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Amorphous CN_x Layers from Neon Electron Cyclotron Resonance Plasmas with N_2 and CH_4 as Precursors

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Deposition of amorphous CN_x thin films on silicon by electron cyclotron resonance plasma-enhanced chemical vapor deposition is investigated. The use of neon instead of argon to form the plasma promotes species activation and leads to deposition on silicon substrates. The influence of precursor flow ratio, addition of hydrogen, and radio frequency power was studied. Optical emission spectroscopy has been used for the diagnosis of active species involved in the deposition process and neither nitrogen nor carbon atomic species were detected. Fourier transform infrared spectroscopy measurements showed as main bands those related to C–N and C=N bonds. Dielectric constants of the films were obtained by spectroscopic ellipsometry: samples grown with the highest methane flow ratios showed absorption throughout all the measured energy range, probably due to free carriers. Present results suggest that CN_x layers consist mainly of C–N and C=N bonds in an amorphous matrix, besides C=C bonds probably in the form of small graphitic clusters.
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The theoretical works of Liu and Cohen on the properties of the hypothetical compound C_3N_4,[1-3] have stimulated much effort in recent years to obtain this material. It is expected to have a structure based on β-Si_3N_4, but with C atoms bonded to nitrogen instead of Si. Its extreme hardness, comparable to that of diamond, and its electronic properties would make it useful for a wide range of applications in materials engineering (as hard coatings, for instance) and microelectronics (as an insulator). In spite of the great number of publications reporting attempted synthesis of crystalline C_3N_4 with properties close to that of diamond, it appears not to have been achieved so far. Continued research in this field is necessary.

Even though many substrates have been tested with results better than silicon,[4,5] this substrate is especially interesting for the potential integration of C_3N_4 in electronic devices. Few works using silicon substrates have been reported, to date, and to the best of our knowledge, in all of them the incorporation of C species is obtained from a solid source.[6-8] The use of gas sources allows growth of higher purity films with low oxygen content, which is a common impurity in C solid sources. Deposition of CN films from gas sources is extremely difficult, because CN-containing species generated as reaction products may have a low sticking coefficient on the Si surface and be relatively volatile on the growing surface.[9]

In this paper we report an attempt to synthesize CN thin films on silicon by microwave electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD). This technique provides a high density of chemically active species at low temperature, allowing the use of very stable precursor gases, such as N_2 and CH_4. A noble gas is used to form and stabilize the plasma. It has been reported that the addition of neon increases the total ionization rate of nitrogen while argon has the opposite effect.[10] Therefore, we used Ne + N_2 + CH_4 plasmas for deposition of thin films. Some of the former experiments were carried out using argon, nitrogen, and methane; however, no deposition was obtained.

We also studied the influence of hydrogen in the grown layers because, as it has been reported, the saturation of dangling bonds by hydrogen atoms significantly reduces the surface free energy.[4]

Experimental

CN films were deposited in a Plasma Quest ECR plasma reactor (model 357) with low-profile configuration in which a collimated plasma column is achieved by placing an additional electromagnet below the substrate holder.[11]

Layers were deposited on (100) p-type Si wafers, with resistivities between 4 and 6 Ω cm. Both sides of the polished substrates were selected in order to perform transmission infrared measurements. Prior to load in the vacuum chamber, the substrates were degreased and the native oxide removed by a buffer etching. During deposition the sample holder was not intentionally heated.

Deposition processes were run using precursor gas mixtures of N_2 and CH_4, with $CH_4/(CH_4 + N_2)$ gas flow ratios between 0.5 and 0.856. Ne gas or Ne + Ar gas mixture was also added in order to maintain stable plasma regime regardless of the precursor gas flow values. In some cases, H_2 gas was also introduced in the chamber to study its role as a possible promoter of CN formation, as suggested by some authors.[4]

Ne, N_2, and H_2 gases were introduced in the chamber by an upper gas inlet directly into the resonance zone; meanwhile CH_4 was introduced just above the sample. The introduction of N_2 in the resonance zone allows maximum energy transfer from the plasma to the N_2 molecules.

