# OPTICAL CHARACTERSTICS OF CARBON BASED SEMICONDUCTORS

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## Abstract

The photoluminescence (PL) in a-C:H:N was measured using a 2.41eV Ar ion laser line for varying N content. The PL results show a lowering of the PL peak energy and a spectral line width broadening as the N content in the film increases. Decomposition of the PL spectra into a series of Gaussian sub-peak levels shows two distinct peaks at 2.2 and 2.1eV and a broad peak at 1.7eV. It is found that the apparent lowering in the PL peak energy and the spectral line width broadening with increasing N content can be understood in terms of an increase in intensity of the sub-peak at 2.1eV with respect to that at the higher energy (2.2eV). The 1.7eV, 2.1eV and 2.2eV sub-peaks are also found in a-C:H without N.

## Introduction

Hydrogenated amorphous carbon (a-C:H) films can be deposited using a plasma enhanced chemical vapour deposition (PECVD) process with a hydrocarbon gas as the source[1]. The ability of carbon to bond in a variety of configurations - $sp^3$ (diamond-like), $sp^2$ (graphite-like), and sp, in amorphous carbon leads to a material which can have a wide range of mechanical, electrical and optical properties depending on the relative fraction of the different bond types[2-6]. Kruangam et. al. [7] and Hamakawa et. al. [8] have reported the use of a-C:H as the active layer in electroluminescent devices. A new alloy, nitrogenated and hydrogenated amorphous carbon (a-C:H:N) obtained when nitrogen is incorporated into the gas mixture , has drawn the interest due to its superior mechanical and optical properties [9] and also as a cold cathode which emits at low electric fields [10]. Materials containing (C-H) bonds show strong room temperature photoluminescence [11-14]. It is thought that this behaviour is due to photo excitation resulting in generation of confined electron hole pairs in $\pi$ and $\pi^*$ states. Since the $\pi$-$\pi^*$ states associated with $sp^2$ sites are surrounded by wider gap $sp^3$ sites, it creates sharp bad edge fluctuations leading to localised band edge states[15]. In this report we present the influence of nitrogen on the room temperature photoluminescence (PL) of amorphous carbon.

## Experimental Work

The a-C:H:N films in this work were deposited by decomposition of methane ($CH_4$) and nitrogen ($N_2$) at 900mTorr, in an inductively coupled PECVD system operated at 27MHz, with variable RF power (600W - 1050W). In inductively coupled PECVD the ionised plasma oscillations are parallel to the substrate, minimising induced self bias voltage with respect to the substrate and secondary back sputtering, which is not the case in conventional capacitively coupled PECVD. Films were deposited on Si {100} substrates for PL studies and on fused quartz substrates for optical measurements. All substrates were chemically cleaned using a standard process prior to deposition [**The cleaning procedure** : boiled in deionized water, heated in trichloro ethylene, rinsed in 2-propanol, washed in deionized water, heated in hydrogen peroxide and ammonium hydroxide, washed in deionized water, heated in a hydrogen peroxide and hydrochloric acid mixture washed in deionized water and spin-dried]. In addition all substrates were given an in situ He plasma clean for 30 seconds in order to sputter clean any remaining impurities.

Optical measurements were carried out on 100nm - 300nm thick films deposited on quartz substrates. Absorption data were collected both in transmission and reflection with near normal incidence in a Philips UV-VIS spectrophotometer (188nm - 900nm). Optical parameters (refractive index - n and absorption constant - k) were computed, by considering reflection and transmission in a multilayer system comprising the film and substrate.

For the PL spectra measurement the 514nm line of an Ar ion laser operated at 600mW was used as the excitation source. The sample was excited at a glancing angle by a modulated laser beam, the PL emission was dispersed by a monochromator and detected by a photomultiplier placed normal to the sample. The amplifier was locked-in with the modulating frequency in order to remove any dc bias induced on the detector by the scattered ambient, and an optical filter in front of the detector is used to exclude the exciting laser line. All PL spectra were corrected for the system response.

