

Effect of the addition of nitrogen gas and annealing on the electrical properties of DLC films deposited by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD)

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Nitrogenated diamond-like carbon films (a-C:H:N) were deposited on Si-wafers by a rf-PECVD method with the addition of nitrogen to the gas mixture of methane and hydrogen. The effect of the additive nitrogen gas and annealing was investigated in the relationship between the bonding structure and electrical properties of the deposited films. As the flow rate of nitrogen gas and annealing temperature were increased, the film thickness decreased. The electrical conductivity of films increased with an increase in the flow rate of nitrogen up to 10 sccm. However a further increase in the flow rate decreased the electrical conductivity rapidly. Also as the annealing temperature was increased, the electrical conductivity of films increased. The structural analysis results show that an increase of the flow rate of nitrogen and annealing temperature favor the formation of sp² bonding in the films. Therefore, It has been confirmed that the increase of the electrical conductivity is due to a structural change by graphitization of the films.

Key words: nitrogenated diamond-like carbon, electrical conductivity, annealing effect.

Introduction

Diamond-like carbon (DLC) films have been considered for many industrial applications, due to their special properties such as high hardness, low friction, high wear resistance, and chemical inertness [1]. On the one hand, there have been several attempts to improve the various properties of DLC films by the addition of elements, such as silicon, nitrogen, fluorine, and various metals [2-5]. The electrical, optical, thermal, and mechanical properties of DLC films with nitrogen additions (a-C:H:N) and the possibility to modify them by choosing the right deposition parameters, make them suitable for a variety of applications [6]. In particular, the possibility of depositing these films on large-area substrates, at low temperatures, has attracted the investigation of this material as a semiconductor and/or dielectric material [7].

Currently, an a-Si:H film can be made into a semiconductor by doping, and is then used in the field of microelectronics extensively. The variation of the electrical conductivity due to the Fermi level shift generated by the change in doping concentration is an obvious evidence of a doping effect [7]. The electrical conduc-

tivity of a DLC film can be increased by the addition of nitrogen or a metal [8, 9]. However, the doping effect is weak and the effect on the electrical conductivity of the DLC film by this doping is not certain [10].

Silva et al. [11] reported that there were nine binding models of nitrogen in the a-C:H:N film, but only three of them contribute to the electrical conductivity. The nitrogen can contribute to the electrical conductivity, when an unpaired electron in the nitrogen atom exists

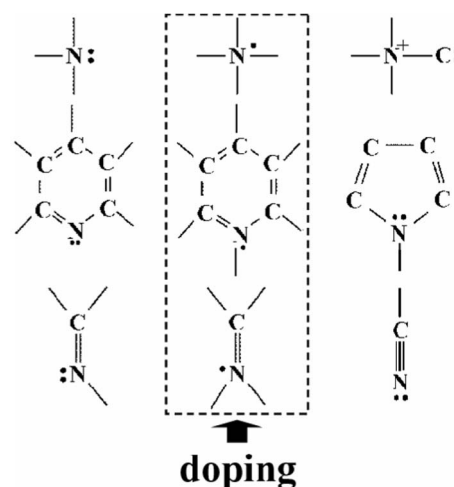


Fig. 1. Possible configurations of nitrogen in a-C:H:N, the lines represent bonds, dots are unpaired, and dot pairs are lone pairs.

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after incorporation of nitrogen into the DLC film. The possible configurations of nitrogen in a-C:H:N film are shown in Fig. 1.

Although, a deposited a-C:H:N film has three binding configurations which contribute to the electrical conductivity, when a hydrocarbon gas is used as a starting material, the deposited a-C:H:N film contains substantial amounts of hydrogen and these hydrogen atoms easily combine with the unpaired electrons. As a result, the effect on the electrical conductivity can lead to a decrease in it.

