Effect of surfactant Sb on In incorporation and thin film morphology of InGaN layers grown by organometallic vapor phase epitaxy

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ABSTRACT

The effects of the surfactant Sb on InGaN grown by organometallic vapor phase epitaxy (OMVPE) were studied. Eight samples of InGaN were grown with Sb concentrations ranging from 0% to 2.5%. Characterization was done by photoluminescence (PL) and atomic force microscopy (AFM). An abrupt change in PL emission peak energy and surface morphology occurred at a certain critical Sb concentration. Above and below this threshold concentration two distinct regimes of surface morphology and PL emission characteristics were observed. This effect was interpreted as due to a surfactant-induced change of surface phase on the InGaN films.

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1. Introduction

InGaN has become a topic of intense research due to its invaluable optoelectronic properties. This ternary III/V semiconductor is a seemingly ideal material for LEDs due to its direct bandgap that is tunable across the visible range by varying the relative amounts of GaN and InN. InGaN is currently used in commercially produced blue and green LEDs, but the material makes poor yellow and red LEDs due to inherent materials quality issues [1].

Epitaxial growth of nitride semiconductors has been challenging and difficult to understand. This can be attributed to many materials problems: lack of a native substrate, lattice mismatch to common substrates, solid phase immiscibility between GaN and InN, comparatively high vapor pressure of InN, and difference in formation enthalpies of GaN and InN [2]. These problems contribute to material defects, inhomogeneous alloying, and phase separation that affect the film quality and emission characteristics.

Surfactants have emerged in recent decades as a powerful tool for controlling epitaxial growth and achieving more desirable film qualities. Surfactants are active surface species that modify surface free energy, have negligible solubility in the bulk, and low desorption coefficients. During the growth process, surfactants accumulate on the surface, changing the thermodynamics and kinetics of growth. The effects of surfactants have been reported for many different material systems and diverse results have been seen.

One of the first reported results of surfactant-mediated epitaxial growth was the change in surface morphology of films. It was observed that by reducing the free energy of the growth surface with a surfactant, 3D islanding of the film was kinetically inhibited [3,4]. Much of the literature attributed this to surfactant-modified atomic surface processes such as surface diffusion and adatom step-edge attachment. Zhang et al. [5] observed an interesting change during the lateral epitaxial overgrowth (LEO) of GaN by organometallic vapor phase epitaxy (OMVPE). A change in the dominant growth facets occurred with the addition of Sb. At 1025 °C, undoped GaN had predominant, sloped growth planes of $\{1\ \bar{1}\ 0\ 1\}$. When Sb was added to the growth process, the predominant growth facets shifted to vertical $\{1\ 1\ \bar{2}\ 0\}$. A similar shift in growth facets occurred at a growth temperature of 1075 °C with sloped $\{1\ 1\ \bar{2}\ 2\}$ facets shifting again to vertical $\{1\ 1\ \bar{2}\ 0\}$ facets with the addition of Sb to the growth process.

Solid composition has also been changed by the addition of surfactant. It has been shown that N incorporation in GaAs is reduced by Sb, Bi, and Tl surfactants [6]. This was attributed to accumulation of surfactants on the growth surface blocking N adsorption and incorporation. Furthermore, Sb surfactant was reported to change impurity concentrations in GaAs. Zn and In dopant concentrations increased significantly with the addition TESb to the OMVPE growth process [7]. The Zn effect was explained theoretically by an intriguing dual surfactant effect

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involving the presence of H on the surface [8,9]. Another study showed an increase in the In composition of InGaN with the addition of Sb to hydride vapor phase epitaxial (HVPE) growth. This was accompanied by a change in the aligning direction of InGaN nanostructures on the surface [10]. In contrast to these results, more recent studies have shown that low concentrations of Sb can suppress In incorporation in InGaN grown by OMVPE [11,12].

