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OMVPE Growth and Gas-Phase Reactions of AlGaN for UV Emitters

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ABSTRACT

Gas-phase parasitic reactions among TMG, TMA, and NH_3, are investigated by monitoring of the growth rate/incorporation efficiency of GaN and AlN using an *in-situ* optical reflectometer. It is suggested that gas phase adduct (TMA: NH_3) reactions not only reduce the incorporation efficiency of TMA but also affect the incorporation behavior of TMGa. The observed phenomena can be explained by either a synergistic gas-phase scavenging effect or a surface site-blocking effect. Relatively low reactor pressures (30-50 Torr) are employed to grow an AlGaN/GaN QW p-n diode structure. The UV emission at 354 nm (FWHM ~ 6 nm) represents the first report of LED operation from an indium-free GaN QW diode.

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DISCLAIMER

INTRODUCTION

GaN is known[1] to exhibit a high equilibrium nitrogen vapor pressure at temperatures typically employed (1000 to 1100°C) during the MOCVD process which demands the supply of a substantial amount of ammonia (NH_3) to minimize the loss of surface nitrogen. However, a high partial pressure of NH_3 in the reaction chamber enhances the formation of the Lewis acid-base complexes (adducts) between NH_3 and metal-organic molecules (such as *trimethylgallium*, TMGa) in the gas phase. Gas-phase pre- (or parasitic) reactions often complicate the growth chemistry by adding extra steps in or even diverting precursor dissociation on the deposition surface.[2] In many cases such gas-phase pre-reactions can also cause the depletion of reactants when large oligomers resulting from adduct decomposition and having with low vapor pressures can not be transported efficiently in the vapor stream.

So far, most of the efforts in III-nitrides have focused on visible (blue and green) light emitters employing InGaN as the active layers. The AlGaN alloy system serves a dual purpose in ultraviolet (UV) optoelectronics and power electronics. Gas-phase interactions during organometallic vapor phase epitaxy (OMVPE) between NH_3 and the two most commonly employed group III metal-organic precursors, TMGa and *trimethylaluminum* (TMAl), need to be understood. Thon and Kuech[3] studied the gas-phase reaction of TMGa with NH_3 and observed a rapid ($<<$ 1 sec) formation of adduct compound, $(CH_3)_3Ga{:}NH_3$. Decomposition products related to a possible oligomer product, such as $[(CH_3)_2Ga{:}NH_2]_n$, were suggested to result from a methane-elimination reaction. The presence of the ($TMGa{:}NH_3$) adducts, nevertheless, does not necessarily have to influence significantly the decomposition of TMGa or the incorporation of Ga as judged by the relative insensitivity of GaN growth rates versus NH_3 pressures.[4]

TMAl has been observed[5] to react with NH_3 into a white crystalline solid at and below room temperature. Chen et al.[4] showed that the Al incorporation (using TMAl) during MOCVD of AlGaN strongly depends on the growth pressure which could be described by a bi-molecular chemical reaction. It is generally accepted that the TMAl:NH_3 preaction is manifested by a reduced Al incorporation efficiency and a sub-linear relationship between the Al compositions in the gas and solid phases during the growth of AlGaN. Various measures such as special gas-injection schemes,[6] short inlet-susceptor separation,[7] higher gas velocity,[8] and reduced reactor pressures [4] have been adopted to alleviate the pre-reaction between TMAl and NH_3 even though the information as to the degree to which gas-phase reactions occur under growth conditions has not been well-established.

In this paper we intend to illustrate experimentally the cause-effect of the incorporation of Al under a range of OMVPE growth conditions. The effect of TMA:NH_3 reaction on the growth rate was studied *in situ* using an optical reflectance monitor[9] which enables us to delineate the susceptibility of the growth rate to pre-reactions over a wide range of gas compositions. We will show that the formation of (TMA:NH_3) adduct not only depletes TMA from the vapor state but also inhibits the incorporation of TMG (by as much as 60%). Once the extent of gas-phase reaction was mapped out over growth parameter space, we attempted the growth of AlGaN/GaN heterostructures. The growth and device fabrication of a short-wavelength indium free GaN quantum well (QW) UV LED, with an emission wavelength at 354 nm, will be reported in this paper.

EXPERIMENTAL

GaN/AlGaN was grown in a high speed rotating (~ 1000 rpm) MOCVD reactor (diameter of the quartz chamber is 4.75"). Two-inch basal plane sapphire wafers were placed on

molybdenum (Mo) susceptor, which is RF inductively heated using a SiC-coated graphite coupling block. Temperature was monitored by a pyrometer focusing on the Mo susceptor surface nearly co-planar with the wafer surface. NH_3, TMGa, and TMAl were used as the N, Ga, and Al precursors, respectively. Hydrogen (H_2) was used as the carrier gas and also to supplement the NH_3 in making up the required flow rate as determined by the reactor pressure and wafer rotating speed.[10] Metal-organic precursors were separated from hydride gases before being injected into top of the growth chamber. The reflectometer uses a tungsten lamp as a light source, illuminating a spot (of 6 mm in diameter) on the sample surface through the reactor port window. Standard two-step growth (550 and 1050 °C for the low and high temperatures, respectively) with GaN low-temperature buffer layer was used in this work.

ALGAN GAS PHASE REACTIONS

We have reported[11] that the *in-situ* reflectance monitor can provide information on surface roughening, growth rates, and even AlGaN alloy compositions. During our initial attempt of growing AlGaN, it was observed that the introduction of TMAl into the reactor (while leaving TMGa and NH_3 flow rates constant) caused an increase of the periodicity (of the reflectance oscillations) during the AlGaN growth, implying a decrease in the growth rate.