Experimental conditions of the three sample series are summarized in Table I. Neon and nitrogen gas flows were maintained at 50 sccm in all cases. Methane flow was varied between 50 and 120 sccm to attain a variation of the $CH_4/(CH_4 + N_2)$ flow ratio as wide as possible, maintaining a pressure of about 5 mTorr. In one deposit we employed 10 sccm Ar and 40 sccm Ne instead of the usual 50 sccm Ne. The second series was carried out with 15 sccm H_2. Finally, a third one was performed under similar conditions as the first series but applying 160 W of radio frequency (rf) power to the plasma. In all processes the microwave power was maintained at 1000 W.

Emissive species in plasmas were detected by optical emission spectroscopy (OES) measured through a quartz window. The collected spectra correspond to a downstream plasma region near the substrates. Thickness of deposited layers was measured by a Dektak profilometer. Fourier transform infrared (FTIR) spectra were obtained using a Bruker IFS-66V spectrometer. They were used to

Table I. Experimental conditions of the deposition processes.

Gas flow (sccm)	Series 1	Series 2	Series 3
N_2	40, 50	50	50
CH_4	50-120	80-120	60-120
Ne	50	50	50
H_2	—	15	—
Ar	0, 10	—	—
Microwave power (W)	1000	1000	1000
RF power (W)	—	—	160

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identify vibrational modes of the different bonds present in the films for comparison among effects of different experimental conditions. Finally, dielectric constants of layers were obtained by spectroscopic ellipsometry (SE) measurements in the range between 1.5 and 4.5 eV, performed with a Uvisel Jobin Yvon system. Energy gap for each layer was estimated from these measurements.

Results and Discussion

Growth kinetics.—The deposition rate, shown in Fig. 1, seems to be linear with the $CH_4/CH_4 + N_2$ flow ratio in the plasma. This may indicate that the flow of CH_4 is the parameter that limits the growth rate of the film. The rise of nitrogen partial pressure has been reported to cause a reduction of the deposition rate in diamond-like carbon film growth,[12,13] which would be equivalent to the observed evolution with increasing CH_4. An enrichment of films in carbon content for high CH_4 flows could be the explanation for the increase of the deposition rate. This enrichment could be produced as a consequence of the higher H radical concentration with rising CH_4 flow, rather than the higher C species concentration in the plasma. It is thought that H radicals saturate dangling bonds in the growing diamond surface, reducing its surface energy.[4] Further, the slight increase of the deposition rate in the second series can be also due to the addition of H_2, which could reduce the surface metastability at low-pressure conditions. Under high CH_4 flows the large amount of dissociated hydrogen makes this effect almost negligible.

Deposition rates in samples performed with Ar in the gas mixture are not shown in this figure, but they were about one order of magnitude less than in the rest of the samples. Previous experiments showed that there is no deposition on substrates when using only Ar as diluent gas.

Optical emission spectroscopy.—OES measurements allowed us to identify the main excited species present in the plasma and to investigate their role in deposition mechanisms. In Fig. 2a and b, the spectra of gas mixtures with Ne + N_2 and Ne + CH_4, respectively, are shown. The main contributions in both of them are the lines of 584 nm and 639 nm of Ne activated atoms. First and second positive systems of the neutral N_2^* molecule are also observed in Fig. 1a, as well as the lines at 390 and 357 nm, due to the first negative N_2^+ system. In spite of the higher activation energy of this ion compared to the atomic one (18.7 and 14 eV), no lines ascribed to the atomic nitrogen detected.

The Ne + CH_4 spectrum shows contributions in 386 and 429 nm due to CH, as well as hydrogen Balmer lines at 433 (H_γ), 485 (H_β), and 656 nm (H_α). Near the Ne lines mentioned, which appear in both spectra, in this case we distinguished secondary lines that could be related to upper excited states of Ne.

All the emission lines mentioned can also be observed in Fig. 2c, which shows the spectrum of typical plasma of the first series of processes. The apparent relative increase of the 386 nm CH line intensity compared to Ne lines is produced by the contribution of the CN cyanoviolet system at 387 nm. This has been reported to be much more intense than the CH one, as a consequence of the low activation energy of the CN specie.[14] The band between 418 and 421 nm belongs also to the cyanoviolet system.[15] The apparent increase of the 337 nm line intensity, belonging to the second positive N_2^* system, is due to the NH contribution, located in 335 nm but, in this case, of similar tabulated intensity. Both contributions are too close to distinguish one from the other.

