Variation of crystallite size of $\text{Al}_{1-x}\text{In}_x\text{N}$ for different values of x and band gap

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Abstract. By using wide angle X-ray scattering (WAXS) technique, we have characterized the epitaxial $\text{Al}_{1-x}\text{In}_x\text{N}$ films (thickness, 150 nm) with $0 < x < 1$ grown by plasma source molecular beam epitaxy on sapphire (0001) at the low substrate temperature of 375°C, by computing the crystallite size in these samples. We observe that the crystallite size decreases with increase in the concentration of indium and that the band gap in these samples has a direct correlation with the crystallite size.

Keywords. WAXS; crystal imperfection parameters; band gap; crystallite shape.

1. Introduction

Materials like InN, AlN and ternary alloys, $\text{Al}_{1-x}\text{In}_x\text{N}$, are mainly used in light emitting and laser diodes which operate in the ultra-violet region. This is due to their direct and wide band gap, which lies between 1.9 and 6.2 eV, at room temperature. Earlier investigations were mainly concerned with the growth of these films (Kubota *et al* 1989; Guo *et al* 1995; Kim *et al* 1997; Peng *et al* 1997; Jain *et al* 2000; Yanaguchi *et al* 2000; Lukitsch *et al* 2001b). Recently, Lukitsch *et al* (2001b) reported the epitaxial growth of $\text{Al}_{1-x}\text{In}_x\text{N}$ films using plasma source molecular beam epitaxy (PSMBE), along with the X-ray diffractometer data for these samples at room temperature. As an extension of this work, we have carried out the profile analysis of these XRD data to compute the microcrystalline parameters like crystallite size and lattice strain in these samples using single order method developed by us (Somashekar and Somashekarappa 1997; Somashekar *et al* 1999). The accuracy of this Fourier method has been established in the recently concluded IUCr round robin test (Balzar *et al* 2004).

2. Theory

Microstructural parameters like crystal size ($\langle N \rangle$) and lattice strain (g in %) are usually determined by employing Fourier method of Warren and Averbach (1950) and Warren (1955, 1969). The intensity of a profile in the direction joining the origin to the centre of the Bragg reflection can be expanded in terms of Fourier cosine series as

$$I(s) = \sum_{n=-\infty}^{\infty} A(n) \cos\{2\pi n d(s - s_0)\}, \quad (1)$$

where $A(n)$ is the product of size coefficients, $A_s(n)$, and lattice distortion (strain coefficient), $A_d(n)$. As per our notation for lattice strain, $g = \Delta d_{hkl}/d_{hkl}$, whereas the mean square strain which is dependent on n is given by (Rothman and Cohen 1971)

$$\langle e_n^2 \rangle = g^2 / n. \quad (2)$$

We have used two asymmetric (exponential and log-normal) column length distribution functions for the computation of microstructural parameters. The exponential function has been used extensively in condensed matter science to explain various phenomena like dielectric relaxation, luminescence decay law and other physical properties (Williams and Watts 1970; Klafter and Shlesinger 1986) and hence, we have used this function to find out the goodness-of-fit compared to the lognormal function.

2.1 Exponential distribution

It is assumed that there are no columns containing fewer than p unit cells but that the number of those longer than this decays exponentially. Thus

$$P(i) = 0; \quad p < i, \quad (3)$$

$$P(i) = a \exp\{-a(i - p)\}; \quad i \geq p, \quad (4)$$

where

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$$\mathbf{a} = \frac{1}{(N-p)}. \quad (5)$$

This gives

$$A_s(n) = A(0)(1 - n/\langle N \rangle); \quad n \leq p, \quad (6)$$

$$A_s(n) = A(0)\{\exp[-\mathbf{a}(n-p)]\}/\mathbf{a}N; \quad n \geq p, \quad (7)$$

where $\mathbf{a}$ represents width of the distribution which has been varied to fit the experimental results, p the smallest number of unit cells in a column (Somashekar *et al* 1989; Hall and Somashekar 1991), $\langle N \rangle$ the number of unit cells counted in a direction perpendicular to the (hkl) Bragg plane, d the spacing of the (hkl) planes, λ the wavelength of X-rays used, D_s the surface weighted crystal size $(= \langle N \rangle d_{hkl})$.

