Study on the Performance Impact of Introducing an InN Buffer Layer at Various Deposition Temperatures on InN Film Grown by ECR-PEMOCVD on Free-Standing Diamond Substrate

Shuaijie Wang *, Xin Guan, Shu Liu and Dong Zhang

School of Renewable Energy, Shenyang Institute of Engineering, Shenyang 110136, China; xin.guan@sina.com (X.G.); ls_jhl@163.com (S.L.); ambitious211@163.com (D.Z.)
* Correspondence: Insolwsj@163.com or D11402027@mail.dlut.edu.cn

Abstract: In this study, InN films are grown at a relatively low temperature by electron cyclotron resonance plasma-enhanced metal organic chemical vapor deposition (ECR-PEMOCVD) on free-standing diamond substrates. Due to the high lattice mismatch rate between InN film and the free-standing diamond substrate, the function of a buffer layer is to build a bridge between the substrate and film to reduce the lattice mismatch between them. Therefore, here, we study the performance impact of introducing an InN buffer layer at various deposition temperatures and explore the optimal buffer layer deposition temperature used to grow relatively high-quality InN films. The experimental results show that when an InN buffer layer is introduced at a deposition temperature of 100 °C, the growth direction of the InN film is perpendicular to the substrate with a high c-axis preferred orientation, the roughness of the surface is minimal, and the particle sizes are consistent with growth in the same direction. Additionally, the carrier mobility is highest, and the carrier concentration is lowest compared with other conditions.

Keywords: InN buffer layer; ECR-PEMOCVD; free-standing diamond substrate

1. Introduction

InN is an important group III nitride material. As compared with other group III nitride materials such as GaN, there are relatively few studies on the growth mechanisms, optical properties, and electrical properties of InN. In recent years, scientists have found that InN has special optical and electrical properties and a wide range of applications; therefore, the study of InN film growth with optical and electrical properties has gradually become a new focus in the field of semiconductors. Recent studies have shown that the band gap width of an InN semiconductor is 0.7 eV at a low temperature and 0.65 eV at room temperature, which is not the previous theoretical value (1.9 eV) [1,2]. This discovery had a profound impact. The spectral range of group III nitride material and its ternary and quaternary alloys has changed from 1.9–6.2 to 0.65–6.2 eV. Photoelectric devices for near-infrared to deep-ultraviolet spectra can be prepared by using group III nitride InGaAlN materials. Therefore, InN is an excellent semiconductor material for long wavelength semiconductor optoelectronic devices and full spectral absorption efficient solar cells [2]. In addition, since the luminescence wavelength of InN-based materials can reach 1.55 µm, there is a wide choice of materials for optical communication devices; therefore, InN brings a new direction for the research and development of optical communication devices [3]. Theoretical studies on electrical properties have shown that InN has better transient and steady-state electron transport characteristics than GaN and AlN. Its low field mobility can reach 3200 cm²/V·s [4], and its peak rate can reach $4.3 \times 10^7$ cm/s [5]; moreover, temperature does not affect the electron transport characteristics. Therefore, InN has unique advantages in the preparation of high-speed and high-frequency transistors.
InN has potential applications in the field of photoelectric devices for near-infrared to deep-ultraviolet spectra, optical communication devices, high-speed and high-frequency transistors, and full spectrum absorption high-efficiency solar cells. Research on the growth and physical properties of high-quality InN film is not as deep as that of other group III nitride materials. Growing methods have improved in recent years, as InN films have been successfully grown on α-Al₂O₃ heterogeneous substrates by metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), plasma-enhanced MBE (PEMBE), and other methods [6–9]; however, several scientific problems exist, which include the following: (1) Conventional MOCVD and MBE methods use NH₃ as the nitrogen source. The decomposition temperatures of NH₃ and InN are 800 and 600 °C, respectively; however, InN should be grown in relatively low temperature conditions, and herein exists an inextricable contradiction. (2) There is a lack of substrate material that can match the thermal expansion coefficient and lattice constant of InN. (3) The heat dissipation of α-Al₂O₃ and other heterogeneous substrates is not good, while high heat dissipation and durability are required by high-frequency power devices.

Due to the low decomposition temperature of InN, its growth temperature is generally less than 600 °C [9]. The equilibrium pressure of nitrogen also increases rapidly with an increase in temperature. In order to effectively inhibit nitrogen volatilization and reduce nitrogen vacancy defects, InN must grow at a relatively low temperature [9]. The conventional MOCVD and MBE methods both use NH₃ as the source of nitrogen reaction. NH₃ can decompose more nitrogen atoms only at higher temperatures, which is an unresolvable contradiction of InN film growth in low temperature conditions (inhibits the volatilization of nitrogen). The growth of InN film in low temperature conditions requires a high concentration of active nitrogen sources, and therefore, plasma-activated nitrogen sources are a better choice.

