

Noble Interactions between Ar and Carbons

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ABSTRACT

Noble interactions between Ar and carbons are observed for carbons, such as carbon nanotubes and carbon blacks by means of mass-analyzed thermal desorption. The absorption states exist at around 300 K as well as at around 100 K. X-ray photoelectron spectroscopy reveals that Ar2p shows the chemical shifts. These results suggest that Ar is in charge and it is in valence state, or gives the evidence of the chemical interaction.

Keywords: Ar; Interaction; Carbon; Valence States

1. Introduction

The compounds of rare gas elements such as Kr and Xe have been reported [1-5].

The examinations of compressibility for C₆₀ using He, Ne and Ar as pressure media and the study of diffusion kinetics in solid C₆₀ have been carried out under the conditions of high pressure at around several kbar [6-9]. In these, the chemical interactions have not been discussed.

We have reported the chemical interactions of rare gases [10], such as He, Ne and Ar, in solid carbon nanotubes. Closed carbon nanotubes (CNTs) show larger amounts of absorption for gases such as hydrogen, He, Ne and Ar than opened CNTs. From these results, we conclude that sites that are preferentially found in endcaps provide more active electronic states for the chemical interaction between rare gases and solid carbon nanotubes.

This paper presents results on the thermal desorption from carbon blacks and the X-ray photoelectron spectra of Ar2p.

2. Experimental

C₆₀ (Hoechst, 99.98% purity) was used without further purification.

Endcaps and endcaps-opened multi wall carbon nanotubes (CMWCNT and OMWCNT, Bucky USA BU-200 and 201, 3 - 10 multi-layer with 2 - 10 nm diameter and 3 - 30 μm length), endcaps and endcaps-opened single wall carbon nanotubes (CSWCNT and OSWCNT, Bucky USA BU-202 and 203, 1.4 - 3 nm diameter and 10 - 50 μm length) were used without further purification. As for

the single and multi-wall carbon nanotubes, there is the only difference in the both end structure, and the another structure is the same.

Carbon black (Seast 3HAF (S3)) and graphitized carbon blacks (3855, 3845 and 3800) were supplied from Tokai Carbon Co. **Table 1** shows the characterization of samples.

After vacuum heating at 653 K or 1073 K, samples were exposed to Ar (Nippon Sanso, >99.99% purity) of 1 to 1.4 atm, at 473 K for 1 to 10 days. After the sample was cooled to liquid nitrogen temperature, the sample tube was evacuated to ultra-high vacuum. *In-situ* measurements of the thermal desorption with the temperature-rise rate of 5 K/min and X-ray photoelectron spectra by using MgK α were carried out.

3. Results and Discussion

Figures 1 and 2 show the thermal desorption of Ar from carbon blacks.

The Ar desorption peaks were observed at around 90 - 100 K in the lower temperature region for all carbon blacks. These peak temperatures were higher than that of boiling point of Ar such as 87 K. Therefore, these results

Table 1. Characteristics of carbon blacks.

Sample	Particle radii/nm	N ₂ specific surface area/m ² /g
Seast 3HAF (S3)	28	79
3855	25	90
3845	40	57
3800	70	27

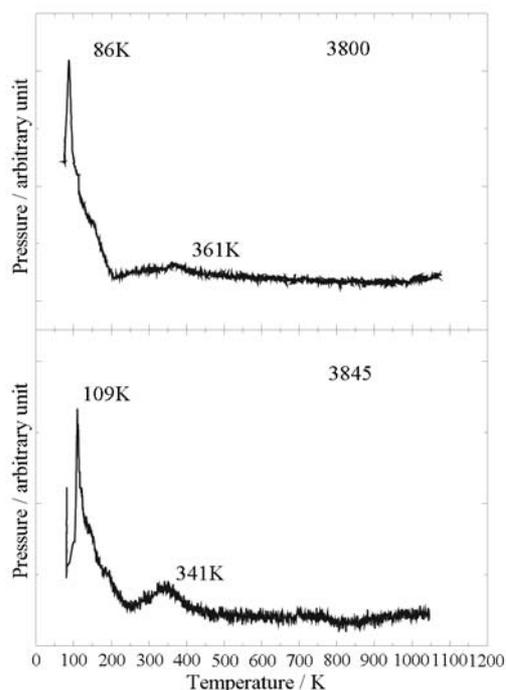


Figure 1. Thermal desorption of Ar from carbon blacks, 3800 and 3845.