Lines centered at 387, 429, and 335 nm, corresponding to CN, CH, and N_2^* + NH respectively, have been chosen to monitor the behavior of plasma with the $CH_4/CH_4 + N_2$ flow ratio in the three series.

In previous experiments with Ar, CH_4, and N_2, in spite of the presence of the 387 nm CN line, we observed the absence of film deposition over the silicon surface. This fact can be due to the low sticking coefficient of this group on Si or to the energetic ion bombardment, as suggested by Clay *et al.* about N_2^+ in rf plasmas.[14]

No substantial changes between deposition rates of the second and third sample series have been appreciated, even though the energy of the ions is expected to be higher under rf field (Fig. 1); thus, we believe that the low sticking coefficient must be the right explanation.

The intensity of the CN emission line decreases drastically with the flow ratio in series 3 (Fig. 3a) despite the increase of the CH one that accomplishes the rising of CH_4 flow (Fig. 3b). Two factors can explain this fact. First, an increase of collisional phenomena caused by excited C_mH_n species present in the plasma. Mass spectroscopic studies point out that these species tend to undergo collisional reactions, rather than de-excitation processes, and thus, they are not visible in optical emission spectra.[14] Then, collisional processes can

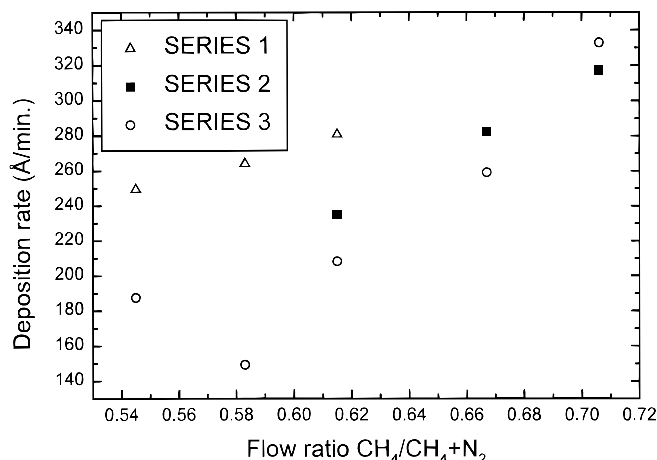

Figure 1. Deposition rates of the three series.

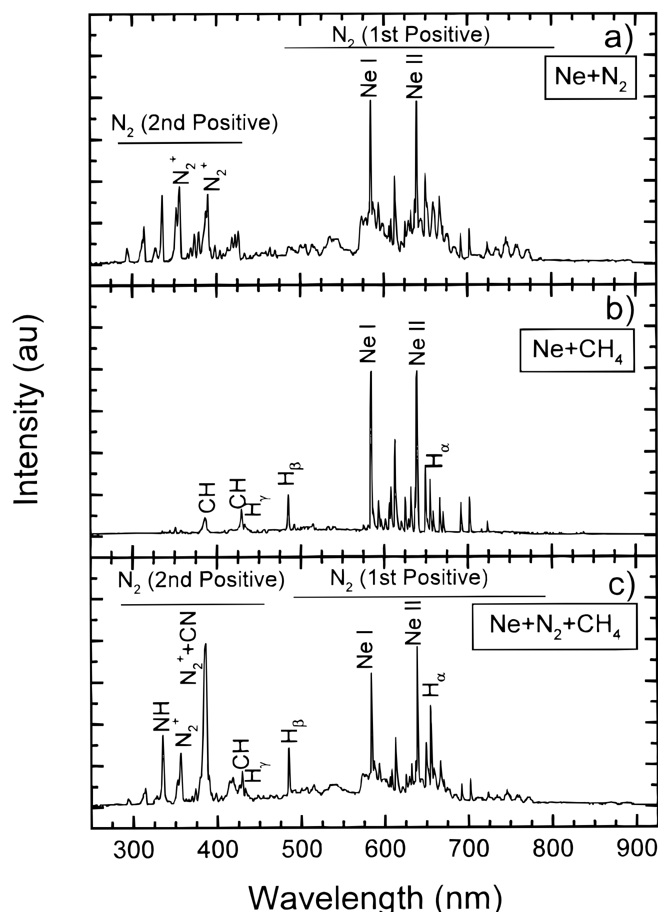

Figure 2. Optical emission spectra of: (a) Ne + N_2, (b) Ne + CH_4, and (c) Ne + N_2 + CH_4 gas mixtures.