Another effect that has been reported in the literature is a surfactant-induced change in microstructure. One example of this was the change in CuPt-B ordering in GaInP with the addition of Sb. Small amounts of Sb were shown to decrease the amount of CuPt-B ordering making a more homogeneous alloy. However, above a certain threshold concentration, Sb induced a new triple period ordered structure [13]. This was attributed to surfactant-induced changes in surface reconstruction. Other studies showed that increasing Sb concentrations led to an increase in the presence of lateral compositional modulation in GaInP that reduced the low temperature PL peak energy [14,15].

Although a broad range of experimental results have been reported, the effects of surfactants on nitride semiconductors have not yet been widely explored. This paper reports the use of an Sb surfactant on the OMVPE growth of InGaN. We have discovered that the Sb surfactant causes a marked shift in bandgap, In incorporation, and surface morphology of the film at a certain critical Sb concentration.

2. Experimental

InGaN was grown on 2 in. (0001) sapphire wafers by OMVPE at 720 °C. The TMIn/(TMIn+TMGa) ratio was 0.64, and the growth rate was 0.39 Å/s. A GaN buffer layer was deposited on the sapphire prior to epitaxial growth of InGaN. In order to test the effects of TMSb on the growth process and resulting film characteristics, different samples were grown with varying values of TMSb/(TMIn+TMGa) in the vapor. The first test batch consisted of samples grown with 0%, 0.5%, 1%, and 2% TMSb. These samples were grown with two different approximate average film thicknesses, 1.5 nm (38 s growth time) and 3 nm (75 s growth time). A subsequent batch was grown with TMSb concentrations of 0.75%, 1.25%, 1.75%, and 2.5%. The growth time for this batch was 75 s for an approximate average film thickness of 3 nm. All other growth parameters were unchanged.

Characterization of the samples was conducted to determine surface morphology, In incorporation, and photoluminescence (PL) spectra. PL was performed with a 349 nm high intensity laser. Atomic force microscopy (AFM) was done with a Brunker Dimension Icon apparatus operating in the quantum nano-mechanical mapping mode.

3. Results and discussion

PL spectra from the samples showed a large characteristic GaN peak from the underlying buffer layer, and a less intense peak from the InGaN film. The GaN peak occurred at the same emission energy for each sample, but an interesting shift occurred in the InGaN peaks. Samples grown with 0–1% Sb all showed the same blue emission peak at 2.7 eV, while samples grown with 1.25–2.5% Sb all showed the same green emission peak at approximately 2.3 eV. This can be seen in Fig. 1 where the normalized PL emission spectrum for each sample is shown from 425 nm to 625 nm. The marked shift in the emission peak from blue to green is seen to occur at a critical concentration of Sb surfactant between 1% and 1.25%. The growth time, or film thickness, was not observed to have any effect on the
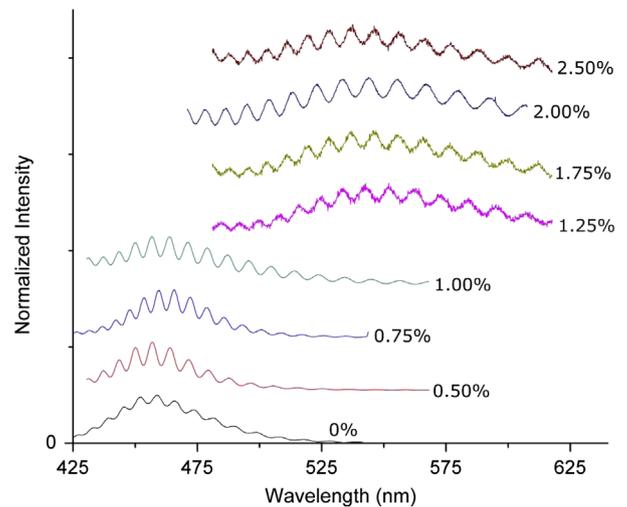
Fig. 1. Normalized PL spectra for InGaN samples grown with varying amounts of surfactant. Percentages represent the amount of TMSb present in the vapor during OMVPE growth.
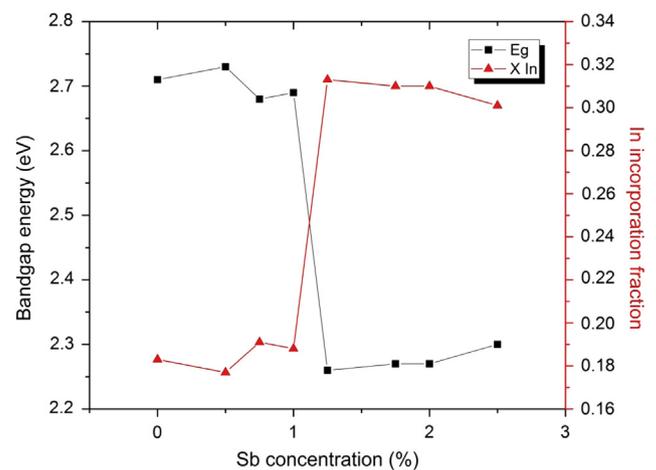
Fig. 2. Bandgap energy and In incorporation as a function of Sb surfactant concentration for OMVPE grown InGaN.

