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Structural and Electrical Properties of Amorphous Hydrogen Carbon–Nitrogen Films *

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Amorphous hydrogenated carbon–nitrogen (a-C:H:(N)) films with different nitrogen contents have been deposited by using rf-sputtering of a high purity graphite target in an Ar–H₂–N₂ atmosphere. Transmittance and reflectance spectra are used to characterize the Tauc gap and absorption coefficients in the wavelength range 0.185–3.2 μm. The temperature dependence of conductivity demonstrates a hopping mechanism of the Fermi level in the temperature range of 77–300 K. The density of state at the Fermi level is derived from the direct current conductivity. The photoluminescence properties of a-C:H:N films were investigated. The photoluminescence peak has a blue shift with increasing excitation energy. These results are discussed on the basis of a model in which the different sp² clusters dispersed in sp³ matrices.

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In the last decade, hydrogenated amorphous carbon (a-C:H) films have received considerable attention owing to their specific properties such as hardness, low friction and chemical inertness. The physical properties and microstructure of a-C:H films have been well studied.^[1–4] Only a few attempts have been made to dope a-C:H films by boron, phosphorus and nitrogen. Kaufman and Metin performed further research on the structure of a-C:H:N films by IR and Raman analyses.^[5,6] They concluded that nitrogen is incorporated into the sp² clusters in the a-C:H films. Grill and Pated observed a decreasing hydrogen content with an increasing nitrogen partial pressure.^[7] Han and Feldman^[8] and Amir and Kalish^[9] found that nitrogen incorporation significantly affects the electrical and optical properties of a-C:H:N films. In this Letter, a-C:H:N films are studied by analysing the contents of C–H and N–H, the Tauc energy gap and absorption coefficients in the wavelength range of 0.185–3.2 μm. Additionally, a measurement of electrical conductivity has been taken to deduce the density of states at the Fermi level. A microstructure model for a-C:H:N films is presented to explain the photoluminescence properties.

Amorphous hydrogenated carbon–nitrogen (a-C:N:H) films were deposited on glass, silicon and Corning glass substrates by rf-sputtering of a high purity graphite target in an Ar–N₂–H₂ atmosphere with gas flow rate ratio (N₂/Ar) between 0 and 0.31 while the H₂ flow rate was fixed at 10 sccm. To obtain the same sputtering yield for carbon with different nitro-

gen gas flow rates, argon gas flow rates were adjusted from 75 to 55 sccm corresponding to nitrogen changing from 0 to 20 sccm.

The transmittance and reflectance spectra were measured by using a Perkin-Elmer UV–VIS–NIR Lambda 900 spectrophotometer in the range of 0.185–3.2 μm. The optical Tauc gap and the absorption coefficient of the samples were evaluated using standard technique. Raman spectra were recorded with a JY T64000 spectrometer, and an argon ion laser with 514.5, 488.0 and 457.9 nm was used as the excitation source. The IR measurements were carried out in the absorption mode by using a Magna-IR560 ESP spectrometer at 4 cm⁻¹ resolution in the range 400–4000 cm⁻¹. The relative absorption coefficients have been calculated for the C–H stretching modes in the range 2850–2950 cm⁻¹ and for the N–H modes in the range 3250–3430 cm⁻¹, taking into account the influence of interference fringes and absorption due to the silicon substrate. The dark conductivity was measured in a vacuum at the temperature range 77–500 K.

In crystalline semiconductors, the optical band gap is a fundamental physical parameter measured with a high accuracy. The optical band gap is still a useful concept in amorphous semiconductors, but has no immediate physical meaning. Moreover, there is some ambiguity about its experimental determination. Most frequently the optical gap is obtained from the Tauc plot:^[10]

