FAST TRACK COMMUNICATION

Surfactant effects of lithium dopant during molecular beam epitaxy of ZnO films

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Abstract
Surfactant effects of lithium dopant during epitaxial growth of ZnO films were
investigated by using reflection high-energy electron diffraction, atomic force
microscopy, and x-ray photoemission spectroscopy (XPS). Three-dimensional
ZnO epitaxial growth was found to be changed into the two-dimensional layer-
by-layer mode after the onset of Li doping, resulting in atomically flat ZnO
surfaces. Li atoms, adsorbed on the growth front, induced 12×12 and 6×6
reconstructions on the polar $ZnO(000\bar{1})$ surface. Further XPS depth profiling
investigations of these reconstructed surfaces demonstrated that most of the Li
atoms were segregated within the outermost 1 nm ZnO surface. It was proposed
that the spontaneous depolarization of the polar ZnO surface caused by the
enrichment of Li dopant would reduce the charge accumulation on the polar
surface to decrease the surface energy and finally result in the transition of
surface morphologies and surface structures.

1. Introduction

Zinc oxide, as a wide band-gap semiconductor with a large exciton binding energy of 60 meV,
has attracted much attention due to the potential applications in short-wavelength optoelectronic
devices such as light emitting diodes and laser diodes [1]. Ascribed to the self-compensation
of some native defects and/or interstitial hydrogen [2, 3], the unintentionally doped ZnO films
usually exhibit strong n-type conductivity, which makes the manufacture of low-resistivity p-
type ZnO difficult. With a number of candidates among group-V and group-I elements, the
optimal choice of acceptor species remains undetermined. Lithium, as a potential p-type dopant
for ZnO, has received particular attention. In recent years, many experimental and theoretical
studies have been carried out on the preparation and the conductive properties of ZnO with Li
dopant. However, the carrier type (n-type, p-type, or semi-insulator) of Li-doped ZnO is still
controversial [4–7]. To optimize the doping process and hence realize p-type conductivity of

ZnO:Li film, it is essential to clarify the doping behavior of Li atoms during the ZnO epitaxial growth.

In addition, surface control in epitaxial growth plays a critical role in the design and the fabrication of device structures, such as quantum wells and p–n junctions, since the growth basically is a surface phenomenon [1]. It was discovered more than a decade ago that, during the epitaxy of Si(111) films, a third element acting as a surface active agent (surfactant) can lead to layer-by-layer growth [8] and drastically improve film quality [9]; this is called surfactant mediated epitaxy (SME). Since then, much effort has been devoted to the SME growth of many hetero- and homoepitaxial systems. The use of small amounts of Mg dopant (or Ga, As), for example, could suppress the three-dimensional (3D) islanding of GaN and engender a typical two-dimensional (2D) layer-by-layer growth [10–13]. However, so far, very little is known about the surfactant effects during ZnO epitaxy. In this letter, we show evidence that the Li dopant acts as a surfactant element during ZnO epitaxial growth. A growth mode transition from 3D to 2D induced by lithium dopant has been revealed, and surface reconstructions have been observed as a result of the participation of Li surfactant.

2. Experimental details

ZnO samples were grown on $MgAl_2O_4(111)$ substrate by radio frequency plasma-assisted molecular beam epitaxy (rf-MBE). According to our previous studies, O-polar ZnO films could be obtained by using an ultrathin Mg wetting layer deposited on an oxygen-plasma-pretreated $MgAl_2O_4(111)$ surface [14]. By delicate control of the Zn/O flux ratio, smooth ZnO surfaces with a 3×3 reconstruction could be achieved despite the great strain caused by the lattice mismatch between film and substrate. Otherwise, a rough surface would be formed in a Volmer–Weber (VW) island growth mode due to the polar nature of the surface and its instability, which have been investigated by Noguera, Diebold, Woell, and coworkers [15–19]. In this study, the rough ZnO films, grown in the 3D mode, have served as the growth templates for surfactant mediated epitaxy of Li-doped ZnO films. The Li flux was in the range from 10^{11} to 10^{12} atoms cm^{-2} s^{-1}, about two orders less than the Zn flux (2.0×10^{14} atoms cm^{-2} s^{-1}). With the onset of doping growth, the dopant-induced surfactant effects were observed and further studied by *in situ* reflection high-energy electron diffraction (RHEED) and *ex situ* atomic force microscopy (AFM). X-ray photoemission spectroscopy (XPS) measurements were performed on a VG MKII spectrometer to investigate the surfactant distribution with the depth from the surface. Atom concentration was calculated using the method of single-element standard sensitivity factors.

