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1996 Chinese Phys. Lett. 13 537

(http://iopscience.iop.org/0256-307X/13/7/016)

CHIN.PHYS.LETT. Vol.13, No.7 (1996) 537

Structural Changes in Nitrogen-Doped a C:H Films

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(Received 6 December 1995)

The influence of nitrogen on the microstructure of a-C:H film is investigated by infrared, photoluminescence (PL), and transmittance-reflectance spectra. It is indicated that nitrogen incorporation into a-C:H network will weaken some C–H bonds, which is confirmed by differential scanning calorimeter experimental results. It is also demonstrated that nitrogen entering into a-C:H film can raise luminescence intensity. On the other hand, nitrogenation will reduce PL thermal stability.

PACS: 68.55.Ln, 73.61.Ng

In recent years, a-C:H films have become well known in solid state physics and technology because of their diamond-like characteristic and their foreseen application.[1,2] Light emitting diodes (LED) based upon a-C:H films acting as active layers have already been prepared.[3,4] However, the performance of these devices was not good enough to allow practical applications. One of the reasons was that an effective doping procedure had not yet been set up for a-C:H films. So, many efforts were made to study the properties of nitrogen doping in a-C:H films. The research results indicated that photoluminescence (PL) intensity can be raised in nitrogen-doped a-C:H film.[5,6] It is a good way to improve the luminescence performance of the optoelectronic devices based upon a-C:H films acting as active layers. On the other hand, nitrogen entering into a-C:H film will cause its microstructure change. The aim of the present study is trying to understand the relationship between microstructure and nitrogen.

In our experiment a-C:H (:N) films were deposited by rf sputtering of a graphite target (purity 99.999%) in Ar-H_2-N_2 atmospheres with various gas flow rate ratios (N_2/Ar) from 0 to 0.31. H_2 flow rate was fixed at 10 sccm. The film thickness was about 0.5 μm. The sputtering power was 300 W. The substrate temperature was 100°C. The samples were prepared on crystalline silicon and glass substrates. PL spectra were obtained by means of a grating spectrometer of the type J-Y Ramanor U 100 and water-cooled photomultipler C 2761 Hamamatsu photonics. The 488.0 nm line of an Ar-ion laser was used as the exciting light. The measurements of the transmittance-reflectance (T-R) spectra were performed with a Perkin-Elmer UV-VIS-NIR Lambda 9 spectrophotometer in the wavelength range 0.2–1.6 μm. The Tauc gaps, E_{04} (the energy at which the absorption coefficients are of $10^4\,\mathrm{cm}^{-1}$), and the absorption coefficients of the samples were evaluated by using standard technique.[7] The infrared (IR) measurements were carried out in the absorption mode by using a Perkin-Elmer FTIR 2000 spectrophotometer in the range 400–4000 cm^{-1}. The integrated intensity of the deconvoluted peaks had been deduced. The a-C:H:N films about 1 μm thick for differential scanning calorimeter (DSC) measurement were deposited on aluminum foils. The aluminum substrates were etched in diluted HCl and the sample powders were washed and rinsed. DSC curves were recorded by a power compensation DSC (Perkin Elmer DSC 7) in argon atmosphere. Isochronal annealing was carried out on the a-C:H and the a-C:H:N films for 30 min. in vaccum (10^{-2} Pa) at annealing temperature varying between 250 and 500° C.

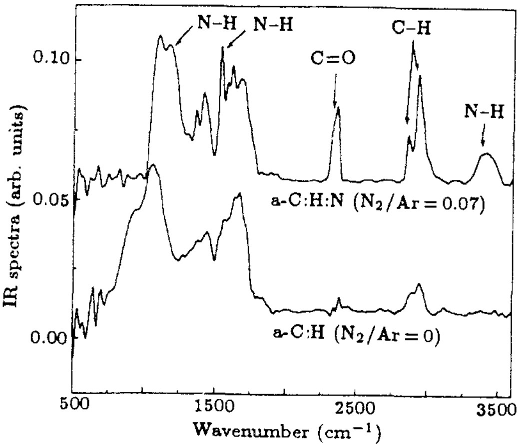

Fig. 1. Infrared absorption spectra of a-C:H ($N_2/Ar=0$) and a-C:H:N films ($N_2/Ar=0.07$).

