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Surface Structure and Surface Kinetics of InN Grown by Plasma-Assisted Atomic Layer Epitaxy: A HREELS Study

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The surface bonding configuration and kinetics of hydrogen desorption from InN grown by plasma-assisted atomic layer epitaxy have been investigated. High resolution electron energy loss spectra exhibited loss peaks assigned to a Fuchs–Kliewer surface phonon, N-N and N-H surface species. The surface N-N vibrations are attributed to surface defects. The observation of N-H but no In-H surface species suggested N-terminated InN. Isothermal desorption data were best fit by the first-order desorption kinetics with an activation energy of (0.88 ± 0.06) eV and pre-exponential factor of $(1.5 \pm 0.5) \times 10^5 \, \text{s}^{-1}$. © *2014 American Vacuum Society.*
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I. INTRODUCTION

Indium nitride, a group-III nitride compound semiconductor, has attracted extensive research interest over the past decade due to its unique electronic properties such as small effective mass, large electronic mobility, high peak and saturation velocities, and small bandgap energy. These properties make InN a potential material for a number of electronic and optoelectronic devices.[1] However, among other group-III nitride semiconductors, InN is less studied due to difficulties in producing good quality InN films ensuing from its low dissociation temperature, high equilibrium vapor pressure for nitrogen, and a lack of suitable lattice matched substrates.[2] InN epilayers have been grown by a number of techniques including metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy, liquid phase epitaxy, and hydride vapor phase epitaxy. Atomic layer epitaxy (ALE) has been found to be a very promising thin film deposition technique due to its ability in producing thin films with excellent conformality.[3,4] This technique has a wide range of advantages such as stoichiometric film growth with large area uniformity, precise thickness control, low temperature deposition, and a gentle deposition for sensitive substrates.[5]

In recent years, the number of publications related to InN research has increased significantly. Most of the studies have been focused on the structural (crystalline), chemical, electrical, and optical properties. However, there are a very few studies on the fundamental surface properties of InN. These studies are very important to gain an understanding of the growth mechanism because surface structure and bonding

affect kinetic processes during growth, which determine the quality of films and the performance of devices.[6] In previous work from the author's research group, Bhatta *et al.*[6] reported on the surface structure and bonding configurations of InN samples grown by high pressure chemical vapor deposition (HPCVD) using high resolution electron energy loss spectroscopy (HREELS). From HREELS measurements, it was concluded that the HPCVD-grown InN surfaces were nitrogen terminated. In other work from the author's group, crystallites tilted away from the c-axis were observed on HPCVD-grown InN and attributed to the effects of high group V/III ratio and lattice mismatch.[7]

During the growth of InN films, surface reactions involving hydrogen are important steps. When a precursor such as trimethylindium (TMI) is decomposed during the growth of InN, surface hydrogen atoms are produced. These surface hydrogen atoms reduce the number of available reaction sites for indium and nitrogen precursors affecting the quality and composition of the films. The surface hydrogen atoms produced during epitaxial growth of InN are usually eliminated by desorption after reacting with adsorbed methyl groups or other hydrogen atoms. It has been reported that an increase in hydrogen partial pressure decreases the deposition rate of InN, and the increase in hydrogen produced in the growth reaction may switch the system from deposition mode to the etching mode.[8] Moreover, InN strongly reacts with atomic hydrogen, resulting in the depletion of nitrogen and formation of In droplets at the surface.[9] It is reported that indium content in atomic layer deposited InGaN is significantly influenced by the amount of hydrogen flowing into the reactor.[10]

Knowing the kinetic parameters for surface reactions is crucial for determining the effects of hydrogen on the growth of InN. However, very few studies have been done and both

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qualitative and quantitative details of many of the important surface reactions occurring during the growth are still unknown.[11] In this work, we have determined the kinetic parameters for hydrogen desorption from the plasma-assisted atomic layer epitaxy (PA-ALE)-grown InN surface using HREELS. In addition, HREELS has been used to study the surface bonding configurations and surface termination of InN grown by PA-ALE.

