Transmission electron microscopy study on the formation of SiNₓ interlayer during InAlN growth on Si (111) substrate

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Abstract

Ternary indium aluminum nitride (InₓAl₁₋ₓN) semiconductor is an attractive material with a wide-range bandgap energy varied from ultraviolet (Eg(AlN): 6.2 eV) to near infrared (Eg(InN): 0.7 eV). With tuning composition, it can be widely used to many optoelectronic device applications. In this thesis, I have studied InₓAl₁₋ₓN film deposited on Si (111) substrate using natural and isotopically enriched nitrogen as reactive gas by reactive magnetron sputter epitaxy (MSE). Four series of experiments were performed, which are I. InAlN presputtering, II. InAlN sputter deposition, III. InAlN direct deposition, and IV. InAlN direct deposition using isotopically enriched nitrogen. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). The θ-2θ XRD scan confirms that the designed composition x = 0.17 of InₓAl₁₋ₓN film was obtained. TEM images shows that an amorphous interlayer with a thickness ranging from 1.2 nm to 1.5 nm was formed between Si substrate and InₓAl₁₋ₓN film. However, high-resolution TEM shows that the interlayer actually contains partial crystalline structures. EDX line profile indicates that the chemical composition of the amorphous interlayer is silicon nitride (SiNₓ). By comparing d-spacing measurement of partial crystalline structures with EDX line profile, it reveals that partial SiNₓ crystal is formed in the interlayer. Nonetheless, the samples (IAD01, IAD02, IAD03, IAD04), grown without presputtering procedure, contain both crystalline SiNₓ and InₓAl₁₋ₓN embedded in the amorphous interlayer. It means that SiNₓ and InₓAl₁₋ₓN film can be directly grown on the substrate in the beginning of deposition. Moreover, the samples (IAD01, IAD03), quenched directly after deposition, have less crystalline structures in the interlayer then the samples (IAD02, IAD04), maintained at 800°C for 20 min.

Keyword

Indium aluminum nitride, silicon nitride, transmission electron microscopy, energy-dispersive X-ray spectroscopy
Abstract

Ternary indium aluminum nitride (In\_xAl\_1-xN) semiconductor is an attractive material with a wide-range bandgap energy varied from ultraviolet (E\_g(AlN): 6.2 eV) to near infrared (E\_g(InN): 0.7 eV). With tuning composition, it can be widely used to many optoelectronic device applications. In this thesis, I have studied In\_xAl\_1-xN film deposited on Si (111) substrate using natural and isotopically enriched nitrogen as reactive gas by reactive magnetron sputter epitaxy (MSE). Four series of experiments were performed, which are I. InAlN presputtering, II. InAlN sputter deposition, III. InAlN direct deposition, and IV. InAlN direct deposition using isotopically enriched nitrogen. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). The θ-2θ XRD scan confirms that the designed composition x = 0.17 of In\_xAl\_1-xN film was obtained. TEM images shows that an amorphous interlayer with a thickness ranging from 1.2 nm to 1.5 nm was formed between Si substrate and In\_xAl\_1-xN film. However, high-resolution TEM shows that the interlayer actually contains partial crystalline structures. EDX line profile indicates that the chemical composition of the amorphous interlayer is silicon nitride (Si\_N\_x). By comparing d-spacing measurement of partial crystalline structures with EDX line profile, it reveals that partial Si\_N\_x crystal is formed in the interlayer. Nonetheless, the samples (IAD01, IAD02, IAD03, IAD04), grown without presputtering procedure, contain both crystalline Si\_N\_x and In\_xAl\_1-xN embedded in the amorphous interlayer. It means that Si\_N\_x and In\_xAl\_1-xN film can be directly grown on the substrate in the beginning of deposition. Moreover, the samples (IAD01, IAD03), quenched directly after deposition, have less crystalline structures in the interlayer then the samples (IAD02, IAD04), maintained at 800°C for 20 min.
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1. Introduction

The group-III nitrides are widely studied for the optical and electronic device applications due to their excellent properties, such as direct and wide-energy bandgaps, high charge carrier mobility, and good thermal conductivity [1-2]. In 1990s, the performance of the group-III nitride semiconductor devices progressed dramatically, and it induced large advances in the solid-state lighting and laser technologies [3-4]. For example, the light-emitting diodes (LEDs), whose bandgaps are in the blue and near-ultraviolet regions, are extensively applied to our daily life [5-6]. Because the bandgap of aluminum nitride (AlN) and indium nitride (InN) are 6.2 eV and 0.7 eV, In$_X$Al$_{1-X}$N can have the bandgap range varied from 6.2 eV to 0.7 eV, which is from ultraviolet to near infrared, depending on the composition x. In addition, In$_{0.18}$Al$_{0.82}$N has the same a-lattice constant to gallium nitride (GaN), which can make strain-free heterostructure used to fabricate high-performance devices [7].

