Reactive Sputtering Growth of Indium Nitride Thin Films on Flexible Substrate Under Different Substrate Temperatures

S. A. Osman, S. S. Ng*, Z. Hassan
Institute of Nano Optoelectronics Research and Technology (INOR), Universiti Sains Malaysia, 11800, USM, Penang, Malaysia
*shashiong@usm.my

Abstract. Indium nitride (InN) thin films were deposited on kapton polyimide substrate by using reactive gas-timing radio frequency (RF) sputtering technique. An indium target with purity of 99.999% was used. Throughout this work, the RF power and gas ratio of argon and nitrogen were maintained at 60 W and 40:60 (Ar:N₂), respectively. The substrate temperature was varied from room temperature to 300°C. The surface morphology, structural and electrical properties of the deposited thin films as a function of the substrate temperature were investigated. All the deposited InN thin films have wurtzite crystal structure with preferred orientation along the (101) direction. The InN (101) peak becomes stronger and sharper as the substrate temperature increases from 100°C to 300°C. In addition, the packing density of the grains increases as the substrate temperature increases. The deposited InN films exhibit n-type conductivity behavior and its Hall mobility increases from 720 cm²/V·s to 2670 cm²/V·s as the substrate temperature increases from room temperature to 300 °C. These results imply that nucleation and crystal growth as well as the crystalline quality were improved at higher substrate temperatures. All the results lead to conclude that the optimal substrate temperature for the deposition of InN was 300 °C.

1. Introduction
Indium nitride (InN) is a potential semiconductor material used in the development of light-emitting diode, laser diode, photodetector, high frequency transistor operating at high power and temperature, and high efficiency low cost solar cell [1–4]. The corporation of InN and its alloys with gallium nitride and aluminum nitride have allowed the extension of light emission from ultraviolet to infrared region [5]. In addition, the low resistivity property of InN layer was used to assist ohmic contact formation to other wide band gap nitrides [6].

Among the III–nitrides, the growth of InN is the most challenging one. This is owing to its low dissociation temperature and the high equilibrium nitrogen (N₂) vapor pressure [7]; hence, suitable conditions for the deposition are very stringent. Therefore, researchers are working hard in finding a promising method to grow good quality InN thin films. To date, InN thin films are grown by molecular beam epitaxy [8], metal-organic vapor phase epitaxy [9], and hydride vapor phase epitaxy [10]. However, most of the methods required the complicated setups, toxic precursor and costly in productions. Consequently, a low-cost, simpler, safe, non-toxic, and scalable method to produce InN-based semiconductors is highly desirable.

Recently, sputtering technique has received enormous attention as an alternative candidate for the growth of InN thin films [11-13]. This technique is relatively simpler, cheaper and scalable as compared...
to the aforementioned growth techniques [14]. Moreover, the special attribute of this technique is the ability to deposit the InN thin films at lower temperatures. Consequently, the challenges such as the high equilibrium N\(_2\) vapor pressure and low dissociation temperature of InN can be overcome. Apart from that, the low temperature growth process would allow less expensive and flexible substrate materials to be used. For instance, the growth of InN thin films on kapton polyimide flexible substrates can be applied for the innovation of low cost flexible optoelectronic semiconductor devices.

Despite, the potential and promise of the sputtered InN thin films on kapton polyimide flexible substrate, relatively little detailed works devoted to this subject have been performed and few references on the sputtering growth of InN thin films on kapton [15]. Consequently, there is still plenty of room for improvement. For this reason, a systematic and in-depth study on the radio frequency (RF) reactive sputtering growth of InN thin films on kapton polyimide flexible substrate was carried out. Special attention was paid to the effects of substrate temperature on the structural, surface morphologies, and electrical properties of the deposited thin films. To access these properties, X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDX) as well as Hall effect measurement were used.

2. Experimental Details

InN thin films were deposited on kapton polyimide substrates (Kapton films type HN) by means of reactive gas-timing method via Auto HHV500 sputter coater. Inch indium (In) target with purity of 99.999% was used, and the sputtering process was performed in a mixture of argon (Ar) and N\(_2\) gasses. In this work, four sets of InN thin films deposited under different substrate temperatures were produced. Prior deposition, the substrates were first cleaned by ultrasonic agitation with ethanol for 15 minutes and later, rinsed with acetone to remove the possible surface contamination. Throughout the deposition process, the RF power and the gas ratio (Ar:N\(_2\)) were maintained constant at 60 W and 40:60, respectively. The resulting InN films thickness was controlled to be around 500 nm. In brief, the reactive sputtering growth conditions were summarized in Table 1. Noted that the experiment was limited to 300 °C because the substrates will start to deform above 300 °C [16].