PL peak energies. Low temperature time-resolved PL measurements have also been done and are in agreement with these results [16]. The spectra also showed interference pattern oscillations which were an important indication that these emissions originated at the top of the samples in the InGaN thin film, and were not due to a possible yellow emission of the underlying GaN. If this were the case, the emissions would be produced within the GaN in a spatially distributed manner and would not give an interference pattern.

The bandgap of each sample was taken from its respective PL peak. The bandgap of $In_xGa_{1-x}N$ depends on the value of x and ranges from that of InN (0.7 eV) to that of GaN (3.4 eV). Eq. (1) gives the bandgap energy as a function of alloy composition and In incorporation was calculated from this relationship [17]. Fig. 2 shows the bandgap and In incorporation in the film as a function of Sb concentration. An abrupt change in the bandgap energy and alloy composition was induced by Sb concentrations above 1%. The bandgap was shifted from 2.3 eV to 2.7 eV corresponding to a shift in In concentration from 18% to 31%. Sadasivam et al. and Baranowski et al. also observed a PL peak shift in InGaN/GaN multi-quantum wells with the addition of Sb. However, they reported a slight blue-shift in the peak position with the addition of much lower Sb concentrations (0% to 0.16%). Their emission peak shifted from 527 nm to 506 nm, corresponding to a change of In concentration

in the InGaN wells from 31% to 28%, a change much smaller in magnitude and opposite in direction than that observed in this work.

$$E_g = 3.42 \ \text{eV} - x2.72 \ \text{eV} - x(1-x)1.43 \ \text{eV} \qquad (1)$$