2.2 Lognormal distribution

The lognormal-size distribution density function (Ribarik *et al* 2001) is given by

$$P(i) = \frac{1}{(2p)^{1/2} \mathbf{s}} \frac{1}{i} \exp \left\{ -\frac{[\log(i/m)]^2}{2\mathbf{s}^2} \right\}, \quad (8)$$

where $\mathbf{s}$ is the variance and m the median of distribution. Using the above equation, we get the equation for size coefficients as

$$A_s(n) = \frac{m^3 \exp[(9/4)(2^{1/2}\mathbf{s})^2]}{3} \operatorname{erfc} \left[\frac{\log(|n|/m)}{2^{1/2}\mathbf{s}} - \frac{3}{2} 2^{1/2}\mathbf{s} \right] - \frac{m^2 \exp(2^{1/2}\mathbf{s})^2}{2} |n| \operatorname{erfc} \left[\frac{\log(|n|/m)}{2^{1/2}\mathbf{s}} - 2^{1/2}\mathbf{s} \right] + \frac{|n|^3}{6} \operatorname{erfc} \left[\frac{\log(|n|/m)}{2^{1/2}\mathbf{s}} \right]. \quad (9)$$

The surface weighted mean column length, $\langle N \rangle_{\text{surf}}$, is given by

Figure 1. Wide angle X-ray diffractograms of $\text{AlN}_{1-x}\text{In}_x\text{N}$: (a) AlN (pure), (b) $(\text{AlN})_{45}(\text{InN})_{55}$, (c) $(\text{AlN})_{72}(\text{InN})_{28}$ and (d) InN (pure).

Figure 2. Experimental and simulated X-ray intensity profiles of $\text{AlN}_{1-x}\text{In}_x\text{N}$: (a) AlN (pure), (b) $(\text{AlN})_{33}(\text{InN})_{67}$, (c) $(\text{AlN})_{45}(\text{InN})_{55}$ and (d) $(\text{AlN})_{72}(\text{InN})_{28}$.

Table 1. Microstructural parameters of $\text{Al}_{1-x}\text{In}_x\text{N}$ films for reflection observed at $2\theta = 31^\circ$.

Sample	Exponential						Lognormal							
	$\langle N \rangle$	g (%)	a^*	D_s (Å)	D_v (Å)	Δ	$\langle L \rangle$	$\langle N \rangle$	g (%)	a^*	D_s (Å)	D_v (Å)	Δ	Band gap (eV)
0-00	120.87	0.3	0.03	405.54	405.61	0.03	129.47	145.45	0.8	0.09	401.36	454.43	0.04	5.03
0-12	110.16	0.7	0.07	278.69	278.67	0.04	105.91	119.15	1.0	0.10	267.84	301.33	0.05	4.17
0-28	80.00	2.1	0.19	210.83	210.81	0.03	88.23	99.26	2.1	0.20	210.16	236.44	0.04	3.25
0-34	90.43	2.0	0.20	256.68	257.48	0.03	96.86	108.97	2.1	0.21	252.32	283.87	0.03	3.17
0-55	89.07	2.5	0.24	269.79	269.82	0.03	93.58	105.28	2.5	0.24	268.10	301.63	0.03	2.50
0-67	70.02	2.1	0.18	206.89	207.55	0.03	76.23	85.76	1.8	0.16	208.11	234.12	0.04	2.50
0-90	39.41	3.0	0.19	127.45	127.91	0.04	43.49	48.93	3.3	0.22	125.64	141.36	0.05	1.83
1-00	131.42	0.7	0.08	384.38	384.38	0.04	135.90	152.89	1.1	0.13	385.96	435.28	0.04	—

$$\langle N \rangle_{\text{surf}} = \frac{2m \exp[(5/4)(2^{1/2} \mathbf{s})^2]}{3}, \quad (10)$$

and the volume weighted mean column length, $\langle N \rangle_{\text{vol}}$, is given by

$$\langle N \rangle_{\text{vol}} = \frac{3m \exp[(7/4)(2^{1/2} \mathbf{s})^2]}{4}. \quad (11)$$

We have used the SIMPLEX minimization program (Press *et al* 1992) to find out unknown parameters like crystallite size (N), lattice strain (g in %), correction for background (BG), width of the crystallite size distribution in the case of exponential distribution function and also lognormal distribution function parameters. Normally these parameters are varied as in the case of SIMPLEX, a multidimensional cube, so as to simulate an intensity profile, which is then compared with the experimental profile. These parameters are varied till the set standard deviation between simulated and experimental profiles is achieved. Normally the standard deviation is <1% of the mean value.