This study is aimed at improving the electrical conductivity of DLC films deposited by a rf-PECVD system with a CH₄-H₂-N₂ mixture where it is easy to uniformly deposit over a wide area at low temperature. Also, an understanding of the relationship between the bonding structure and the electrical properties of the deposited films by varying the flow rate of nitrogen gas and the annealing temperature to follow modification of the electrical properties is needed.

Experimental Procedures

The rf-PECVD system used consisted of a capacitively-coupled, asymmetric plasma reactor driven by a 13.56 MHz rf power supply. A negative bias voltage was generated at the lower electrode where the rf power was applied and the source gases were supplied uniformly by a shower-head distributor system. In particular, the pressure in the chamber during deposition processing was precisely controlled with an automatic pressure controller system containing a booster pump and throat valve.

A p-type silicon (100) wafer was used for deposition substrates and these were cleaned using an ultrasonic cleaner and then dried by nitrogen gas before being loaded into the reactor. The substrate was placed on the lower electrode. A methane (99.99%) and hydrogen (99.99%) gas mixture was used as the reaction gas, whilst nitrogen (99.8%) was used as an additive gas. The pressure in the reactor was initially established at 9.3×10^{-6} Pa, and then the substrate surface was etched by a hydrogen plasma for 10 minutes in the reactor with a rf power of 80 W before the deposition process. The flow rate of hydrogen gas was fixed at 50 sccm and the pressure was kept at 11.2 Pa.

After the etching process was completed, the vacuum pressure was re-established at 9.3×10^{-6} Pa and then the reaction gases were introduced into the reactor chamber. The methane and hydrogen flow rates were fixed at 20 sccm and 40 sccm, respectively and the nitrogen gas (N₂) flow rate was varied from 0 to 15 sccm. During the deposition, the working pressure and bias voltage were fixed at 11.6 Pa, 575 V (87 W), respectively. The deposition conditions are listed in Table 1. The specimens were annealed separately at a temperature of 300 and 400 in an air atmosphere for 30 minutes.

Table 1. Typical experimental conditions used in this study

Substrate	p-type Si (100) wafer
Reaction gas	CH ₄ , H ₂ , N ₂
Biased negative voltage	575 V
Base pressure	9.3×10^{-6} Pa
Working pressure	11.6 Pa
N ₂ flow rate	0-15 sccm
CH ₄ , H ₂ flow rate	20, 40 sccm
Deposition time	1 h
Annealing temperatures	300, 400 °C
Annealing time	0.5 h

The thickness of the deposited DLC films was measured by cross-sectional observations with a scanning electron microscope (SEM, Jeol, JSM-5900LV, Japan). Fourier transform infrared spectroscopy (FT-IR, Nicolet, Magna-IR 760 spectrometer, USA) was used to investigate the chemical structures of the grown films in the wavenumber range from 500 to 4000 cm⁻¹. The binding energy of coating elements was monitored by X-ray Photoelectron Spectroscopy (XPS, PHI 5600ci, USA) to investigate the bonding state in the coatings. XPS measurements were carried out using monochromated Al K α radiation with an energy of 1486.6 eV.

Raman spectroscopy with an Ar ion laser of 35 mW power at a green wave length of 514.5 nm was used to analyze the change of material properties of the deposited films in the wavenumber range from 1000-1800 cm⁻¹. A peak analysis using the Gaussian line shape for the deconvolution of the Raman spectra was used to establish the Raman parameter (position and FWHM) and ratio of the I_D/I_G was estimated. Current-voltage (I-V) curves (microcurrent, HP 4140B, USA) were used to investigate the electrical properties.