Due to the improvement of growth methods in recent years, InN films have been successfully grown on α-Al₂O₃ and other heterogeneous substrates by magnetron sputtering [5], metal–organic chemical vapor deposition (MOCVD) [6–9], atomic layer deposition (ALD) [10], molecular beam epitaxy (MBE) [11], plasma-enhanced molecular beam epitaxy (PEMBE), and other methods [4,10,12–18]. However, the heat dissipation performance of these substrates is poor; therefore, it is still difficult to select appropriate substrate materials for high frequency and power devices [19–21]. Diamond is characterized by high thermal conductivity and excellent heat resistance. The thermal conductivity of diamond is 1515W/m·K. The atoms in diamond are bonded in the form of covalent bonds with high energy, which results in fast energy transfer of atoms in vibration and less decay, and therefore its thermal conductivity is excellent. Generally, diamond begins to burn in air at about 850 °C, and graphitization begins at about 1000 °C without oxygen, which leads to good heat resistance. At the same time, diamond is not corroded by strong acids, strong alkalis, and other chemical agents. Therefore, low temperature growth of high-quality InN films on free-standing diamond substrates is the key point for InN-based optoelectronics and high-frequency power devices.

In this study, electron cyclotron resonance plasma-enhanced metal organic chemical vapor deposition (ECR-PEMOCVD) was used to solve the above problems [22]. A novel cavity coupled magnetic multistage microwave ECR plasma source is used in ECR-PEMOCVD, and microwave coupling efficiency can be up to 95%. This device can generate highly activated plasma with high energy electrons (5–50 eV), low energy ions (<2 eV), and large area uniform non-magnetized high activated plasma at an air pressure of 10⁻²–10⁻¹ Pa, which is especially suitable for studying the growth of films in a large area and at a low temperature without high energy ion damage. As compared with magnetron sputtering and MBE, the chemical ratio of InN films can be precisely controlled by adjusting the gas flow rate using ECR-PEMOCVD. N₂ is used as the reaction source, which can provide adequate activation energy, N atoms, and N ions at a low temperature (<600 °C), and herein, the InN key binding energy is enhanced. The InN buffer layer is prepared by nitrogen (N₂) and trimethyl indium (TMIn) mixed gas on the substrate surface to solve
the mismatch of thermal expansion coefficient and lattice constant between InN films and substrates [23–25]. At the same time, the use of free-standing diamond as the substrate with the properties of high thermal conductivity and excellent heat resistance can achieve InN film growth at a low temperature. Previous experiments have determined the best deposition temperature and N2 flow rate for InN film growing at a low temperature on free-standing diamond substrate by ECR-PEMOCVD. When the deposition temperature is 400 °C, InN films with high c-axis preferential orientations can be obtained. A higher temperature results in a rougher film surface and deteriorating crystallization quality. The preferential orientation, optimal surface morphology, and electrical properties of InN films can be obtained at 400 °C [26]. When the N2 flow rate is 80 sccm, InN films have excellent preferential orientation, surface morphology, and atomic ratio [27].

However, we found that the mobility of InN film was still relatively low (48.5 cm2/V·s), and the carrier concentration was relatively high (9.2 × 1019 cm−3) [26]. This may have been caused by the lattice mismatch between the InN film and diamond substrate, which was found to be as high as 18.3%. We aimed to solve this problem by introducing an InN buffer layer to match the lattice constants, which would improve the quality and performance of InN film. Therefore, in this study, we conducted our experimental research on the “performance impact of introducing InN buffer layers on InN films” based on the above process parameters. Introducing an InN buffer layer at the appropriate deposition temperature can improve the migration energy of surface atoms, and therefore, the atoms can find a suitable location to form the InN buffer layer. However, if the temperature is too high, atoms are prone to secondary re-crystallization under the action of high migration energy, and an excellent buffer layer cannot be formed, which results in poor morphology of subsequent InN films. Therefore, in this study, the deposition temperatures for the introduction of the InN buffer layers ranged from room temperature to 200 °C.

2. Experimental Methods, Equipment, and Procedures

At present, molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) are the most mature and advanced methods for the deposition of semiconductor thin films. However, the defects of these two methods are also very significant, which has a significant impact on their possible applications.

(1) The MBE method cannot evaporate samples with a high melting point, and its control force of group V elements is insufficient; therefore, only a small batch of samples can be prepared. First, although InN and other group III nitride samples can achieve low temperature epitaxial growth by PEMBE, the high ion damage problem cannot be ignored. Secondly, the MBE method can only be used in ultra-high vacuum systems, which reduces its range of applications. Thirdly, the MBE method is only suitable for small batch productions, and therefore its application in industry is difficult [26].

(2) One disadvantage of the MOCVD method is the relatively high deposition temperature, which causes impurities to diffuse from substrates to growth films. The abrupt change in the impurity distribution at the interface results in a lack of high enough purity and a low-quality interface for epitaxial materials. In addition, high temperature conditions complicate device preparation, and film doping is best suited to a low temperature. Higher growth pressure results in inefficient configurations of detection and analysis instruments in the growth chamber, which makes it impossible to control the size of atomic growth. However, mass production is the biggest advantage of this approach [27].

In this study, the equipment used for InN film growth was a second-generation ECR-PEMOCVD device (ESPD-U) equipped with a reflection high-energy electron diffraction (RHEED) monitoring system, which combined the advantages of MBE and MOCVD. An ECR plasma source was used in this device.