Taking advantage of *in-situ* growth rate monitoring, we have now conducted a series of experiments aimed at illustrating the complex nature of the gas-phase reactions when both TMGa and TMAl are used with NH_3. Figure 1 shows a typical reflectance trace during a particular study of the gas-phase reactions. In this experiment, the TMGa and TMAl flow rates were fixed at around 60 μmole/min. TMGa, TMAl, and both TMGa and TMAl were open sequentially to allow a measurement of the growth rates of GaN (region (i)), AlN (region (ii)), and AlGaN (region (iii)), respectively, at a given gas composition (a layer of GaN was inserted after AlN

growth to improve the surface morphology and verify the measured growth rate of GaN). We then changed the gas composition (partial pressures of H_2 and NH_3 independently, from region (A) to (B) in Fig. 1) and repeated the same valve operation. (The total reactor pressure equals the sum of the partial pressures of H_2 and NH_3 since TMGa and TMAl flows contribute negligible pressures.) Such an *in-situ* probe allows a single growth run to provide the data necessary to construct three-dimensional plots of the growth rates of GaN (Fig. 2(a)), AlN (Fig. 2(b)), and AlGaN (Fig. 2(c)) versus partial pressures of both H_2 and NH_3.

It is clear from Fig. 2(a) that the reported gas phase reactions between TMGa and NH_3 do not result in much (if any) of a decrease in growth efficiency when the H_2 partial pressure is less than 20 Torr. The decreased growth rate shown at higher H_2 pressure may be due to the etching of GaN by a H_2 surface reaction.[12] Alternatively, this may be due to an indirect effect of decreasing the rate of the decomposition reaction[13] needed to compensate for the loss of nitrogen at high temperatures.[1] The trend of the growth rate of AlN versus NH_3 shows distinctly different behavior. An increase of NH_3 (with H_2 pressures below 20 Torr) leads to a rapid decrease of AlN incorporation. We note that the above observation is in qualitative agreement with the previous report[4] of a bi-molecular reaction between TMAl and NH_3.

The growth rate of AlGaN (with both TMGa and TMAl open) is shown in Fig. 2(c). It is interesting to note that the measured growth rate of AlGaN is always less than the sum of the growth rates of the individual binary compounds. An "interaction parameter" Ω is therefore defined as $(GR_{AlGaN}/(GR_{AlN} + GR_{GaN}))$ which is plotted in Fig. 2(d). An Ω value approaching unity suggests an independent and additive incorporation of TMAl and TMGa. An Ω much less than unity implies that additional interactions between the respective adduct compounds, either in the gas phase or on the gas-solid interface, have inhibited the incorporation of certain species.

Comparing Fig. 2(b) and 2(d), one could argue that the reduction of Ω follows the general trend of the reduction of AlN growth rates (which in turn suggests an increase in gas-phase adduct reactions related to species such as $[(CH_3)_2Al{:}NH_2]_n$[14]). Such reactions are seen to inhibit the incorporation of TMGa, down to less than 40% at an NH_3 partial pressure of 58 Torr. We speculate that the reduction of TMGa incorporation is due to either a scavenging effect of $TMAl{:}NH_3$ adducts or their reaction products on TMGa (or $TMGa{:}NH_3$ adducts) in the gas phase. Alternatively, this may be due to a site-blocking effect[15] in which the competitive adsorption of $TMAl{:}NH_3$ decomposition products decreases the TMGa reraction rate on the surface.

Ideally the Lewis-base precursors should be separated physically for as long as possible from the Lewis-acid precursors before they reach the growth surface. Implementation of this concept, however, is often at the expense of growth uniformity over a large area due to the lack of gas mixing. The spacing between inlet and growth surface essentially determines the reaction time. In our system, the separation between the inlet and the susceptor surface is around 4". Under typical growth conditions, this amounts to a potential reaction time in the gas-phase of ~ 1 second, which serves to emphasize the facile nature of TMAl: NH_3 reaction. Another parameter one could vary is the partial pressures of the reactants. A lower reactor or NH_3 pressure not only reduces the chemical reaction rate but also increases the flow velocity, which in turn reduces the interaction time. It is worth noting that both thermodynamics calculations[12] and kinetics arguments[16] suggest the need to maintain minimum values of V/III flow ratios and NH_3 partial pressures based on morphological, structural, and optical criteria.

ALGAN/GAN QW UV LEDS

AlGaN UV LED structures were attempted once the information of the gas-phase prereaction of $TMAl:NH_3$ had been established. It is worth noting that there has been no report, to the best of our knowledge, on the AlGaN/GaN QW p-n junction LEDs thus far. Photoluminescence (PL) has been applied to undoped[17] and Si-doped[18] AlGaN/GaN quantum wells (QWs) with linewidths varying from 80 to 110 meV at room temperature. Stimulated emission by optical pumping was also achieved in the latter report. Both Amano et al.[19] and Kuga et al.[20] have reported AlGaN/GaN double heterostructure (DH) diodes with emission peaks centered around 375 and 420 nm, respectively. In both cases the widths of emission peaks are in excess of 250 meV (or 40 nm), indicative of recombination through localized centers.