Results and Discussion

The variation of flow rate of nitrogen in the reaction gas and annealing temperature were both found to have a significant influence on the growth rate of the

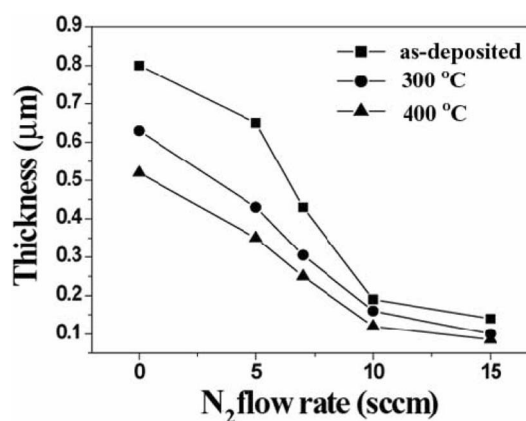


Fig. 2. Thickness of annealed and unannealed a-C:H:N films as functions of nitrogen flow rate.

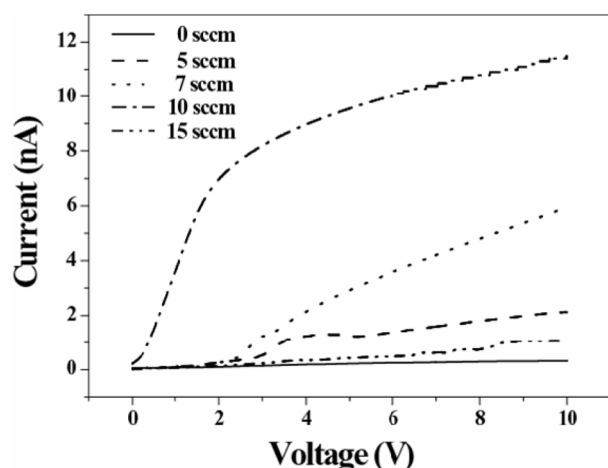


Fig. 3. I-V curves of the a-C:H:N films for various nitrogen flow rates.

deposited films. As can be seen in Fig. 2, the thickness decreased from 0.8 μm to 0.2 μm as the flow rate of nitrogen increased. This decrease may be due to the onset of a type of chemical sputtering process arising from activated N_2^+ ion bombardment of the growing film surface [12].

The thickness of films showed a tendency to decrease as the annealing temperature increased. The reason for this is assumed to be that oxygen from the air was adsorbed on the film surface during the annealing process and formed carbon dioxide, which effused out from the surface. This oxidation reaction resulted in a decrease of the film thickness during the annealing process in an air atmosphere [13].

The I-V curves of a-C:H:N films as a function of the nitrogen flow rate are shown in Fig. 3. From these results, it is seen that the electrical conductivity of the films increases with an increase in the nitrogen flow rate from 0 to 10 sccm. However, when the nitrogen flow rate in the mixed gas was 15 sccm, the electrical conductivity of films rapidly decreased. This suggests that the increase of the electrical conductivity of films by nitrogen additions is a critical value. For the deposition conditions used here, the highest electrical conductivity value was when the nitrogen flow rate in the mixed gas was 10 sccm.

FT-IR was used to investigate the relationship between electrical conductivity and structural modification. From the FT-IR analysis, it was found that the C-H stretching band at 2920 cm^{-1} decreased and the N-H stretching band in the 3300-3600 cm^{-1} range increased, when the nitrogen flow rate increased (Fig. 4). This suggests that the number of nitrogen atoms bound to hydrogen atoms in the films increased with an increase in the nitrogen flow rate. Also, an increase of the absorption band in the 2200-2300 cm^{-1} range caused by the absorption of nitrile group stretching bonds was seen. This implies that carbon-nitrogen triple bonds existed. Hence, it is assumed that the rapid reduction in

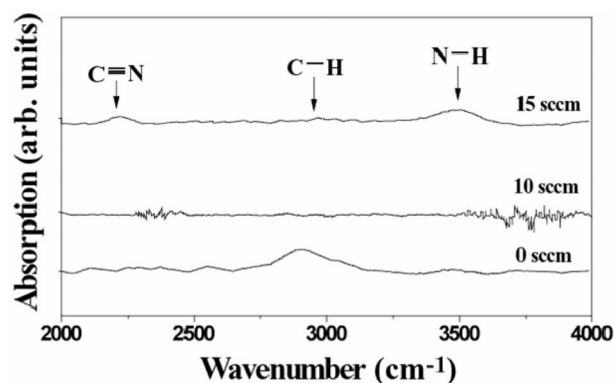


Fig. 4. FT-IR spectra of a-C:H:N films for various nitrogen flow rates.