## Results and Discussion

The PL spectra measured from films with varying N content from no detectable N to 30 at% N [The N content was determined using scanning neutral mass spectroscopy (SNMS) with a structure factor adjusted for the density of a-C:H:N] are shown in Fig. 1. The PL peak energy position moves from 2.23eV for the film with no N to 2.12eV for the film with the highest nitrogen content. The Tauc optical band gap of the nitrogenated films remains constant at around 2.7eV for all nitrogen ratios while that of a-C:H without nitrogen is 3.0eV. With nitrogen incorporation into the film, the refractive index of the material n, does not shift from its behaviour without nitrogen in the film, as shown in Fig. 2a. The behaviour of the absorption constant k also remains the same with varying nitrogen contents [Fig. 2b]. However it shifts from its position at 0 at% N with the presence of nitrogen in the film. The deconvolution of the composite PL envelope for all the a-C:H:N and a-C:H films reveals two prominent Gaussian sub-peaks around 2.1eV and 2.2eV, and another relatively broad minor peak around 1.7-1.8eV. The apparent shift in peak position of the composite PL envelope with increasing N content is due to the change in the relative intensities of the two prominent sub-peaks with variation in nitrogen content, see Fig. 3a-Fig. 3d. As nitrogen content increases, the intensity of the sub-peak at 2.1eV increases with respect to that at 2.2eV, this effect is manifested as an apparent shift in PL peak position of the composite envelope towards lower energies. The relationship between the relative intensity of the sub-peaks and the measured PL peak is clearly seen in Fig.

4. In Fig. 4 the N ratios of 0.4, 1 and 3 correspond to N contents of 3.6 at%, 9 at% and 27 at%. The highest ratio of N is expected to be at the saturation level of N in a-C:H:N, 30 at%, as also measured previously [15]. When the ratio of $P_{S1(2.1eV)}$ / $P_{S2(2.2eV)}$ and the composite PL peak is plotted against N content, the change in peak position with N content closely corresponds to the inverse change of the major sub-peak ratio. This is a strong evidence for the apparent shift in peak position of the composite envelope being due to intensity competition between these two sub-peaks. It is not due to any movement of the recombination centre within the band-gap as the N content increases.

As N content in the film increases the density of states related to N-centre, which on the basis of the PL results we propose to be ~2.1eV above the π edge, increases making the intensity of PL associated with that centre higher. As shown in Fig. 5, the spectral width of the composite spectra gets broader with N content in the film. The spectral widths are comparable with those reported previously for similar materials [16]. The spectral broadening seen can be understood within the same context of there being two dominant recombination centres. The width of the two sub-peaks remains unchanged with changing N content, with a width of 0.18eV for the sub-peak at 2.2eV and 0.31eV for the sub-peak at 2.1eV. This shows that inclusion of nitrogen does not influence the line shape. Rather, nitrogenation leads to a higher intensity of the PL sub-peak at 2.1eV. Although the width of the sub-peaks remains unchanged, as relative N content, intensity increases, the intensity level at which half maximum occurs goes up. This is reflected as a broadening in the composite PL profile.

## Conclusions

In this work we have studied the effect of nitrogen on photoluminescence in a-C:H:N, and we suggest that the apparent shift in PL peak and line with broadening of the PL spectra with nitrogen content is in fact due to increased intensity of a nitrogen associated recombination centre at 2.1eV from the π edge, within the bandgap electronic density of states (DOS). The fact that the spectral width of the PL sub-peak associated with N does not change as the N content is increased up to the saturation value, also points to the N states associated with this centre being very strongly localised. We conclude that the PL is a very sensitive measurement of relative variation in such DOS in a-C:H due to inclusion of N compared to conventional optical absorption.