The LED structure consists of a 3 μm GaN:Si ($n \sim 2x10^{18}cm^{-3}$) grown on sapphire using a LT GaN buffer layer, an $Al_{0.2}Ga_{0.8}N$:Si ($n \sim 2x10^{18}cm^{-3}$) barrier layer of 0.1 μm thick, four GaN quantum wells (~ 30Å undoped) separated by undoped $Al_{0.2}Ga_{0.8}N$ barrier layers (~ 70Å), a p-$Al_{0.2}Ga_{0.8}N$ ([Mg] ~ $1.0x10^{20}cm^{-3}$) of 0.1 μm thick, a p-$Al_{0.1}Ga_{0.9}N$ ([Mg] ~ $1x10^{20}cm^{-3}$) layer of 0.2 μm thick to help current spreading, and a p-GaN ([Mg] ~ $1x10^{20}cm^{-3}$) contact layer of 0.1 μm thick. Step-graded regions were introduced between each composition change except the QW region. For the SCH structure reported here, the LT GaN and the Si-doped GaN were grown at 140 Torr, the rest of the structure was grown between 30 to 40 Torr. After growth the AlGaN/GaN SCH sample was annealed in the reactor at 850°C under flowing nitrogen (140 Torr) for 20 min to activate the Mg acceptors. An additional anneal was performed outside of the reactor at 1050 °C for 15 sec in nitrogen. The sample was etched (using inductively-coupled plasma etching) 1.2 μm deep to expose the n-GaN region. Ni/Au and Ti/Al were employed as p- and n-type contacts, respectively.

Figure 3(a) shows the current-voltage (I-V) characteristics of a processed diode with a mesa diameter of 100 μm. The top p-type contact has a circular ring pattern to facilitate light emission from the center of the mesa. We note, however, that the limited p-type conductivity in GaN and AlGaN significantly limits lateral current spreading and the effective device area is much less than the physical dimension of the mesa. The forward turn-on occurs at around 4 V. Electroluminescence (EL) is collected using a 200 μm core fiber positioned at about 2 mm from the top of the device. Figure 3(b) shows the EL spectrum a 5 mA injection level. The emission at 354 nm agrees well with the PL peak position reported earlier,[17] and is the shortest wavelength reported from a GaN-based light emitting diode. The FWHM of the emission peak is around 6 nm, which compares favorably with the reports of 30 to 45 nm from GaN-based DH diodes. We are in the process of measuring the integrated light output power as well as the quantum efficiency, and the results will be reported elsewhere.

CONCLUSION

In conclusion, we have studied the gas-phase reactions during the OMVPE growth of AlGaN. The presence of [TMA:NH_3] adduct was found to influence and hinder the incorporation of TMGa, possibly through a gas-phase scavenging or surface site-blocking effect. The observed parasitic reactions can be alleviated by configuring the reactor design or operating at a reduced pressure. An AlGaN/GaN p-n QW LED was grown at reduced reactor pressure regime. The observed UV emission at 354 nm represents the shortest wavelength emission from a GaN-based injection device.

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FIGURE CAPTIONS

Figure 1. A portion of reflectance trace during a gas-phase reaction study. Regions (i), (ii), and (iii) correspond to GaN, AlN, and AlGaN, respectively.

Figure 2. The measured growth rates of (a) GaN, (b) AlN, and (c) AlGaN (from Figure 1) versus H_2 and NH_3 partial pressures. A plot of the interaction parameter Ω (refer to text for definition) versus H_2 and NH_3 is shown in (d).

Figure 3. Forward I-V characteristics (a) and emission spectrum (b) of an AlGaN/GaN p-n diode structure.

REFERENCES

[1] Z. A. Munir and A. W. Searcy, J. Appl. Phys. **42**, 4223 (1965); C. D. Thurmond and R. A. Logan, *J. Electrochem. Soc.* **119**, 622 (1972); A. Koukitu, N. Takahashi, and H. Seki, *Jpn. J. Appl. Phys.* **36**, L1136 (1997).

[2] R. H. Moss, *J. Cryst. Growth* **68**, 78 (1984).

[3] A. Thon and T. F. Kuech, *Appl. Phys. Lett.* **69**, 55 (1996).

[4] C. H. Chen, H. Liu, D. Steigerwald, W. Imler, C. P. Kuo, M. G. Craford, M. Ludowise, S. Lester, and J. Amano, *J. Electron. Mat.* **25**, 1004 (1996).

[5] L. V. Interrante, L. E. Carpenter II, C. Whitmarsh, W. Lee, M. Garbauskas, and G. A. Slack, *Mat. Res. Soc. Proc.* **73**, 359 (1986).

[6] S. Nakamura, Jpn. J. Appl. Phys. 30, 1348 (1991); M. Matloubian and M. Gershenzon, *J. Electron. Mat.* **14**, 633 (1985).

[7] W. Van der Stricht, I. Moerman, P. Demeester, J. A. Crawley, and E. J. Thrush, *J. Cryst. Growth* **170**, 344 (1997).

[8] Y. Koida, H. Itoh, N. Sawaki, I. Akasaki, and M. Hashimoto, *J. Electrochem. Soc.* **133**, 1956 (1986).

[9] J. Han, T. -B. Ng, R. M. Biefeld, M. H. Crawford, and D. M. Follstaedt, *Appl. Phys. Lett.* **71**, 3114 (1997).

[10] W. G. Breiland and G. H. Evans, *J. Electrochem. Soc.* **138**, 1806 (1991).

[11] T. -B. Ng, J. Han, R. M. Biefeld, and M. V. Weckwerth, *J. Electron. Mat.* **27**, 190 (1998).

[12] A. Koukitu, N. Takahashi, and H. Seki, *Jpn. J. Appl. Phys.* **36**, L1136 (1997).

[13] M. E. Bartram (unpublished)

[14] L. V. Interrante, G. A. Sigel, M. Garbauskas, C. Hejna, and G. A. Slack, *Inorg. Chem.* **28**, 252 (1989).

[15] O. Briot, J. P. Alexis, B. Gil, and R. L. Aulombard, *Mat. Res. Soc. Symp. Proc.* **395,** 207 (1996).

