Non-polar ZnO Thin Films and LED Devices

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Keywords: Non-polar, ZnO, LED

Abstract. ZnO materials have been researched in recent 30 years as a hot topic. ZnO is a third generation of semiconductor, it can be prepared into various forms of films and nanostructures, and they have excellent optical properties, electrical properties and magnetic properties. Because the polar ZnO’s quantum wells have a strong electric field, this will have a great impact on its optical properties. But non-polar ZnO has reduced such a strong electric field, so it greatly improved the luminescent performance. It’s more excellent than polar ZnO in the optical performance. In recent years, non-polar ZnO thin films’ research became increasingly evident. This article summed up the performances, preparations and applications of non-polar ZnO, and there are some suggestions. All of these are good to the further study of non-polar ZnO.

Introduction

As a direct band gap semiconductor material, ZnO’s forbidden band width is 3.37eV at room temperature. ZnO would be more easily grown along [0001] (c-axis), Due to the wurtzite structure in (0001) plane have higher energy under ordinary conditions. Because it’s lack of mirror symmetry, the spontaneous polarization have been caused in the [0001] direction, the [0001] direction is ZnO polar axis direction, the hetero-interface growth in this direction produce polarization charge due to the spontaneous polarization and piezoelectric effect. So there is a built-in electric field in the multiple quantum wells which make the quantum well’s band change, and then the equivalent charge centers between electron energy potential well and the hole energy potential well do not coincide in space. Internal electric field separate the quantum’s electron and hole, and reduce their radiative recombination’s probability, and lead emission spectra to red-shift, make the light emitting diodes and lasers’ internal the quantum efficiency reduce, All of this will affect the optical and electronic properties of devices [1].The key to solving this problem is to avoid polarization, That is enable ZnO film’s growth without polarization electric field, so we need to form non-polar ZnO thin films. On the ZnO’s plane {11̅20} and {10̅–0₁}, their direction is parallel to the c axis, and the number of zinc atoms and oxygen atoms is same, that is to say they are non-polarity. {11̅20} plane is a-plane, {10̅–0₁} plane is m-plane. a-plane and m-plane non-polar ZnO haven’t spontaneous polarization along the growth direction. It will undoubtedly play a very big role to improve devices’ optical properties and electrical properties. But the high quality non-polar ZnO thin films’ preparation is very difficult, the main problem is how to further reduce the defect density and improve the performance of the device substantively. This article will focus on the structure, preparation methods, performance and the application technology on LED of non-polar ZnO thin films. At last, we conclude the research direction in future.
Non-polar ZnO’s structure and detection

ZnO has three different crystal structures such as Quartet of rock salt mine (cube-NaCl), the cubic zinc blende and hexagonal wurtzite structure. ZnO is hexagonal wurtzite structure at Room temperature which belong to hexagonal system. It’s lattice constant \( a=3.249 \, \text{Å}, \, c=5.206 \, 9 \, \text{Å} \). Each Zn atom is in a tetrahedral gap formed by four adjacent oxygen atoms, but the zinc atom occupied half void of the tetrahedral, and the oxygen atoms’ arrangement is the same as zinc atoms’ [2]. The type of molecular structure is between ionic bond’s and covalent bond’s. Spacing between zinc and oxygen atoms is \( d_{\text{Zn-O}}=1.94 \, \text{Å} \), The coordination number is 4:4. Wurtzite ZnO’s exciton binding energy is 60 meV at room temperature which is much higher than another third generation semiconductor material GaN’s. This indicated that ZnO’s exciton is stable at room temperature, so we can achieve high efficiency stimulated emission at room temperature or higher temperatures. Due to the influence of preparation conditions, there always be some defects such as point defects [3], dislocations [4], grain boundaries [5], surface configuration [6] and interface configuration [7] in ZnO thin films. These defects have a significant impact on optical properties and electrical properties of non-polar ZnO.

Non-polar ZnO thin film’s internal and external structure, composition and properties often used x-ray diffraction, atomic force microscope, scanning electron microscope and Photoluminescence to detect.

Preparation of technical methods of non-polar ZnO thin films

Substrate’s selection principles. The substrate’s different structures have a great influence on the growth of non-polar ZnO thin films, so the selection of the substrate is critical. According to numerous studies and related theoretical knowledge, the substrate’s selection principle can be summed up such as the substrate’s structure and the epitaxy’s should be identical or similar with each other, they should have a small degree of lattice constant mismatch, thus, so the formed films have lower crystal defect density and better performance. The better optical, thermal and electrical properties of the substrate the better thermal conductivity, electrical conductivity and transmittance the device will have. The Chemical properties of the substrate should be stable during the preparation of the film, it should be not easy to corrosion and decomposition, and it couldn’t affect the quality of epitaxial films during the chemical reaction with the epitaxial film. Good mechanical properties of the substrate make the processing (antifriction, polishing and cutting) easy; The better interface-specific of the substrate, the better nucleation and strong adhesion the epitaxial material will have. At last, the Shape of the substrate should be easily made, so you can get higher quality extension.