3. Results and discussion

It has been revealed that the use of a low dose of surfactant may change the mobility of deposited atoms on a surface, and then result in the growth mode transition of epitaxial films [8, 12, 13]. Here, we describe the RHEED observations of the growth mode transition during dopant-mediated ZnO epitaxy. Figure 1 shows RHEED evolution from the rough surface of undoped ZnO film to the flat Li-mediated surface, with electron beam incident azimuths along $[11\bar{2}0]_{ZnO}$ and $[10\bar{1}0]_{ZnO}$ directions, respectively. Patterns of the island-featured surface of undoped ZnO are shown in figures 1(a) and (b), which are spotty and dim. When ZnO SME growth began, the spotty patterns were found gradually to elongate. About 30 min later, the spotty patterns were completely replaced by sharp streaky ones, as shown in figures 1(c) and (d), which indicated the accomplishment of the transition from the 3D VW growth to the 2D Frank-van der Merwe (FM) mode. The suppressed ZnO islanding and the modified smooth
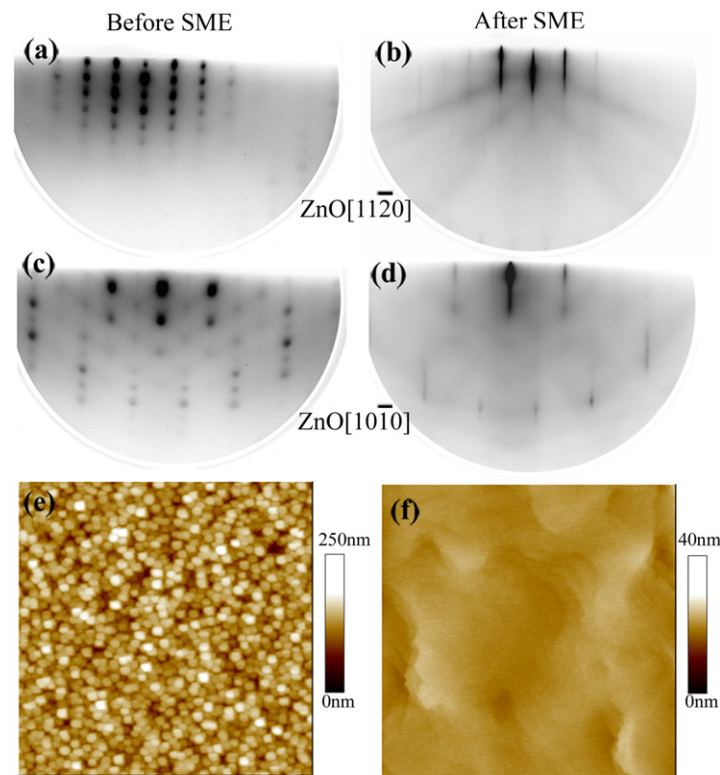
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Figure 1. RHEED patterns and AFM images of ZnO surfaces, (a), (b), (e) without Li surfactant, and (c), (d), (f) with Li surfactant. AFM image size is 5 μm × 5 μm.

(This figure is in colour only in the electronic version)

surface demonstrate the surfactant action of Li dopant during the SME growth. Furthermore, the clear Kikuchi lines and Kikuchi bands in figures 1(c) and (d) imply that the crystal quality of Li-doped ZnO film is greatly improved.

To further identify the growth mode transition, surface morphologies of the above-mentioned ZnO films were studied by AFM. Figure 1(e) shows the AFM image of a rough ZnO surface before SME. Typical VW growth results in the island-featured surface, whose root mean square (RMS) roughness is as high as 21.0 nm in a scanned area of 5 × 5 μm^2. The islands are uniform with diameters of around 100 nm and heights near 100 nm. On the other hand, the ZnO surface after Li doping is very flat, with an RMS roughness as small as 1.3 nm, as shown in figure 1(f). Large terraces with a maximum width of more than 1 μm can be observed on smooth ZnO surfaces. The step height (0.28 nm) is similar to the distance between two consecutive Zn–O bilayers along the c-axis in a wurtzite ZnO lattice (0.26 nm).