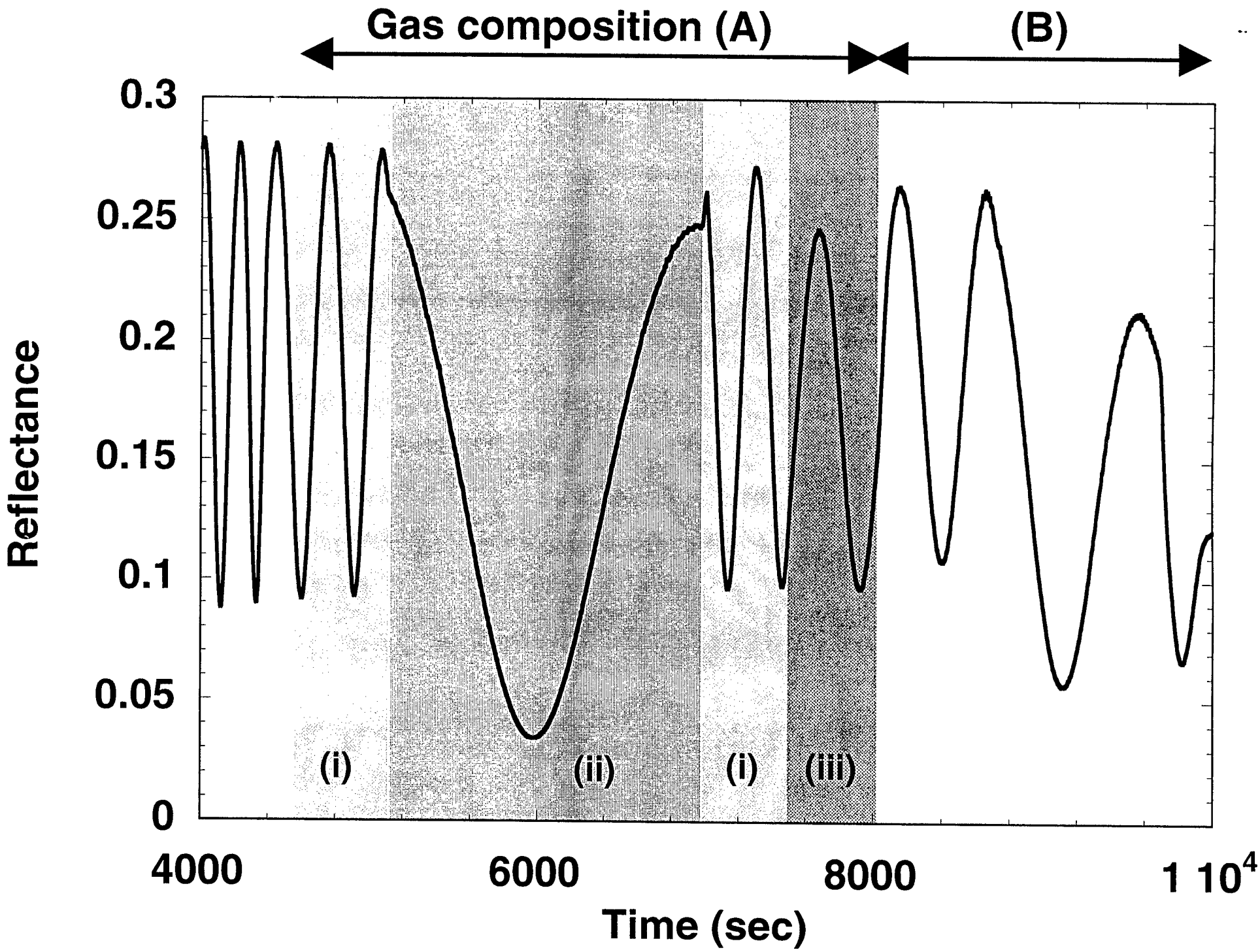
[16] D. D. Koleske, A. E. Wickenden, R. L. Henry, W. J. Desisto, and R. J. Gorman, *Mat. Res. Soc. Symp. Proc.* Fall 1997, D5.27.

[17] M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, W. Kim, and H. Morkoc, *Appl. Phys. Lett.* **69**, 2453 (1996).