| Parameters                      | Values                                           |
|---------------------------------|-------------------------------------------------|
| Target                          | Indium (99.999%)                                |
| Target diameter                 | 3 inches                                        |
| Substrate                       | Kapton polyimide                                |
| RF power                        | 60 W                                            |
| Ar:N\(_2\) gas ratio            | 40:60                                           |
| Substrate temperature (T\(_s\)) | *RT, 100 °C, 200 °C, 300 °C                     |
| Deposition time                 | 3 hours                                         |
| Base pressure                   | 2.5×10\(^{-5}\) Torr                            |
| Sputtering pressure             | 2.2×10\(^{-2}\) Torr                            |

*RT - Room temperature

Various characterization techniques were used to investigate the structural, carrier concentration, mobility and properties of the deposited thin films. Structural and growth orientation of the deposited thin films were investigated using XRD (PANalytical X’Pert Pro MRD). EDX and FESEM (NOVA NANOSEM 450) were used to access the elemental composition and morphology of the films. Lastly, the carrier concentration and mobility of the deposited films were determined by using Hall effect
system (Hall system accent HL5500PC). For the Hall effect measurements, silver (Ag) contacts were used and were deposited onto InN surface through a metal mask via thermal evaporator.

3. Results and discussion

Figure 1 illustrates the XRD diffraction patterns of bare kapton polyimide substrate, and InN thin films grown on the substrate at various substrate temperatures. The XRD patterns were measured under the 2theta-omega (2θ-ω) scan mode. From the XRD patterns, two prominent peaks originated from the substrate can be clearly observed at 22.05° and 26.25°. While a peak corresponding to wurtzite InN (002), (101), (102) and (103) was detected at 31.3°, 33.1°, 43.3° and 56.9° for all the InN thin films [Figures 1 (b) to (e)]. The strongest InN peak, i.e., InN(101) diffraction peak becomes sharper as the substrate temperature increases from 100 °C to 300 °C [17]. These changes can be attributed to the increment of the crystallite size (as shown in Table 2) as the crystallite gained more kinetic energy at higher temperature [18].

![Figure 1. XRD patterns of (a) bare kapton polyimide, and InN thin films grown on kapton polyimide at different substrate temperatures: (b) room temperature (c) 100 °C, (d) 200 °C, and (e) 300 °C.](image)

Detail analysis on, i.e. the crystallite size, dislocation density and stress for the films deposited at different substrate temperatures were performed. The crystallite size (D), dislocation density (δ) and stress (σ) of the InN thin film deposited at different substrate temperatures were calculated based on the most intense diffracted peak [i.e., InN(101)], and the results were shown in Table 2. The crystallite size, (D) of the deposited InN thin films was estimated by using Scherrer’s equation [19]:

\[
D = \frac{k\lambda}{\beta \cos\theta}.
\]

Here, \( k \) is shape factor with value of 0.89, \( \lambda \) is wavelength of the incident beam with value of 0.154 nm, \( \beta \) is the FWHM of the diffracted peak, and \( \theta \) is diffraction angle. The dislocation density (δ) of InN films is evaluated using the formula [20]:

\[
\delta = \frac{1}{D}.
\]
While, the stress develops in InN crystalline was evaluated using the following equation [21]:

$$\sigma = E (da - do)/2doY$$

(3)

where $E$ and $Y$ are the Young modulus (149 GPa) [22] and the Poisson’s ratio (0.17) [23] of InN, respectively, $da$ and $do$ are the d spacing of the bulk and InN, respectively.

Table 2. The crystallite size, dislocation density, stress and FWHM of RF sputtered InN thin films at different substrate temperatures. The results were extract from the InN(101) diffraction peak.

| $T_s$ [$^\circ$C] | Crystallite size, $D$ [Å] | Dislocation density, $\delta$ [$\times 10^{15}$ /m$^2$] | Stress, $\delta$ [GPa] | FWHM [$^\circ$] |
|------------------|--------------------------|-----------------|-----------------|-----------------|
| RT               | 23.70                    | 1.78            | 0.1410          | 1.20            |
| 100              | 23.72                    | 1.78            | 0.1865          | 0.96            |
| 200              | 23.73                    | 1.78            | 0.3135          | 0.72            |
| 300              | 23.80                    | 1.77            | 0.6075          | 0.48            |

From Table 2, it was found that the FWHM of the strongest (101) peak decreases gradually with increasing substrate temperature from room temperature to 300 $^\circ$C. While there was a little increment of crystalline size and little apparent variation the dislocation density as the substrate temperature increases. These results implied that nucleation and crystal growth as well as the crystalline quality were improved at higher substrate temperatures. The larger crystallizes were obtained at higher temperature at 300 $^\circ$C which might cause by the improvement of the nucleation and crystal growth. Apart from that, it was found that the magnitude of the stress increases significantly as the substrate temperature increases. This phenomenon is attributed to the mismatch in the thermal expansion coefficient between InN thin films and the kapton polyimide substrate. It is interesting to note here that the deposited InN thin films remain uncrack.