Recently, more and more efforts have been devoted to develop the growth of III-nitride on silicon (Si). The advantages of using Si substrate include large wafer size up to 18 inch, ultrahigh crystal quality, low cost, and compatible to integrated circuits (IC) industry. However, when the group-III nitride is grown on Si substrate, there is an amorphous silicon nitride (SiNx) interlayer formed between substrate and film. The nucleation stage of film growth is strongly influenced by SiNx [8]. Although there is an amorphous interlayer between Si substrate and group-III nitrides, the films were still grown epitaxially on Si substrates [9-10]. Some studies have indicated that the crystalline- $\beta$–Si$_3$N$_4$ layer is formed in the beginning of film growth, and then becomes amorphous layer [11-12]. However, some studies found that the epitaxial growth of group-III nitride film is formed directly on Si substrate without the SiNx interlayer, and SiNx is subsequently formed because of nitrogen diffusion to the interface [13].

The motivation of this thesis is to figure out the mechanism of the SiNx interlayer formation. By reactive magnetron sputter epitaxy (MSE), In$_X$Al$_{1-X}$N film is deposited on Si (111) substrate. In order to know timing of the SiNx interlayer formation, experiments are designed in four series to separate each steps of MSE technique. The growth rate performances from metal targets is investigated by X-ray diffraction (XRD), and the structure and composition is characterized by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX).
Besides, the material in the interlayer can be also studied.
2. Magnetron sputter deposition

2.1 The concept of sputtering

The concept of sputter deposition is a process of generating atoms from the target material by the bombardment with energetic ions, and then the sputtered atoms reach and condense on the substrate to form a thin film. In this deposition mechanism, the deposition chamber must be at vacuum condition. Ultra-high vacuum (less than $10^{-8}$ Torr) condition is recommended to reduce the incorporation of impurities from the background residue gas during deposition. Besides, higher vacuum condition can increase the mean free path of sputtered atoms to travel to the substrate.

In the beginning, a sputtering gas is introduced into the chamber (Ar or N$_2$ are used in this work). By applying a negative potential to the target material, the sputtering gas is discharged to ions and form a plasma state. The positive ions are accelerated toward and bombard the target by the applied negative potential. The energy of ions transfer to the target during striking. If it is high enough to overcome the surface binding energy of the target, atoms of the target can be sputtered away. There is only some part of the energy transfer from ions to the target atoms and the fraction is given by [14]:

$$E = \frac{4M_1M_t}{(M_1+M_t)^2}$$

(2.1)

where $E$ is the transferred energy, $M_1$ is the mass of the sputtering ion, and $M_t$ is the mass of the target atom. The sputtering yield is the number of sputtered atoms from the target per incident ion. It is a measurement to gain the efficiency of sputtering process [15].

While bombarding the target, the interaction also generates secondary electrons from the target. The secondary electrons are important to keep the discharging process for plasma. The secondary electrons are accelerated away from the target because of the applied negative potential, and further ionize the sputtering gas by scattering. Furthermore, the result of the sputtering ions may be reflection or neutralization after the bombardment. The reflected neutral atoms may reach the substrate with a sufficient energy and induce the effect of particle bombarding on the film atoms. The sputtering ions can also be implanted in the target. A schematic of the sputtering process is plotted in Figure 2.1.
Figure 2.1. The illustration of the sputtering process.

2.2 Magnetron sputtering

Magnetron sputtering is a technique to enhance the ionization possibility of the gas by magnetic field during sputtering. The permanent magnets are mounted at the backside of the target. After the secondary electrons are ejected from the target and accelerated away by the electric field from the applied potential, the electrons move in a cycloid motion with the Lorentz force near the target surface by the effect of magnetic and electric fields. According to this mechanism, the secondary electrons can be trapped near the target until energy losing, the plasma can be confined close to the target surface, and the ionization probability of the sputtering gas in this region can subsequently be increased. Thence, plasma can be sustained with a lower target potential and a lower working pressure.

There are three types of magnetrons as shown in Figure 2.2. In balanced magnetron, the field lines are coupled because the center and outer poles are equally strong. However, only some of field lines are coupled because of unequally strength of poles in the case of unbalanced magnetron. The unbalanced magnetron type II is used for film deposition in this thesis. Because the center magnet cannot catch all the field lines from the outer ring magnet, some secondary electrons can travel along the field lines which leave away to chamber space and the substrate. These electrons can ionize the sputtering gas and the plasma can be extended close to the substrate, which can influence the film deposition process due to the ion bombardment [16-17].
In order to form a compound film on the substrate, chemical reactions between the sputtering gas and the target material is employed, which is called reactive sputtering.

### 2.3 Reactive magnetron sputter epitaxy

Epitaxy is defined as a crystalline film grown on a crystalline substrate, and one of in-plane orientations of the film and substrate are parallel to each other. If the epitaxial film and the substrate are the same materials, the growth is called homoepitaxy; otherwise it is referred to heteroepitaxy. Thence, MSE means that a film can be grown epitaxially on a substrate by magnetron sputter deposition.

