# **Formation of porosity in sputtered amorphous hydrogenated carbon films**

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Results are reported of the porosity and the microstructure of amorphous hydrogenated carbon films produced by direct current (d.c.) sputtering. The as-deposited films were initially slightly mesoporous. Heating the material in a vacuum, however, produced a highly porous material. The amount of porosity and the pore size distribution were directly related to the quantity of material which was outgassed during heating. The dependence on the baking temperature of the degree of  $sp<sup>2</sup>$  hybridization in the films had the same form as the dependence of the porosity and of the quantity of outgassing. The plasmon-energy data for the films was related to the process of morphology and composition reconstruction during the heating. The outgassing quantity was strongly dependent on the oxygen content of the as-prepared material. The morphology changes in the material can be regarded as a carbon-activation process involving the incorporation of oxygen in the film during deposition, followed by the outgassing of carbon-oxygen compounds during heating in vacuum. Many of the properties of the hydrogenated amorphous carbon  $(a-C:H)$  film were very similar to those exhibited by conventional activated carbons, and it is therefore concluded that the porous baked a-C: H film is a form of activated carbon.

# **1. Introduction**

Hydrogenated amorphous carbon (a-C:H) prepared by reactive sputtering has a number of applications including in optical and wear-resistant coatings. The physical properties of this material were extensively studied in the 1980s  $\lceil 1-3 \rceil$ . One of the important properties of these films is their morphology, which can vary from being very dense to being rather porous, depending on the deposition conditions and on the subsequent treatments  $[4, 5]$ . Many techniques, such as scanning electron microscopy (SEM), small-angle X-ray scattering and gas adsorption, can be used to investigate these morphology properties. The gasadsorption method, in particular, can provide detailed information on the morphology of porous materials, especially for pores of molecular dimensions. This method was used in this work to study the morphology of a-C:H films produced by direct current (d.c) sputtering.

Until recently, little attention has been paid to the mechanism of the porosity formation in a-C: H materials. Previous papers  $[6, 7]$  have presented some results on the porosity and the annealing behaviour of the films. This paper provides detailed information on the formation of the porosity in a-C:H films and the way in which the porosity of heat-treated films depends on the outgassing quantity and on the oxygen content in the films. The oxygen content was measured using Rutherford backscattering spectroscopy (RBS). The electron-energy-loss technique was used to provide information on the microstructure of the films. A model is proposed to explain the mechanism

of the morphology reconstruction of the films during heating. It is argued that the process of porosity formation is similar to the process involved in the production of conventional active carbons, and that the baked a-C:H films are, indeed, a form of active carbon.

## **2. Experimental procedure**

Amorphous hydrogenated carbon films can be deposited by d.c. magnetron sputtering decomposition of acetylene in a cylindrical sputtering apparatus. The cathode of the sputtering apparatus used was a 40 mm diameter stainless-steel, water-cooled tube, aligned parallel to a  $0.03$  T magnetic filed  $\lceil 8, 9 \rceil$ . In this process, carbon is deposited onto all the surfaces in the chamber, including the cathode. Some of the carbon reaching the substrate is therefore deposited directly from the discharge, and some is sputtered from the cathode. If the concentration of the reactive gas is sufficiently high, the deposition rate onto the cathode is greater than the rate of removal by sputtering. Under these conditions, the cathode becomes completely covered with carbon. The material deposited, when the cathode is completely covered, is a form of hydrogenated carbon; it is called a-C:H-R film in this paper. Another form of hydrogenated carbon, called a-C:H-S film in this paper, can be obtained by sputtering the fully covered cathode in pure argon gas.

A quartz-crystal microbalance (QCM) technique was used to measure the porosity of the films in this study. The QCM apparatus which was used has been

reported in detail elsewhere [6, 7]. This technique was shown recently to be capable of generating useful information on the morphology of porous or rough surfaces of thin films [7, 10, 11]. The mass of the deposited films, and the amount of adsorbed gas on the films, can be determined using [12].

$$
\Delta f/f_{\rm q} = -\Delta m/m_{\rm q} \tag{1}
$$

where  $\Delta m$  and  $m_q$  are the areal mass densities of the deposited film (or adsorbed gases) and of the quartz crystal, respectively, and  $\Delta f$  and  $f_a$  are the change of frequency and the frequency of the quartz crystal, respectively.

Following deposition, the coated quartz crystal was placed in an ion-pumped ultrahigh vacuum (UHV) system and evacuated to a pressure of less than  $1 \times 10^{-6}$  Pa. All the measurements and the heat treatments were performed in this system. The adsorption quantity, or porosity, of the heated films was measured after baking without exposing the specimens in air, because heated films can chemisorb or trap significant numbers of molecules from air. The mass of each film was determined by measuring the frequency of the quartz crystal before and after deposition of the film. The quantity of material which was outgasssed from the a-C:H film due to heating in vacuum was also determined using this method by measuring the change of frequency of a quartz crystal due to the baking process. Benzene was used as the adsorbate in all the isothermal adsorption experiments and it was purified by a freeze-thaw method. All the isotherms were measured at room temperature. A point-by-point measurement method was used for obtaining adsorption isotherms to ensure that equilibrium was reached under all conditions, because the adsorption rate was very low at low-cowerage, especially for low-porosity microporous films ['7].