II. EXPERIMENT

The two sets of InN samples used in this study were grown by PA-ALE as described in detail by Nepal *et al.*[12] The first set of samples was grown on Si(100) at 200, 220, 240, and 260 °C. The second set of samples was grown at 240 °C on Si(100), Si(111), and sapphire(0001). All substrates were solvent cleaned and rinsed with deionized water before any further surface pretreatments. The Si(111) surface was additionally pretreated with HF. After *ex situ* cleaning with deionized water and acid pretreatment, the substrates were then treated *in situ* with 50 SCCM N_2 plasma at 300 W prior to the growth of InN in an argon ambient. TMI (semiconductor grade purity), a group III-precursor, was pulsed for 60 ms to saturate the growth surface and added to 30 SCCM flow of ultrahigh purity (UHP) argon carrier gas while 100 SCCM of UHP argon was introduced separately through the plasma source. This total flow of argon resulted in a reactor pressure to 166 mTorr. The amount of TMI used to saturate the sample surface during the corresponding pulse was 10^6 L. In order to enhance the saturation of the sample surface with TMI molecules, the main pumping valve was closed for 5 s after each TMI pulse. Then, the chamber was purged with UHP Ar for 10 s to remove unadsorbed precursor. Subsequently, a 20 s long, 300 W UHP N_2 (50 SCCM) plasma pulse was used to provide a group-V precursor. Unreacted precursors and by-products were removed by purging the deposition chamber with UHP Ar for 10 s. This completed one deposition cycle. In order to synthesize InN epilayers, 800 cycles of ALE were employed. The InN layer thickness was measured using a variable angle spectroscopic ellipsometry and used to calculate the average growth rate per cycle. The calculated value of the average growth rate of InN layers was 0.51 Å/cycle. So, 800 cycles of ALE growth resulted to 408 Å thick InN layers.

Samples were then transferred to an ultrahigh vacuum (UHV) surface analysis chamber during which they were exposed to atmosphere. The UHV chamber had a base pressure of 1.5×10^{-10} Torr. The sample was mounted on a tantalum sample holder and held in place by tantalum clips. Sample heating was achieved by bombardment of electrons from the back of the tantalum sample holder. The temperature of the sample was measured with a chromel–alumel thermocouple. Auger electron spectroscopy (AES) was performed to monitor the surface cleanliness. AES of the as-inserted sample showed oxygen and carbon contamination due to exposure of the sample to atmosphere. Sample cleaning was performed by sputtering the sample surface with 1 keV nitrogen ions followed by atomic hydrogen cleaning

or atomic deuterium cleaning (ADC). The details of the cleaning the sample by sputtering followed by atomic hydrogen cleaning have been published elsewhere.[6,7,11] AES spectra after a few cycles of cleaning confirmed that the InN surface was free from contaminants. In order to study the surface structure, low energy electron diffraction (LEED) experiments were performed on the cleaned samples. However, no significant LEED patterns were observed. The bonding configurations of the surface species on the samples were investigated using HREEL spectrometer. HREEL spectra were achieved in a specular geometry with an incident and scattered angle of 60° from the normal. The energy of the incident electrons was 7.0 eV.

In order to determine the surface kinetic parameters, two series of isothermal desorption experiments were performed on the same sample which was grown on Si(100) at 240 °C. To avoid the confounding effects of background hydrogen, deuterium was used to emulate the surface interaction with hydrogen. In each series, the sample was heated from room temperature to a target value at the rate of 1 °C/s. Once the sample reached the target value, it was heated isothermally at different temperatures between 200 and 375 °C for 900 s in the first series and between 200 and 425 °C for 90 s in the second series. The surface was restored to its original condition through atomic deuterium cleaning before each isothermal heating treatment. Before choosing the particular temperature ranges and hold durations, several experiments were performed to study the desorption of hydrogen from the sample at different temperatures and hold durations. The complete desorption was observed at 375 and 425 °C on annealing for 900 and 90 s, respectively. The two series of experiments were performed to extract the kinetic parameters of hydrogen desorption by fitting the two experimental data. A number of intermediate experiments were performed between 200 and 375 °C in the first series and between 200 and 425 °C in the second series. However, only six or seven data were chosen to make the plots.