Initially, sputtered atoms transport from the target to the substrate and condense on or desorb from substrate surface. The adsorbed atoms on the substrate is called as adatoms. These adatoms diffuse on the substrate surface and interact with other adatoms. If the adatom gains enough energy to overcome the binding energy with substrate, the adatom can also leave from the surface resulting in desorption. The interaction of adatoms will form small clusters to minimize the total free energy, and further only when clusters reach to the critical size, they will become stable nuclei. This is so-called nucleation stage. While nuclei size increases, they get close to each other and can merge to each other. This is the coalescence stage. This procedure is repeated during film growth.

![Diagram of 3 types of magnetrons](image)
According to the performance of growth process described above, there are three major growth modes [18].

I. Frank-van der Merwe (FM) mode:
This is a two-dimensional (2D) layer-by-layer growth mode. Because the binding energy between adatoms and substrate is stronger than between adatoms, adatoms easily form monolayer on the substrate.

II. Volmer-Weber (VW) mode:
This is a three-dimensional (3D) island growth mode. This case is inversely to FM growth mode. Because the binding energy between adatoms is stronger than the one between adatoms and substrate, clusters are easily formed on the substrate and then coalesce to large 3D islands.

III. Stranski-Krastanov (SK) mode:
This is a mixed growth mode. 2D layer-by-layer growth forms first and it transfers to 3D island growth.

The film growth process is strongly related to the adatom mobility and lifetime. Figure 2.3 shows a schematics of a MSE system. A heater, which is behind the substrate holder, can apply thermal heat to the substrate. When growth temperature is high, the density of stable nuclei decrease because of thermodynamic effect increasing adatom mobility to form a layer-by-layer growth. However, high temperature can induce more impurities to be desorbed from surroundings and to be incorporated into film growth. To enhance adatom kinetics, the substrate can also be biased to apply a negative potential, which can promote higher adatom migration to form epitaxial growth. And the growth temperature can be lower. However, too higher substrate bias can enhance ion bombardment to form point defects and deteriorates film quality during growth.

In the reactive magnetron sputter epitaxy, sputter gas can react with the target and form a thin compound layer on the target surface. Then, the compound is sputtered away and deposits on the substrate instead of only pure metal film. Because the compound layer on the target may reduce the sputtering yield, an optimization of growth parameters is needed.
Figure 2.3. The illustration of the sputtering deposition system
3. Characterization techniques

3.1 Transmission Electron Microscopy (TEM)

3.1.1 Introduction

TEM techniques are widely applied in academia and industry because TEM provides not only material images but also structural, crystallographic, and compositional information by different operation modes and imaging techniques. The principle of a TEM is similar to an optical microscopy in many ways. However, optical microscopes have the resolution limitation, which can only achieve down to ~200 nm, because of long wavelength of the light.

To overcome this limitation, electrons have been introduced to be used as the radiation source. The dualism principle between particle and wave defines that electrons have wave characteristics and the wavelength is \( \lambda = \frac{h}{p} \). Electrons have the short wavelength related to the energy. By replacing electrons as the radiation source instead of light, the first TEM was built by Ruska and Knoll in 1932. Besides, because the radiation source is based on electrons instead of light, the lenses in the microscopy are magnetic. According to the advantage of short wavelength, a TEM can give images in atomic resolution.

Nevertheless, there are some typical limitations of TEM. First, images are only greyscale without color. Second, because of the small volume of analyzing sample, it may not represent the entire sample [19]. Third, the sample can be damaged by the electron beam. Furthermore, preparation of sample is a necessary but destructive procedure [20]. In this thesis, FEI Tecnai F20 named as-Galadriel and FEI double-corrected Titan named as-Arwen were used for analyses, shown in Figure 3.1.
3.1.2 The principle of TEM

TEM should be operated at high vacuum condition (less than $10^{-6}$ Torr) or else electrons cannot reach the sample because of the long mean free path. The electrons are generated from the electron gun, and they are accelerated by a voltage which is around 60 kV to 400 kV. The electron beam with high energy can give higher atomic resolution. For example, electrons which are accelerated by 200 kV (the condition in Galadriel) have wavelength of 2.5 pm.

The electron beam is focused to a small area on the sample by a set of electromagnetic lenses which are the condenser lens system. After the beam is incident on the sample whose thickness is less than 100 nm, both transmission and scattering of electrons occur. The sample is at the objective plane of the objective lens. The transmitted and scattered electrons are focused by objective lens and the image is magnified by intermediate lens and projector lens. Then, the image is projected on a fluorescent screen or recorded by a CCD camera [21]. The schematic structure of the TEM is shown in Figure 3.2.
3.1.3 Lens aberrations

Although TEM is a versatile instrument, electromagnetic lenses have aberrations which are referred to lens effect and limit resolution. There are different kinds of aberrations which have several effects on electrons, and common aberrations includes chromatic aberration, and spherical aberration [22]. The same effect of these three aberrations increases the inclination angle of the electrons on the optical axis.

The chromatic aberration results in a limit on the image transfer and a loss of information. It influences to decrease the energy of electrons and then makes the inability to focus electrons with energy variations on the same point of the optical axis. The spherical aberration results in a limit on the resolution. It relates to that electrons scattered with different angles from sample focus on different points of the optical axis. It brings about a phase shift of electrons and the non-accuracy of image interpretation. Take the delocalization of image due to the spherical aberration for example, shown in Figure 3.3. Figure 3.3 (a) shows that the delocalization affects the image. In the interlayer, there is crystallinity on the bottom due to Si substrate and on the top due to Al protective layer. However, the interlayer isn’t influenced by the
crystal substrate and protective layer in Figure 3.3 (b).