The discharge mode of the ECR-PEMOCVD device generates gas discharge through electron cyclotron resonance (ECR), which generates non-equilibrium plasma. Therefore, it has the characteristics of high electron temperature and low ion temperature, which can avoid high energy ion damage to the growth surfaces of films. A common way to excite an
ECR discharge is to input microwaves with a frequency of 2.45 GHz into a plasma-formed space. The direction of the electric field can rotate around the magnetic field by applying a magnetic field to the axis of the resonator. Electrons are accelerated as they spin under the influence of this electromagnetic field. Under optimal flux density, if the microwave frequency is equal to the electron cyclotron frequency, electron cyclotron resonance is generated (the energy becomes higher when the electron gyroscopic radius becomes larger and higher). Then, the electron will absorb microwave energy and ionize neutral gas molecules into the plasma through collision [22].

The procedure for growing the InN film samples using the ECR-PEMOCVD method was as follows:

1. The first step is ultrasonic cleaning of the substrate surface. The purpose is to remove surface stains in order to prevent material contamination. The procedure is to put the free-standing diamond substrate into acetone solution for 10 min, ethanol solution for 10 min, and deionized aqueous solution for 10 min. Finally, it is blow-dried with N2.

2. The second step is to clean the free-standing diamond substrate under a condition of plasma gas discharge. The surface of the substrate is cleaned in a hydrogen plasma environment at room temperature for 30 min.

3. The third step is to introduce the buffer layer in order to effectively alleviate the rate of lattice mismatch between the InN film and free-standing diamond substrate. After cleaning the substrate, the InN buffer layer is prepared in 30 min.

4. The final step is the growth of InN film on the InN buffer layer for 180 min.

Four InN film samples were prepared. Table 1 shows the preparation parameters of the InN films without a buffer layer or with a buffer layer at various deposition temperatures.

Table 1. Deposition parameters of InN films without a buffer layer or with a buffer layer at various deposition temperatures.

| Samples | Procedure        | Deposition Temperature (°C) | N2 Flow Rate (sccm) | TMIn Flow Rate (sccm) | H2 Flow Rate (sccm) | Microwave Power (W) |
|---------|------------------|-----------------------------|---------------------|-----------------------|---------------------|---------------------|
| 1       | No buffer layer  | 25                          | 0                   | 0                     | 60                  | 650                 |
|         | InN film         | 400                         | 0                   | 0.6                   | 0                   | 650                 |
| 2       | Buffer layer     | room temperature            | 60                  | 0.3                   | 0                   | 650                 |
|         | InN film         | 400                         | 80                  | 0.6                   | 0                   | 650                 |
| 3       | Buffer layer     | 100                         | 60                  | 0.3                   | 0                   | 650                 |
|         | InN film         | 400                         | 80                  | 0.6                   | 0                   | 650                 |
| 4       | Buffer layer     | 200                         | 60                  | 0.3                   | 0                   | 650                 |
|         | InN film         | 400                         | 80                  | 0.6                   | 0                   | 650                 |

After preparation, the InN film samples were characterized and analyzed using the following methods:

1. Reflection high-energy electron diffraction (RHEED)

   RHEED was used to observe the pattern and process of film epitaxial growth. A Model RDA-004G RHEED device (R-DEC, Sapporo, Japan) was used in this study. The electron beam diameter was 90 µm, the insulation voltage was DC30 KV, and the working pressure range was $10^{-4}$-$10^{-9}$ Pa.

2. X-ray diffraction (XRD)

   XRD is used to obtain the atomic distribution, molecular structure, and composition information of materials. The XRD device used in this study, an ARL EQUINOX 3000 instrument for XRD (Thermo Scientific, Waltham, MA, USA), was used, which featured a unique curved position sensitive detector for real-time simultaneous acquisition of a full pattern, enabling faster analysis, in situ experimentations, and crystalline phase development and phase transitions. This XRD technology allows for greater flexibility and has quicker process response times.

3. Scanning electron microscope (SEM)
An SEM is a device used for large-scale analysis, which is widely used for detecting the ultrastructure morphology and composition of various solid surfaces. A model JSM-6360LV scanning electron microscope was used in this study (JEOL, Tokyo, Japan). The acceleration voltage range was 0.5–30 kV, the amplification was 80,000–300,000 times, and the secondary electron resolution was 3 and 4 nm under high and low vacuum conditions, respectively.

(4) Atomic force microscope (ATM)

An AFM is a device capable of comprehensively analyzing solid surface structures. A model AFM5500M atomic force microscope with a four-inch automatic motor (Hitachi, Tokyo, Japan) was used in this study. It provided an automatic operation platform in cantilever replacement, laser alignment, and test parameter settings. A high-precision scanner and low-noise three-axis sensor greatly improved the measurement accuracy.