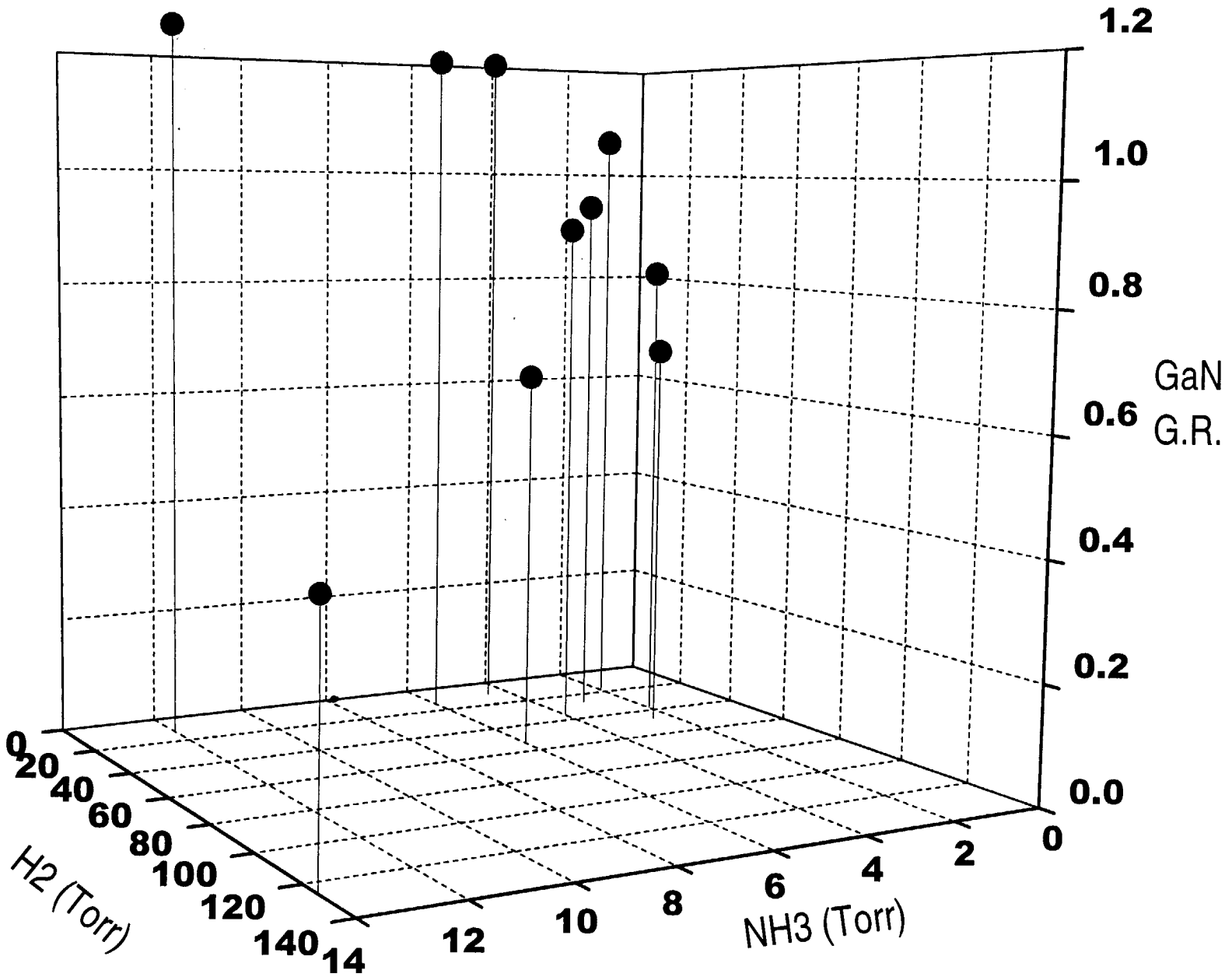
[18] T. J. Schmidt, X. H. Yang, W. Shan, J. J. Song, A. Salvador, W. Kim, O. Aktas, A. Botchkarev, and H. Morkoc, *Appl. Phys. Lett.* **68,** 1820 (1996).

[19] I. Akasaki and H. Amano, *Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials*, Tsukuba, p327 (1992).

[20] Y. Kuga, T. Shirai, M. Haruyama, H. Kawanishi, and Y. Suematsu, *Jpn. J. Appl. Phys.* **34,** 4085 (1995).



Han et al. Fig 1



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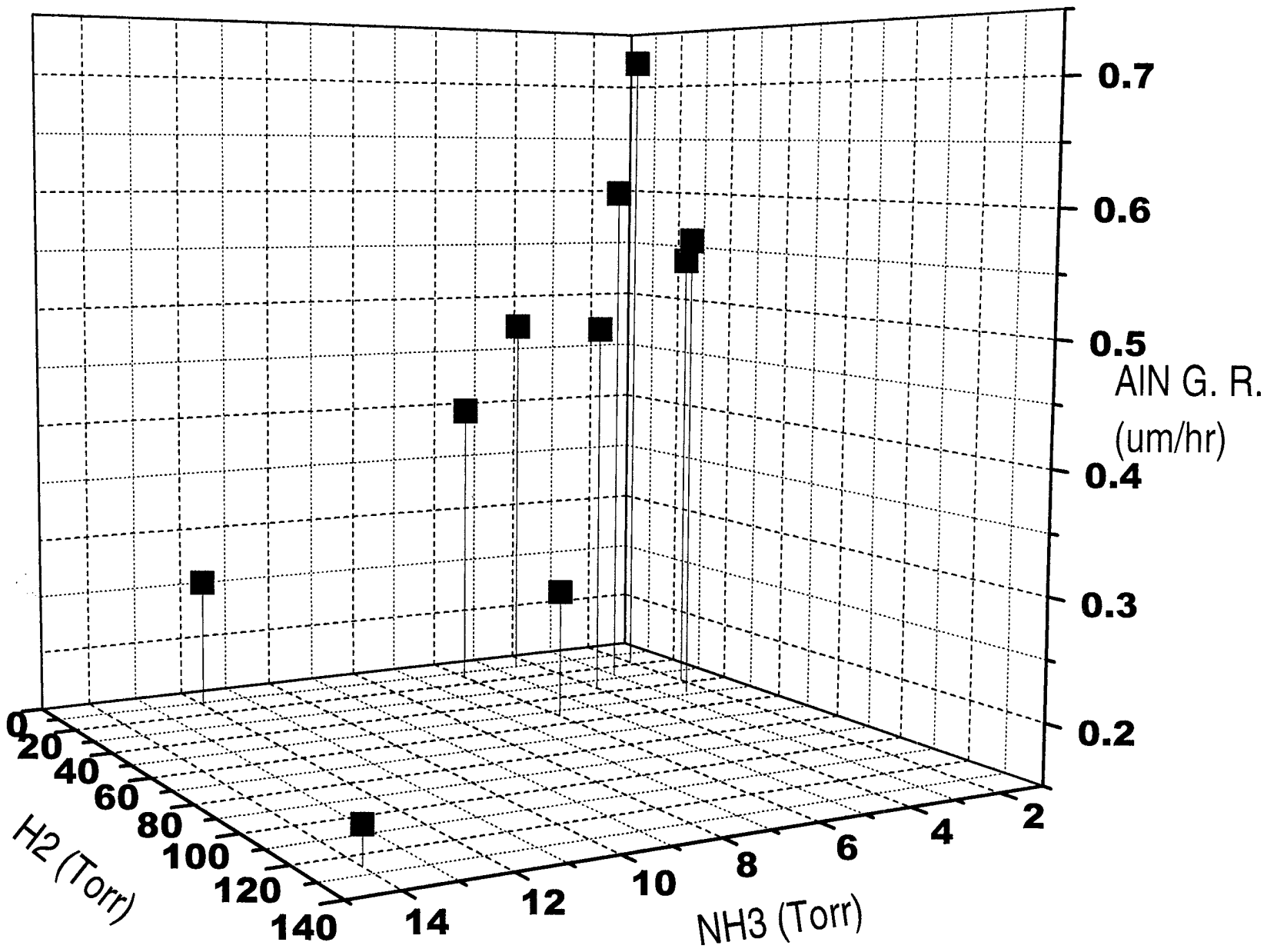