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g)$$

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by linear extrapolation to zero, where α is the absorption coefficient and B is a proportion constant. This method is based on the assumption of a constant momentum matrix element and of a density of states at the valence and conduction band edges varying with the square root of energy. It has been shown recently that the Tauc method gives a good estimate of the optical gap E_g because the error in the matrix element is approximately compensated by the error in the assumed density of states distribution at the band edges.^[11] The B value that is the slope of the linear part of the Tauc plot in terms of disorder had been interpreted by several authors^[12–14] based on the model of Mott and Davis.^[15] The values of E_g and B are also given in Table 1, and it can be seen that the optical energy gap decreases with the increase of the N_2/Ar ratio. Robertson and O'Reilly^[16] developed a model for a-C:H samples and found that the value of optical energy gap E_g is controlled by the extent of the graphitic phase, and its value is given by $E_g \sim 1/N^{1/2}$, where N is the number of the sixfold rings fused in compact clusters. Therefore a decrease of E_g indicates an increase of the size of the graphitic layers. On the other hand, the optical absorption of the heaviest doped sample in the low energy side (less than the energy gap) is larger than that of the less doped film. This may be explained by the fact that the heaviest doped sample shows a more developed graphitic phase. The absorption coefficient on the low energy side increases with the increase of N_2/Ar .

Table 1. Optical energy gap E_g and B values with gas flow rate ratios (N_2/Ar).

N_2/Ar	E_g (eV)	B ($\mu eV \cdot cm$) ^{-1/2}	Film thickness (μm)
0	1.80	255	0.33
0.07	1.64	220	0.35
0.14	1.62	240	0.33
0.22	1.60	250	0.34
0.31	1.55	240	0.41

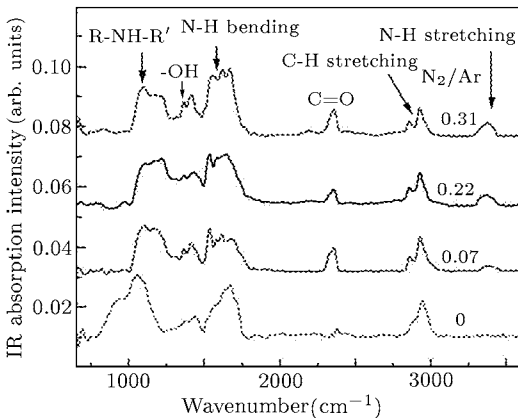


Fig. 1. IR absorption spectra of a-C:H:N films with different gas flow rate ratios of N_2/Ar .

The infrared spectra are shown in Fig. 1. The IR line located at 3340 cm^{-1} is due to N–H stretching vibrations which have a slow increase in intensity with the increase of N_2/Ar . The corresponding bending vibration should then occur near 1600 cm^{-1} , where it is indeed detected. However, it may be superimposed by intrinsic absorption sp^2 hybridized regions, which may also be enhanced by nitrogenation. The line at 1210 cm^{-1} is most likely to be related to the molecular structure of R–NH–R' in a-C:H:N. This is because of the type of R–NH–R' correlated with the 1210 cm^{-1} vibration mode, where at least one of the groups (R, R') must be aromatic. Hence, we can conclude that the incorporated nitrogen atoms are most probably bound to carbon atoms of the aromatic clusters, so that we can observe the NH group vibration lines. Nitrogen atoms entering into a-C:H film may also cause some deformation in the border regions of the clusters, which leads to an increase in the absorption of the intrinsic sp^2 vibrations.^[5] The relative absorption coefficients α_{C-H} and α_{NH} for the CH_x and NH_y vibration modes for a set of a-C:H:N samples are calculated from the IR spectra and the results are in agreement with those data of Kaufman and Metin^[5] and Grill and Patel.^[7] The increase of N_2/Ar is the reason for the enhancement in α_{NH} and the decrease in α_{CH} . This is because the N–H has a bonding energy of 3.7 eV, which is higher than 3.5 eV for C–H. Thus the hydrogen should preferentially bond to nitrogen in the a-C:H:N films, resulting in an increase in IR in the $1340\text{--}1620\text{ cm}^{-1}$ region. It is well known that hydrogen incorporation should lead to a stronger network in the a-C:H films. The decrease in hydrogen content due to nitrogen incorporation into a-C:H films will lead to an extension sp^2 cluster in a-C:H:N than in a-C:H. When N doping takes place in a-C:H films, a logarithmic dependence of direct current conductivity σ on temperature is expected. However, the dependence of $\log(\sigma)$ is linear to $T^{-1/4}$ in the temperature range from 77 K to 300 K, which is a typical electron transport by variable-range hopping (VRH) at the Fermi level. This demonstrates that doping effect does not occur in these a-C:H:N films. In amorphous semiconductors, the Fermi level is located in the middle of the band gap. The π and π^* bands are closer to the Fermi level than the σ and σ^* bands. Since the aromatic clusters are extending, the π and π^* band broadens and the density of states at the Fermi level increases. A high density of states at the Fermi level prevents nitrogen doping into the a-C:H film. For the relationship $\log(\sigma) \sim (1/T)^{-1/4}$, the density of states at the Fermi level $[N(E_F)]$ can be deduced from the formula $\sigma(T) \sim \sigma_o \exp[-(\alpha^3/kN(E_F))^{1/4}/T]^{-1/4}$, where k is the Boltzmann constant and α^{-1} is assumed to be 0.1 nm,^[18] as listed in Table 2. When the