III. RESULTS AND DISCUSSION

HREEL spectra of InN grown on Si(100) at 240 °C acquired after atomic hydrogen cleaning and atomic deuterium cleaning are shown in Fig. 1. A loss peak observed at 550 cm^{-1} is assigned to the Fuchs–Kliewer surface phonon.[13] Loss peaks observed at 3260 cm^{-1} for the atomic hydrogen cleaned surface and 2410 cm^{-1} for the atomic deuterium cleaned surface are assigned to N-H and N-D stretching vibrations, respectively. These assignments are in excellent agreement with the assignments made by Bhatta *et al.*[6] on atomic hydrogen cleaned and atomic deuterium cleaned surfaces of InN grown by HPCVD. In contrast to the previous work on HPCVD-grown InN, two prominent peaks at 1240 and 2020 cm^{-1} are observed from both atomic hydrogen cleaned and atomic deuterium cleaned surfaces of PA-ALE-grown InN. These peaks are not related to hydrogen because no isotope shift is observed between atomic hydrogen cleaned and atomic deuterium cleaned surfaces. The authors suggest that these loss peaks are due to surface
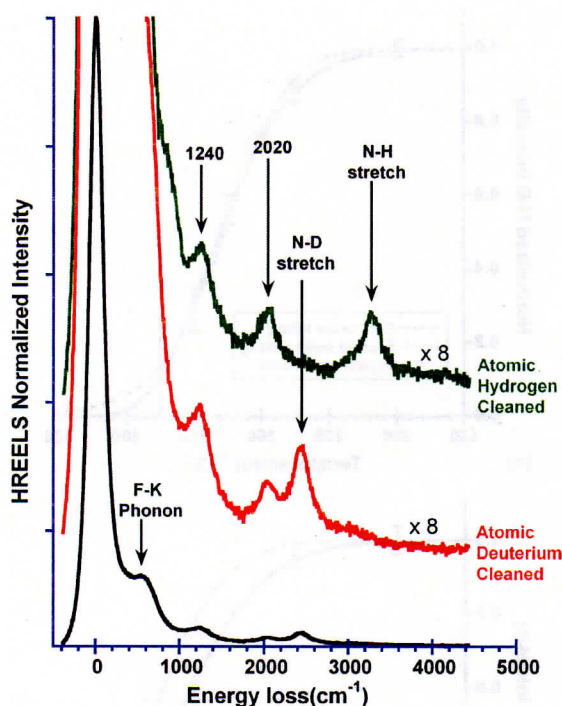
FIG. 1. (Color online) HREELS of InN after atomic hydrogen and atomic deuterium cleaning. Spectra were acquired in the specular direction with an incident electron energy of 7.0 eV.

N-N vibrational modes.[11] It is reported that GaH stretch has nearly the same frequency on the GaP, GaAs, and GaN surfaces.[14–16] The In-H stretch would be expected to have a similar frequency on InP, InAs, and InN surfaces, just as the GaH stretch has nearly the same frequency on the GaP, GaAs, and GaN surfaces. On InP surfaces, the In-H stretch has been reported at 1650–1700 cm^{-1} in HREELS experiments[17–19] and at 1630–1680 cm^{-1} from calculations.[20] However, the present study showed no HREELS loss features in this range indicating no In-H on the hydrogenated InN surface. Though In-H termination may be thermodynamically unstable at elevated temperatures, it may exist at lower temperatures, such as near room temperature.[7] HREELS spectra (not shown) were also taken from the sample dosed with hydrogen at temperature as low as 60 °C. But no loss feature related to In-H was observed in the HREEL spectra. It is suggested that surface indium atoms are either not present or not available for reaction with atomic hydrogen. If indium atoms were present and reactive, exposure to atomic hydrogen near room temperature should have produced In-H vibrations in HREELS. The observation of surface N-H vibrations but no In-H vibrations demonstrates N-termination of the InN.

HREELS experiments were also performed on a number of InN samples to study the dependence of surface bonding configurations on growth temperatures and substrates. The experiments performed on the samples grown on Si(100) at 200 and 220 °C did not give the significant results since the contaminations (carbon and oxygen) were incorporated in the samples. However, the experiments performed on the sample grown on Si(100) at 260 °C showed similar HREELS

results (not shown) to those shown in Fig. 1, indicating nitrogen terminated surfaces and presence of N-N modes of vibration. In addition, HREELS experiments on InN samples grown on Si(111) and sapphire at 240 °C also revealed similar results as shown in Fig. 1 for Si(100), independent of the substrate. These results show that the surface defects responsible for the vibrational peaks at 1240 and 2020 cm^{-1}, attributed here as N-N species, are produced under a range of PA-ALE conditions and for growth on various substrates. In each case, the sample surfaces were free from contaminants after a few cycles of cleaning, suggesting that little or no contaminants were incorporated in the samples (<1 at. %).

HREEL spectra from the InN surface grown on Si(100) at 240 °C acquired after annealing the atomic deuterium cleaned surface to various temperatures for 900 s are shown in Fig. 2. The surface was restored to the same condition by sputtering and atomic deuterium cleaning before each desorption experiment. Heating to 275 °C produced only a small decrease in the intensity of N-D peak but increasing annealing temperatures produced larger losses in intensity up to 375 °C, which effectively removed deuterium from InN surface as shown in Fig. 2. The results of a similar experiment on the sample with anneal times of 90 s (data not shown) showed that as the temperature increased, the N-D peak intensity decreased, disappearing after annealing at 425 °C. In both cases, the peaks at 1240 and 2020 cm^{-1} remained unchanged even after removing the deuterium completely from the sample surface. This further supports that these loss peaks are not related to hydrogen vibrational modes. With higher annealing temperatures, N-H stretching vibrational peaks appear in each spectrum at 3260 cm^{-1} and are attributed to the readsorption of hydrogen liberated from the sample mount during the heating.[21]