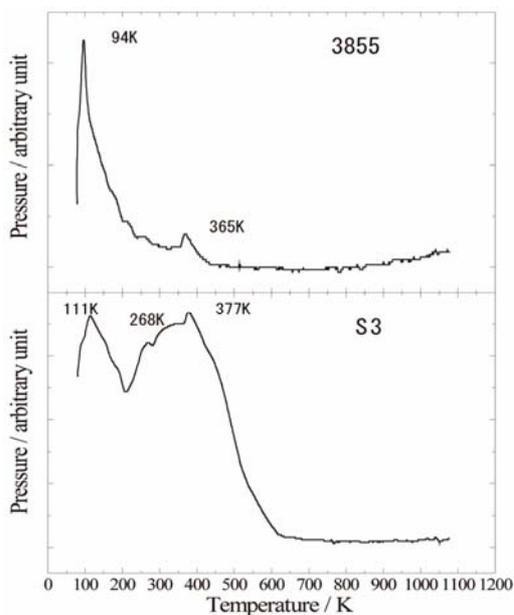


Figure 2. Thermal desorption of Ar from carbon blacks, 3855 and S3.

suggest the stronger interaction than van der Waals interaction.

In addition, the Ar desorption peaks were observed at around 350 K in the higher temperature region than room temperature. Therefore, these results suggest the chemical interaction between Ar and carbon blacks.

Figure 3 shows the X-ray photoelectron spectra of

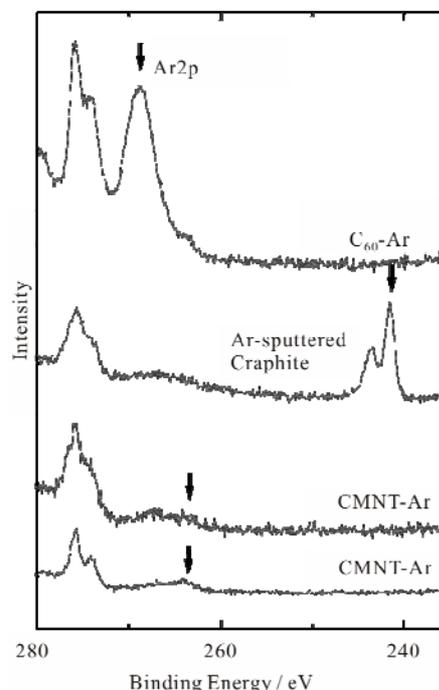


Figure 3. The x-ray photoelectron spectra of Ar_{2p} for C₆₀, graphite and closed and open multiwall carbon nanotubes.

Ar_{2p} for C₆₀ and closed and open multiwall carbon nanotubes exposed to Ar gas at around room temperature, and the Ar⁺-sputtered graphite.

The peaks appeared at around 275 eV are assigned to the peaks due to the X-ray impurities.

For Ar⁺-sputtered graphite, Ar_{2p_{1/2}}-Ar_{2p_{3/2}} peaks were observed. This spin-orbit interaction indicates that Ar exists as the neutral molecule in the graphite. On the other hand, for C₆₀, Ar_{2p} peak was not observed at around 241 eV and the peak appears at around 269 eV, showing the large chemical shift to that for the Ar⁺-sputtered graphite at around 241 eV. The spin-orbit interaction was also not observed.

For the closed and open multiwall carbon nanotubes, although the signal intensities were weak, Ar_{2p} peaks were observed at around 264 eV, showing also the large chemical shift to that for the Ar⁺-sputtered graphite at around 241 eV.

Figure 4 shows the X-ray photoelectron spectra of Ar_{2p} for the Ar⁺-sputtered carbon blacks. Although characteristics of the thermal desorption were different from amorphous-type carbon black and graphitized carbon blacks, the Ar_{2p} peaks were observed at around 242 and 244 eV. The spin-orbit interaction was observed for the all spectra.

For the Ar⁺-sputtered graphite, the difference between C1s and Ar_{2p_{3/2}} was observed as 43.3 eV, and the splitting width of the spin-orbit interaction was 2.2 eV. For carbon blacks, the difference between C1s and Ar_{2p_{3/2}}

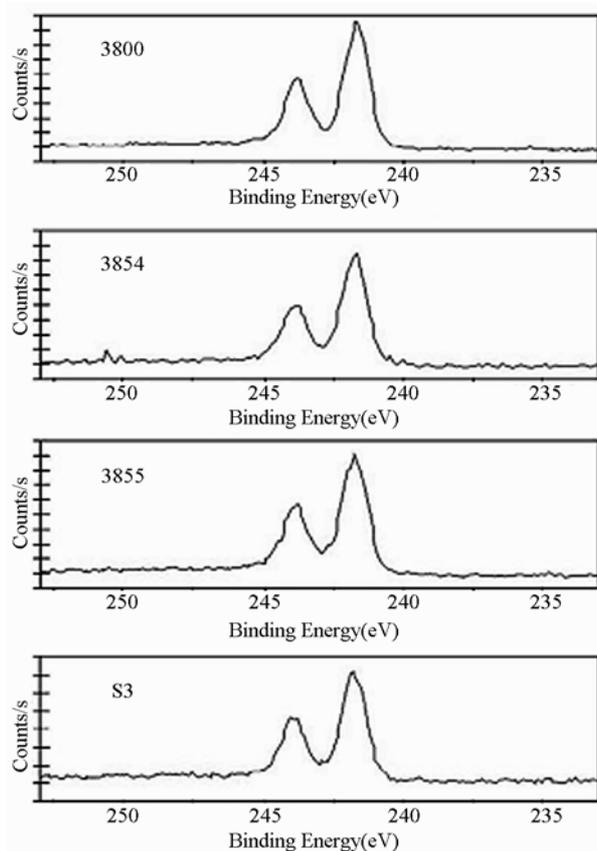


Figure 4. The X-ray photoelectron spectra of Ar₂p for carbon blacks.