Figure 3.3. Cross-sectional HR-TEM images in same area (a) with and (b) without delocalization effect.

3.2 X-ray Diffraction (XRD)

XRD is commonly used to study the structure and crystallinity of materials. It is a non-destructive technique and it is not needed for sample preparation in lots of cases. It can be used to get information of crystallographic structure, epitaxial relations, and composition of the sample [23-24]. By applying a high voltage to accelerate electrons in a vacuum tube, the metal target which is struck by electrons can generate X-ray. Common materials of metal targets are copper, chromium, and molybdenum [25]. In this thesis, copper are used for the target. Moreover, in order to filter out Cu K\textsubscript{β} X-rays, Nickel (Ni) is used as the filter at the exit of tube. The rest useful X-rays for detecting is Cu K\textsubscript{α} whose wavelength \( \lambda \) is 1.54 Å.

The principle of XRD is based on scattering. When X-rays are incident on the sample, the X-rays diffract and interfere with each other. Due to periodic atomic planes in crystalline material, X-rays with a wavelength whose magnitude is same order as atomic distances can scatter and interfere constructively. According to Bragg’s law, constructive interference occurs only when the path length difference of two X-rays differs by an integer number of wavelengths, shown in Figure 3.4. The Bragg’s law:

\[
    n\lambda = 2d \sin \theta \tag{4.1}
\]

where \( n \) is an integer number, \( \lambda \) is the wavelength of X-rays, \( d \) is the lattice plane distance and \( \theta \) is the diffraction angle. Bragg’s law states the maximum of diffraction
intensity appears when there is an integer number of wavelength. Besides satisfying Bragg’s law, the intensity of diffracted X-ray is related to many factors, such as polarization factor, Lorentz factor, structure factor, etc. [23].

![Diagram of XRD following Bragg's law](image)

Figure 3.4. The schematic principle of XRD following Bragg’s law.
4. In$_X$Al$_{1-X}$N thin film growth

4.1 MSE system

All samples were grown by a DC reactive magnetron epitaxy named as Ragnarök, shown in Figure 4.1. The base pressure of around 2x10$^{-9}$ Torr of the chamber can be achieved with a combination of a turbo molecular pump and an oil mechanical pump. Four metal targets were mounted on type-II unbalanced magnetrons in the bottom of the chamber. Two of them are 75 mm-diameter targets and the others are 50 mm-diameter. High purity 75 mm-diameter aluminum (99.9999%) and indium (99.9999%) target sources were used for film growth. Sputtering gas pipes were connected to the chamber. N$_2$ (99.999999%) and Ar (99.999999%) were used in the thesis. Moreover, in order to deposit In$_X$Al$_{1-X}^{15}$N film, the nitrogen isotope $^{15}$N$_2$ (98%) was used. During sputtering process, electronic mass flow controller can control the sputtering gas flow rate, and the pressure is 5 mTorr. Si substrates are placed on the sample holder. In order to grow uniform film on the substrate, the substrate holder are rotated with a speed of 30 rpm.

![Figure 4.1. The MSE system, named as-Ragnarök, is used in this thesis.](image)

4.2 Experimental details

Before film deposition, Si substrates were dipped into hydrofluoric acid (HF) solution to etch away native silicon oxide (SiO$_2$) film according to the RCA cleaning procedure. The solution ratio of HF (48–51%) with deionized (D.I.) water is 1 to 3.
Place and leave Si substrates in HF solution for 2 min, and then rinse substrates with D.I. water twice.

After placing Si substrates on the sample holder and transferring in the deposition chamber, indirectly heat Si substrates for degassing procedure to 1000°C for 10 min by heater which is behind the sample holder. There are four series experiments, which are I. InAlN presputtering, II. InAlN sputter deposition, III. InAlN direct deposition, and IV. InAlN direct deposition using nitrogen isotope. For In$_x$Al$_{1-x}$N thin film growth, 75 mm-diameter Al and In target sources are co-sputtered by N$_2$ sputtering gas at a total pressure of 5 mTorr at 800°C. For Al protective layer growth, a 15 nm Al layer was sputtered at 17°C by Ar at a total working pressure of 5 mTorr for 6 min. The Al magnetron power was kept at 30 W.

I. InAlN presputtering

In this series, the procedure is only presputtering by closing shutters of metal targets and substrate. The power of the Al and In magnetrons are 300 W and 8 W respectively, and the presputtering process is 2 min. There is one sample, named as IAP01, in this series. The schematic structure of sample is shown in Figure 4.2 and the growth condition is listed in Table 4.1.