To date, there has been no published work on the desorption of hydrogen from the ALE-grown InN surface. However, there have been a few reports on the desorption of
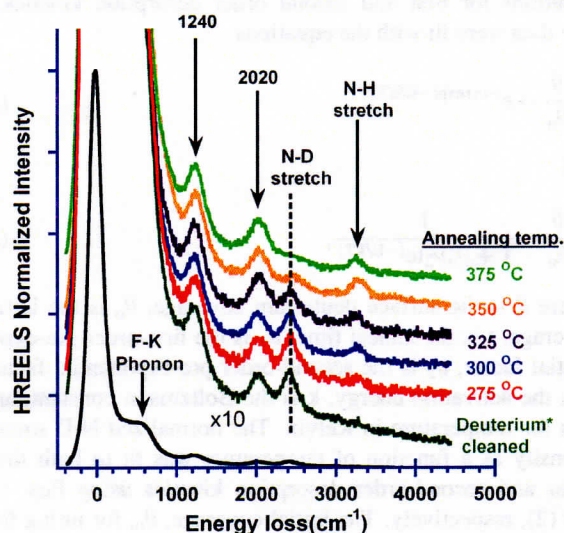

FIG. 2. (Color online) HREEL spectra after InN sample preparation by ADC and after heating to 275, 300, 325, 350, and 375 °C for 900 s. The surface was restored to the same initial state with ADC prior to each heat treatment.

hydrogen from InN and GaN surfaces grown by other techniques. Bhatta *et al.*[11] reported the desorption of hydrogen from HPCVD-grown N-terminated InN surface at 425 °C annealed for 900 s or at 500 °C annealed for 30 s. Bellitto *et al.*[22] observed a complete disappearance of Ga-H stretch intensity from MOCVD-grown GaN surface after briefly heating at 380 °C. Sung *et al.*[23] reported the desorption of hydrogen from the nitrogen sites on a metal organic vapor phase epitaxy grown GaN surface at 850 °C. Chiang *et al.*[24] reported hydrogen desorption from Ga-sites of a GaN surface at 250 °C and from N-sites at 500 °C. The desorption temperature from N-sites on ALE-grown InN reported in this work is lower than that reported for N-sites on InN and GaN grown by other techniques.[21–24] Rendulic *et al.*[25] studied the role of surface defects in the desorption of hydrogen on Ni(111) surface. They reported that surface defects introduced nonactivated adsorption sites, which lowered the desorption temperature. In this study, the HREELS spectra showed the prominent loss peaks related to N-N vibrations indicating the presence of a significant amount of surface defects. Therefore, we suggest that the observation of lower desorption temperature of hydrogen from ALE-grown InN surface is attributed to the presence of surface defects.

The kinetic parameters have also been determined from the HREEL spectra. Relative surface coverages were obtained by integrating the area under N-D stretching vibrational peak in each normalized HREEL spectrum. The normalized N-D stretch intensity is assumed to be proportional to the surface coverage[26] and is plotted as a function of annealing temperature [shown in Figs. 3(a) and 3(b)]. During atomic deuterium cleaning, the sample was annealed to 325 °C. However, the exposure with atomic deuterium was continued until the sample was cooled down to ~200 °C. For this reason, N-D stretch intensities after atomic deuterium cleaning are plotted as equivalent to a 200 °C anneal.

To determine the kinetic parameters for hydrogen desorption, the integrated N-D stretch intensities were fit using equations for first and second order desorption kinetics.[11] The data were fit with the equations

$$\frac{\theta}{\theta_o} = e^{-\nu_1 t \exp(-E/kT)}, \tag{1}$$

and

$$\frac{\theta}{\theta_o} = \frac{1}{1 + \theta_o \nu_2 t e^{(-E/kT)}}, \tag{2}$$