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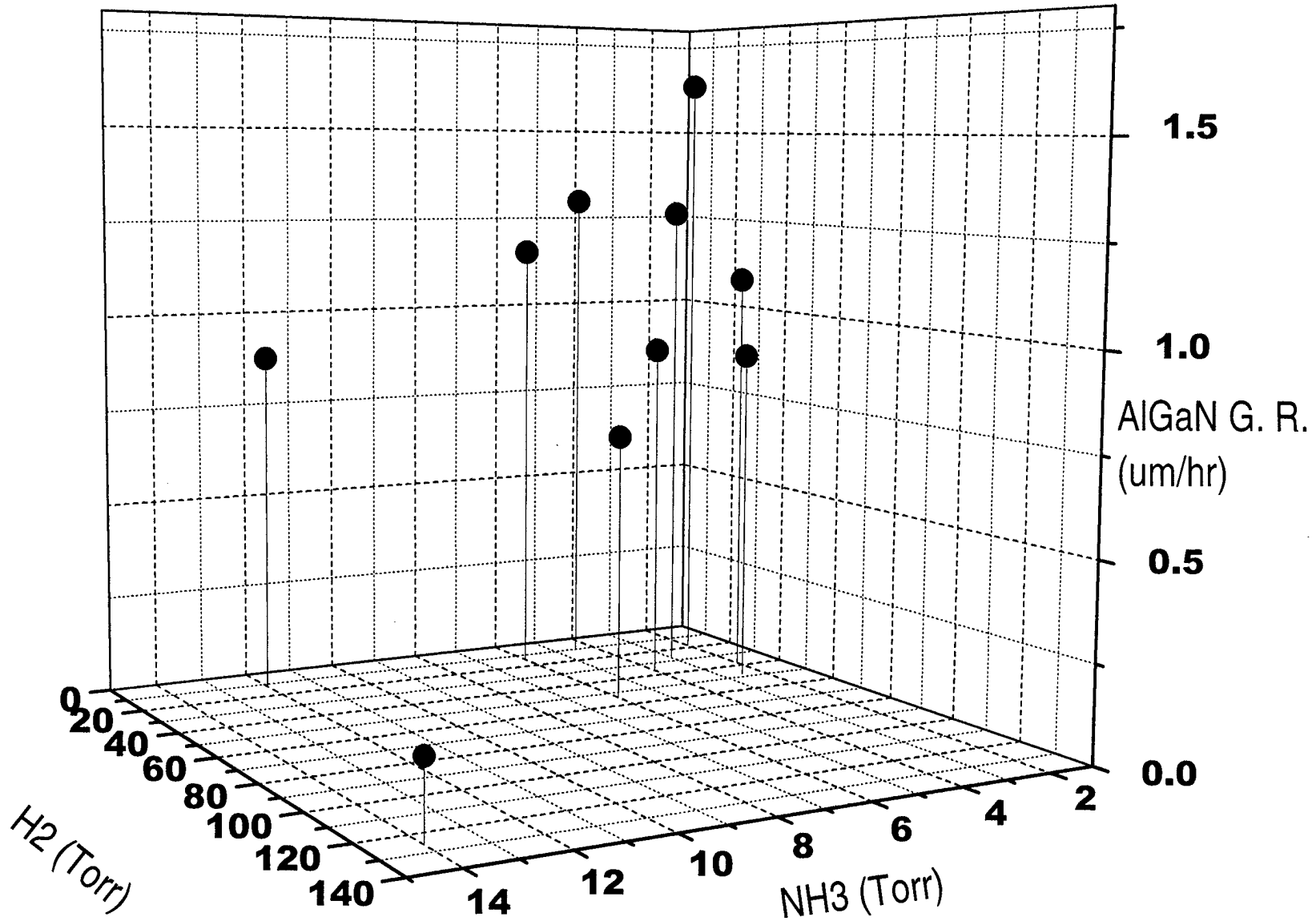