(5) Hall effect system

In this study, a Hall effect system (ACCENT HL5500PC) was used. This system is composed of a main engine, a system controller, and a temperature controller. It can be used to test the electrical properties of semiconductors and thin film materials. At the same time, the temperature change of materials can be measured through a liquid nitrogen cooling system. The equipment has the characteristics of fast testing speed and accurate data, which can be used for testing carrier concentration, resistivity, carrier mobility, and other electrical properties at normal or variable temperatures.

3. Characterization Analysis of InN Films

3.1. Analysis of Growth Patterns

Reflected high-energy electron diffraction (RHEED) was used to characterize the growth patterns of the InN film samples. Figure 1 shows the RHEED images of InN films at various buffer layer deposition temperatures. As can be seen from Figure 1, the RHEED image of the film sample prepared without a buffer layer was fuzzy and presented a continuous ring pattern, which indicates that the film had poor crystallization performance. When the InN buffer layer was introduced with the deposition temperature of the buffer layer increased from room temperature to 100 °C, the RHEED images of the InN film gradually changed from a continuous ring to a disconnected ring, and the image definition became higher. However, when the deposition temperature of the buffer layer was increased from 100 to 200 °C, the RHEED images of the prepared sample gradually changed from a broken ring to a continuous ring.

![RHEED images](image)

(a) without buffer layer (b) with buffer layer, room temperature

(c) with buffer layer, 100 °C (d) with buffer layer, 200 °C

Figure 1. The RHEED images of InN films without a buffer layer or with a buffer layer at various deposition temperatures: (a) without buffer layer; (b) with buffer layer, room temperature; (c) with buffer layer, 100 °C; (d) with buffer layer, 200 °C.
The results show that an InN buffer layer and the deposition temperature have a significant influence on InN film growth. When the buffer layer deposition temperature is 100 °C, the prepared film sample has a clear RHEED image, which shows a broken ring. Moreover, the sample has better crystallization performance with growth direction perpendicular to the substrate and a high c-axis preferred orientation. However, the film samples without a buffer layer or with a buffer layer at the other deposition temperatures have poor crystalline properties.

3.2. Analysis of Grain Size

The grain size of the InN film samples was characterized using X-ray diffraction (XRD). Figure 2 shows the XRD spectra of InN films at various buffer layer deposition temperatures. It can be seen from Figure 2 that the highest diffraction peak of the prepared InN film sample was 31.3°, namely the diffraction peak of the InN (0002) plane.

The test shows that when the InN buffer layer is introduced at a deposition temperature of 100 °C, the diffraction peak strength is significantly stronger than that at other temperatures. The InN film sample grows perpendicular to the substrate, which presents a high c-axis preferred orientation [28–31].

Free-standing diamond substrate was used to prepare the InN films because it has a large lattice mismatch with InN. It is difficult to prepare high-quality film without a buffer layer; therefore, herein an InN low temperature buffer layer is a necessary preparation condition. When the InN films were prepared by ECR-PEMOCVD, the nitrogen reaction source was N\(_2\). Due to the low N\(_2\) dissociation rate and low particle migration energy at lower InN buffer layer deposition temperatures, the crystallization quality of the InN buffer layer film was poor and did not provide a good quality buffer layer for the subsequent growth of InN film. However, when the deposition temperature of the InN buffer layer was further increased, although hionization reaction efficiency of N\(_2\) and migration energy of particles were improved, the higher temperature led to interface defects, which deteriorated the quality of InN film prepared by subsequent heating. Therefore, the best crystallization performance of the InN film was when the InN buffer layer deposition temperature was 100 °C. The analysis result was the same for RHEED.

In order to further study the effect of the deposited InN buffer layer on the crystallization performance of InN film, the grain size of the InN film was calculated according to Scherrer formula [26]:

\[
d = \frac{k\lambda}{B \cos \theta}
\]

Figure 2. The XRD spectrum of InN films without a buffer layer or with a buffer layer at various deposition temperatures: (a) without buffer layer; (b) with buffer layer, room temperature; (c) with buffer layer, 100 °C; (d) with buffer layer, 200 °C.
where \( d \) is the grain size, \( \lambda \) is the wavelength of CuK\(_x\) rays (0.15406 nm), \( \theta \) is the Bragg diffraction angle, and \( B \) is the FWHM of InN film.

At the same time, the change rule of the c-axis stress on InN films with a buffer layer at various deposition temperatures was analyzed by a stress formula:

\[
\sigma = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \frac{c - c_0}{c_0} = -319.5 \frac{c - c_0}{c_0} \text{ (Gpa)}
\]

(2)

In the above formula, \( c_{11}, c_{12}, c_{13}, \) and \( c_{33} \) are the elastic constants of the InN bulk single crystal (\( c_{11} = 223 \text{ GPa}, c_{33} = 224 \text{ GPa}, c_{12} = 115 \text{ GPa}, c_{13} = 92 \text{ GPa} \)); \( c \) and \( c_0 \) are the c-axis lattice constants of InN film and InN bulk single crystals, respectively (\( c_0 = 0.5760 \text{ nm} \)). Grain size, c-axis lattice constant, and the stress of InN film can be calculated from the diffraction peak position and full width at half maximum (FWHM) of the (0002) crystal plane. Table 2 summarizes the test and analysis data of InN films at various buffer deposition temperatures. Under certain experimental conditions, the absorption capacity of substances with different impurity contents to X-ray is different; herein, distribution state, orientation, and stress of trace phase affect test results. In addition, due to the instability of materials, phase transformation and oxidation may also occur. When the X-ray hits the film during the test, phase transformation and phase after oxidation may appear, which can also affect the test results.