Four classes of a-C: H films were prepared in order to study the effect of oxygen on the outgassing, and therefore on the porosity: reactively sputtered films  $(150 \text{ Pal s}^{-1})$  with acetylene  $(167 \text{ Pal s}^{-1})$ ; films of a-C:H-S sputtered in pure argon  $(150 \text{ Pal s}^{-1})$  from a fully covered cathode; and  $a-C:H-10$ , and  $a-C:H-30$ films, sputtered under similar conditions to those for the reactively sputtered film except that argon gas was mixed with 10% and 30% oxygen, respectively. The oxygen content in the deposited a-C:H films was determined by using RBS. This technique is wellsuited to the non-destructive determination of the elemental composition of compounds without the need for reference standards, if the atomic ratio of the elemental composition is not less than a few per cent. The oxygen content in the a-C:H films was measured in the RBS experiment using 2.0 MeV He ions with a normal incident angle and a  $165^\circ$  scattering angle.

The RBS data was confirmed qualitatively by measuring the infrared (i.r.) absorption spectrum for the films. In the i.r. spectra, absorption near  $1700 \text{ cm}^{-1}$  increased with increases in the oxygen content (as determined by the RBS technique). Absorption near  $1700 \text{ cm}^{-1}$  indicated the presence of  $C = O$  bonds [5], since this absorption is present as a strong band in many ketones and aldehydes containing oxygen.

Electron-energy-loss spectroscopy (EELS) using a Gatan 666 Peels system attached to a Philips EM 430 electron microscope, was used to determine the plasmon-energy and the shape of the carbon K-edge-shellcore loss feature. The plasmon-energy gives a useful measure of the atomic density of the network via the relationship

$$
\omega_{\rm p}^2 = \frac{\rm ne^2}{\epsilon_0 m} \tag{2}
$$

where  $\omega_p$  is the plasmon frequency, *n* is the number of the free electrons per unit volume and  $m$  is the electronic mass [13]. This formula works well for a wide range of materials if n is taken to be the number of valence electrons per unit volume. The  $sp<sup>2</sup>$  fraction was determined from the normalized intensity of the  $\pi^*$  feature of the carbon K-edge in the manner described by Berger *et al.* [14]. The result for the  $sp^2$ fraction was calibrated using a spectrum obtained from a  $C_{60}$  film. It is known that  $C_{60}$  films contain  $100\%$  sp<sup>2</sup> bonds.

## **3. Results**

## 3.1. General adsorption data

Typical adsorption isotherms of benzene for the a-C:H-R films baked at different temperatures are shown in Fig. 1. The relative pressure is defined, in this case, as the pressure, P, of benzene vapour divided by the saturated vapour pressure of this material,  $P_0$ . These data were obtained for a reactively sputtered a- $C: H-R$  film which was approximately 0.5  $\mu$ m thick. The film was deposited onto both sides of a quartz crystal. The slope of the isotherms of all the a-C:H films are found to be essentially identical for films measured in the thickness range 50nm to about  $1.0 \,\mu$ m. We therefore conclude that the adsorption capacity of the film is proportional to the mass of a sample. This result implies that a-C: H films produced in this way, both as-prepared and after baking, are uniformly porous, and that the pore size distribution is not affected by the thickness. In addition, the adsorption of benzene onto the external surface of the films is negligible in this thickness range. We define the volume of the internal pores of the films as the amount of gas adsorbed at a relative pressure of  $P/P_0 = 0.9$ . The pore volume in the a-C:H-R films was found to be approximately 0.1, 0.2 and 0.4 for films in the asprepared state, and baked at 350 and at 450 °C respectively.

The isotherms of the as-prepared films shown in Fig. 1 can be classified as type II, whilst the isotherms of the 350 °C baked films are more typical of type I, where types I and II are defined in [15]. However, following baking at  $450^{\circ}$ C, the isotherms become pseudotype II with a large contribution from the microporosity. The open knee near  $P/P_0 = 0.1$ , and the significant mesopore adsorption occurring in the range  $P/P_0 > 0.2$ , indicate that a wide range of pore sizes exists in the films baked at  $450^{\circ}$ C. Upon increasing the baking temperature to  $500^{\circ}$ C, the isotherms



*Figure 1* Isothermal adsorption data for benzene on the a-C: H-R films prepared by reactive decomposition of acetylene in a d.c. magnetron discharge: ( $\circ$ ) as-prepared; (+) baked at 350 °C for 1 h, ( $\triangle$ ) baked at 450 °C for 1 h; ( $\bullet$ ) baked at 500 °C for 1 h, and ( $\circ$ ) baked at  $500\,^{\circ}\text{C}$  for 21 h.

again approached type I. It is interesting that the films baked at  $500^{\circ}$ C had a smaller adsorption capacity than that of the films baked at  $450^{\circ}$ C. This effect can be understood in terms of a collapse in the films during baking at  $500^{\circ}$ C, which is consistent with previous SEM observations of a reduction in the thickness of the a-C:H films due to the extended heating of the film at 500  $^{\circ}$ C [5].