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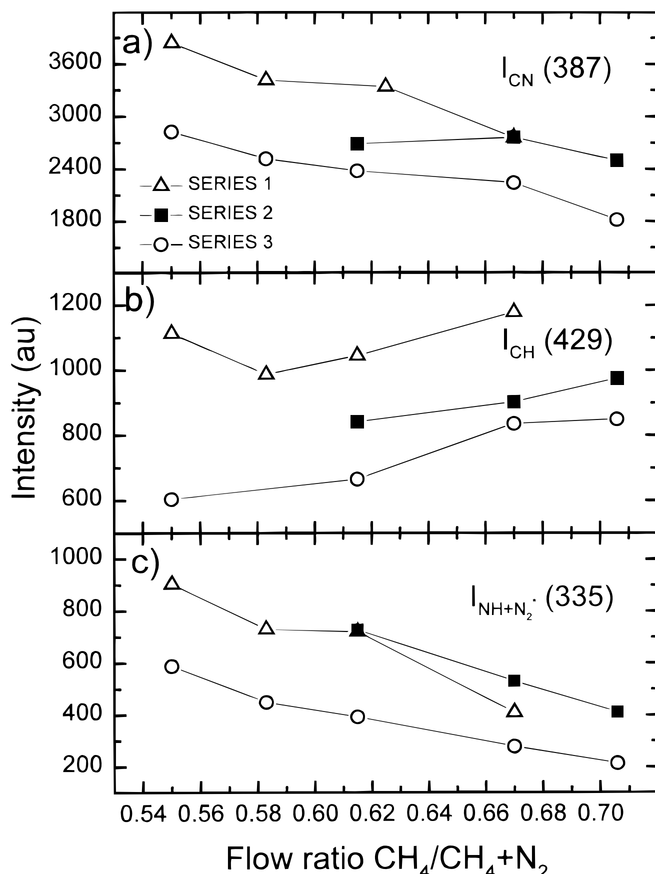

Figure 3. Evolution of the (a) 387 (CN), (b) 429 (CH), and (c) 335 (NH + N_2^*) nm emission lines.

favor the breaking of CN bonds in volatile species, promoting the incorporation of separated C and N on the substrate. The second factor may be the minor density of activated nitrogen species in the plasma, as deduced from the decreasing intensity with the flow rate of the NH + N_2^* line (Fig. 3c). The deposition rate evolution in Fig. 1 supports the first explanation: separated incorporation of C and N in the films.

Infrared characterization.—Figure 4 shows the FTIR spectra that have been considered most representative for the qualitative analysis

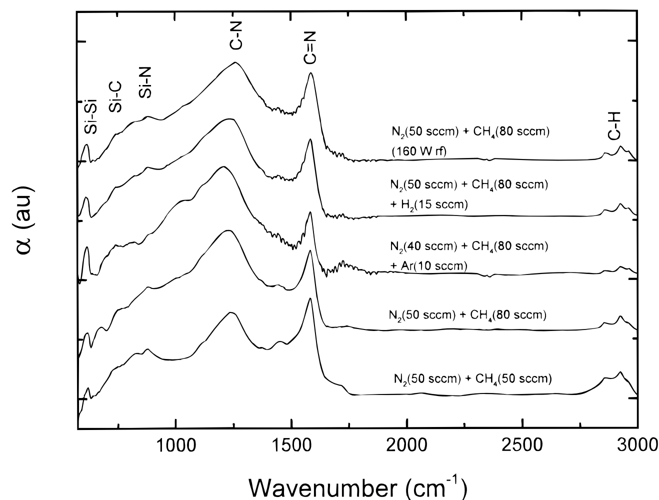

Figure 4. Representative FTIR spectra of some samples. In all cases the Ne flow was 50 sccm.

of the films' chemical composition. In all cases the main bands are centered at about 1250 and 1600 cm^{-1}. These two bands can be associated to the stretching mode of C–N and C=N bonds at 1350 and 1500 cm^{-1}.[16,17] The single bond band has been reported to be located between 1100 and 1250 cm^{-1} depending on the crystalline structure.[19] In our case the peak is clearly broadened, meaning that the samples must be amorphous with a microstructure of mixed crystalline phases. The second one, at the sp^2 zone (1600 cm^{-1}), could also be due to C=C bonds,[18] but the slight increase of its area with the N_2 flow supports the first assignment.

