계면공학에 기초한 우르차이트 결정의 극성 조절

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Polarity Control of Wurtzite Crystal by Interface Engineering

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Abstract : The general method and mechanism for the polarity control of heteroepitaxial wurtzite films, such as ZnO and GaN, by interface engineering via plasma-assisted molecular beam epitaxy are addressed. We proposed the principle and method controlling the crystal polarity of ZnO on GaN and GaN on ZnO. The crystal polarity of the lower film was maintained by forming a heterointerfce without any interface layer between the upper and the lower layers. However the crystal polarity could be changed by forming the heterointerface with the interface layer having an inversion center. The principle and method suggested here give us a promising tool to fabricate polarity inverted heterostructures, which applicable to invent novel heterostructures and devices.

Key Words : Polarity, Wurtzite, Interface Engineering, Molecular Beam Epitaxy (MBE)

1. Introduction

Gallium Nitride (GaN) and related III-V nitrides have been extensively explored for applications to optical devices in the ultra-violet (UV) region and high-speed electronic devices as well. Most recently Zinc Oxide (ZnO) and related II-VI oxides have emerged as novel photonic materials for the UV region owing to their wide bandgaps and very large exciton binding energy, which give rise to enhanced nonlinear optical properties. Those materials are of wurtzite crystal structure and are lack of inversion symmetry along the <0001> direction thus have a polarity. When wurtzite epilayers are grown with strain, piezoelectric field is generated in the epilayers due to built-in strain. However, It even when there is no strain, the spontaneous polarization field lies along the +c or -c directions depending on the polarity, and negative charge accumulates at the +c plane, while positive charge at the –c plane. This polarization is estimated to be -0.057C/m^2 for ZnO and -0.029 C/m^{2}for GaN, which is much larger than piezoelectric polarization due to built-in strain, in general.

The polarity of wurtzite structure semiconductors, such as ZnO or GaN, has been receiving increasing interests because of its strong effects, which resulted from built-in field by spontaneous and piezoelectric polarization, on properties of films and applications for devices [1-5]. Hence, the control of crystal polarization is one of most crucial issues in epitaxy of wurzite structure materials.

The purpose of this study is to introduce a general method to control the crystal polarity by engineering the interface in epitaxy of wurtzite-structure materials and to demonstrate several examples of control of crystal polarity in the growth of ZnO and GaN based on this general principle.

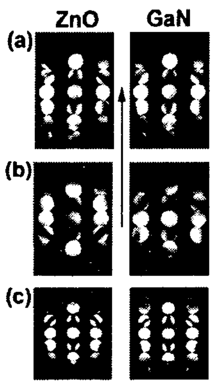
2. Experimental

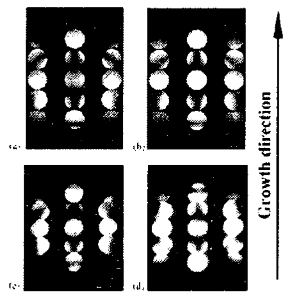
ZnO epilayers are grown by plasma-assisted molecular beam epitaxy (P-MBE). Commercial c-plane sapphire or MOCVD grown GaN template on sapphire are used for substrates. An effusion Zn cell, Mg cell, Ga cell, and RF O-plasma are used for Zn, Mg, Ga, and O sources, respectively. The growth processes are monitored by *in-situ* reflection high-energy electron diffraction (RHEED). The polarity of ZnO films is determined using the convergent beam electron diffraction (CBED).

3. Results and Discussion

The growth of Zn-polar ZnO layers would be possible if we could form N-Ga-O-Zn bonding at the interface but it is not so easy because of high reactivity of Ga with oxygen, which leads to the formation of an oxide layer at the interface during the initial growth of ZnO. Hence Zn pretreatments has been adopted to protect oxidation by preventing preferential reaction of a Ga-polar GaN surface with energetic O plasma and thereby helps grow Zn-polar ZnO layers. Zn preexposure time is about 3min. In order to invert polarity from a cation-polar to an anion-polar surface, we have converted the bond sequence by oxidizing the GaN surface prior to ZnO epitaxy. A Ga_2O_3 interface layer, which was formed by oxidizing Ga-polar GaN templates with O plasma (or growing Ga_2O_3 directly), has been inserted in between the ZnO layer and the GaN template. Since Ga_2O_3 has inversion symmetry with O surfaces both at the top and bottom, the resultant ZnO layers should show O polarity. The polarity of the ZnO films has been confirmed by CBED.

Figure 1(a) shows experimental CBED patterns of an upper ZnO and a lower GaN film from a Zn preexposed sample. The arrow indicates the growth direction. Figure 1(b) shows experimental CBED patterns of an upper ZnO and a lower GaN films from an O-plasma preexposed sample. In order to determine the polarity without ambiguity, comparisons with simulated CBED patterns from ZnO and GaN are performed. Figure 1(c) shows simulated CBED patterns from wurtzite ZnO and GaN. The simulated patterns correspond to 28- and 45-nm-thick ZnO and GaN, in which the upward directions are aligned to Zn- and Ga-polar, respectively. Comparison of the experimental and simulated CBED patterns directly indicates that the polarity of ZnO film with O-plasma preexposure is of O-polar and that of ZnO film with Zn preexposure is of Zn-polar.





Figures 1 and 2. CBED patterns for the ZnO on GaN (left figure set) and the GaN on ZnO (right figure set).

Recently, successful growth of Ga-polar GaN epilayers on O-polar ZnO templates pre-deposited on c-plane sapphire by NH_3 pre-exposure onto ZnO templates has been reported. Prior to GaN growth, 10 sccm-NH_3 gas was exposed onto the ZnO template to grow a Zn_3N_2 layer, which should allow the growth of Ga-polar Gan on O-polar ZnO. Figure 2(a) and (b) show simulated CBED patterns of (a) O-polar ZnO and (b) N-polar GaN obtained for a thickness of 26nm with the zone axis of [11-20]. Figure 2(c) and (d) show measured CBED patterns with the same zone axis of the (c) ZnO template and (d) GaN layer from a GaN/ZnO/c-sapphire sample. By comparing the simulated CBED pattern of O-polar ZnO with the measured one (figure 2(a) and (c)), it is clear that ZnO template has O polarity. The measured CBED pattern of the GaN (figure 2(d)) unequivocally show that the GaN layer has Ga polar through a comparison with the simulated CBED pattern of N-polar GaN (figure 2(b)).

4. Conclusions

The growth of O-polar(anion-polar) ZnO on Ga-polar (cation-polar) becomes possible by the formation of the Ga_2O_3 interface layer with a monoclinic structure in between the GaN and ZnO films. The monoclinic Ga_2O_3 interface layer has a center of symmetry, since the space group of Ga_2O_3 is *C2/m*. While Ga-polar GaN was grown on O-polar ZnO with a Zn_3N_2 interface layer in between. The Zn_3N_2 has a cubic structure with a space group of Ia3, which possesses inversion symmetry. Such an interface layers with inversion symmetry can invert crystal polarity and the methods demonstrated in this paper can be applied to fabricate polarity controlled and/or polarity inverted heterostructures.

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