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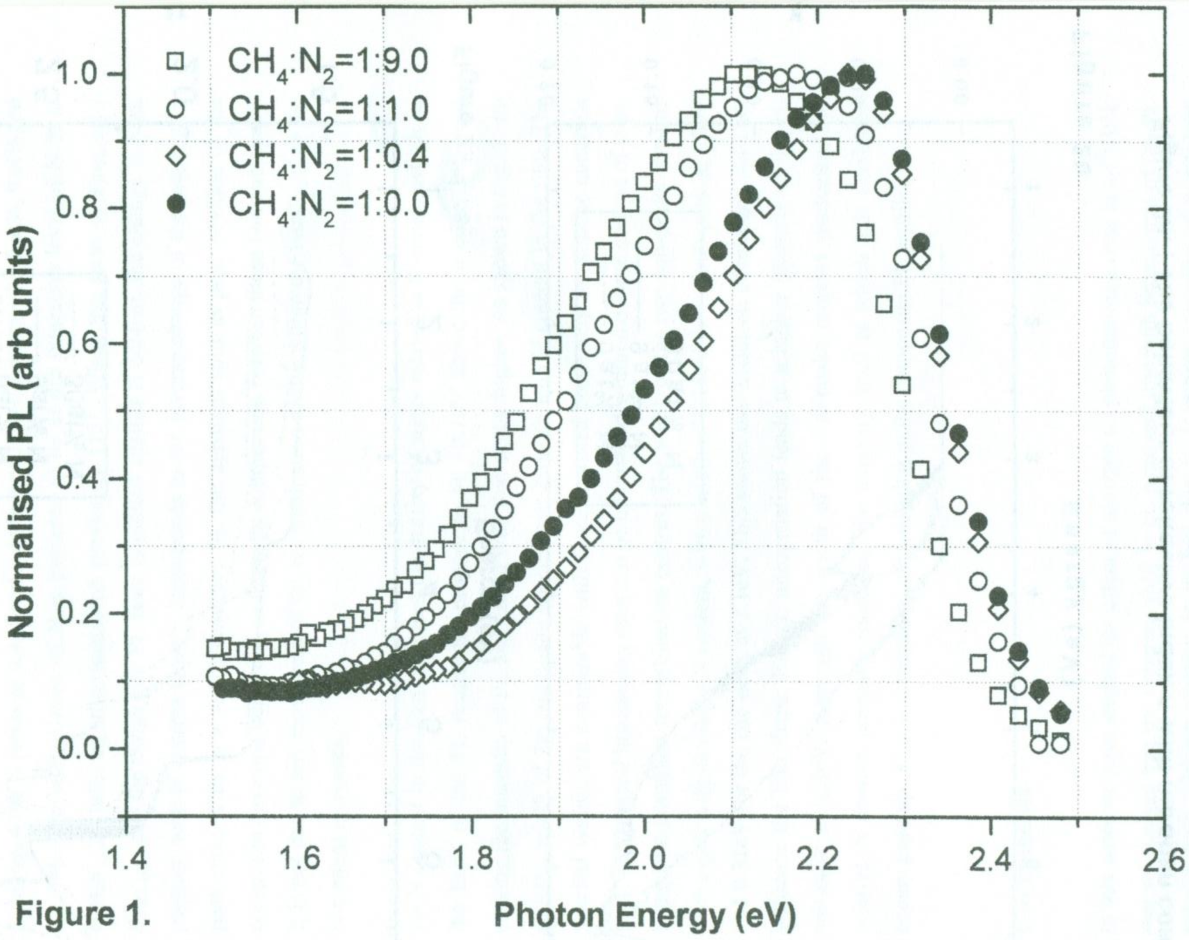

**Figure 1.**

PL spectra of a-C:H:N with varying N contents from no detectable N to ~30% N. Excitation energy used was the 2.41eV Ar ion laser line. As N content in the film increases, PL peak position shifts from higher photon energy of 2.23eV to 2.12eV. The spectral width of the spectra also broadens with N content in the film.