Si–Si, Si–C, and Si–N stretching bands were detected too, probably due to the deepest layers where, during the first stages of the deposition, these kind of bonds could be formed with the silicon substrate. C–H bonds were also found in the samples. This band does not increase when adding H_2 gas to the plasma, thus we believe that C–H bonds must be formed by radicals from CH_4.

There are only slight differences among the spectra of the films grown with and without H_2, perhaps a small narrowing of the C–N band, more symmetrical in the second case. This must indicate that the methane decomposition produces such a large quantity of hydrogen that the effects of the added flow of H_2 in the deposition conditions are negligible.

The rf power did not show a great influence either. The relative decrease of the double C=N band with respect to the C–N one suggests an effect of ion bombardment in the films, as consequence of rf on one hand and the higher value of the CH_4 flow on the other.

The addition of Ar to the gas mixture does not produce important changes in bond structure. The appearance of a shoulder at 1030 cm^{-1} in the IR spectrum suggests the presence of a nonstoichiometric thin oxide film, grown in the substrate surface at the first stages of the plasma process. Initial oxidation from degassed H_2O would be easier to take place when adding Ar, due to the lower deposition rate observed under these conditions.

Spectroscopic ellipsometry.—Figure 5 shows the ellipsometric spectra of two films of the first series, both of them grown with 50 sccm Ne, 50 sccm N_2, and 60 sccm (Fig. 5a) or 80 sccm (Fig. 5b) of CH_4. Because of the lack of interference oscillations, we have assumed the films to be absorbent enough to consider that the substrate cannot be seen by this technique and, therefore, those measurements lead to the true dielectric constants of deposited layers.

We have tried to fit all the spectra using the classic DHO model (damped harmonic oscillator) that approximates the dielectric constant by a sum of Lorentz damped oscillators[20]

$$\epsilon(E) = 1 + \sum_j \frac{C_j}{(1 - X^2) - iX\gamma_j} \qquad X = \frac{E}{E_j} \qquad [1]$$

where E_j, C_j, and γ_j are the energy, amplitude, and the damping parameter of each oscillator, respectively. Fittings needed more than one oscillator and, even in this way, good results have not been obtained because of the presence of absorption by free electrons. In this way we can only get an estimation of the fitting parameters for the lowest-carbon-content samples. We obtained a value for the energy of the main oscillator between 2.6 and 2.8 eV, amplitude of 0.9-1.3, and damping parameter of 0.3 approximately.

We tried then to estimate the energy of the optical gap using the experimental data and a function of the energy with the form

$$f(E) = [\epsilon_i(E)]^{1/2}E \qquad [2]$$

usually known as Tauc formula. The results of these fittings, as can be seen in Fig. 6, prove that the increase in the $CH_4/(CH_4 + N_2)$ gas ratio in the plasma leads to an apparent reduction in the gap energy, probably caused by a higher carbon concentration, may be as graphitic clusters. This metallic character is clearly seen in Fig. 5b (where the CH_4 flow ratio was 0.62); the increase of the dielectric constants below 1.6 eV is typical of absorption by free electrons.

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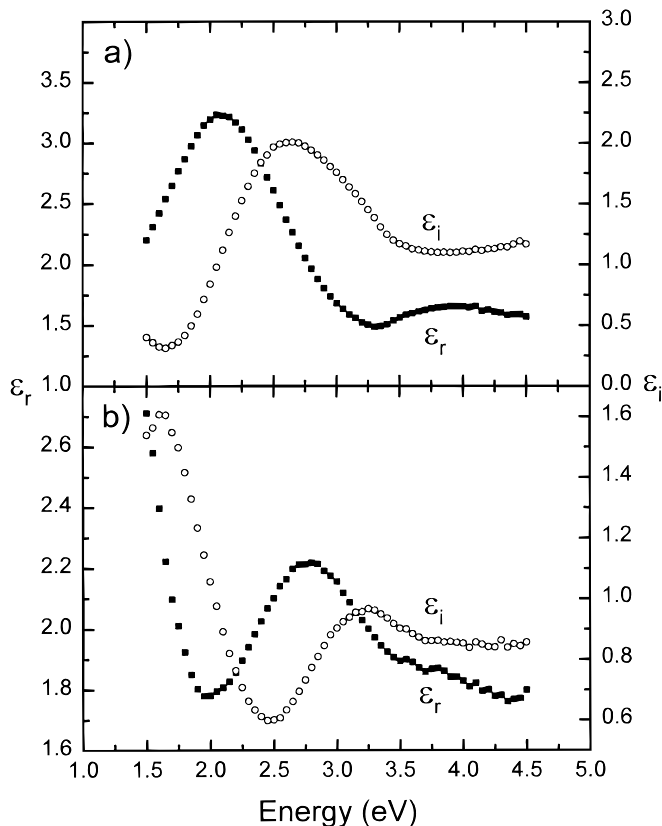