In order to investigate the influence of nitrogen on the microstructure of a-C:H film, the IR spectra are used to characterize a-C:H(:N) films as deposited and as annealed at increasing temperatures. The IR spectra of the a-C:H films with and without nitrogen are shown in Fig. 1. It is clear in Fig. 1 that the characteristic absorption lines of N–H bond appear at 1210, 1600 and 3400 cm^{-1}, respectively.[8–10] In these peaks, the peak at 1600 cm^{-1} may overlap with the IR absorption peak of sp^2 carbon at 1600 cm^{-1}. Because the IR spectra of a-C:H and a-C:H:N in the range of 900–1700 cm^{-1} are rich of overlapping peaks,[8,9] it is very difficult to identify those peaks. However, there are some characteristic absorption lines in the range of 2850–2950 cm^{-1} for two sets of samples. These lines are CH_n stretching vibration modes in the sp^3 or sp^2 sites. These lines can be used to evaluate C–H bond strength, and its content in a-C:H films.[9] For the sake of comparing these data, the Gaussian line shape function is applied to analyze these IR absorption lines. In order to compare and simplify, we only show the ratios of the integrated intensities of the 2880 and 2950 cm^{-1} lines as annealed at increasing temperature to those of the 2880 and 2950 cm^{-1} lines as deposited for two samples in Figs. 2(a) and 2(b). From Fig. 2, the ratios I_{2880} and I_{2950} gradually decrease at annealing temperatures below 350° C, and rapidly decrease at annealing temperatures above 350° C for a-C:H:N film. When a-C:H:N film is heat-treated at 400° C for 30 min, these absorption lines completely disappear. On the contrary, the ratios I_{2880} and I_{2950} for a-C:H film become slowly decreasing at annealing temperature over 350° C, even though the annealing temperature gets to 500° C, the strong IR peaks at 2880 and 2950 cm^{-1} can be observed. On the other hand, owing to N entering into a-C:H network, the IR peaks of a-C:H film at 2880 and 2950 cm^{-1} shift to 2860 and 2930 cm^{-1}, respectively. From these results, it can be indicated that nitrogen entering into a-C:H films will weaken some C–H bonds.

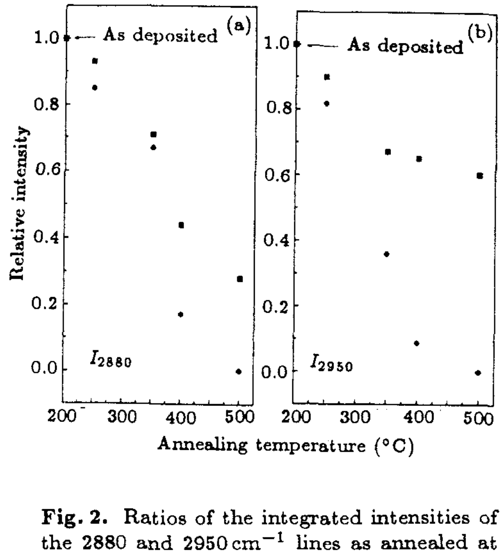

Fig. 2. Ratios of the integrated intensities of the 2880 and 2950 cm^{-1} lines as annealed at increasing temperature to those of the 2880 and 2950 cm^{-1} lines as deposited for two samples. (a) IR stretching mode at 2880 cm^{-1}. (b) IR stretching mode at 2950 cm^{-1}. ■: a-C:H ($N-2/Ar=0$), ●: a-C:H:N ($N_2/Ar=0.07$).

At first, let us consider N entering into sp^3 network, which will give rise to decreasing average coordination number.[6] As a result, the internal stress is reduced. Many experimental results have indicated that the compressive internal stress of a-C:H film is a reverse function of the nitrogen content.[11,12] Nitrogen entering into a-C:H film leads to PL intensity increasing, which is correlated with N entering into sp^3 network.[6] On the other hand, since the electronegativity of nitrogen is larger than that of carbon, the electron clouds between C–N bonds tend to N atom, as a result, the part of C–C, and C–H bonds will be weakened in sp^3 network. This is in agreement with our experimental observation. The second case, when N atoms enter into sp^2 clusters, the average coordination number is constant, so internal stress relief is not correlated with this process. Considering N entering into sp^2 clusters that is not responsible for radiative recombination process, the PL intensity is non-monotonously relative to the nitrogen content in a-C:H films.[6] In any case, nitrogen incorporation into a-C:H film will weaken some C–C, C–H bonds in the sp^3 or sp^2 clusters. For the sake of further understanding the influence of nitrogen on a-C:H microstructure, we have studied the correlation of the energy gap values with annealing temperature. It is shown that the Tauc gap and E_{04} values decrease with the rise of annealing temperature (Fig. 3). The main reason is that sp^2 cluster size increases as a result of the transition from sp^3 to sp^2 clusters.[13] With the annealing temperature increasing, the C–H bonds are broken and reconstructed as hydrogen effusion from a-C:H film takes place. This process is directly observed by DSC experiment (Fig. 4). Comparing the result of a-C:H:N film with that of a-C:H film,[14] it is indicated that an endothermic peak exists at 380°C for a-C:H:N film. This low temperature endothermic peak is correlated with the breaking of the C–H, and C–C bonds in a-C:H:N network. However, the first endothermic peak of a-C:H film is located at 500°C. So it can be deduced that the breaking of C–H bonds and the network reconstruction take place more easily in a-C:H:N than in a-C:H. These results are also supported by the quadrupole mass experiment.[11]