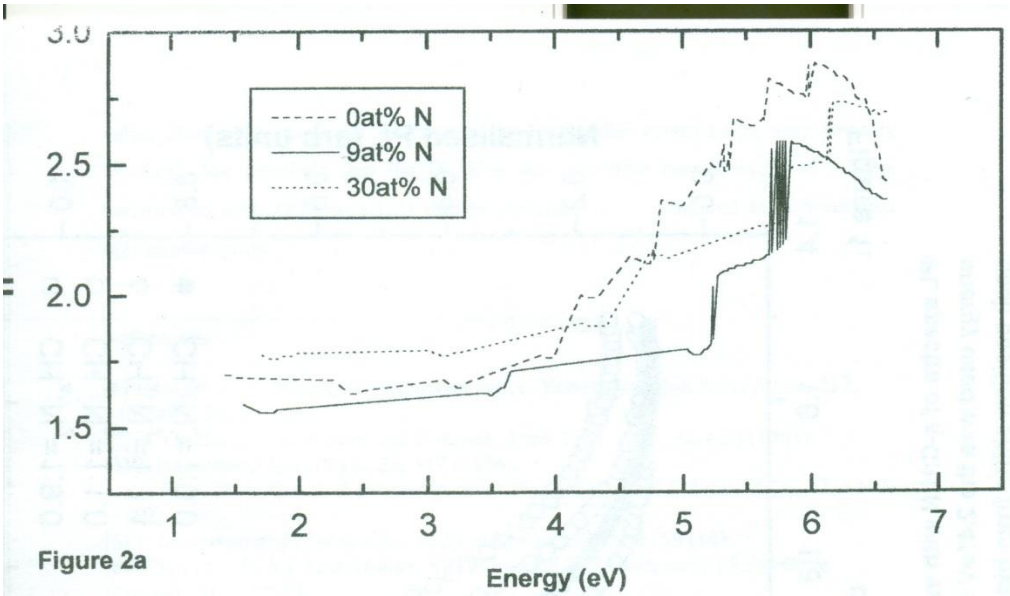

**Figure 2a**

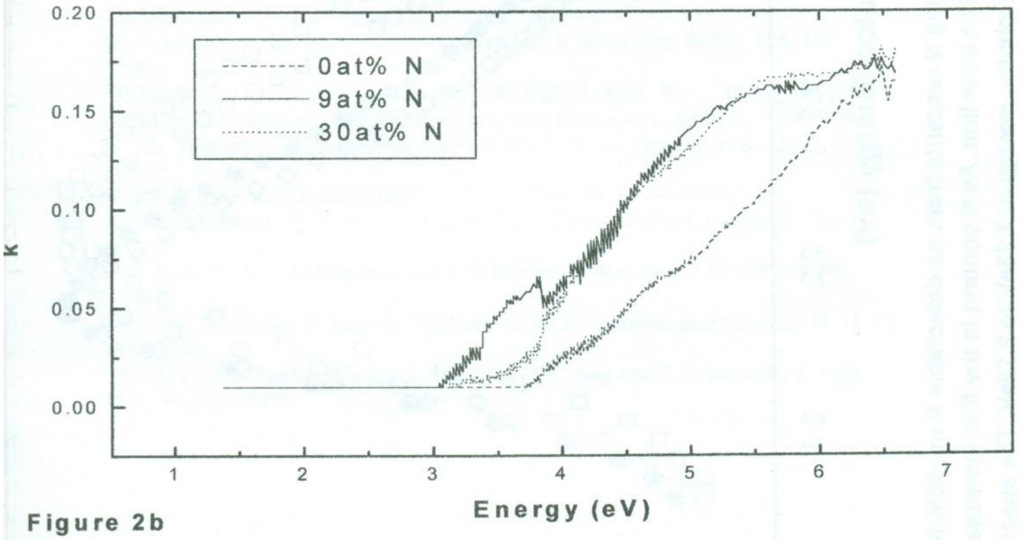

**Figure 2b**

**Figure 2a. : The behaviour of refractive index n with nitrogen content for three different N levels in the film. Incorporation of N does not affect the behaviour of n with photon energy.**

**Figure 2b. : The absorption constant k, shifts from nitrogen free position indicating the presence of N in the film. However it does not change further with varying N content.**

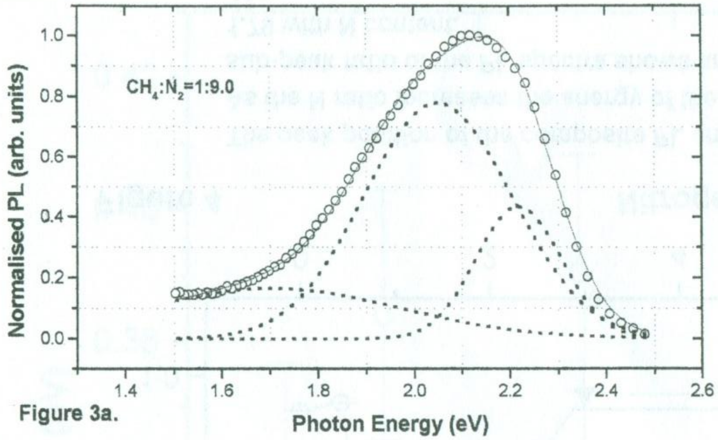

Figure 3a.