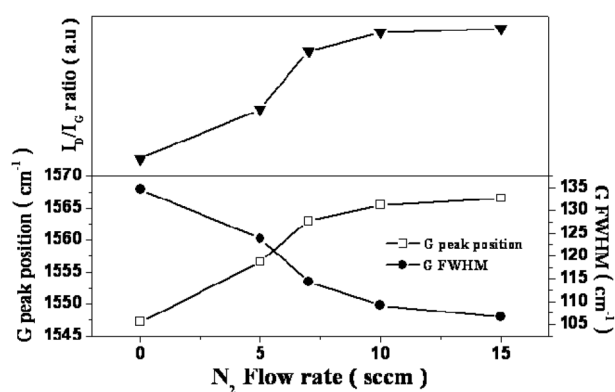


Fig. 5. I_D/I_G ratio, G peak position, and FWHM for various nitrogen flow rates.

the electrical conductivity at a nitrogen flow rate of 15 sccm is due to the formation of nitrile (CN) bonds (that is triple bonds between carbon and nitrogen) during the deposition process. It is known that the formation of these nitrile bonds increase the band gap [14]. Another possible contribution to the rapid reduction in the electrical conductivity is due to the bonding (N-H) of hydrogen atoms and unpaired electrons from carbon-nitrogen atom in the model proposed by Silva et al. [11].

A Raman spectral analysis was also carried out and Fig. 5 shows the I_D/I_G ratio, G peak position, and full width at half maximum (FWHM) as a function of the nitrogen flow rate. With an increase in the nitrogen flow rate, the I_D/I_G ratio increased and G peak position shifted from 1547 to 1566 cm^{-1} . The FWHM of the G peak decreased from 134 to 106 cm^{-1} . These results indicate an increase of the sp^2 content in the films. Finally, the results indicate that the nitrogen incorporation in the films favors the formation of sp^2 units and an increase of the sp^2 cluster size [11, 15]. It further suggests that carbon atoms in aromatic sp^2 clusters are substituted by nitrogen atoms [7].

The I_D/I_G ratio is an indication of the sp^2 aromatic cluster size (L_a) and this ratio is inversely proportional to the sp^2 cluster size [16]. Therefore, as the flow rate

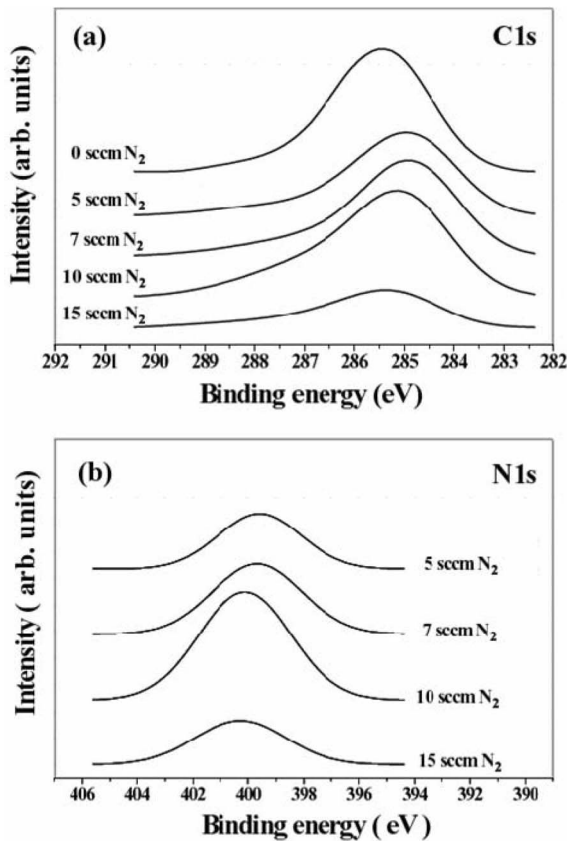


Fig. 6. XPS spectra of a-C:H:N films deposited at various nitrogen flow rates; (a) C 1s and (b) N 1s.

of nitrogen increased, the a-C:H:N films becoming more graphite-like from the Raman spectrum analysis.

