are larger than those for the Zn-polar ZnO surface. The interaction of pentacene and O-polar ZnO is suppressed because of charge accumulation. The strong interaction between pentacene and Zn-polar ZnO can more easily modulate the electronic state. This suggests that the interfaces of organic/polar materials have potential in advanced electronics. Hall-effect measurement for pentacene/Zn-polar ZnO revealed that electron concentration of ZnO in the heterostructure is about 10 times higher than that of ZnO single crystal substrate. This suggests that the electrons in pentacene are partially transferred to superinterface of pentacene/ZnO.

References


(2005).


Chapter 7: Summary

This thesis has been devoted to the study on morphology control and polarization engineering of ZnO-based heterostructures. The main results in this work are summarized as follows.

In Chapter 2, surface preparation process of polar ZnO single crystal substrates, especially Zn-polar ZnO (0001) are discussed. Thermal annealing process in air, in vacuum, and in oxygen ambient cannot remove the topmost surface damaged layers and resulted in surface segregation. These results indicate that preparation of stoichiometric surface before annealing is important for obtaining epitaxy-ready Zn-polar ZnO surfaces. Atomically-flat surface of the Zn-polar ZnO substrates are realized by using wet-chemical etching by HF and UV-ozone cleaning which can remove the surface damaged layer without any pit formation.

In Chapter 3, growth mode of homoepitaxial films on polarity-controlled ZnO substrates by the pulsed laser deposition is discussed. In order to prepare an atomically-flat ZnO homoepitaxial films with polarity-controlled structure, VI/II ratio, growth rate and substrate temperature are controlled. Surface morphology of ZnO thin films on Zn-polar ZnO substrates is improved through high temperature growth technique. Zn-rich flux promotes pit formation and O-rich flux yields the three-dimensional growth. The difference of the growth processes on Zn-polar and O-polar substrates was also discussed. The difference should be due to the difference in the number of surface dangling bond of oxygen adatoms, i.e. three dangling bonds for Zn-polar ZnO and one for O-polar ZnO. This difference results in the difference in the growth rate of films, minimum temperature for two-dimensional growth and more...
between Zn- and O-polar ZnO. These results indicate that in order to obtain atomically-flat Zn-polar ZnO films, approaches such as low-speed growth, high-temperature growth or oxygen-rich flux condition compared with O-polar ZnO is important. Atom scattering spectroscopy revealed that near-surface structure of homoepitaxial ZnO films is identical to those of the single crystal substrate and simulated pattern using unstrained 2-nm-thick ZnO surface suggesting that the surface quality including the defect density and surface strains also equivalent. The surfaces of these samples show upward band bending regardless of the polarity of ZnO, as revealed by X-ray photoelectron spectroscopy. We can conclude that the surface energy bands of all the samples (Zn- and O-polar ZnO single crystals and those of homoepitaxial films) are upwardly bended probably originated that the defect density of the epitaxial films at near-surface is as low as the single crystal substrates.

In Chapter 4, the author tried to prepare thin films of a ZnO-based diluted magnetic semiconductor Zn$_{1-x}$Mn$_x$O (ZnMnO, $x \sim 0.12$) and its growth morphology is discussed by using knowledge obtained in Chapter 3. Solution state of Mn ions and strain by substrates were characterized by XRD, and the polarity effects on these properties of ZnMnO thin films were discussed. Extremely low temperature growth induces the secondary phase of Mn$_2$O$_3$ revealed by X-ray diffraction. At high-temperature growth at 800 °C, ZnMnO films with flat surface morphology were obtained at higher growth rate contrary to our expectations. X-ray diffraction measurements revealed this is because Mn ions were not incorporated completely due to its solid soluble limit. By increasing the growth rate, preferential formation of ZnO becomes dominant and the surface roughness improved. These results suggest the difference in the Mn incorporation efficiency between on Zn-polar (\~8 at.%) and on
Chapter 5 and Chapter 6 focused on the growth morphology and polarity-dependent interface formation in organic semiconductor/polar ZnO heterostructures in order to control the electronic properties of organic semiconductor by polarization of ZnO. By using the ultraslow deposition method, two-dimensional growth of pentacene ultrathin films was observed on SiO₂, but the aggregation of pentacene molecules was recognized on ZnO substrate above 6 MLs regardless of its polarity. At a substrate temperature as high as 64 °C, the surface morphology of the pentacene on O-polar ZnO is identical to that on Zn-polar ZnO. However, the ratio between the bulk phase and film phase of pentacene apparently increases during the aggregation in pentacene/Zn-polar ZnO samples, which was not observed in pentacene/O-polar ZnO. At a lower substrate temperature, on the other hand, surface morphology exhibits a clear difference between the both polarities; pentacene films on the Zn-polar ZnO show three-dimensional growth from the early stage of the deposition originating from the surface diffusibility of pentacene molecules on the ZnO surfaces. The electronic band structures of both ZnO surfaces bend downward by ~0.3 eV as revealed by XPS. Further, the values of binding energy and the degree of the downward band bending become larger with approaching the pentacene/ZnO interface and those values of O-polar ZnO surface are larger than those of Zn-polar ZnO surface. The interaction at pentacene/O-polar ZnO is suppressed due to the existence of charge accumulation. On the other hand, the strong interaction between pentacene and Zn-polar ZnO can more easily modulate the electronic state. Hall-effect measurement for pentacene/Zn-polar ZnO revealed that electron concentration of ZnO increased about 10 times higher than that of ZnO single crystal substrate suggesting that the electrons in
pentacene are partially transferred to superinterface of pentacene/ZnO.

Results described above establish the controllability of polarization applicable even in practical electronic devices. Much more tunable polarization-controlled heterostructure can be realized using (Zn,Mn,Mg)O by overcoming solid solution limit of Mn.
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### Original Articles Regarding This Thesis

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<td>4</td>
<td>Near-surface structure of polar ZnO surfaces prepared by pulsed laser deposition</td>
<td>T. Nakamura, A. Ashida, T. Yoshimura, N. Fujimura</td>
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<td>Chapter 3</td>
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<td>Fabrication and Magneto-Transport Properties of ( \text{Zn}<em>{0.88-x}\text{Mg},\text{Mn}</em>{0.12}\text{O}/\text{ZnO} ) Heterostructures Grown on ZnO Single-Crystal Substrates</td>
<td>K. Masuko, T. Nakamura, A. Ashida, T. Yoshimura, N. Fujimura</td>
<td>Advances in Science and Technology 75, pp. 1-8 (2010).</td>
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Effect of Substrate Polarity on the Growth Process of Pentacene Films on Polarity-Controlled ZnO Substrates

T. Nakamura
T. Nagata
R. Hayakawa
S. Oh
N. Hiroshiba
T. Yoshimura
N. Fujimura
T. Chikyow
Y. Wakayama


Chapter 5

Effects of crystallographic polarity on the electronic state at pentacene/ZnO interfaces

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T. Nagata
R. Hayakawa
S. Oh
N. Hiroshiba
T. Yoshimura
N. Fujimura
T. Chikyow
Y. Wakayama


Chapter 6

Other Article Regarding This Thesis

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