where θ is the surface deuterium coverage, θ_o is the initial coverage, t is the anneal time, ν_1 is the first-order pre-exponential factor, ν_2 is the second-order pre-exponential factor, E is the activation energy, k is the Boltzmann constant, and T is the temperature in Kelvin. The normalized N-D stretch intensity as a function of temperature was fit to both first-order and second-order desorption kinetics using Eqs. (1) and (2), respectively. The initial coverage, θ_o, for fitting following the second order desorption kinetics was assumed to be 1. First- and second-order fits to data for 900 and 90 s anneals are shown in Figs. 3(a) and 3(b), respectively. The
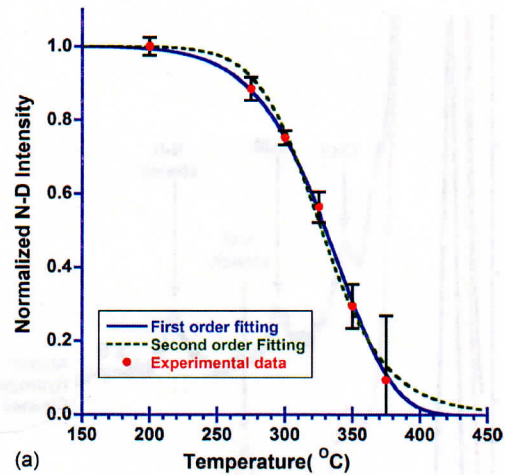
(a)
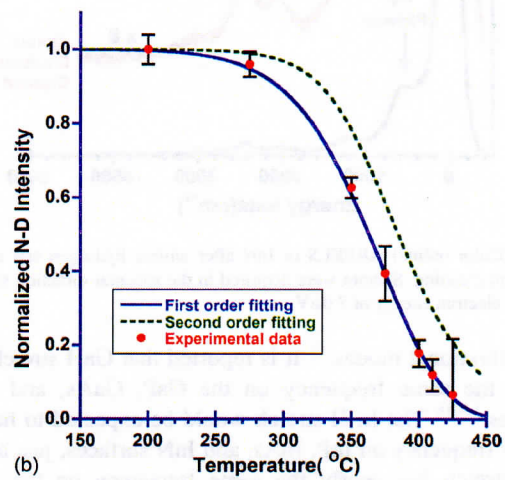
(b)

FIG. 3. (Color online) Fitting of first and second-order desorption kinetics to deuterium coverage (obtained from HREELS N-D stretch intensity) for InN sample after preparation by atomic deuterium cleaning and after heating for (a) 900 s to 275, 300, 325, 350, and 375 °C and (b) 90 s to 275, 350, 375, 400, 410, and 425 °C. Equations and parameters used in the fitting are described in the text.

experimental data for 900 s anneal were fit very well by second order desorption kinetics with an activation energy of (1.31 ± 0.14) eV and pre-exponential factor of $(1.2 \pm 0.3) \times 10^8$ cm^2 s^{-1}, but these parameters could not fit well for 90 s anneal data. On the other hand, first-order desorption kinetics fit both 900 and 90 s anneal data very well with the same set of activation energy and pre-exponential factor. This analysis yielded first-order desorption kinetics with activation energy of (0.88 ± 0.06) eV and a pre-exponential factor of $(1.5 \pm 0.5) \times 10^5$ s^{-1}. Bhatta *et al.*[11] reported that desorption of hydrogen from HPCVD-grown InN samples was best described by second-order kinetics with an activation energy of (1.3 ± 0.2) eV.

The chemical properties of surfaces can be controlled to a large extent by defects. It is reported that defect sites are often more reactive sites and hence lower the activation energy of particular reactions.[27] We suggest that surface defect sites result in first-order desorption process for hydrogen recombination being dominant on this surface and resulting in a lower activation energy[27] and temperature[25] than observed

in the case of HPCVD-grown InN. The nature of these defects is unknown, however, we can speculate that if InN surfaces have N-N bonds, those nitrogen atoms must be bonded securely to the surface (probably with two In-N bonds) or else the two nitrogen atoms would be unstable toward desorption as N_2. Some sort of bridging structure is suggested instead of a terminal N-N structure. This could suggest the presence of In vacancies on the surface.

IV. SUMMARY AND CONCLUSIONS

In summary, the surface bonding configuration and kinetics of recombinant desorption of hydrogen from PA-ALE-grown InN were investigated using high resolution electron energy loss spectroscopy. HREELS showed surface N-N vibrational modes at 1240 and 2020 cm^{-1}, indicating the presence of surface defects. Hydrogenated and deuterated InN surfaces showed N-H and N-D stretch vibrations, respectively, while no In-H modes were observed, indicating N-terminated InN. Complete desorption of surface hydrogen was observed after heating to 375 °C for 900 s or 425 °C for 90 s. First-order kinetics best described the desorption of hydrogen from InN surface with an activation energy of (0.88 ± 0.06) eV and a pre-exponential factor of $(1.5 \pm 0.5) \times 10^5 \, s^{-1}$. The lower values of activation energy and desorption temperature than previously reported on HPCVD-grown InN samples along with first-order desorption kinetics were attributed to the presence of surface defects.

ACKNOWLEDGMENTS

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