![Figure 4.2. The illustration of the sample structure of InAlN presputtering.](image)

Table 4.1. The growth condition of InAlN presputtering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>3” Al target power</th>
<th>3” In target power</th>
<th>$^{14}$N$_2$ gas flow</th>
<th>Growth temperature</th>
<th>Presputtering time</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAP01</td>
<td>300 W</td>
<td>8 W</td>
<td>5 mTorr</td>
<td>800°C</td>
<td>2 min</td>
</tr>
</tbody>
</table>

II. InAlN sputter deposition

In this series, the growth of In$_x$Al$_{1-x}$N thin film was used a normal MSE procedure. After presputtering for 2 min, open shutters to deposition In$_x$Al$_{1-x}$N film on the substrate for 10 min. The power of the Al and In magnetrons are 300 W and 10 W respectively. The schematic structure of sample is shown in Figure 4.3 and the
growth condition is listed in Table 4.2.

![Sample Structure Diagram](image)

**Figure 4.3.** The illustration of the sample structure of InAlN sputter deposition

<table>
<thead>
<tr>
<th>Sample</th>
<th>3” Al target power</th>
<th>3” In target power</th>
<th>14N₂ gas flow</th>
<th>Growth temperature</th>
<th>Presputtering time</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAS01</td>
<td>300 W</td>
<td>10 W</td>
<td>5 mTorr</td>
<td>800°C</td>
<td>2 min</td>
<td>10 min</td>
</tr>
</tbody>
</table>

**III. InAlN direct deposition**

In this series of experiment, the InₓAl₁₋ₓN films were directly grown on Si substrates without closing shutters. There are four samples, named as IAD01, IAD02, IAD03, and IAD04. For IAD01 and IAD02, the growth time is 20 sec to deposit ~2 nm thin film thickness. For IAD03 and IAD04, the growth time is 105 sec to deposit ~10 nm film thickness. In addition, there is one more step including quenching or 20 min waiting after deposition. For IAD01 and IAD03, samples were immediately cooled down to 17°C after deposition. For IAD02 and IAD04, samples were maintained at 800°C for 20 min after deposition, and then cooled down to 17°C. The schematic structure of sample is shown in Figure 4.4 and the growth condition is listed in Table 4.3.

![Sample Structure Diagram](image)

**Figure 4.4.** The illustration of the sample structure of InAlN direct deposition.
<table>
<thead>
<tr>
<th>Sample</th>
<th>3” Al target power</th>
<th>3” In target power</th>
<th>$^{14}$N$_2$ gas flow</th>
<th>Growth temperature</th>
<th>Growth time</th>
<th>$^{15}$N$_2$ gas flow</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAD01</td>
<td>300 W</td>
<td>10 W</td>
<td>5 mTorr</td>
<td>800°C</td>
<td>20 sec</td>
<td>Quench</td>
<td></td>
</tr>
<tr>
<td>IAD02</td>
<td>300 W</td>
<td>10 W</td>
<td>5 mTorr</td>
<td>800°C</td>
<td>20 sec</td>
<td>Wait for 20 min</td>
<td></td>
</tr>
<tr>
<td>IAD03</td>
<td>300 W</td>
<td>10 W</td>
<td>5 mTorr</td>
<td>800°C</td>
<td>105 sec</td>
<td>Quench</td>
<td></td>
</tr>
<tr>
<td>IAD04</td>
<td>300 W</td>
<td>10 W</td>
<td>5 mTorr</td>
<td>800°C</td>
<td>105 sec</td>
<td>Wait for 20 min</td>
<td></td>
</tr>
</tbody>
</table>

**IV. InAlN direct deposition using isotopically enriched nitrogen**

There are two samples, named as IAD05 and IAD07. In this series, the nitrogen isotope ($^{15}$N$_2$) was used as sputtering gas to grow In$_X$Al$_{1-X}$N film. For IAD05, the In$_X$Al$_{1-X}$N film of 2 nm thickness is grown first, and then deposit In$_X$Al$_{1-X}$N film of 10 nm thickness. For IAD07, the order of the film deposition is inversely to IAD05. The schematic structures of IAD05 and IAD07 are shown in Figure 4.5 and the growth conditions are listed in Table 4.4 and 4.5 respectively.

![Figure 4.5. The illustrations of the sample structure of IAD05 and IAD07.](image)

**Table 4.4. The growth condition of IAD05.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>3” Al target power</th>
<th>3” In target power</th>
<th>Growth temperature</th>
<th>$^{14}$N$_2$ gas flow</th>
<th>Growth time</th>
<th>$^{15}$N$_2$ gas flow</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAD05</td>
<td>300 W</td>
<td>10 W</td>
<td>800°C</td>
<td>5 mTorr</td>
<td>20 sec</td>
<td>5 mTorr</td>
<td>105 sec</td>
</tr>
</tbody>
</table>
Table 4.5. The growth condition of IAD07.