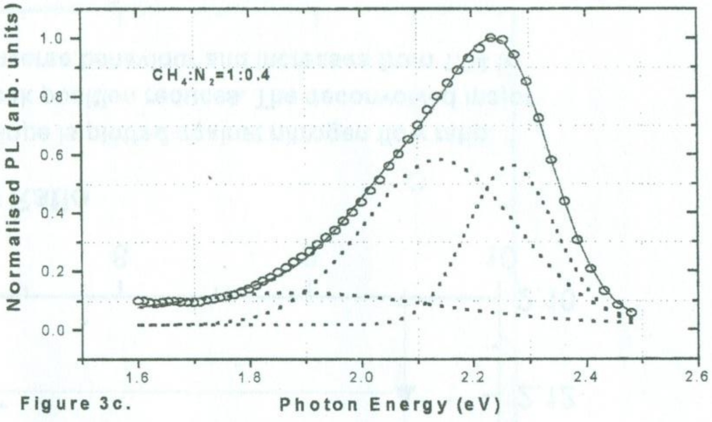

Figure 3c.

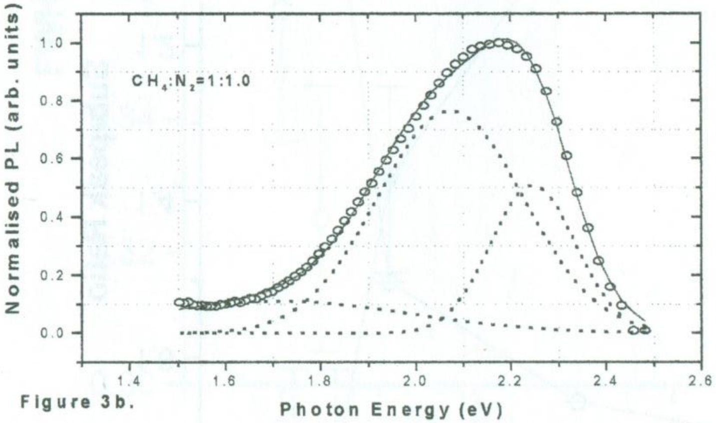

Figure 3b.

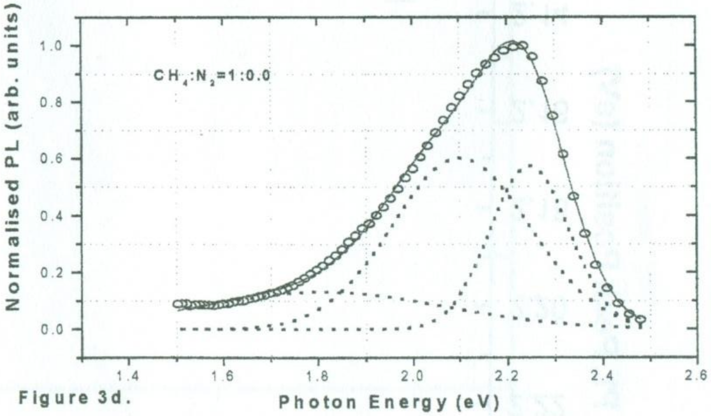

Figure 3d.