In order to identify the bonding state of a-C:H:N films, the XPS spectra on the C 1s and N 1s were analyzed. Figures 6(a) and 6(b) show the typical XPS C 1s and N 1s spectra of the films deposited at various N_2 flow rates. Compared with the spectrum of a pure DLC, the C 1s spectra of a-C:H:N films are broad and asymmetric towards higher binding energies. This suggests that there are several bonding configurations related to carbon atoms in the deposited films. Also the N 1s spectra show a broad peak corresponding to some bonding configurations of the N atoms. Using a Gaussian function fitting routine after the inelastic background subtraction, the C 1s spectra were deconvoluted into three sub-peaks corresponding to the different bonding states of C atoms. With a similar routine the N 1s spectra were deconvoluted into two sub-peaks corresponding to the different chemical bonding states. Figures 7(a) and 7(b) show the typical deconvoluted XPS C 1s and N 1s spectra of a-C:H:N films deposited at a N_2 flow rate of 5 sccm. In the C 1s spectra, the peaks at binding energies of ~ 284.6 eV and ~ 285.5 eV are contributed to by the sp^2 C-C and sp^3 C-C bond atoms, respectively. The peak with the highest binding energy (287.8 eV) value in the C 1s spectra was assigned to the bonding states of C with O. This is possibly produced by surface

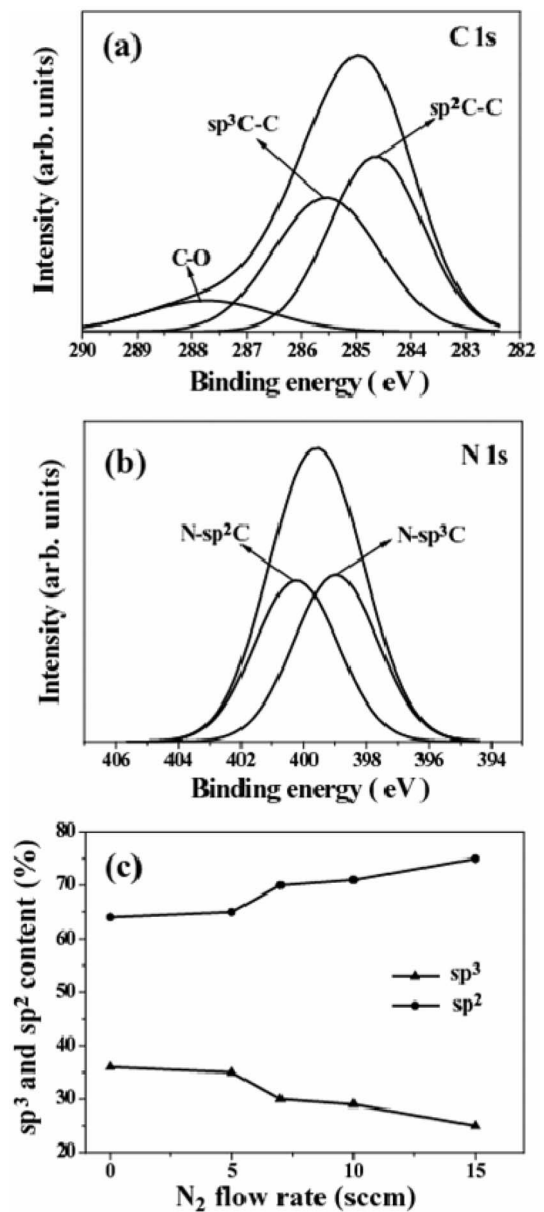


Fig. 7. (a) Deconvoluted with a Gaussian Function XPS C 1s spectrum and (b) N 1s spectrum of a-C:H:N film deposited at a N_2 flow rate of 5 sccm. (c) the sp^2 and sp^3 bond contents as a function of N_2 flow rates.