<table>
<thead>
<tr>
<th>Sample</th>
<th>3” Al target power</th>
<th>3” In target power</th>
<th>Growth temperature</th>
<th>$^{15}$N$_2$ gas flow</th>
<th>Growth time</th>
<th>$^{14}$N$_2$ gas flow</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAD07</td>
<td>300 W</td>
<td>10 W</td>
<td>800°C</td>
<td>5 mTorr</td>
<td>20 sec</td>
<td>5 mTorr</td>
<td>105 sec</td>
</tr>
</tbody>
</table>
5. Results and discussion

5.1 The composition of the In$_x$Al$_{1-x}$N film

Because of replacing new metal targets, a calibration of sputtering condition was done before this thesis work. The composition of the In$_x$Al$_{1-x}$N film can be determined by Vegard’s rule [26]:

$$C_{\text{In}_x\text{Al}_{1-x}\text{N}} = C_{\text{InN}}X + C_{\text{AlN}}(1 - X) \quad (5.1)$$

where $C_{\text{In}_x\text{Al}_{1-x}\text{N}}$, $C_{\text{InN}}$, $C_{\text{AlN}}$ are the \textit{c} lattice parameters of In$_x$Al$_{1-x}$N, InN, and AlN respectively. The lattice parameters $C_{\text{InN}}$ and $C_{\text{AlN}}$ are 0.571 nm and 0.498 nm, respectively. A symmetric 0-20 XRD scan of IAS01 is shown in Figure 5.1. The scan range is from 26° to 40° to cover Si (111) and Al (111) peaks. According to In$_x$Al$_{1-x}$N peak position, an In-content, $x$, of 0.17 is obtained, calculated by Vegard’s rule. However, the calculation doesn’t consider about the strain effect. The composition ($x=0.17$) indicates that the growth rates from Al and In targets are not different to previous growth conditions. The new condition will be used in this thesis work.

![Figure 5.1. A symmetric 0-20 XRD scan of IAS01.](image-url)
5.2 TEM images of sample structure

5.2.1 InAlN presputtering

IAP01

Figure 5.2 shows the HR-TEM images of IAP01. In Figure 5.2 (a) and (b), the total thickness of film is ~10 nm. Although, only presputtering procedure was applied to this experiment, there is a ~1.2 nm amorphous interlayer grown between Si substrate and Al protective layer. It indicates that the amorphous layer was formed on the substrate before shutter opened to grow InAlN in normal MSE procedure. Besides, there are grains in Al protective layer, and the orientations are different. The inset in Figure 5.2 (a) is the fast Fourier transform (FFT) which is chosen in the Si substrate area. By calculating the ratio of diffraction spot distances, the electron beam direction, zone axis, can be indexed as [0 1 1].

![Figure 5.2. Cross-sectional HR-TEM images of IAP01.](image)

5.2.2 InAlN sputter deposition

IAS01

Figure 5.3 shows the HR-TEM images of IAS01. The d-spacing of Si (111) is 3.326 Å, and the d-spacing of wurtzite AlN and InN equal to c/2 are 2.491 Å and 2.859 Å, respectively. By measuring d-spacing, it can confirm the material of film. In Figure 5.2 (a), the d-spacing of the upper InXAl1-XN layer is larger than the lower layer. It shows that In incorporation is less in the beginning of deposition, and
increases during deposition. In addition, it is obviously that there is an interlayer, which thickness is 1.46 nm, between Si substrate and In$_x$Al$_{1-x}$N film. Figure 5.2 (b) is a high-magnification TEM image. Although the interlayer shows mostly an amorphous structure, there are some partial crystalline structures embedded in the layer. The d-spacing of these partial crystalline structures is in the range from 2.9 Å to 3.3 Å which indicates that these crystals are not from In$_x$Al$_{1-x}$N. However, it is hard to determine that this d-spacing is from crystalline SiN$_x$ because the FFT of these partial crystalline structures is too small to get the clear diffraction pattern to give the orientation. Besides, there are two stable structures of crystalline SiN$_x$ which are trigonal $\alpha$–Si$_3$N$_4$ and hexagonal $\beta$–Si$_3$N$_4$. It also increase difficulty in identifying the crystalline structure of SiN$_x$. Figure 5.4 is the EDX line profile of IAS01, which provides element’s distributions from substrate to film. By comparing the thickness of the interlayer from HR-TEM images with the EDX profile, it shows that there are Si and N distributions at early stage of the interlayer. Therefore, it indicates that the interlayer is SiN$_x$, and the partial crystalline structure may be $\alpha$–Si$_3$N$_4$ (111) (d-spacing is 3.18 Å), $\alpha$–Si$_3$N$_4$ (201) (d-spacing is 2.87 Å), or $\beta$–Si$_3$N$_4$ (200) (d-spacing is 3.31 Å) [27]. Furthermore, based on Al and In signals, it shows that In incorporation is less in the beginning of film growth, which corresponds to the result from Figure 5.2 (a).