Table 2. Test and analysis data of InN films without a buffer layer or with a buffer layer at various deposition temperatures.

| Samples | Deposition Temperature of Buffer Layer (°C) | 2\( \theta \) (°) | FWHM (°) | Grain Size (nm) | c-Axis Lattice Constant (nm) | Stress (GPa) |
|---------|---------------------------------|-----------------|-----------|----------------|-----------------------------|-------------|
| a       | Without buffer layer            | 31.23           | 0.28      | 31             | 0.5731                     | 0.78        |
| b       | With buffer layer, room temperature | 31.27          | 0.21      | 43             | 0.5714                     | 2.00        |
| c       | With buffer layer, 100 °C       | 31.31           | 0.17      | 51             | 0.5708                     | 2.88        |
| d       | With buffer layer, 200 °C       | 31.28           | 0.24      | 44             | 0.5728                     | 1.28        |

As can be seen from Table 2, the crystallization performance of the prepared film sample without a buffer layer was poor. When the deposition temperature of the InN buffer layer was increased from room temperature to 100 °C, the lattice constant of the c-axis decreased, grain size increased, and FWHM decreased gradually. The lattice constant of the c-axis increased, FWHM increased, and grain size decreased gradually as the deposition temperature increases from 100 to 200 °C. The XRD analysis results show that when the deposition temperature of the buffer layer was 100 °C, the InN film sample had the smallest FWHM (0.17°) and the largest grain size (51 nm). At the same time, the film was in a state of c-axis compressive stress (a-axis tensile stress), and the maximum stress value was 2.88 Gpa.

The factors affecting InN film stress are relatively complex. The size of film stress can be affected by lattice mismatch, film composition, film dislocation, and thermal expansion coefficient mismatch. As can be seen from Table 2, the c-axis lattice constant of samples under all conditions was lower than that of the InN bulk single crystal (\( c_0 = 0.5760 \text{ nm} \)), and all InN film samples were in a state of c-axis compressive stress (or a-axis tensile stress), which was mainly due to the lattice mismatch and thermal expansion coefficient mismatch between the InN film and the diamond substrate.

First, from the perspective of the lattice matching relationship, Figure 3 shows the relationship of lattice match between the InN c-plane and the diamond (111) plane. An analysis of Figure 3 shows that the mismatch of the epitaxial lattice between the InN c-plane and the diamond (111) plane could lead to a-axis tensile stress (c-axis compressive stress) of the InN film. Because the a-axis lattice constant of InN (0.3548 nm) should have matched \( \sqrt{3} \) times the cell constant of the diamond (111) plane (\( \sqrt{3} \times 0.2522 \text{ nm} \approx 0.4368 \text{ nm} \)), their lattice mismatch was as high as 18.3%, which means that the InN film was in a state of a-axis tensile stress.
was relatively good because the crystal quality of epitaxial film was better, and the film where

was in a state of c-axis compressive stress (a-axis tensile stress), and the maximum stress

value was 2.88 Gpa. was in a state of c-axis compressive stress (a-axis tensile stress), which was mainly due to the lattice mismatch and thermal expansion coefficient mismatch. As can be seen from Table 2, the c-axis lattice constant of samples be affected by lattice mismatch, film composition, film dislocation, and thermal expansion

was relatively good because the crystal quality of epitaxial film was better, and the film

$T_g$ and $T_r$ are deposition temperature and room temperature, respectively; $\alpha_{sub}(2 \times 10^{-6}/K)$ is the thermal expansion coefficient of diamond film; $\alpha_{film}(4 \times 10^{-6}/K)$ is the a-axis thermal expansion coefficient of the InN film.

The InN film grows in a c-axis orientation (c-axis of the InN film is perpendicular to the diamond substrate surface and a-axis is parallel to the diamond substrate surface). It is obvious that the a-axis of the InN film will shrink faster than that of the diamond substrate during cooling, which results in a-axis tensile stress (c-axis compressive stress).

As seen in Table 2, the c-axis compressive stress did not increase linearly with an increase in the deposition temperature of the InN buffer layer. There was a significant reduction at 200 °C, which means that the thermal mismatch stress of InN film may have an obvious relaxation process during the cooling process. However, it is more likely that stress is relieved by more defects in InN film at higher temperatures. Overall, among all the samples, the highest c-axis stress (2.88 GPa) of InN film was obtained with a buffer layer deposition temperature of 100 °C, which implies that the crystal quality of the sample was relatively good because the crystal quality of epitaxial film was better, and the film stress is usually larger during heteroepitaxy growth. Therefore, InN film growth on freestanding diamond substrate has better crystal quality when the InN buffer layer deposition temperature is 100 °C.