oxidation during the exposure to the atmosphere. In the N 1s spectra, according to published data [19], the peak at a binding energy of ~ 398.3 eV is attributed to N atoms bonded to sp^3 -coordinated C atoms, and the second peak at the binding energy of ~ 400 eV is attributed to substitutional N atoms in an sp^2 graphite-like configuration bonded to sp^2 -coordinated C atoms. The contents of sp^2 and sp^3 bonds in the deposited films can be determined by the ratio of the corresponding peak area over the total C 1s peak area [20]. Figure 7(c) shows the sp^2 and sp^3 bond contents as a function of N_2 flow rates. As the N_2 flow rate increased, the sp^3 content decreased, while the sp^2 bonds content increased. These results indicate that the incorporation of nitrogen atoms

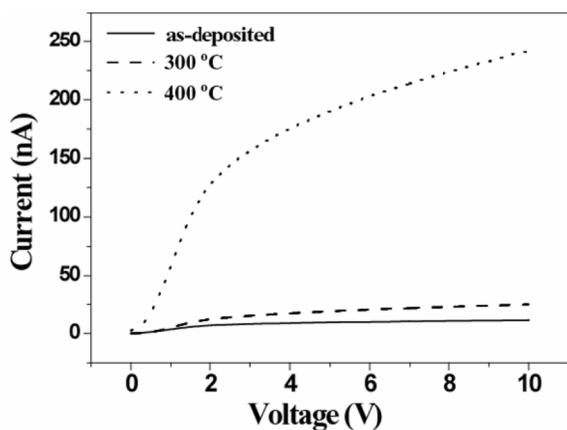


Fig. 8. I-V curves of the a-C:H:N films deposited with 10 sccm of nitrogen gas before and after annealed at 300 and 400 °C.

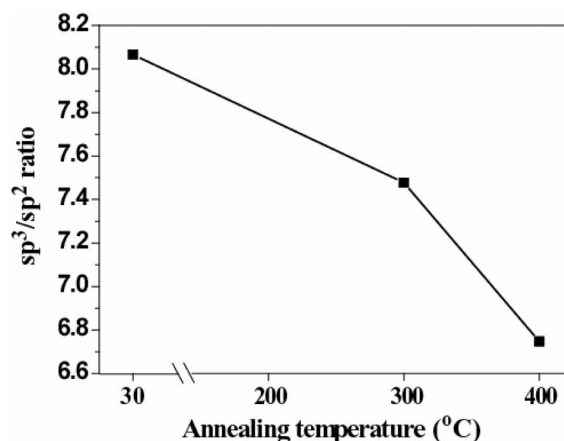


Fig. 10. sp^3/sp^2 ratios as a function of annealing temperature.

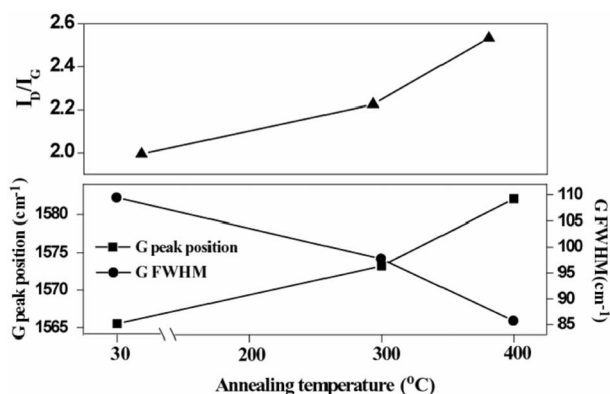


Fig. 9. I_D/I_G ratio, G peak position, and G peak width versus annealing temperature.

into the films promotes the development of sp^2 bonds.