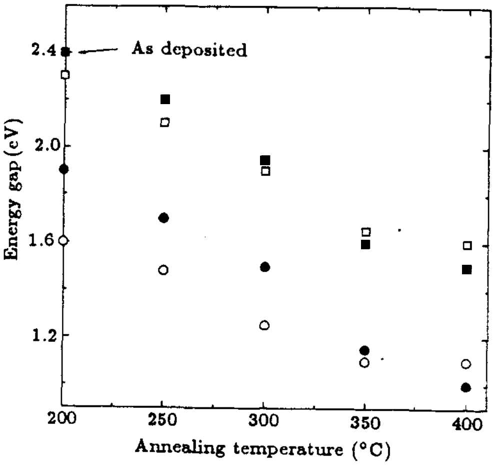

Fig. 3. Tauc gap and E_{04} of a-C:H ($N_2/Ar=0$) and a-C:H:N ($N_2/Ar=0.07$) films as function of annealing temperature. ■: E_{04} for a-C:H film. □: E_{04} for a-C:H:N film. ●: Tauc gap for a-C:H film. ○: Tauc gap for a-C:H:N film.

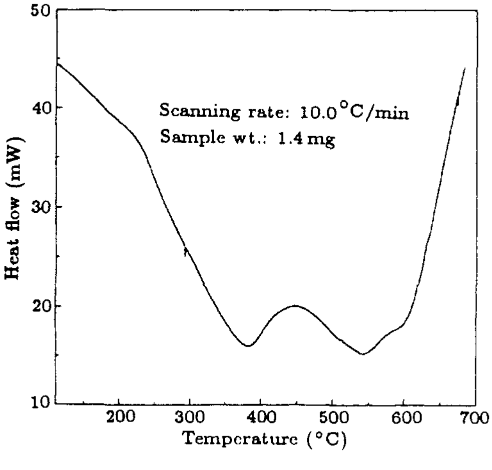

Fig. 4. DSC traces for a-C:H:N ($N_2/Ar=0.07$) powders (1.4 mg) obtained by power compensation calorimeters.

From Fig. 3, the annealing makes the Tauc gap and E_{04} values decrease, which is due to transition from sp^3 to sp^2 clusters. This will weaken sp^3 potential confinement action, so that the PL intensity decreases. In order to investigate the effect of annealing on PL intensity, the a-C:H and a-C:H:N samples had been heat-treated at 250°C for 30 min. From Fig. 5, it can be observed that PL intensities decrease for a-C:H films with and without nitrogen annealed at 250°C. By comparing PL results, we can observe that the luminescence intensity of a-C:H:N film has a larger change than that of a-C:H film. As discussed above, nitrogen incorporation into a-C:H film makes some C–H, C–C bonds weaken, so that some C–H and C–C bonds are easily broken by an annealing process, which will produce some dangling bonds. These dangling bonds as non-radiative recombination centers may play an important role in the luminescence process. The results also indicate that nitrogen incorporation into a-C:H will weaken some C–H bonds so that new defects are produced by low temperature annealing.

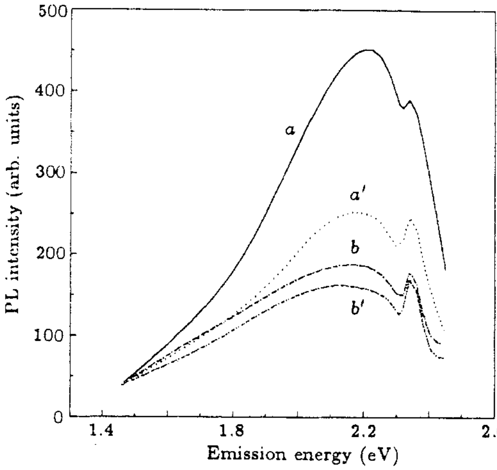

Fig. 5. PL intensity versus annealing temperature, *a*: as-deposited a-C:H:N ($N_2/Ar=0.07$) film, *a'*: a-C:H:N film annealed at 250°C; *b*: as-deposited a-C:H ($N_2/Ar=0$) film, *b'*: a-C:H film annealed at 250°C.

In conclusion, nitrogen incorporation into a-C:H films will weaken some C–H bonds and leads to increasing undistorted sp^2 clusters that are responsible for radiative recombination process. The breaking of the C–H bonds and C–C bonds is easier in a-C:H:N film than that in a-C:H. Thus more dangling bonds as non-radiative recombination centers in a-C:H:N film can be produced at low temperature annealing. So annealing causing PL signal decrease is easy for a-C:H:N film. In other words, nitrogenation will reduce PL thermal stability.

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