3.3. Analysis of the Surface Structure Morphology

The InN film samples were characterized and analyzed by a scanning electron microscope (SEM). Figure 4 shows the SEM images of InN films without a buffer layer or with a buffer layer at various deposition temperatures. The SEM test results showed that the grain size of the film samples was disorderly and rough without an InN buffer layer. With an InN buffer layer and the deposition temperature of the buffer layer increased from room temperature to 100 °C, the density of islands on the surface of the InN film increased, and

Figure 3. The relationship of lattice match between the InN c-plane and the diamond (111) plane.
particles were clearly visible. The island growth mechanism of large islands merging with small islands could be observed, and the film gradually changed from island growth mode to layer–island combination growth mode. When the temperature reached 100 °C, it can be seen from Figure 4 that particles were growing, the particle boundary was significantly reduced, and stability was increased, which means an excellent layer growth mode was achieved. However, when the temperature was increased from 100 to 200 °C, the density of islands on the film surface was reduced, particles became disorderly, and the particle boundary was not obvious.

![SEM images of InN films with buffer layer at various deposition temperatures](image)

**Figure 4.** The SEM images of InN films without a buffer layer or with a buffer layer at various deposition temperatures: (a) without buffer layer; (b) with buffer layer, room temperature; (c) with buffer layer, 100 °C; (d) with buffer layer, 200 °C.

An explanation for the abovementioned characteristics is that an appropriate deposition temperature of the buffer layer improves the migration energy of atoms on the surface, which allows them to find a suitable position to combine in the InN buffer layer. However, atoms are prone to secondary crystallization under the action of excessively high migration energy due to a higher buffer layer deposition temperature; therefore, an excellent buffer layer cannot be formed, which results in poor morphology of subsequent InN film layers.

### 3.4. Surface Particle Distribution Analysis

An atomic force microscope (AFM) was used to analyze the surface particle distribution of the films. Figure 5 shows the AFM images of the InN films without a buffer layer or with a buffer layer at various deposition temperatures. As can be seen from Figure 5, when an InN buffer layer was not introduced, the sample had poor flatness, ambiguous particle boundaries, and disorderly particles. When the InN buffer layer was introduced and the
deposition temperature was increased from room temperature to 100 °C, the density of islands on the surface increased, and grainy boundaries were clearly visible. The mechanism of merging large and small islands could be observed, and the image presents a uniform two-dimensional plane. However, when the deposition temperature continued to increase from 100 to 200 °C, the density of islands on the surface decreased, the particle boundaries changed from clear to fuzzy, and particles became disorderly.

Figure 5. The AFM images of InN films without a buffer layer or with a buffer layer at various deposition temperatures: (a) without buffer layer; (b) with buffer layer, room temperature; (c) with buffer layer, 100 °C; (d) with buffer layer, 200 °C.

The test result shows that deposition temperature of the InN buffer layer had a significant influence on InN film growth. When the temperature was 100 °C, InN film had good surface morphology, the particle boundaries were clearly visible, and layer–island combination growth mode was formed [32–34]. Further analysis shows that the surface roughness of InN film samples without an InN buffer layer was very large. When the InN buffer layer was introduced with the deposition temperature increasing from room temperature to 100 °C, the surface roughness decreased from 3.7 to 2.4 nm, the particle sizes gradually became consistent, and they grew in the same direction. When the temperature was increased from 100 to 200 °C, the surface roughness gradually increased, and the particle growth was disorderly. According to the analysis of Figure 5, InN film had the best morphological characteristics when the deposition temperature of the InN buffer layer was 100 °C.

3.5. Analysis of Electrical Properties

The electrical properties of InN films were tested using a Hall effect system. Table 3 shows the electrical properties of the InN films without a buffer layer or with a buffer layer at various deposition temperatures. Because the free-standing diamond substrate...
was insulated, all data were derived from InN. Testing with the Hall effect system can produce some systematic errors due to the existence of a geomagnetic field. Furthermore, the Hall effect system can have a variety of other effects, since the voltage between poles measured in experiments are not equal to the real values of Hall voltage. It contains additional voltage caused by various side effects. As shown in Table 3, the InN films all exhibited the conductivity of an n-type semiconductor, which is a unique feature of unintentionally doped InN films. This is related to the inherent defects in the films [26]. The carrier mobility of InN film was obviously not ideal (20.4 cm$^2$/V·s), and the carrier concentration was high ($2.04 \times 10^{20}$ cm$^{-3}$) without a buffer layer. When an InN buffer layer was introduced with the deposition temperature increasing from room temperature to 100 °C, the carrier concentration decreased to a minimum value ($4.3 \times 10^{18}$ cm$^{-3}$), while the mobility increased to a maximum value (185 cm$^2$/V·s). The trend was reversed when the temperature increased from 100 to 200 °C. The result shows that the introduction of a buffer layer greatly improves the carrier mobility of InN film.