was observed as 42.6 ± 0.1 eV, and the splitting width of the spin-orbit interaction was 3.0 eV. By the comparison with the Ar⁺-sputtered graphite, the difference between C1s and Ar₂p_{3/2} became to be lower and the splitting width of the spin-orbit interaction increased for the carbon blacks. These results indicate that the ad-/ab-sorption states observed at around 90 - 100 K and 350 K are due to the weak and strong chemical interactions.

4. Conclusions

Carbons show the noble interaction with Ar due to the characteristic structures and those electronic states. The X-ray photoelectron spectroscopy results in the chemical interaction between Ar and carbons such as C₆₀, CNTs, and carbon blacks. Carbons have possibilities of the diversity of chemical interactions with designs of structure and those electronic states.

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REFERENCES

- [1] S. R. Gunn, "Heat of Formation of Krypton Difluoride," *The Journal of Physical Chemistry*, Vol. 71, No. 9, 1967, pp. 2934-2937. [doi:10.1021/j100868a025](https://doi.org/10.1021/j100868a025)
- [2] L. V. Streng and A. G. Streng, "Formation of Xenon Difluoride from Xenon and Oxygen Difluoride or Fluorine in Pyrex Glass at Room Temperature," *Inorganic Chemistry*, Vol. 4, No. 9, 1965, pp. 1370-1371. [doi:10.1021/ic50031a035](https://doi.org/10.1021/ic50031a035)
- [3] H. H. Claassen, H. Selig and J. G. Malm, "Xenon Tetrafluoride," *Journal of the American Chemical Society*, Vol. 84, No. 18, 1962, pp. 3593-3593. [doi:10.1021/ja00877a042](https://doi.org/10.1021/ja00877a042)
- [4] R. D. Burbank and G. R. Jones, "Structure of the Cubic Phase of Xenon Hexafluoride at 193 deg.K," *Journal of the American Chemical Society*, Vol. 96, No. 1, 1974, pp. 43-48.
- [5] J. L. Huston, "Xenon Dioxide Difluoride: Isolation and Some Properties," *The Journal of Physical Chemistry*, Vol. 71, No. 10, 1967, pp. 3339-3341.
- [6] B. Morosin, Z.-B. Hu, J. D. Jorgensen, S. Short, J. E. Schirber and G. H. Kwei, "Ne Intercalated C₆₀: Diffusion Kinetics," *Physical Review B*, Vol. 59, No. 9, 1999, pp. 6051-6057. [doi:10.1103/PhysRevB.59.6051](https://doi.org/10.1103/PhysRevB.59.6051)
- [7] B. Morosin, J. D. Jorgensen, S. Short, G. H. Kwei and J. E. Schirber, "Ne-Intercalated C₆₀: Pressure Dependence of Ne-Site Occupancies," *Physical Review B*, Vol. 53, No. 3, 1996, pp. 1675-1678. [doi:10.1103/PhysRevB.53.1675](https://doi.org/10.1103/PhysRevB.53.1675)
- [8] J. E. Schirber, G. H. Kwei, J. D. Jorgensen, R. L. Hitterman and B. Morosin, "Room-Temperature Compressibility of C₆₀: Intercalation Effects with He, Ne, and Ar," *Physical Review B*, Vol. 51, No. 17, 1995, pp. 12014-12017. [doi:10.1103/PhysRevB.51.12014](https://doi.org/10.1103/PhysRevB.51.12014)
- [9] G. A. Samara, L. V. Hansen, R. A. Assink, B. Morosin, J. E. Schirber and D. Loy, "Effects of Pressure and Ambient Species on the Orientational Ordering in Solid C₆₀," *Physical Review B*, Vol. 47, No. 8, 1993, pp. 4756-4764. [doi:10.1103/PhysRevB.47.4756](https://doi.org/10.1103/PhysRevB.47.4756)
- [10] K. Ichimura, K. Imaeda, C.-W. Jin and H. Inokuchi, "Super van der Waals Interaction of Fullerenes and Carbon Nanotubes with Rare Gases and Hydrogen-Storage Characteristics," *Physica B: Condensed Matter*, Vol. 323, No. 1-4, 2002, pp.137-139, and references in there. [doi:10.1016/S0921-4526\(02\)00879-7](https://doi.org/10.1016/S0921-4526(02)00879-7)