Figure 2 shows the surface morphology of InN thin films grown at different substrate temperatures, i.e., ranging from room temperature to 300 $^\circ$C. It was found that the InN thin film deposited at room temperature exhibits bigger and inconsistent grain sizes (Figure 2a). The grain size decreases gradually, and the surface became smoother or uniform with increasing substrate temperature, as shown in Figs 2b-2c. The behavior of the grain size as a function of substrate temperature is contrary to the conventional behavior where the grain size tends to be small with increasing substrate temperature [24]. At present, this odd behavior still remains unclear. We believe that it is most likely due to the increase of the amount of the stable InN phase at higher substrate temperature. At lower substrate temperature (room temperature), the grain may probably consist of indium oxynitride (InNO) compounds [25]. Therefore, the grain size is much bigger. Further analysis is needed to verify this subject.

To examine the elemental compositions of the deposited thin films, EDX measurements were performed and the obtained results were summarized in Figure 3. It was found that all samples contain indium, nitrogen and oxygen elements. The presence of oxygen in the deposited films might originate from kapton polyimide substrate. Nevertheless, it should be pointed out here that the oxygen is a common contaminant of InN in non-equilibrium RF sputtering deposition [26]. Figure 4 shows the chemical structure of kapton polyimide substrate [27]. From Figure 3, it was found that the atomic percentages of indium and nitrogen components were increased with increasing substrate temperature, while the oxygen component shows the opposite trend. This phenomenon is possibly due to the increment of the formation of stable InN phase as compared to that of the In$_2$O$_3$ or InNO phase. Consequently, the atomic percentage of oxygen decreases as the substrate temperature increased.
Van der Pauw Hall effect technique was applied to access the Hall mobility, carrier concentration, and resistivity of the deposited films. The obtained results were tabulated in Table 3. From Table 3, it can be seen that the value of resistivity decreases with increasing of substrate temperature. The Hall effect measurement shows that the films exhibit n-type conductivity. Figure 5 shows the Hall mobility and carrier concentration as a function of the substrate temperature. It can be seen that Hall mobility...
increases with increasing of substrate temperature, i.e., from 720 cm$^2$/V-s (at room temperature) to 2670 cm$^2$/V-s (at 300 °C). The obtained Hall mobility values are about 530 cm$^2$/V-s lower than that of bulk InN. This is most probably due to the high density of dislocations of the deposited InN thin films. The carrier concentration decreases, and the Hall mobility increases with increase of substrate temperatures. For substrate temperature of 300 °C, highest Hall mobility of 2670 cm$^2$/V-s was obtained and it might be due to the highest InN films thickness obtained at this substrate temperature. The observed decrease in carrier concentration with increasing substrate temperature can be attributed to several factors. These factors include homogenous background concentration, inhomogeneous carrier distribution in the InN films due to defect, and localized electron accumulation due to specific sheet concentration at the surface [28]. The sheet resistivity decreases is most likely due to the increase in mobility of the charge carriers [29].

**Table 3.** Hall effect results of RF sputtered InN thin films on kapton polyimide at room temperature and various substrate temperatures.

| \( T_s \) [°C] | Hall mobility [cm$^2$/V-s] | Carrier concentration [cm$^3$] | Resistivity [ohm/cm] |
|---------------|-----------------------------|-----------------------------|-------------------|
| RT            | 720                         | 2.37×10$^{21}$              | 2550              |
| 100           | 1410                        | 2.56×10$^{21}$              | 116               |
| 200           | 2260                        | 1.18×10$^{21}$              | 111               |
| 300           | 2670                        | 1.39×10$^{21}$              | 111               |

![Figure 5](image.jpg)

**Figure 5.** Hall mobility and carrier concentration of the InN films as a function of the substrate temperatures.
4. Conclusions
To summarize, InN thin films were successfully grown on kapton polyimide substrate by using reactive RF sputtering. The influences of the substrate temperatures on the structural, morphologies and electrical properties were investigated. The results showed that the deposited InN thin films grown on flexible substrate have wurtzite crystal structure with preferred orientation along the InN (101) direction. As the substrate temperature increases, the packing density and the Hall mobility increased. Through this study, it was revealed that the substrate temperature has played an important role in defining the properties of the InN thin films grown by RF sputtering technique.

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