The large, abrupt change in In incorporation observed here is suggestive of a phase change, in this case, a phase change of the surface reconstruction induced by the addition of Sb to the surface. Wixom et al. [18,19] calculated the surface phase diagrams for GaP
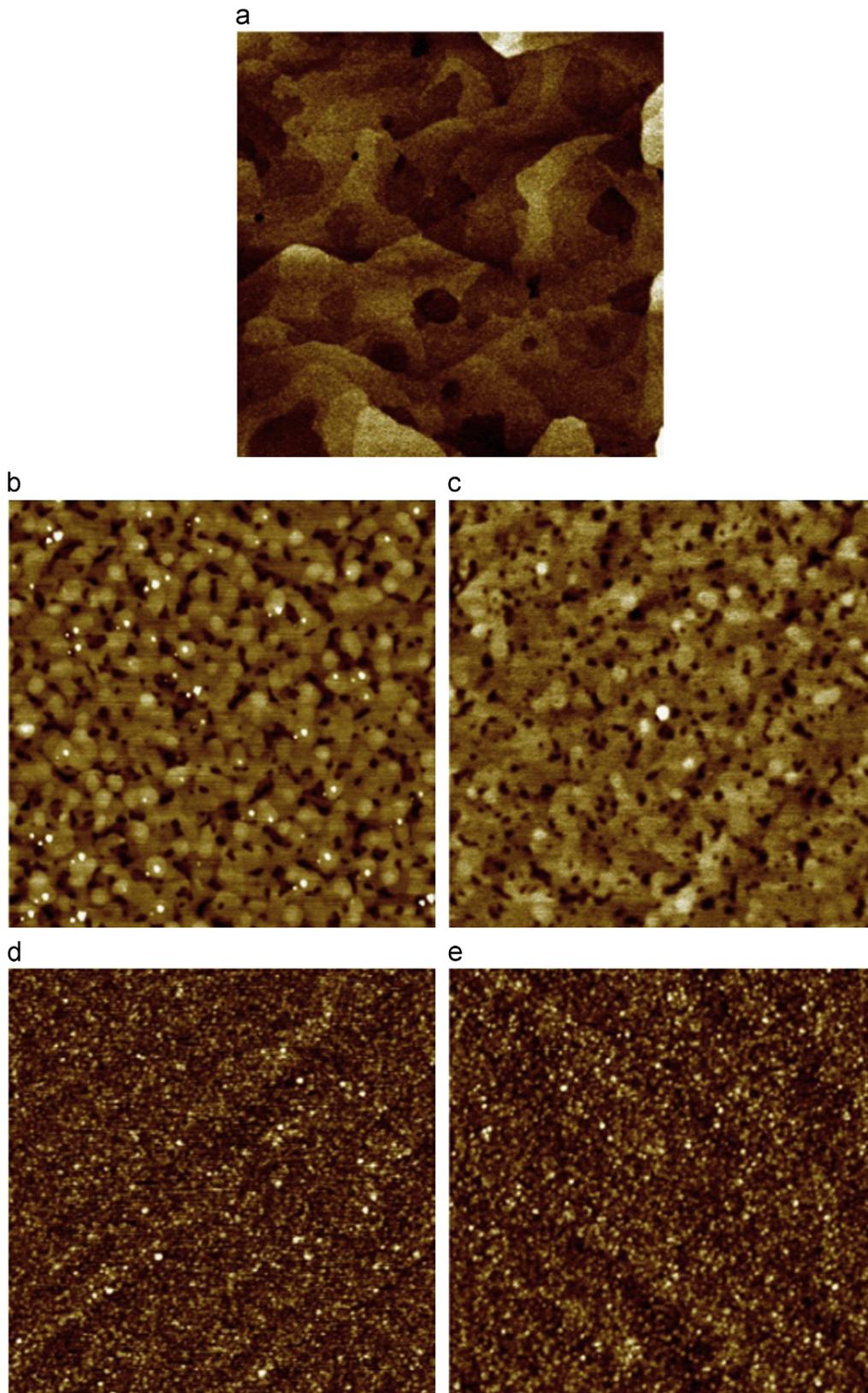
Fig. 3. 1×1 micron AFM images of InGaN samples grown with (Sb/III)$_v$ ratios of (a) 0%, (b) 0.5%, (c) 1%, (d) 1.25%, (e) 2%. Images (b) and (c) show the same relative island size and density and are characteristic of samples grown with Sb concentrations below the critical value. Images (d) and (e) show the same relative island size and density and are characteristic of samples grown with Sb concentrations above the critical value.

and InP as a function of Sb, showing a number of different surface reconstructions depending on the Sb concentration in the vapor phase. Of course, the surface reconstructions involving Sb on GaN are unknown. Studies on GaInP have clearly shown that the structure (i.e. reconstruction) of the growth surface can have profound effects on the microstructure, in this case, the atomic scale ordering of the material [13–15,18]. Different surface reconstructions provide the thermodynamic driving force for different microstructures and hence, markedly different bandgap energies. Surface reconstruction has also been shown to change the morphology of GaAs grown by OMVPE by changing surface diffusion and attachment at step edges [20–21].