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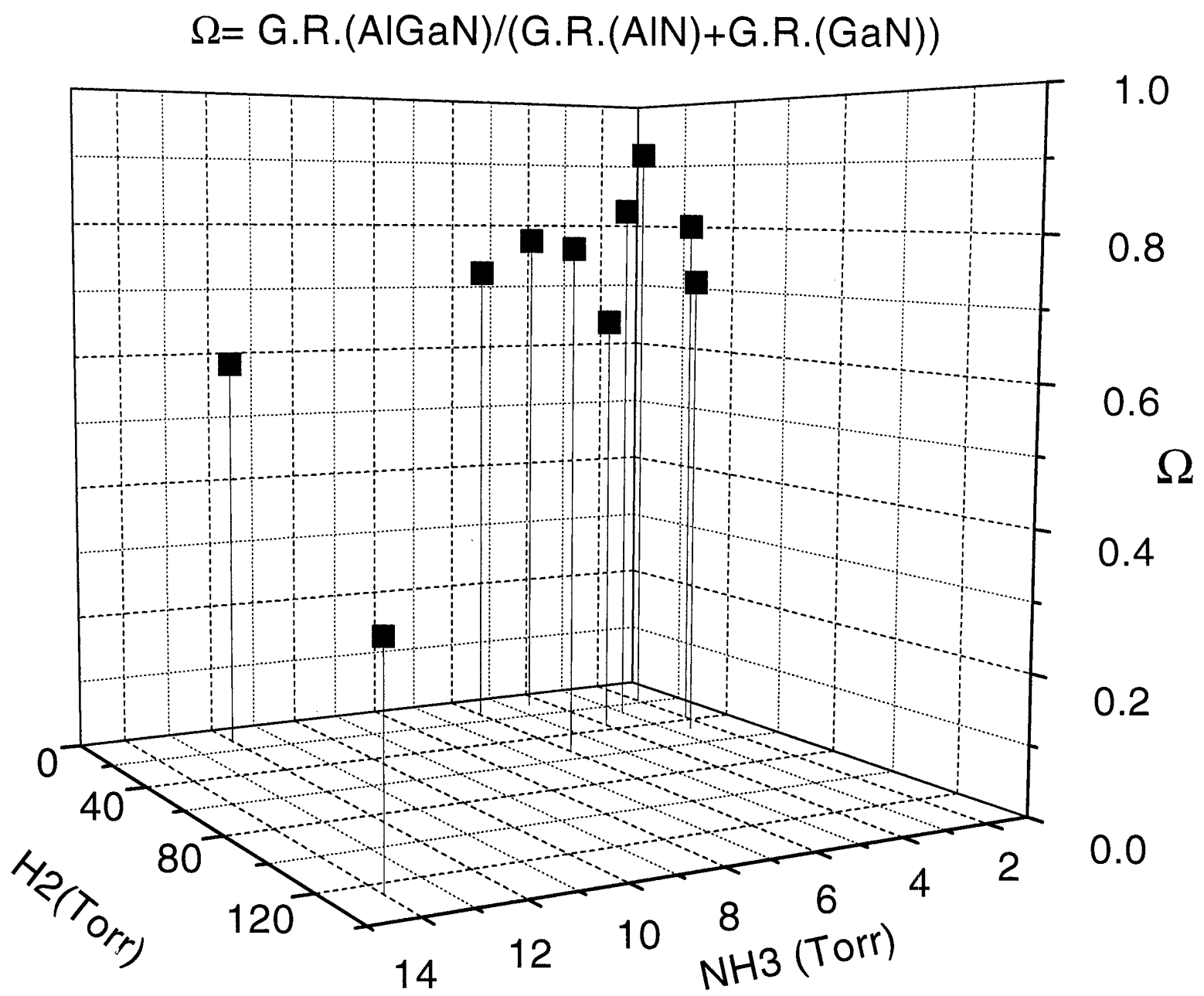

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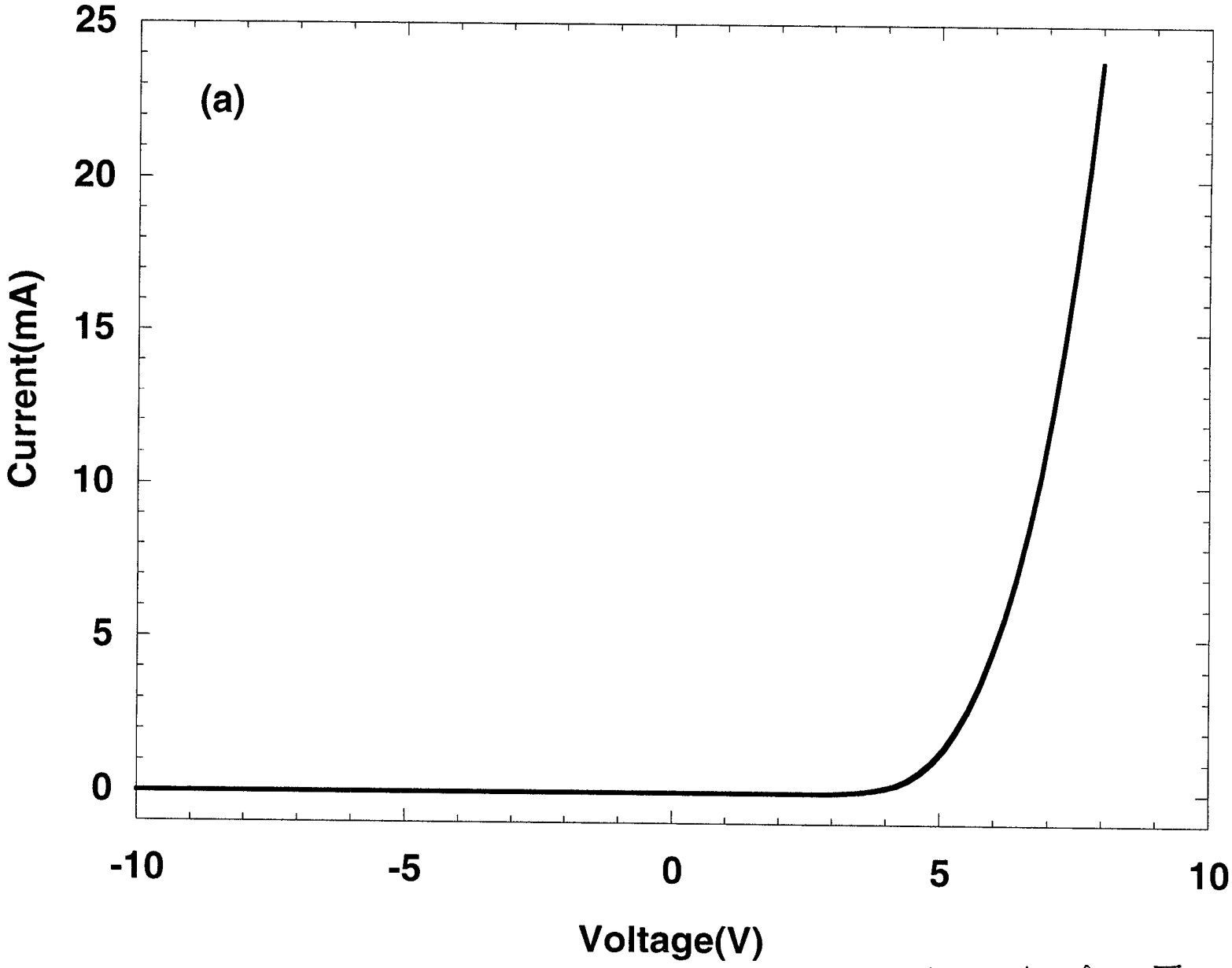