![Figure 5.3. Cross-sectional HR-TEM images of IAS01.](image)
5.2.3 InAlN direct deposition

IAD01

Figure 5.5 shows the HR-TEM images of IAD01. In Figure 5.5, the thickness of In\(_x\)Al\(_{1-x}\)N film is \(~2.99\) nm. In Figure 5.5 (a), the total thickness of film is 17.57 nm. Figure 5.5 (b) shows that there are grains of Al protective layer and parts of In\(_x\)Al\(_{1-x}\)N film are not covered with Al layer. In Figure 5.5 (c) and (d), In\(_x\)Al\(_{1-x}\)N film is covered without and with Al protective layer respectively in higher magnification. There is an amorphous interlayer between Si substrate and In\(_x\)Al\(_{1-x}\)N film, and partial crystalline structures are in the interlayer. In Figure 5.5 (c), there are still partial crystalline structures in the interlayer although there is no Al layer covering, and it indicates that partial crystalline structures is not related to Al layer. Figure 5.5 (e) is the sectional image chosen from Figure 5.5 (d). In Figure 5.5 (e), the thickness of the interlayer is \(~1.42\) nm. Besides, it also shows that some parts of In\(_x\)Al\(_{1-x}\)N film are directly grown on Si substrate. Figure 5.6 is the EDX line profile of IAD01. By comparing the thickness of the interlayer from HR-TEM images with the EDX profile, it shows that there are Si and N distributions in the interlayer. According to the d-spacing measurement in Figure 5.5 (e) and elemental distribution in EDX profile, the partial
crystals in the interlayer mixes with crystalline SiN$_X$ and In$_X$Al$_{1-X}$N. It indicates that some crystalline SiN$_X$ and In$_X$Al$_{1-X}$N can be formed in the beginning of deposition.

Figure 5.5. Cross-sectional HR-TEM images of IAD01.
Figure 5.6. EDX line profile of IAD01.

IAD02

Figure 5.7 shows the HR-TEM images of IAD02. The thickness of In$_{X}$Al$_{1-X}$N film is $\sim$2.91 nm. In Figure 5.7 (a), the total thickness of film is 15.13 nm. In Figure 5.7 (b), there is an amorphous interlayer between Si substrate and In$_{X}$Al$_{1-X}$N film. Figure 5.7 (c) is the sectional image chosen from Figure 5.7 (b). It shows that the thickness of the interlayer is $\sim$1.45 nm and there are partial crystalline structures in the interlayer. It also shows some parts of In$_{X}$Al$_{1-X}$N are directly grown on Si substrate. Moreover, by d-spacing measurement of these crystals, some crystalline structure are crystalline Si$_X$ and some are In$_{X}$Al$_{1-X}$N. Therefore, in the beginning of deposition, some crystalline Si$_X$ and In$_{X}$Al$_{1-X}$N can be formed.
IAD03

Figure 5.8 shows the HR-TEM images of IAD03. The thickness of In$_X$Al$_{1-X}$N film is ~7.7 nm. In Figure 5.8 (b), there is an amorphous interlayer, whose thickness is 1.45 nm, between Si substrate and In$_X$Al$_{1-X}$N film. Figure 5.8 (c) is the sectional image chosen from Figure 5.8 (b). In Figure 5.8 (c), there are partial crystalline structures in the interlayer, and some parts of In$_X$Al$_{1-X}$N film are directly grown on Si substrate. Figure 5.9 is the EDX line profile of IAD03. By comparing the thickness of the interlayer from HR-TEM images with the EDX profile, it shows that there are Si and N distributions in the interlayer. The partial crystals in the interlayer are crystalline SiN$_X$ and In$_X$Al$_{1-X}$N and it means that some crystalline SiN$_X$ and In$_X$Al$_{1-X}$N can be formed in the beginning of deposition.
Figure 5.8. Cross-sectional HR-TEM images of IAD03.

Figure 5.9. EDX line profile of IAD03.
IAD04

Figure 5.10 shows the HR-TEM images of IAD04. The thickness of In$_x$Al$_{1-x}$N film is \(~8.5\) nm. Figure 5.10 (b) shows that there is an amorphous interlayer, whose thickness is \(1.22\) nm, between Si substrate and In$_x$Al$_{1-x}$N film. Figure 5.10 (c) is the sectional image chosen from Figure 5.10 (b). In Figure 5.10 (c), there are partial crystalline structures in the interlayer, and some parts of In$_x$Al$_{1-x}$N film are directly grown on Si substrate. According to d-spacing measurement, the partial crystals are crystalline Si$_x$N$_y$ and In$_x$Al$_{1-x}$N. Thence, it indicates that some crystalline Si$_x$N$_y$ and In$_x$Al$_{1-x}$N can be formed in the beginning of deposition.

![Figure 5.10. Cross-sectional HR-TEM images of IAD04.](image)