**Table 3.** Electrical properties of InN thin films without a buffer layer or with a buffer layer at various deposition temperatures.

| Samples | Deposition Temperature of Buffer Layer (°C) | Carrier Mobility (cm$^2$/V·s) | Carrier Concentration (cm$^{-3}$) | Conductivity (S·cm$^{-1}$) |
|---------|------------------------------------------|-------------------------------|-----------------------------------|----------------------------|
| a       | Without buffer layer                      | 20.4                          | $2.0 \times 10^{20}$             | 652.8                     |
| b       | With buffer layer, room temperature       | 48.5                          | $9.2 \times 10^{19}$             | 713.9                     |
| c       | With buffer layer, 100 °C                 | 185.0                         | $4.3 \times 10^{18}$             | 127.3                     |
| d       | With buffer layer, 200 °C                 | 90.3                          | $9.4 \times 10^{18}$             | 135.8                     |

The main reason for the high background electron concentration is the generation of nitrogen vacancies during the growth of InN films. Donor impurities in the InN films are nitrogen vacancies, which are easily generated because of the higher nitrogen partial pressure. The decrease in the carrier mobility of InN films is mainly due to grain boundary scattering and defect scattering. An appropriate InN buffer layer deposition temperature further improves the atom mobility of InN films, which indicates that an InN buffer layer can reduce defect density in subsequent InN films [35–37]. The Hall test results show that InN film grown on free-standing diamond substrate has the best carrier mobility when the InN buffer layer deposition temperature is 100 °C.

4. Conclusions

In this study, InN films are grown by ECR-PEMOCVD with the introduction of an InN buffer layer at various deposition temperatures. The properties are characterized and analyzed, and the results show that an InN buffer layer has a significant influence on the optimal growth of the InN film (0002) plane. The RHEED and XRD analyses show that InN film has the highest crystal quality when an InN buffer layer is introduced, and the deposition temperature is 100 °C; the growth direction is perpendicular to the substrate with a high c-axis preferred orientation. The largest grain size (51 nm) and the maximum c-axis stress (2.88 GPa) mean that the crystal quality under this condition is relatively good. The SEM and AFM test analyses show that InN film has the highest density of islands on the surface, and the grain boundary is clearly visible when the deposition temperature of the InN buffer layer is 100 °C. The surface roughness is only 2.4 nm, and the particle size gradually becomes consistent and grows in the same direction. The Hall system test analysis shows that the InN film has the lowest background electron concentration ($4.3 \times 10^{18}$ cm$^{-3}$) and the highest carrier mobility (185 cm$^2$/V·s) when the deposition temperature of the InN buffer layer is 100 °C, which means that the electrical performance is optimal compared with other conditions.

An InN buffer layer is the innovation of this study. In previous work, we found that the proper technological parameters for InN film growth by ECR-PEMOCVD without introducing a buffer layer were a deposition temperature of 400 °C, a nitrogen flow rate of
80 sccm, and a TMIn flow rate of 0.6 sccm [26,27]. Under these conditions, the grain size of InN was 47 nm, the surface roughness was 3.7 nm, the background electron concentration was $9.2 \times 10^{19}$ cm$^{-3}$, and the carrier mobility was 48.5 cm$^2$/V·s [26,27]. When an InN buffer layer was introduced with a deposition temperature of 100 °C, the grain size of InN film was 51 nm (4 nm larger) and the surface roughness was 2.4 nm (1.3 nm less). The background electron concentration of InN film was $4.3 \times 10^{18}$ cm$^{-3}$ (one order of magnitude less), and the carrier mobility was 185 cm$^2$/V·s (3.8 times higher). These results show that the introduction of an InN buffer layer improves the crystal quality, surface flatness, and electrical properties of InN film, which further improve the performance of the InN film.

**Author Contributions:** Conceptualization, S.W.; methodology, S.W.; software, S.L.; validation, D.Z.; formal analysis, S.W.; investigation, X.G.; resources, D.Z.; data curation, D.Z.; writing—original draft preparation, S.W.; writing—review and editing, X.G.; visualization, X.G.; supervision, S.L.; project administration, D.Z.; funding acquisition, S.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by [Educational Department of Liaoning Province] Grant Nos. [JL-2022] and [Technology Innovation Talent Fund of Shenyang] Grant No. [RC210143].