Overall, structure, thermal expansion coefficient and chemical stability of the substrate should match with epitaxial film; taking the needs of industry into account, the cost of the cost of substrate materials should be low.

The preparation of non-polar ZnO. In order to generate high quality non-polar ZnO, and because a-plane ZnO structure is not as same as the m-plane ZnO’s, We choice the method and the substrate based on a- plane ZnO thin films or m-plane ZnO thin films we want. It is summarized in Table 1.
Table 1 The preparation method of the non-polar ZnO

<table>
<thead>
<tr>
<th>Goal Orientation</th>
<th>Substrate and Orientation</th>
<th>Growth Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-plane (10 1 0)ZnO</td>
<td>(10 1 0) Sapphire, ZnO, (100)LiGaO₂, (100)LaAlO₃</td>
<td>MOVPE[8]; MBE[9]; MOVPE[18, 19]</td>
</tr>
<tr>
<td></td>
<td>(10 1 0) Sapphire, ZnO, (100)LiGaO₂, (100)LaAlO₃</td>
<td>MBE[10]; PLD[11]</td>
</tr>
<tr>
<td></td>
<td>RF magnetron sputtering</td>
<td>[12]; PLD[17]</td>
</tr>
<tr>
<td></td>
<td>(10 1 0) Sapphire, ZnO, (100)LiGaO₂, (100)LaAlO₃</td>
<td>CVD[13]</td>
</tr>
<tr>
<td></td>
<td>CVD[14]; MOCVD[15];</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MBE[16]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PLD[17]</td>
<td></td>
</tr>
<tr>
<td>a-plane (11 2 0)ZnO</td>
<td>(11 2 0) Sapphire, ZnO, (100)LiAlO₂, (100)(La, Sr)(Al, Ta)O₃, (100)SrTiO₃, (320)r-LiAlO₂, (001)Si, (01 1 2)LiTaO₃, (010)LiGaO₂</td>
<td>MOVPE[24, 25]</td>
</tr>
<tr>
<td></td>
<td>MOVPE[26]; PLD[27]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CVD[28]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RF magnetron sputtering</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>MOVPE[30]; PLD[31]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PLD[32]</td>
<td></td>
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<tr>
<td></td>
<td>MBE[12]</td>
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</tr>
<tr>
<td></td>
<td>RF magnetron sputtering</td>
<td>[33]</td>
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</table>

In the above method, the main methods of preparing is metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), of course, the film also has some other manufacturing methods, such as pulsed magnetron sputtering (PMS)[34]. Growth conditions has significant influence on the crystal quality and surface morphology of the non-polar ZnO thin films during the growth process, so it is important to control the growth conditions such as temperature, VI / II ratio and oxygen pressure. In The hetero epitaxial growth, according to the substrate’s selection principle, a-plane ZnO should be grown on the a-plane sapphire, m-plane ZnO should be grown on the m-plane sapphire. The growth direction on sapphire substrate also depends on the growth conditions. Moriyama and Fujita reported the growth of m-plane ZnO on Sapphire substrates[9], they found that high temperature (800 ° C) and high VI/II ratio (2. 8x10⁴) is very good for the growth of m-plane ZnO, but at the low growth temperature (500 ° C) and the low VI / II ratio (5.4 x 10³), it produced other planes. Other studies also found that the presence of other planes in the interface of the internal ZnO / Al₂O₃ film [26]. In the epitaxial growth, the lattice mismatch has a crucial impact on the epitaxial layer’s growth. r-plane and m-plane sapphire substrate’s high lattice mismatch make the crystalline quality of the non-polar ZnO films significantly reduce, so the quality of non-polar ZnO thin films is not high at present[8]. There is a solution to reduce the lattice mismatch between ZnO thin films and sapphire substrate that used GaN or SiNx as the buffer layer on the Sapphire substrate surface[12], high quality crystals of a-plane ZnO thin films can be received as result.

It is well known that homo-epitaxial growth is better than hetero-epitaxial growth according to the substrate’s selection principles. Especially the homo-epitaxial growth with on lattice mismatch is expected to get smooth surfaces and low density lattice defects non-polar ZnO thin films.
Kashiwaba et al. [14] get a-plane ZnO thin films deposited on the single crystal ZnO (1\(\<\frac{11}{2}\>0\)) substrate and r-plane (1\(\<\frac{1}{1}\>0\)2) Sapphire substrate respectively, and carried out a comparative study, they found that the value of the half-peak width in the homo-epitaxial ZnO thin films (0002) is smaller than hetero-epitaxial ZnO thin films’ and it’s optical properties is better than Hetero-epitaxial ZnO thin films by the measurement of GID. Abe et al. [15] obtained ZnO epitaxial thin films using (11\(\<\frac{1}{2}\>0\) ZnO substrate, they found that the Surface morphology and crystalline quality had markedly improved. These studies suggested that using homo-epitaxial growth to get high quality non-polar ZnO will become the main trend.