Furthermore, we found that Li surfactant induced some well-defined reconstructions on the flat ZnO(000$\bar{1}$)–O surfaces. RHEED patterns of the 12 × 12 and 6 × 6 reconstructions are shown in figure 2, in which the long and sharp streaky patterns with high-order Laue zones can be clearly observed. Figures 2(a) and (b) are the patterns of the 6 × 6 reconstructed surface. Strong Bragg-reflection streaks from the basic c-plane lattice of wurtzite ZnO and the superlattice reflections from the 6 × 6 structure coexist in the patterns. The $\frac{1}{3}$- and $\frac{2}{3}$-order streaks are sharper and brighter than the $\frac{1}{6}$-, $\frac{3}{6}$-, and $\frac{5}{6}$-order streaks in both azimuths.
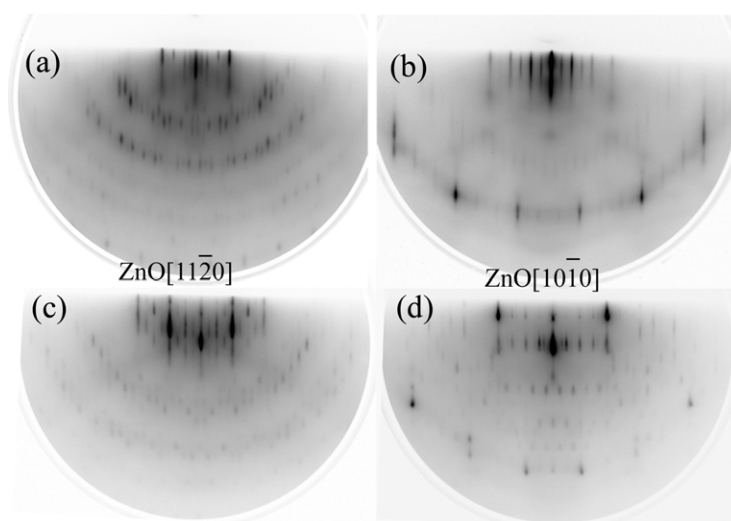
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Figure 2. RHEED patterns of ZnO reconstructed surfaces. (a) 6×, (b) ×6, (c) 12×, and (d) ×12.
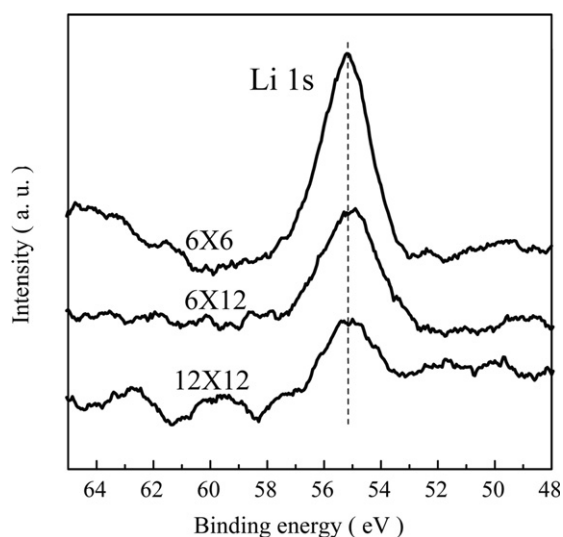

Figure 3. Li 1s core-level XPS spectra on varied reconstructed surfaces, demonstrating the relationship of reconstructions with Li surfactant coverage (atom concentration) on the ZnO surface.

Likewise, in RHEED patterns of the 12×12 reconstruction (figures 2(c) and (d)), the $\frac{1}{4}$-, $\frac{2}{4}$-, and $\frac{3}{4}$-order patterns are sharper than other fractional-order streaks. Other than the 6×6 and 12×12 reconstructions, we also observed two more Li-induced reconstructions, i.e. the 6×12 and 12×6. Normally, surfactant induced reconstructions have a close relationship with the coverage of surfactant atoms on surfaces. Phase transition happens, for example, between different Sb-induced Si(111) surface structures when Sb coverage changes [20]. Similarly, Li-induced ZnO reconstructions transferred from the 12×12 to the 6×12 (or 12×6) and to the 6×6 structure with increase of the amount of Li atoms on the ZnO(000$\bar{1}$) surface. From core-level XPS spectra of these reconstructed surfaces, as shown in figure 3, it can be found that the
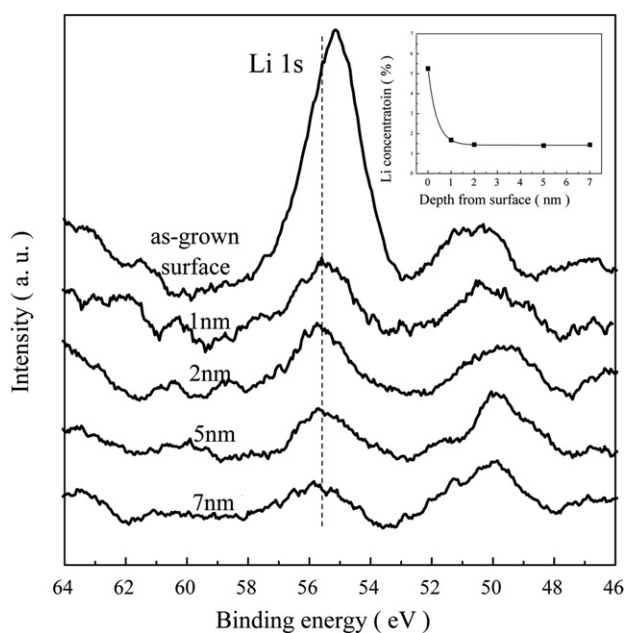
Figure 4. XPS depth-profile analysis of Li 1s core-level spectra, (a) the as-grown surface with the 6×6 reconstruction, and the sputtered surfaces with a depth of (b) 1 nm, (c) 2 nm, (d) 5 nm, and (e) 7 nm. The inset shows the relationship of Li atom concentration to the sputtering depth. The peak at 50.0 eV is Mg 2p, which comes from the cutting edge of the $MgAl_2O_4$ substrate.