temperature is greater than 300 K, the dependence of $\log(\sigma)$ on T^{-1} is linear, which demonstrates a thermal excitation process. Based on the relationship of $\log(\sigma)$ versus $(\Delta E/k)T^{-1}$, the thermal excitation energy ΔE can be deduced. Above room temperature, the thermal excitation energy is about the half of the energy gap, which indicates that the electrons are thermally excited from the Fermi level to an extend state. The electrical conductivity of the films at room temperature increases with an increase in N_2/Ar .

Table 2. Densities of states at the Fermi level, conductivity at room temperature and thermal excitation energy versus N_2/Ar .

N_2/Ar	$N(E_F)$ ($eV^{-1} cm^{-3}$)	σ_{room} ($S cm^{-1}$)	ΔE (eV)
0	2.66×10^{21}	3.2×10^{-8}	0.86
0.07	3.67×10^{20}	5.0×10^{-7}	0.73
0.14	2.60×10^{20}	1.0×10^{-6}	0.71
0.22	7.90×10^{19}	3.6×10^{-6}	0.68
0.31	1.95×10^{19}	1.0×10^{-5}	0.65

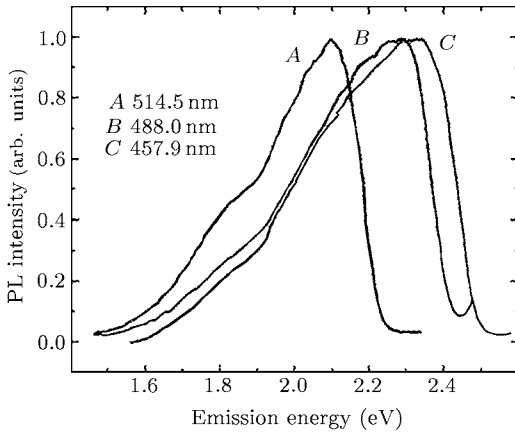


Fig. 2. Photoluminescence spectra of a-C:H:N film with different excitation energies with $N_2/Ar=0.07$.

In general, the sp^3 matrix forms a network with a larger optical energy gap ($E_g \geq 6$ eV), in which the sp^2 clusters are embedded. Here the size of sp^2 clusters has a distribution related to the optical energy gap ($E_g \leq 3$ eV). We can assume that the carriers are free to move within the clusters, but almost forbidden to move from one cluster to another. Since sp^2 clusters have different sizes and shapes they have differ-

ent optical energy gaps.^[4,17] The photoluminescence signal shifts to the high energy side with the increase of excitation energy in a-C:H:N film ($N_2/Ar=0.07$), as shown in Fig. 2. For the low nitrogen incorporated into a-C:H:N films ($N_2/Ar=0.07-0.31$), the photoluminescence spectra give a similar change. This explains why sp^2 clusters with different sizes are responsible for luminescence centres. Different excitation energies will excite different sp^2 clusters with different energy gaps.

A set of a-C:H:N films were prepared at the IR spectra showing an increase in the N-H content in the a-C:H:N films and a decrease in the C-H content. The decrease effect of the optical energy gap demonstrated that nitrogen could cause the growth of sp^2 aromatic clusters. Furthermore, conductivity measurement shows that the $\log(\sigma)$ depended linearly on $(1/T)^{-1/4}$ for all films in the temperature range from 77–300 K, which demonstrates that at the Fermi level, 3D-VRH is the main transportation mechanism. The density of states at the Fermi level is estimated. In the a-C:H:N network, different sp^2 clusters disperse into sp^3 matrices. The sp^2 clusters with different E_g are effectively excited by different excitation energies.

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