The film deposited with a nitrogen flow rate of 10 sccm was annealed at temperatures of 300 and 400 °C in ambient air and the resulting I-V curves of a-C:H:N films are shown in Fig. 8. The electrical conductivity of films increased with an increase in the annealing temperature. It is thus confirmed that the electrical conductivity of a-C:H:N films may be improved by an annealing process.

In the results obtained from FT-IR analysis, peaks from $C\equiv N$ and the N-H band can not be observed and in particular, the absorption intensity of the C-H stretching band at 2920 cm^{-1} appeared very weakly.

Also, a Raman spectral analysis was carried out. The variation of the I_D/I_G ratio, G peak position, and FWHM of the G peak with annealing temperature are shown in Fig. 9. These results after annealing are similar to those before annealing (Fig. 5) in terms of the effect of the variation of the nitrogen flow rate.

From the viewpoint of the electronic structure near the energy band gap, the band gap depends primarily on the $sp^2:sp^3$ ratio. The σ bonds of the carbon sp^3 sites generate bonding (σ) and antibonding (σ^*) band states, separated by a wide band gap which is close to 5-6 eV, similar to that of diamond. The π bonds of the carbon

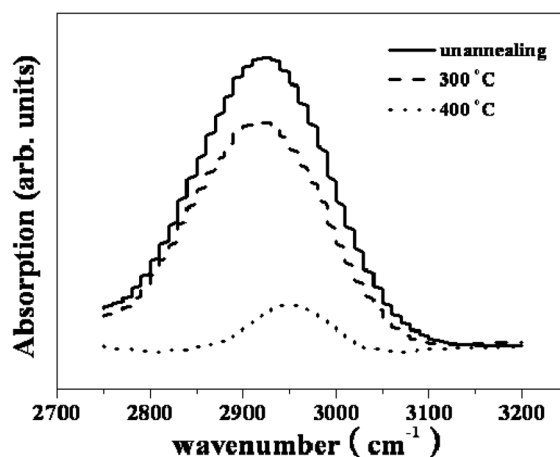


Fig. 11. FT-IR spectra of a-C:H:N films deposited with 10 sccm of nitrogen gas before and after being annealed at 300 and 400 °C.

sp^2 sites form weaker bonds, which introduce bonding (π) and antibonding (π^*) states within the $\sigma-\sigma^*$ gap. They usually lie closest to the Fermi level, E_F [17, 18]. They will therefore form both valence band and conduction band states in films. Startga et al. [17] and Robertson and O'Reilly [18] have shown that the band gap decreased with an increase in the sp^2 content and a decrease in the amount of hydrogen atoms. If the decomposed carbon from the annealing process is in a sp^3 configuration, it will not affect the electrical conductivity. However, if the decomposed carbon is in a sp^2 configuration and if the content of hydrogen is decreased by the decomposition of C-H, this will contribute to the electrical conductivity.

Figure 10 shows the sp^3/sp^2 ratio in films as a function of annealing temperature. It can be seen that the sp^2 fraction increased with increasing annealing temperature. Figure 11 shows the FT-IR spectra of a-C:H:N films deposited with 10 sccm of nitrogen gas before and after annealed at 300 and 400 °C. The total areas of the absorbed peaks in the range of $2750-3100\text{ cm}^{-1}$, C-H stretching vibration range, indicated the relative content of hydrogen [21]. The total areas of the absorbed

peaks decreased with increasing annealing temperature indicating a decrease of the hydrogen content in thin films. Finally, it has been possible to confirm that the improvement in the electrical conductivity of a-C:H:N films by the annealing process is due to the reduction of the hydrogen content and the graphitization of the films by the formation of more sp^2 bonds.