Assuming that the InGaN surface reconstruction is dependent on the Sb concentration, the abrupt changes in In incorporation seen in Fig. 2 could be due to a surface phase change at the critical Sb concentration. In contrast to this explanation of the results, changes in surface kinetics due to Sb on the surface would presumably give a smoothly varying dependence of In incorporation on $(Sb/III)_v$, as opposed to the abrupt change observed.

The abrupt change in bandgap and solid composition was also reflected in the surface morphology of the films seen by AFM, and coincided with the idea of a surface phase change due to surfactant coverage. The 1×1 μm AFM images in Fig. 3 shows various InGaN sample surfaces grown using several Sb concentrations. Fig. 3(a) show the surface of InGaN produced with no surfactant present during growth. Fig. 3(b) and (c) show surfactant-mediated growth below the critical Sb concentration while Fig. 3(d) and (e) were grown with Sb above the critical concentration. The 1.5 nm and 3 nm film thicknesses exhibited identical results. These images clearly show a different surface morphology above and below the critical Sb concentration.

Island density increased and island size decreased with the addition of Sb to the growth process. Samples grown with Sb concentrations from 0.5% to 1%, showed a distinct morphology that did not change substantially with increasing Sb. Island size and density remained relatively constant in this regime. Samples grown with Sb concentrations from 1.25% to 2.5% showed another distinct morphology with no substantial change in island size or density with increasing Sb. The abrupt change observed in surface morphology and PL emission spectra at a particular Sb surface coverage is difficult to explain only in terms of surfactant modified atomic surface processes such as diffusion and step-edge attachment, but more likely indicates a surfactant-induced change in surface reconstruction.

Other surfactant studies on the nitrides showed similar phenomenon that could be explained in terms of a surface phase change. The abrupt change in the growth facets of LEO GaN with the addition of Sb (Zhang et al. [5]) could be attributed to a change in surface reconstruction. The authors attributed this to Sb affecting the fundamental surface processes during growth, such as adsorption/desorption, diffusion, and surface decomposition of precursors. However, given the sudden, striking change in the shape of these LEO GaN stripes, in light of the observations reported here, these results could also be interpreted as a surfactant-induced surface phase change leading to new film morphology.

Other evidence that could be interpreted as a surfactant-induced phase change was seen in HVPE grown InGaN with Sb. Ok et al. [10] reported a surfactant-induced shift in the orientation of hexagonal InGaN nanostructures. Without Sb, these structures were vertically aligned with the growth plane. With the addition of Sb, they grew parallel to the growth plane. The apparent density of nanostructures on the surface also appeared to be much lower when grown in the presence of Sb (from Fig. 4 of Ok et al.). The PL emission spectra of their samples showed a striking similarity to our data. The emission peak of the surfactant-enhanced sample was shifted to a much lower energy, indicating a higher In incorporation in the film, consistent with our samples that were grown with Sb concentrations above the critical value. The abrupt change in surface morphology, PL peak energy, and the associated solid composition, could be interpreted as due to a surface phase change just as we have interpreted our results.

4. Summary

We have shown the effects of Sb surfactant on OMVPE grown InGaN thin films. Samples were grown with Sb concentrations ranging from 0% to 2.5% while all other growth conditions were unchanged. Samples were characterized by PL and AFM. These methods revealed an abrupt change in bandgap, solid composition, and surface morphology of the films at a certain critical surfactant concentration. Above and below this threshold concentration of approximately 1% Sb, two distinct regimes of surface morphology and PL emission characteristics were observed. This effect was interpreted as due to a surfactant-induced change of surface phase on the InGaN films.

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