5.2.4 InAlN direct deposition using isotopically enriched nitrogen

IAD05

Figure 5.11 shows the HR-TEM images of IAD05. The thickness of In$_x$Al$_{1-x}$N film is \(~4.61\) nm. In Figure 5.11 (b), there is an amorphous interlayer between Si substrate and In$_x$Al$_{1-x}$N film. Figure 5.11 (c) is the sectional image chosen from Figure 5.11 (b). Figure 5.11 (c) shows that the thickness of the interlayer is \(1.22\) nm and there are partial crystalline structures in the interlayer. Besides, some parts of
In$_x$Al$_{1-x}$N film are directly grown on Si substrate. Figure 5.12 is the EDX line profile of IAD05. However, the EDX profile shows different results, where In signal rises before N signal, from other samples. It means that there is In distribution in Si substrate. Therefore, the time of flight secondary ion-mass spectroscopy (ToF-SIMS) profile can be introduced to support the results from HR-TEM. Figure 5.13 is a ToF-SIMS depth profile of IAD05 in negative mode. In Figure 5.13, it clearly shows that SiN$^-$ signal rises before AlN$^-$ and InN$^-$ signals, and it indicates that SiNx is the dominated material between Si substrate and In$_x$Al$_{1-x}$N film. Since the sample holder used to load three samples for deposition, and the central one is used to ToF-SIMS analysis and the outer one is to TEM investigation. The growth condition may be different between central and outer regions. Hence, we cannot rule out the possibility of deposition condition which makes result differences between ToF-SIMS profile and EDX profile. By accompanying ToF-SIMS profile and HR-TEM images, it shows that the interlayer is SiNx. It also indicates that some crystalline SiNx and In$_x$Al$_{1-x}$N can be formed in the beginning of deposition.

Figure 5.11. Cross-sectional HR-TEM images of IAD05.
Figure 5.12. EDX line profile of IAD05.

Figure 5.13. ToF-SIMS depth profile of IAD05 in negative mode.
There is no HR-TEM image of IAD07. Figure 5.14 is the EDX line profile of IAD07. In Figure 5.14, it shows that N signal rises before Al and In signals and it means that there is a SiN\text{\textsubscript{X}} interlayer between Si substrate and In\textsubscript{X}Al\textsubscript{1-X}N film.

![EDX line profile of IAD07](image)

**Figure 5.14.** EDX line profile of IAD07.

### 5.2.5 Discussion

From these four series of experiments, a SiN\textsubscript{X} interlayer grown between Si substrate and In\textsubscript{X}Al\textsubscript{1-X}N film can be seen in all samples. The thickness of the interlayer is in the range from 1.2 nm to 1.5 nm. In addition, there are partial crystalline structures in the interlayer. In InAlN sputter deposition series, according to d-spacing measurement, it shows that the partial crystalline structures are mostly referred to crystalline SiN\textsubscript{X}. However, in InAlN direct deposition series, some partial crystalline structures are crystalline SiN\textsubscript{X} and some are In\textsubscript{X}Al\textsubscript{1-X}N which is directly grown on the substrate. The difference between these two series is with and without presputtering procedure. Hence, the presputtering procedure provides a chance to have higher nitrogen ion ratio to Al and In to reactive with Si substrate and form SiN\textsubscript{X}. In addition, In\textsubscript{X}Al\textsubscript{1-X}N film can be directly deposited accompanying with SiN\textsubscript{X} during deposition without closing shutters of substrate and targets. In InAlN direct deposition series, there is a variable which is quenching or 20 min waiting after
deposition. The number of crystalline structures in the interlayer from samples, maintained at 800°C for 20 min, is more than samples, quenched directly. Comparing IAD05 with InAlN direct deposition series, the crystal quality of IAD05 is not as good as InAlN direct deposition series. In HR-TEM of IAD05, the In$_x$Al$_{1-x}$N film is disorder because the film is grown in discontinuous way. The In$_x$Al$_{1-x}$N film is grown first, and then deposit In$_x$Al$_{1-x}$\textsuperscript{15}N film on it.
6. Conclusion

In\textsubscript{X}Al\textsubscript{1-x}N film deposited on Si (111) substrates is realized by MSE technique in this thesis work. There are four implemented series of experiments, which are I. InAlN presputtering, II. InAlN sputter deposition, III. InAlN direct deposition, and IV. InAlN direct deposition using isotopically enriched nitrogen. Samples were investigated to figure out the mechanism of the interlayer growth by XRD, and TEM.

The symmetric $\theta$-$2\theta$ XRD shows that the composition $x$ of In\textsubscript{X}Al\textsubscript{1-x}N film is 0.17. In\textsubscript{X}Al\textsubscript{1-x}N growth rate has no big difference after changing Al and In targets.

According to HR-TEM images, an amorphous interlayer, whose thickness is in the range from 1.2 nm to 1.5 nm, is formed between Si substrate and In\textsubscript{X}Al\textsubscript{1-x}N film. Based on the EDX profile with respected thickness of the interlayer measured from HR-TEM images, the interlayer is mostly associated to Si\textsubscript{N\textsubscript{x}}. In this interlayer, there are partially crystalline structures. By comparing d-spacing measurement of partial crystalline structures and EDX line profile, the material can be known and it indicates that the partially crystalline is also Si\textsubscript{N\textsubscript{x}}. According to InAlN sputter deposition series and InAlN direct deposition series, In\textsubscript{X}Al\textsubscript{1-x}N film can be directly deposited accompanying with Si\textsubscript{N\textsubscript{x}} growth on the Si substrate during deposition without presputtering procedure. Thence, some Si\textsubscript{N\textsubscript{x}} crystal and In\textsubscript{X}Al\textsubscript{1-x}N film can be formed at the same time in the beginning of deposition. In InAlN direct deposition series, the interlayer of samples (IAD02, IAD04), maintained at 800°C for 20 min, have more crystalline structures than samples (IAD01, IAD03), quenched directly.
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