**Figure 3 : The PL spectrum at the highest N content is in 3a. Deconvolution yields three Gussian sub-peaks. The intensity ratio of two major sub-peaks, ~2.1eV to ~2.2eV is 1.79. In 3b the deconvolution shows similar sub-peaks as in 3a. But as N content goes down, major sub-peak ratio also goes down to 1.5. Further reduction in N content brings the deconvolved major sub-peak ratio down to 1.03. Deconvolved spectrum of the film containing no detectable N has a major sub-peak ratio of 1.04.**

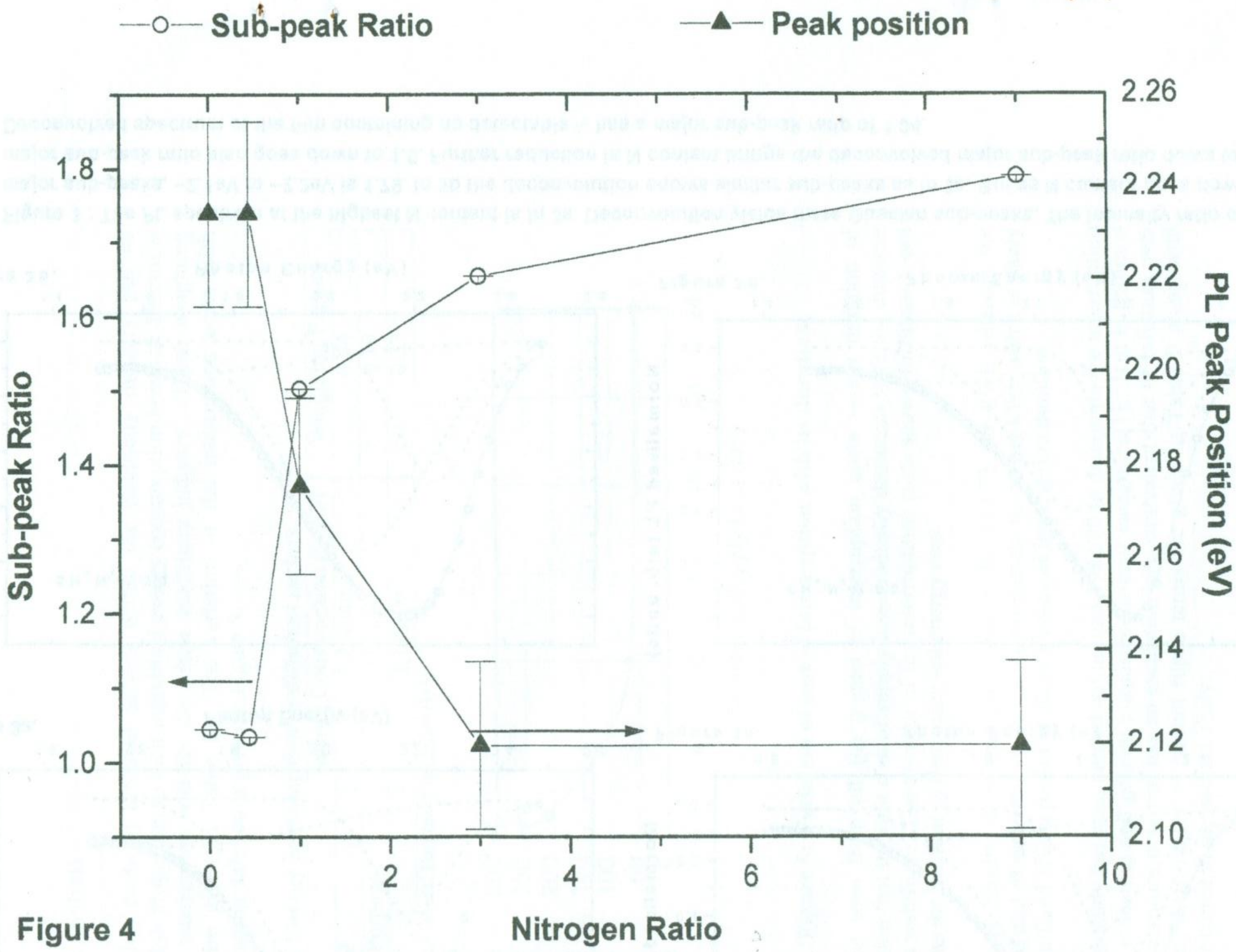

**Figure 4**

The peak position of the composite PL envelope is plotted against nitrogen flow ratio. As the N ratio increases the energy of the peak position reduces. The deconvolved major sub-peak ratio of the PL spectra shows an inverse behaviour and increases from 1.04 to 1.79 with N content.