**ZnO thin films’ performance and testing**

**Non-polar ZnO thin films’ luminescent properties and testing.** The optical band gap of material takes a leading role on the emission characteristics of the LED chip. At first, we discuss the film thickness’s impact to the optical band gap. The derivation of optical band gap (\(E_0\)) is: Simplified the optical absorption coefficient

\[ a = \frac{1}{d}\ln\left(\frac{1}{T}\right) \]  

In the formula:

- \(T\): transmittance
- \(d\): the thickness of the thin film

According Manifacier model [35], because wurtzite ZnO is direct band gap semiconductor material, the optical absorption of direct band gap jump can be given by the following equation:

\[ (ah\nu)^2 = A(h\nu - E_g) \]  

\[ (1/d)^2\ln^2\left(\frac{1}{T}\right) = A\left(\frac{h\nu}{\lambda}\right)^2 \]  

In the formula

- \(v\): \(\frac{c}{\lambda}\)
- \(A\): Constants of the direct band gap transition
- \(h\): Planck’s constant, 6.626 \times 10^{-34} \text{ J} \cdot \text{s}
- \(\nu\): Photon frequency
- \(\lambda\): Optical wavelength

Bring the transmittance (\(T\)), the optical wavelength (\(\lambda\)), the film thickness (\(d\)) into the above formula. Analysis shows that along with the film thickness increases, the band gap decreases. So you can control the thickness of film to influence the optical performance. Wuhan University Dong et al. [36] followed this approach got the AZO thin films[ZnO: 2\% (mass fraction) Al\(_2\)O\(_3\) target], they had studied film thickness’s the effect to the structural and optical properties of thin films. With the thickness increases, the crystal quality of the film becomes excellent; and the growth mode had transformed from vertical growth to lateral growth. Because the resistivity of AZO thin films largely depend on carrier concentration and carrier mobility and the carrier mobility increasing make the resistivity decrease, so the optical band gap increased from 3.58eV to 3.90eV.
The optical properties of non-polar ZnO films often studied by PL spectra and PR spectra under normal conditions. By comparing the optical properties between non-polar ZnO films and polar ZnO films, the first feature can be find that the optical properties is anisotropic, the second feature is the additional emission band caused by the low crystallinity layer and stacking fault defects.

The electrical properties and detection of non-polar ZnO thin films. Non-polar ZnO thin films’ electrical properties mainly refer to resistivity. The size of resistivity can be measured by four-point probe resistivity tester. But the resistivity of the film always greater than it in the bulk material under the same condition of carrier concentration, this is because there are some scattered bodies such as surface scattering and grain boundary scattering in the film body. Because ZnO is single crystal, so the surface scattering is the main scattering to considerate, the surface scattering consists of elastic scattering and inelastic scattering. If the inelastic scattering occurs, it will slow down the velocity of the carrier, thereby reducing the mobility of the carrier, and the resistivity will become larger. Thin film’s resistivity is associated with the thickness of the film itself, the specific relationships can refer Fuchs - Sondheim equation; It is also affected by the doped species and doped concentration. In short, it is a combined effect.

Polar ZnO and non-polar ZnO are very different in electrical properties. As we all know, resistivity largely depend on the carrier concentration and carrier mobility, carrier mobility is largely decided by defect density and dispersion mechanisms. Non-polar ZnO’s defect density is higher than polar ZnO’s, so non-polar ZnO’s electron mobility is lower.

Non-polar ZnO thin films’ application in LED devices

substrate etching. Etching the substrate has many benefits. On the one hand, it can effectively reduce the ZnO epitaxial films’ dislocation density, the active region’s non-radiative complex and reverse leakage current. So it can improve the life of the LED. On the other hand, the light emitted of the active region through multiple scattering between the interface of ZnO and sapphire substrate which changed the light’s total reflection angle and increase the probability of flip LED’s light emitting from the sapphire substrate. In turn, it enhanced light’s extraction efficiency.

The substrate modification methods include dry etching and wet etching. According to different needs choose different methods for etching substrate. Simultaneously, in order to get better performance chip, the substrate need to be etched with different patterns. Currently, there are many methods to etching the substrate, such as photolithography processing, electron beam micro-machining, ion beam micro-machining, laser beam micro-machining, ultrasonic machining, micro EDM, electrochemical micro-machining, micro electroforming, LIGA technology processing and quasi-LIGA processing technology. Each of them has their own processing size, resolution and...
accuracy and others. You can choose different ways according to different needs. Specific methods you can consult other reference material [37].

**Conclusion**

Non polar ZnO overcomes the negative effects of strong internal electrostatic field, so it has great potential application prospect in short wavelength optoelectronic devices. But because the low quality of crystalline of non polar ZnO, high defect density and large surface roughness, it is very difficult to generate the non polar ZnO of high quality. In order to get non polar ZnO films of high quality, researchers continue to improve precise control of growth parameters, and the method of homogeneous epitaxial growth or on the substrate in a variety of ways to improve the crystal quality of the buffer layer, reduce the defect density and reduce the surface roughness.

At present, further understanding of the non polar ZnO exists many problems, the P type doping and the structure of multiple quantum are not very clear, so further research on non polar ZnO is necessary. At the same time, it is also very important for its application in devices. In short, before making the non polarity Oxide Zinc be widely used and commercialized in optoelectronic equipment, a lot of necessary and meticulous works need to be done.

**References**


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