Experimental Determination of the N 1s/C 1s Relative Sensitivity Factor for XPS

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The relative sensitivity factor is practically useful for semi-quantitative analysis by X-ray photoelectron spectroscopy (XPS). The accurate values relative to C 1s peak, however, are not simply determined, since the carbonaceous contamination level on the standard samples is not always estimated correctly.

We are dealing with the carbonization and graphitization of organic polymer films such as polyimide films which are known to be good precursors of highly oriented graphite films. It is known that upon the carbonization of nitrogen-containing polymers such as polyimides, the nitrogen atoms remain in the carbonized films¹⁻³ and affect the graphitization subsequently carried out.⁴ Therefore, information on the chemical state and amount of nitrogen remaining in the carbonized films is essentially important. We have been studying the carbonization of different types of nitrogen-containing polymer films up to 1200°C by XPS, and have reported on the transitions of the states of nitrogen with the carbonization time and temperature.^{3,5} So far, it has not been possible to estimate the surface composition of nitrogen accurately, because with some samples the relative intensity of N 1s peak to C 1s peak was proportional to the matrix composition determined by elemental analysis, but not with others. By accumulating a number of XPS data on various polymer films with different thicknesses, however, the difficulty was found to be due to the uniformity of carbonization, which depends on the thickness of the precursor films. In the present work, the relative sensitivity factor of N 1s/C 1s was determined by a statistical treatment of the experimental data.

Experimental

Three types of polyimide films (Kapton, NOVAX and Upilex) and poly-*p*-phenylene-1,3,4-oxadiazole (POD) film on hand were used: the structure and thickness of the films are shown in Fig. 1. The N/C mole ratios in the film are all different. Carbonization was carried out at temperatures between 500 and 1200°C for 1 h in a flow of high-purity argon. The heating rate was 400 K

h⁻¹. After carbonization, the specimens were kept in a silica gel desiccator of non-grease type.

The XPS measurements were carried out at the normal position by irradiating Mg K α X-rays (15 kV, 20 mA) with a VG Scientific ESCALAB MkII. The analyzer energy was fixed at 20 eV. The X-ray satellites were subtracted by the VG Eclipse data system. The binding energy, E_B , was corrected by referring to the E_B of Au 4f_{7/2} electrons (84.0 eV) for gold particles sputtered on sample films. The integral intensities were calculated by subtracting background by the Shirley method;⁶ although this procedure is only an approximation⁷, it is useful and valid for uncomplicated spectra having similar background levels at both sides of the peak.^{7,8} The energy ranges for background subtraction were selected to include shake-up satellites and plasmon peak.

The elemental analysis of carbonized film was carried out by a conventional combustion method: about 3 mg of sample was heated up to 900°C in a flow of oxygen-

Fig. 1 Structure and thickness of the polymer films used.

Fig. 2 XPS spectra for carbonized Upilex films: (A) C 1s region, bar indicates 5000 cps, and (B) N 1s region, bar indicates 100 cps.

containing helium gas to analyze for H, C and N mass%.

Results and Discussion

Examples of the spectrum and background profile are shown in Fig. 2. The start and the end of background lines were selected at the nearest end of the flat background region, typically, 280–295 eV for C 1s peak and 394–410 eV for N 1s peak. The E_B ranges were not exactly the same for each spectrum due to different S/N ratios of the spectrum, as shown in Fig. 2(B), but were taken as similarly as possible. This procedure is important, since the shake-up satellites and plasmon peak of the C 1s peak become pronounced for specimens carbonized around 1000°C, as shown in Fig. 2(A). Figure 2(B) also suggests that the background should be determined manually, and not by automatic processing by computer software when the S/N ratio of spectrum is not very high. At least two components are distinguishable from the N 1s spectra without peak separation: this becomes pronounced above 600°C, and a higher E_B component survives with increasing temperature and/or time. A lower E_B component around 399 eV is assigned to pyridine type nitrogen and the higher one to nitrogen atoms doped substitutionally in hexagonal carbon layers. Details were reported elsewhere.^{3,5}

The peak intensity ratio, $I[N\ 1s]/I[C\ 1s]$, was plotted against the matrix composition by elemental analysis. Figure 3 is for carbonized Kapton and Upilex films,

and Fig. 4 is for carbonized POD films: the carbonization temperature is not indicated in Fig. 3 for simplicity, but for each sample the upper right point is 500°C and the lower left point is 1200°C. From these results, it is clear that the surface composition of carbonized Kapton and Upilex film is comparable to that of the matrix independent of the temperature, but not for POD. The results for NOVAX, which has a similar molecular structure to that of Kapton and Upilex films but is 50 μm in thickness (Fig. 1), also showed a non-linear relationship similar to that of POD of 50 μm . If the data between 800 and 1200°C in Fig. 4 were taken, they would show some linearity, though we should not be misled by this fact. Evidently, the 50 μm films used here were not carbonized uniformly under the present condition. It is reported that polyimide films having a thickness $\geq 50\ \mu\text{m}$ do not show a uniform graphite structure even after graphitization at 2950°C, whereas 25 μm films showed a well developed graphite structure.⁹ The present results suggest that ununiformity occurs at the stage of carbonization when the film thickness exceeds a certain limit.

On the 15 data for Kapton and Upilex films in Fig. 3, the linear least squares fitting was carried out and the following relation was obtained:

$$y = -0.00202 + 1.75x \quad r = 0.976,$$

where y is $I[N\ 1s]/I[C\ 1s]$, x is N/C mole ratio, and r is an interrelation coefficient. The dotted line in Fig. 3 was drawn according to the above relationship. The value of y -intercept is not zero, but is negligibly small

Fig. 3 Relation between the relative intensity by XPS and the matrix composition by elemental analysis for carbonized Kapton (●) and Upilex (◆) films.

compared with the slope ($\approx 0.1\%$). The correlation analysis showed that the above result is highly significant and that the slope is 1.751 ± 0.079 at the 1% significant level (99% confidence limits). These results suggest that the surface composition of carbonized Kapton and Upilex films is actually the same as that of the matrix. Consequently, the value 1.75 is useful as the relative sensitivity factor, $s[\text{N } 1s]/s[\text{C } 1s]$.

Finally, although the present data were taken at a constant analyzer pass energy of 20 eV, several data taken at 50 eV with the same specimens coincided with the present ones in Figs. 3 and 4. Therefore, the relative sensitivity factor can be used for a semi-quantitative analysis, when an instrument similar to the present one, namely a concentric hemispherical analyzer, is operated by the same mode. An advantage of the present method is that we can discuss the results based on the known experimental error, though the method is not always applicable. When we use a theoretical equation which is the product of the mean free path for photoelectron, the photoemission cross section, the transfer function of the instrument, and so on, it is rather difficult to estimate the degree of confidence, since some values are empirical approximations.

Fig. 4 Relation between the relative intensity by XPS and the matrix composition by elemental analysis for carbonized POD films: carbonization temperature is indicated.

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