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Bechstedt, F.; Furthmüller, J. Do we know the fundamental energy gap of InN? *J. Cryst. Growth* 2002, 246, 315–319. [CrossRef]
2. Sharma, V.; Ahuja, B.L. Unusual electronic properties of InN. *Phys. Lett. A* 2008, 372, 5377–5380. [CrossRef]
3. Mukundan, S.; Chandan, G.; Mohan, L.; Roul, B.; Krupanidhi, S.B. Structural and optical characterization of nonpolar (10-10) m-InN/m-GaN epilayers grown by PAMBE. *J. Cryst. Growth* 2016, 433, 74–79. [CrossRef]
4. Polyakov, V.M.; Schwierz, F. Low-field electron mobility in wurtzite InN. *Appl. Phys. Lett.* 2006, 88, 032101. [CrossRef]
5. Pan, W.; Dimakis, E.; Wang, G.T.; Moustakas, T.D.; Tsui, D.C. Two-dimensional electron gas in monolayer InN quantum wells. *Appl. Phys. Lett.* 2014, 105, 213503. [CrossRef]
6. Qaeed, M.A.; Ibrahim, K.; Saron, K.M.; Salhin, A. Optical and structural properties of indium nitride nanoparticles synthesized by chemical method at low temperature. *Sol. Energy Mater. Sol. Cells* 2013, 97, 614–619. [CrossRef]
7. Yang, F.; Zhang, Y.T.; Han, X.; Li, P.-C.; Jiang, J.-Y.; Huang, Z.; Yin, J.-Z.; Zhao, D.-G.; Zhang, B.-L.; Du, G.-T. Growth parametric study of N-polar InGaN films by metalorganic chemical vapor deposition. *Superlattices Microstruct.* 2016, 91, 259–268. [CrossRef]
8. Zhao, S.R.; Zetian, M. Recent advances on p-Type III-Nitride Nanowires by molecularbeam epitaxy. *Crystals* 2017, 7, 268. [CrossRef]
9. Sarwar, A.T.M.G.; Yang, F.; Esser, B.D.; Kent, T.F.; McComb, D.W.; Myers, R.C. Self-assembled InN micro-mushrooms by upside-down pendeoepitaxy. *J. Cryst. Growth* 2016, 443, 90–97.
10. Bi, Z.X.; Zhang, R.; Xie, Z.L.; Xiu, X.; Ye, Y.; Liu, B.; Gu, S.; Shen, B.; Shi, Y.; Zheng, Y. The growth temperature dependence of in aggregation in two-step MOCVD grown InN films on sapphire. *Mater. Lett.* 2004, 58, 3641–3644. [CrossRef]
11. Le, B.H.; Zhao, S.R.; Tran, N.H.; Mi, Z. Electrically injected near-infrared light emission from single InN nanowire p-i-n diode. *Appl. Phys. Lett.* 2014, 105, 231124. [CrossRef]
12. Zhao, Y.; Wang, H.; Zhuang, S.; Wu, G.; Leng, J.; Li, W.; Gao, F.; Zhang, B.; Du, G. Near infrared electroluminescence from n-InN/p-NiO/GaN light-emitting diode fabricated by PAMBE. *Opt. Commun.* 2016, 371, 128–131. [CrossRef]
13. Nanishi, Y.; Saito, Y.; Yamaguchi, T. RF-Molecular beam epitaxy growth and properties of inn and related alloys. *Ipn. J. Appl. Phys. Part 1* 2003, 42, 2549–2559. [CrossRef]
14. Siekacz, M.; Wolny, P.; Ernst, T.; Grzanka, E.; Staszczak, G.; Suski, T.; Feduniewicz-Zmuda, A.; Sawicka, M.; Moneta, J.; Anikeeva, M.; et al. Impact of the substrate lattice constant on the emission properties of InGaN/GaN short-period superlattices grown by plasma assisted MBE. *Superlattices Microstruct.* 2019, 133, 106209. [CrossRef]
15. Zhao, Y.; Wang, H.; Wu, G.G.; Jing, Q.; Gao, F.; Li, W.; Zhang, B.; Du, G. Effect of nitridation on structure, electrical and optical properties of InN epilayers grown on sapphire by PAMBE. *Vacuum* 2015, 111, 15–18. [CrossRef]
16. Wang, X.Q.; Che, S.B.; Ishitani, Y.; Yoshikawa, A. Hole mobility in Mg doped p-type InN films. *Appl. Phys. Lett.* 2008, 92, 132108. [CrossRef]
17. Tsai, C.H. Nanoindentation study of indium nitride thin films grown using RF plasma-assisted molecular beam epitaxy. *Vacuum* 2012, 86, 1328–1332. [CrossRef]

18. Kumar, M.; Rajpalke, M.K.; Bhat, T.N.; Roul, B.; Sinha, N.; Kalghatgi, A.; Krupanidhi, S. Growth of InN layers on Si(111) using ultra thin silicon nitride buffer layer by NPA-MBE. *Mater. Lett.* 2013, 95, 135–138. [CrossRef]

19. Terziyska, P.T.; Butcher KS, A.; Gogova, D.; Alexandrov, D.; Binsted, P.; Wu, G. InN nanopillars grown from In-rich conditions by migration enhanced afterglow technique. *Mater. Lett.* 2013, 106, 155–157. [CrossRef]

20. Xu, Y.; Gu, B.; Qin, F.W. Electron cyclotron resonance plasma enhanced metalorganic chemical vapor deposition system with monitoring in situ for epitaxial growth of group-III nitrides. *J. Vac. Sci. Technol. A* 2004, 22, 302–308. [CrossRef]

21. Zhang, D.; Bai, Y.Z.; Qin, F.W.; Jia, J.; Wang, J.; Li, X.Z.; Zhen, Z.; Li, Q.; Li, H.; Wang, J.; Tang, G.; Zhang, J.; Bai, D. Strain dependent electronic structure and optical properties tuning of InN/PtX$_2$ (X = S, Se) van der waals heterostructures. *Vacuum* 2019, 168, 108805. [CrossRef]