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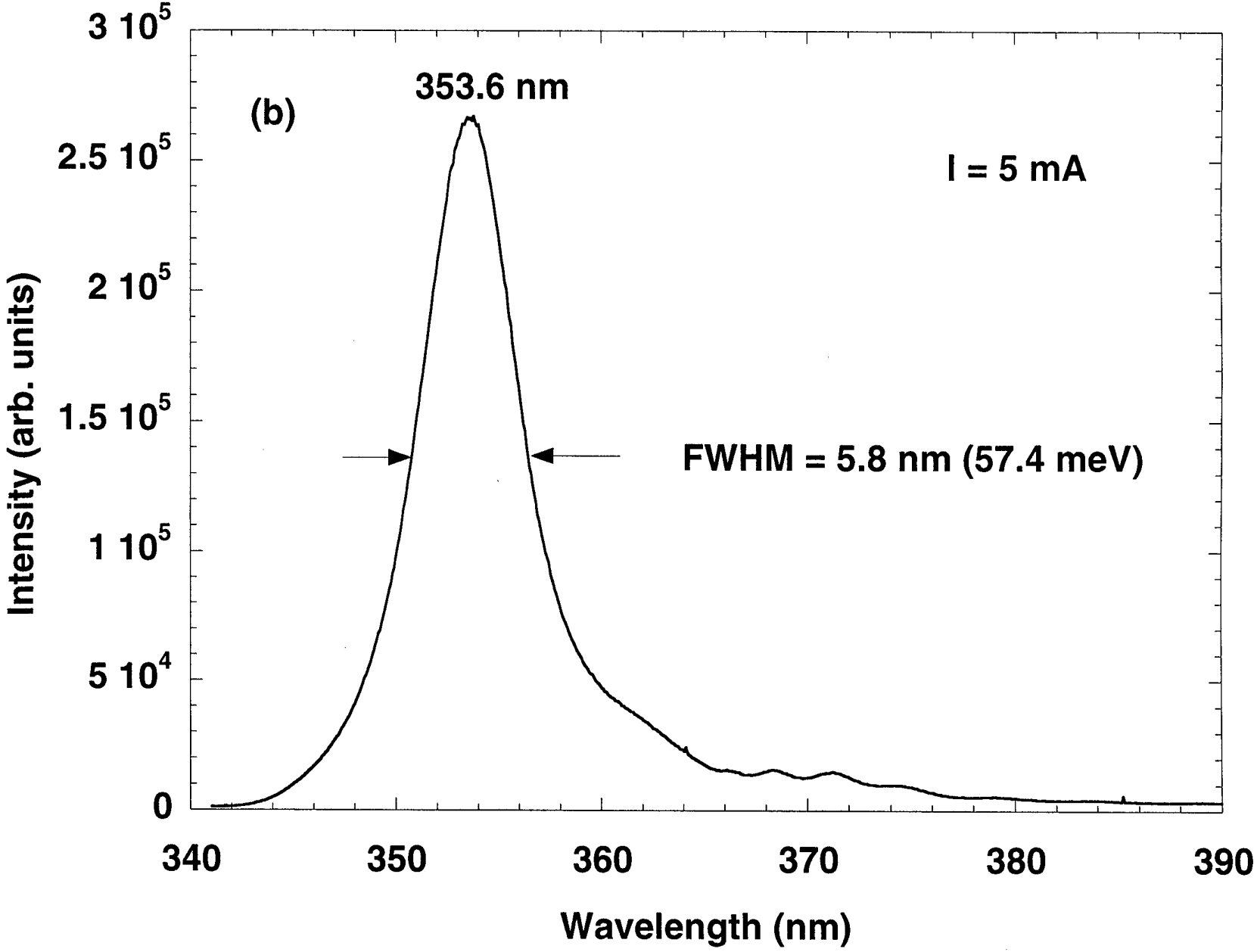

Han et al. Fig. 3(b)

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