Figure 5. Dielectric function of the samples of the first series performed with 50 sccm Ne flow, 50 sccm N_2 and (a) 60 sccm CH_4, (b) 80 sccm CH_4.

Conclusions

Amorphous CN films have been deposited from CH_4 and N_2 in a low-profile configuration ECR system, varying the gas mixture, flow ratio, and rf power. In all cases the deposition rate of these films increases with the $CH_4/(CH_4 + N_2)$ gas flow ratio. Enrichment in carbon content of the films for high flows of CH_4 could be the explanation for the increase. We believe that this is a combined effect of rising H radical concentration (which reduces the surface energy) and collisional phenomena caused by excited C_mH_n species (which break CN bonds). The decrease of the CN optical emission line intensity can be related to the incorporation of atomic species in the film. The presence of Ne gas in the mixture is essential to produce active species for the growth of CN films, although neither nitrogen nor carbon atomic species have been detected near the growing surface.

FTIR spectra of samples grown in different conditions show two bands that can be associated to the stretching mode of C–N and C=N bonds at 1350 and 1500 cm^{-1}, respectively. The broadening of the first band can be associated with an amorphous material with a microstructure of mixed crystalline phases. The intensity of the C=N band is lower than that of C–N in all cases except for low CH_4 flows and absence of rf power, perhaps due to minor collisional effects over C=N bonds.

Because of the high film absorption, spectroscopic ellipsometry measurements gave away the dielectric constants of the deposited layers. Samples grown with higher CH_4 flow ratios show metallic character, probably due to graphitic clusters. From these measurements, a value for the energy of the main oscillator between 2.6 and 2.8 eV has been obtained in low-carbon content samples. The values of the optical gap energy obtained from these measurements are between 1.6 and 0.3 eV, with an apparent reduction for higher flow ratios.

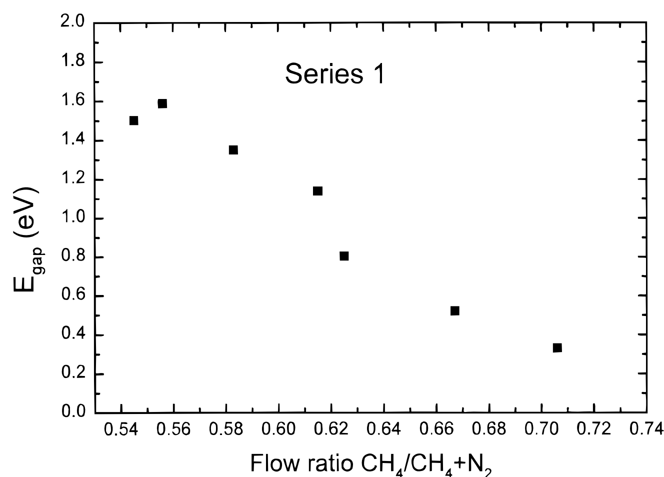

Figure 6. Gap energy of the third series obtained from fitting of the ellipsometric spectra.

Present results suggest that CN-deposited films consist of C–N and C=N, sp^3 and sp^2 bonded, in an amorphous matrix with probable presence of small clusters of some crystalline phases. However, besides CN bands the presence of C=C bands in graphitic clusters cannot be discarded. The decrease of the apparent energy gap with the CH_4 flow suggests some kind of free carrier absorption, probably due to the increase of graphitic clusters.

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