Influence of Silicon Concentration and Heat Treatment on Electronic Properties of Pyrocarbon

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Temperature dependence of diamagnetic susceptibilities of pure and silicon-containing pyrolytic carbon deposited at 1900 K and 13.3 kPa total pressure have been investigated in order to estimate the Fermi level postition and its variations with silicon concentration and heat treatment temperature.

The obtained results suggest that heat treatment causes the lifting of the Fermi level of pyrocarbon, as a consequence of the graphitisation. The same effect takes place in presence of silicon and increases with its concentration. The presence of silicon also enhances the lifting of the Fermi level caused by heat treatment.

1. Introduction

A number of papers concerning the properties of medium-temperature pyrocarbons containing small amounts of silicon, have already been published (1-5). Silicon concentration in these works didn´t exceed 0.2 wt% in order to avoid formation of silicon carbide. The reported results indicate that small amount of silicon improves the structural properties of the pyrocarbon. The effect increases with silicon concentration showing a maximum at about 0.14% Si. The conclusion was that silicon acts as a graphitisation catalyst, but the way it acts wasn´t quite clear. In recent papers (4,5) the existence of two components in the pyrocarbon, one of which shows the properties of an almost perfect graphite, the other of common turbostatic structure, is proposed.

The papers dealing with electronic properties of silicon-containing pyrocarbon are, rather scare. In our previous paper we reported the results of investigations of some magnetic and galvanomagnetic properties (6). The Hall coefficient was positive, indicating the holes as a main charge carriers, and increased with silicon concentration, showing the maximum at about 0.1% Si. The Hall mobility of the charge carriers behaved in the same way. The values of the anisotropy of diamagnetic susceptibility and its longitudinal and transversal components increase with silicon concentration up to the maximum values, reached for 0.1% Si. Such results led us to a conclusion that presence of silicon promotes the graphitisation, which agreed with the conclusion mentioned before.

A later analysis of the experimental results indicates that there are some properties which do not obey the regularity which has appeared to be general, they change with silicon concentration showing no maxima or minima. The behaviour was characteristic of the properties independent of crystallite orientation, such as average susceptibility and components of the diamagnetic susceptibility tensor. Behaviour of these properties, is different from the behaviour of "bulk" properties of pyrocarbon, which show maxima as about 0.1% Si. It may be an indication that influence of silicon on the strukcture within the crystallites should be distinguished from influence on the structure of the pyrocarbon as a whole.

The aim of the present work is to estimate the position of Fermi level and its dependence on silicon concentration and heat treatment temperature in order to make the situation more clear. The model of bidimensional free electron gas, proposed by Marchand (7), and based on Stoner's treatment of the temperature dependence of free electron susceptibility (8) enabled us to calculate the energetic difference between the top of the valence band and Fermi level postition, ε_o. According to this model, the temperature dependence of the Landau magnetism is given by

$$K=K_o(1 - e^{-\frac{\varepsilon_o}{kT}}) \qquad (1.1)$$

K being Landau magnetism (the anisotropic susceptibility of free electrons), K_o - Landau magnetism at absolute zero and k-Boltzmann's constant. As K takes part in the value of average susceptibility $\bar{\chi}$, which is readily measurable, it is more convenient to work with $\bar{\chi}$. By simple transformation it is easy to show that the temperature dependence of $\bar{\chi}$ can be expressed by

$$\bar{\chi}= C_1- \frac{K_o}{3} e^{-\frac{\varepsilon_o}{kT}} \qquad (1.2)$$

where C_1 is a constant composed of susceptibility terms independent of temperature. Consequently when ln $(1- \frac{\bar{\chi}}{C_1})$ is ploted against 1/T, a straight line having the slope equal to ε_o/k is to be obtained. By fitting functional parameters until the accordance among calculated and experimentaly obtained values of $\bar{\chi}$ is achieved (i.e. straight line is obtained), the values of ε_o can be estimated.

2. Experimental

The pyricarbon samples were prepared in platelets form by CVD procedure at 1900K and 13,3 kPa total pressure. The silicon was introduced by codeposition from $SiCl_4$.

The samples were heat treated in a graphite furnace up to 2800K in inert atmosphere of argon under standard pressure. In all the cases the treatment lasted three hours.

The determination of the susceptibility values was performed by means of Faraday method and critical angle method. The temperature range of the studies was usually 77-300K and in some cases extended up to 650K.

3. Results and discussion

The obtained results are presented in two following tables. In the Table 1. the dependence of ε_o values on Si content is given, while Table 2. shows the influence of heat treatment temperature on ε_o values for the pure pyrocarbon and that containing 0.09% Si.

Table 1.

Si/C (%)	0.00	0.05	0.06	0.09	0.16
$\varepsilon_o x10^2$ (eV)	3.00	2.73	2.68	2.61	2.54

Table 1. shows that ε_o values decrease with increasing Si-content, indicating the lifting of Fermi level, the characteristic fact for the graphitisation process. It is to be noticed that there is no indication for the existence of a minimum of ε_o in the vicinity of 0.1% Si. Such a behaviour of ε_o seems to support the proposition that silicon acts in two different ways on the properties of pyrocarbon.

In order to compare the observed effects with effects caused by graphitisation, we subjected the samples of pure pyrocarbon and those with 0.09% Si to the heat treatment. The results are given in Table 2. The graphitisation process, which advances with increasing

Table 2.

HTT (K)	Si/C (%)	$\varepsilon_o x10^2$ (eV)
as	0.00	3.00
deposited	0.09	2.61
2273	0.00	2.72
	0.09	2.39
2573	0.00	2.65
	0.09	2.20
2773	0.00	2.29
	0.09	2.08

heat treatment temperature lifts the Fermi level and ε_o values diminish. It seems clear now that influence of silicon on electronic structure of pyrocarbon is analogous to that of heat treatment. The pyrocarbon containing 0.09% Si shows always the ε_o values smaller than those of pure pyrocarbon which means that effects caused by heat treatment are enhanced by the presence of silicon.

The results of this work supportt the main conclusions of the previous works by supplying a more direct evidence of the influence of silicon on electronic structure of pyrocarbons. However, the way silicon intervenes is still not clear.

4. Conclusion

According to the presented results we can conclude that effects of the presence of small quantities of silicon on the electronic structure of pyrocarbon are analogous to the effects of the heat treatment. The presence of the silicon during the heat treatment enhances the graphitisation.

Thus silicon can be regarded as a promotor of graphitisation, which is in agreement with previous conclusions based on behaviour of other properties.

The behaviour of ε_o being independent on crystallite orientation and size, unlike other properties shows no maxima/minima when ploted against silicon concentration, and corresponds to the behaviour of average susceptibility and components of susceptibility tensor. This fact seems to support the proposition that the influence of silicon on the electronic structure and properties within the crystallites sould be distinguished from its influence on the structure of pyrocarbon "en gros".

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