Conclusions

As the flow rate of nitrogen gas was increased, the electrical conductivity was improved which was caused by formation of more sp^2 bonding and a reduction of H atoms in the films. However, at a nitrogen flow rate of 15 sccm, the decrease of electrical conductivity is due to the formation of $C\equiv N$ (nitrile) bonds, which increase the band gap by a reduction in the interlinks between sp^2 clusters in the films and the formation N-H bonds saturated by H atoms. The structural change of a-C:H:N films by annealing is closely related to the electrical conductivity. The effect of annealing leads to an increase of sp^2 bonded clusters and a decrease of the hydrogen content in the films. The graphitization of the films and reduction of the hydrogen content by annealing leads to an improvement of the electrical conductivity.

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References

1. K. Baba and R. Hatada, *Surf. Coat. Technol.* 136 (2001) 192-196.
2. S.S. Camargo Jr., R.A. Santos, A.L. Baia Neto, R. Carius and F. Finger, *Thin Solid Films* 332 (1998) 130-135.
3. J. Schwan, V. Batori, S. Ulrich, H. Ehrhardt, and S.R.P. Silva, *J. Appl. Phys.* 84 (1998) 2071-2081.
4. T.W. Mountsier and J.A. Samuels, *Thin Solid Films* 332 (1998) 362-368.
5. W.J. Meng and B.A. Gillispie, *J. Appl. Phys.* 84 (1998) 4314-4321.
6. M. Guerino, M. Massi, H.S. Maciel, C. Otani, R.D. Mansano, P. Verdonck, and J. Libardi, *Diam. Rel. Mater.* 13 (2004) 316-319.
7. M. Guerino, M. Massi, H.S. Maciel, C. Otani, and R.D. Mansano, *Microelectronics Journal* 34 (2003) 639-641.
8. H. Dimigen, H. Hubsch, and R. Memming, *Appl. Phys. Lett.* 50 (1987) 1056-1058.
9. A. Grill, V. Patel, and S.A. Cohen, *Diam. Rel. Mater.* 3 (1994) 281-284.
10. A. Grill, *Thin Solid Films* 355-356 (1999) 189-193.
11. S.R.P. Silva, J. Robertson, G.A. J. Amaratunga, B. Raftery, L.M. Brown, J. Schwan, D.F. Franceschini, and G. Mariotto, *J. Appl. Phys.* 81 (1997) 2626-2634.
12. K.J. Clay, S.P. Speakman, G.A.J. Amaratunga, and S.R.P. Silva, *J. Appl. Phys.* 79 (1996) 7227-7233.
13. W.J. Yang, Y.H. Choa, T. Sekino, K.B. Shim, K. Niihara, and K.H. Auh, *Thin Solid Films* 434 (2003) 49-54.
14. M.S. Hwang and C. Lee, *Mater. Sci. Eng. B75* (2000) 24-28.
15. A.C. Ferrari and J. Robertson, *Phys. Rev. B* 61 (2000) 14095-14107.
16. A. Ilie, A.C. Ferrari, T. Yagi, and J. Robertson, *Appl. Phys. Lett.* 76 (2000) 2627-2629.
17. E. Startga, G.W. Bak, and M. Dluźniewski, *Vacuum* 74 (2004) 325-330.
18. J. Robertson and E.P. O'Reilly, *Phys. Rev. B* 35 (1987) 2946-2957.
19. C.W. Ong, X.A. Zhao, Y.C. Tsang, C.L. Choy, and P.W. Chan, *J. Mater. Sci.* 32 (1997) 2347-2352.
20. Y.S. Zou, W. Wang, G.H. Song, H. Du, J. Gong, R.F. Huang, and L.S. Wen, *Mater. Lett.* 58 (2004) 3271-3275.
21. V. Anita, T. Butuda, T. Maeda, K Takizawa, N. Saito, and O. Takai, *Diam. Rel. Mater.* 13 (2004) 1993-1996.