Li 1s peaks become weaker and weaker for the 6×6, 6×12 (or 12×6), and 12×12 surfaces in that order. These XPS results clarified the relationship between the type of ZnO reconstructions and the coverage of Li surfactants, which was consistent with RHEED observations. Basically, these findings provide us with an effective approach to judge the relative concentrations of Li dopant on the $ZnO(000\bar{1})$ surface by affirming different reconstructions during the epitaxial growth of ZnO:Li films.

Surfactant distribution in films is an important issue for SME. To study the distribution of lithium dopant near the ZnO surface, XPS depth profiling was performed on the Li-doped ZnO sample with the 6×6 surface. A series of core-level XPS spectra recorded during the removal of the outermost 7 nm-thick ZnO layer are shown in figure 4. From the spectrum of the as-grown reconstructed surface, the relatively strong Li 1s peak indicates that, on the outermost surface, an Li atom concentration of 5.3% is the highest. The peak intensity greatly reduced after the first sputtering, which reflected an obvious decrease of Li concentration in this process. For successively sputtered surfaces, Li concentrations did not change too much. They kept similar values of around 1.5%, $\frac{1}{3}-\frac{1}{4}$ of that of the as-grown surface. Hereby, the depth profiling proves that most of the Li surfactant atoms float within the outermost 1 nm-thick subsurface and only a small number of them incorporate into the bulk as dopant atoms. Furthermore, an energy shift of the Li 1s peak from 55.1 eV (of the reconstructed surface) to 55.6 eV (in the bulk) could be observed when the first nanometer surface was removed. It implies that Li atoms on the surface have different bonding configurations (chemical states) from those in bulk ZnO, which results in the energy shift of the XPS peak. Thus, the enriched Li atoms are speculated to function as the adatoms to induce new ZnO surface structures, similar to some reconstructions on GaN polar surfaces with the participation of Ga adatoms [12, 21–23]. So far, atomic models of

Li-induced reconstructions on the $ZnO(000\bar{1})$ surface are unclear and further investigations are in progress.

The underlying mechanism for the surface segregation of Li dopant is proposed as the spontaneous depolarization of the polar ZnO surface caused by the participation of Li surfactant atoms in the surface structure. It is well known that there are excessive positive charges accumulated on the ideal O-terminated $ZnO(000\bar{1})$ polar surface, which will lead to the instability of the surface with a divergent surface energy. Recently, some new advances in possible ways to quench the surface polarity and reduce the surface energy of charged polar surfaces have been reported [15–19]. Some methods to realize that are listed as follows: (1) to form rough surface with facets, (2) to change the stoichiometric relation of surface elements, (3) to induce some structure impurities or to form surface reconstructions, (4) to transfer charge partially from one polar plane to another one. By one of these processes or a combination of two or three of them, the polar nature of the surface can be effectively decreased. In our case, the Li^+ ion with one positive charge is not an isoelectronic impurity for the polar ZnO surface. During the epitaxial growth, an exchange process, in which one underlying Li^+ ion replaces one newly deposited Zn^{2+} ion, will lead to one positive-charge reduction on the outermost surface. In this way, the surface-charge accumulation and surface energy can be drastically decreased by the segregation of Li dopants. The incorporation of Li from surface into the bulk was found to be difficult because a de-exchange of the underlying Zn^{2+} ions with the Li^+ ions on the surface increases the surface energy due to the accumulation of surface charges. Therefore, the exchange process driven by the spontaneous depolarization of the polar ZnO surface hinders the ZnO 3D islanding and finally leads to the surface enrichment of Li dopant during the Li-modified ZnO epitaxy. The strong floating ability of Li surfactant induces the formation of surface reconstructions on the growth front of ZnO epitaxial films, which results in a convergent surface energy.

4. Conclusion

In summary, surfactant effects of lithium dopant in ZnO epitaxial growth were investigated on O-polar ZnO surfaces. The Li-induced growth mode transition from 3D to 2D was determined by RHEED observations as well as AFM characterizations. Li atoms were found floating within the outermost 1 nm of the ZnO surface, resulting in the continuous formation of surface reconstructions. Various Li-induced surface reconstructions provide us with a real-time method to judge the relative coverage of Li dopant on the growth front during the doping of ZnO.

Acknowledgments

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