3. Experimental

Ternary alloy films were deposited by PSMBE utilizing a hollow cathode source lined with MBE grade aluminum or indium. Base pressures of the PSMBE system are in the 10^{-9} – 10^{-10} torr range and films are deposited at a dynamic pressure of 3–4 mtorr. Plasmas in the respective In and Al hollow cathode sources are created utilizing r.f. power sources and purified N_2 and Ar gases. C-plane sapphire substrates were ultrasonically cleaned in trichloroethylene, acetone and methanol for 15 min, sequentially, then etched in heated (80°C) acid mixture ($H_3PO_4 : H_2SO_4 = 1 : 3$) for 1 h to remove the damage caused by mechanical polishing. The substrate was preheated to 800°C for 1 h in the growth chamber under ultra high vacuum conditions and then cooled down to 375°C before the deposition of films. Substrates were kept at constant temperature as well as at a negative bias to accelerate the ionic species emerging from the hollow cathode. The films were characterized using XRD with a 12 kW Rigaku Diffractometer. Figure 1 shows representative X-ray recording of the sample, $Al_{0.66}In_{0.34}N$.

4. Results and discussion

Figure 2 shows the comparison between simulated and experimental profiles for $Al_{0.66}In_{0.34}N$ with Bragg angle at $2\theta = 34.4^\circ$ which represents the (0002) reflection, with appropriate model parameters. These calculations were carried out for all the six samples with x varying from 0.0 to 1.0. The computed microcrystalline parameters like crystallite size (number of unit cells) $\langle N \rangle$, lattice strain (g in %), the enthalpy, a^* , the surface weighted crystallite size and the standard deviations of these parameters are given

in table 1. Here the enthalpy essentially implies, according to Hosemann (1982), a measure of energy required for the formation of polymer network by controlling the level of g and crystal size in a material and this has been computed by using the equation

$$a^* = [N]^{1/2} g. \quad (12)$$

We observe that these values are in the range 0.1–0.2 as reported by Hosemann (1982) for ceramic materials. We have also reproduced in table 1, the band gap values for $Al_{1-x}In_xN$ for various x values obtained from an earlier reported paper (Lukitsch *et al* 2001a). The goodness-of-fit while computing these parameters is < 1% for all the samples. We also find that the lattice strain, on an average, decreases with increase in the concentration of In; even though it is not as pronounced as the variation of crystallite size, it is significant. Here we would like to recall the observation

Figure 3. Variation of crystal size distribution along $[xxx]$ direction in $AlN_{1-x}In_xN$: (a) AlN (pure), (b) $(AlN)_{10}(InN)_{90}$ and (c) $(AlN)_{45}(InN)_{55}$.

Figure 4. Variation of crystal size distribution along $[xxx]$ direction in $\text{AlN}_{1-x}\text{In}_x\text{N}$: (d) $(\text{AlN})_{72}(\text{InN})_{28}$ and (e) InN (pure).

made earlier with regard to the bowing in a semiconductor, which arises due to fluctuations in the average potential because of the random distribution of different atoms at different sites in the crystal (Goano *et al* 2000). This is due to the fact that the different technique of sample growth involves changes in microstructure like crystallite size, strain, defects and also fluctuations in the local In content. Our computation shows the presence of strain in the samples and their variation with the content of In. Further, we observe that there is a significant variation of crystallite size with x in $\text{Al}_{1-x}\text{In}_x\text{N}$ samples. This is shown in table 1. Figures 3 and 4 show the variation of crystal size distributions for various concentrations of In. In fact, we have presented both exponential and lognormal experimentally computed crystal size distribution functions and we observe that both functions give exceptionally good agreement between simulated and experimental profiles. In this paper we have shown that not only lognormal function but also exponential function can be used to compute microstructural parameters. With increase in concentration of In, the crystallite size decreases as is evident from table 1, indicating increase in disorder of the alloys with addition of In which is quite natural. A comparison of energy gap with crystallite size

Figure 5. Variation of crystal size with band gap.

in $\text{Al}_{1-x}\text{In}_x\text{N}$ for various values of x is shown in figure 5. This clearly indicates a surprising result, wherein, the band gap increases with increase in crystallite size. Normally, this is referred to as band gap bowing with increase in concentration of x . It is evident from figure 5 that the decrease in band gap has now been quantified in terms of associated decrease in crystallite size values which, in turn, leads to fluctuations in the average potential. Even though this conclusion is in agreement with the one drawn by Goano *et al* (2000), we assert here that we have quantified this aspect using X-ray profile analysis.

5. Conclusions

AFM measurements of these samples showed that for AlN film, the mean grain size was 100 nm (1000 Å) and for the film with $x = 0.34$, the mean grain size was 200 nm (2000 Å), whereas crystal size was 377 Å and for film with $x = 0.34$, we observed average surface weighted crystal size of 256 Å. AFM measurements give the lateral size whereas the X-ray method gives only the vertical size. Broadly, we feel that our methodology seems to give a proper estimation of crystallite size in AlInN films and hence the dependence of the band gap on the shape of these crystallites here.

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