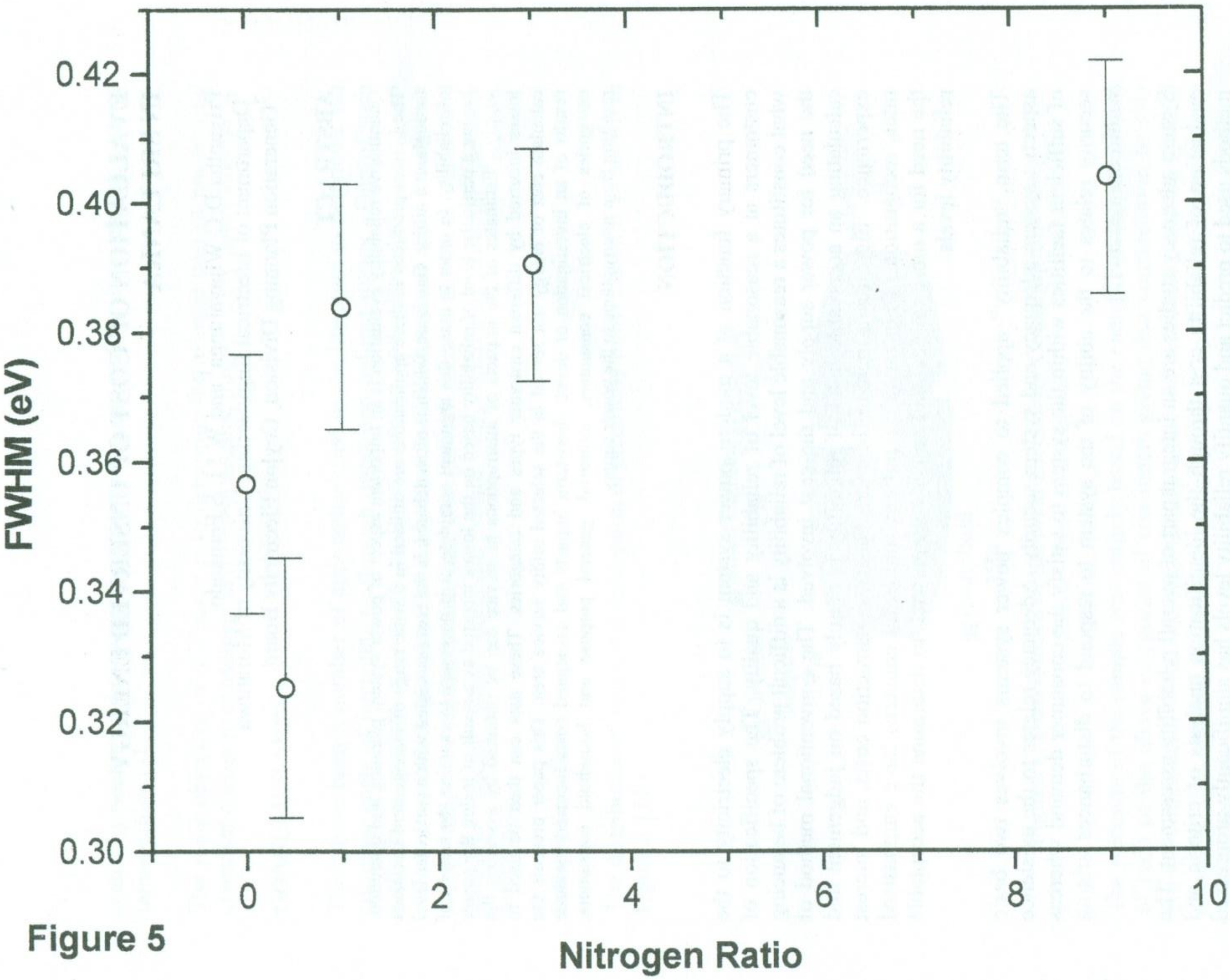

Figure 5

The spectral width of the composite PL envelope as N content increases