#### 3.2. Outgassing effects

Outgassing occurred when the samples were heated. This mass loss due to the outgassing was found to be proportional to the mass of an as-prepared film. The proportionality of outgassing to the mass of an asprepared film indicates that the outgassing plays an important role in the formation of porosity during the heating process. The typical dependence of the Brunauer-Emmett-Teller (BET) surface area and porosity on the outgassing fraction for the films is given in Fig. 2. The BET surface area was derived using a method described by, for example, Gregg and Sing  $[15]$ . The BET area is in units of  $m<sup>2</sup>$  for the per gram mass of the heat-treated material and it is assumed that the molecular area of benzene is  $0.36$  nm<sup>2</sup>; the porosity is defined as the volume of benzene liquid adsorbed at a relative pressure of  $P/P_0 = 0.9$  per gram of the heat-treated material. The outgassing fraction is defined as the ratio of the mass loss to the initial mass of the film. The data were obtained from a-C:H-R films which were sequentially baked at 350, 450 and  $500 \degree C$ , and which were then baked for an extended period at  $500^{\circ}$ C.

The BET area rapidly increased with the outgassing fraction up to 35%, and then it increased only slightly for larger values of mass loss. The porosity was measured as 0.45 for a mass loss of 35%. Heating the film at 500 $\degree$ C resulted in further outgassing of the material to over 50%, while the porosity remained almost constant. However, the total adsorption quantity decreased during this process, as shown in Fig. 1. This



*Figure 2* The effect of the outgassing due to baking on  $(\bigcirc)$  the porosity and  $(①)$  on the adsorption capacity of the a-C: H-R films.

can be interpreted as a collapse effect, in which the thickness of the film decreased with the heating at  $500^{\circ}$ C but its porosity effectively remained constant. In this high-mass-loss range, the increase in the BET area and the maintenance of the porosity indicated that heating the films at 500  $^{\circ}$ C resulted in a reduction of the amount of mesopores in the films, since the micropores will have a larger surface are than that of the same volume of mesopores.

The result above indicates that the morphology of the baked a-C:H films directly depends on the amount of outgassing. Information about the mechanism of morphology reconstruction can thus be obtained by considering the effect of outgassing on the pore size distribution of the films. In the following discussion, we will use the fractal Frenkel-Halsey-Hill (FHH) equation [16] as a mechanism to characterize the pore size distribution for the films studied in the relative pressure range 0.3-0.95. The fractal dimension is in the range of 2-3. Smaller values of the fractal dimension indicate the existence of larger mesoporosities in a film; an ideal micropore adsorption isotherm exhibits a horizontal plateau in the mesopore adsorption range; thus its fractal dimension is near to 3. The fractal dimension therefore provides a parameter which assists in the discussion of the dependence of the pore size distribution on the mass loss from the a-C: H films.

The dependence of the fractal dimension on the outgassing for the films is shown in Fig. 3. For small values of outgassing ( $\leq 10\%$ ), the fractal dimension rapidly increased from about 2.45 up to approximately 2.95. This indicates that the outgassing first opened the micropores, but not the mesopores, in the films. Further outgassing, to about 30%, led to a decrease of the fractal dimension to 2.85. This decrease in the fractal dimension can be interpreted as a relative increase in the mesopores in the film. Since the overall porosity of the films baked at  $450^{\circ}$ C increased due to this outgassing, this indicated that both micropores and mesopores were created, and that the volume of the mesopores exceeded the volume of the micropores. For further outgassing, up to about 50%, the fractal dimension increased again and it approached 2.95. As stated above, we believe that this is due to the collapse of the films with the mesopores having been preferentially removed during this reconstruction.



*Figure 3* The fractal dimension of the a-C: H-R films as a function of the outgassing fraction.

## 3.3. The effect of oxygen

Previous studies using a thermomanometric technique [9, 17] have qualitatively shown that the outgassing materials from the a-C:H film consist mainly of CO and a small amount of  $CO<sub>2</sub>$ . The oxygen which is incorporated into the a-C: H films is presumed to exist as a remnant gas in the deposition chamber, or as an impurity in acetylene and argon. The origin of the porosity of our baked hydrogenated amorphous carbon films is therefore thought to arise from the outgassing of carbon-oxygen structures. In order to confirm the assumption that oxygen evolution from a-C:H films dominates the outgassing process during heating, we prepared a group of  $a-C:H-R$ ,  $a-C:H-S$ . a-C:H-10 and a-C:H-30 films using gas mixtures of argon and acetylene containing different amounts of oxygen, as defined above. All these films were approximately  $0.5 \mu m$  thick.

The ratios of oxygen to carbon in these films, as determined using the RBS method, are given in Table I. Table I also presents previous pyrolysis (PY) data [17] on the oxygen-to-carbon ratio for a-C:H-R and a-C:H-S films. Good agreement exists between these two measurements.

These films were then baked in a vacuum in order to measure the amount of material which was outgassed due to heating. Fig. 4 presents data of the proportional mass loss, relative to the as-deposited mass, as a function of the baking temperature. The heating time was 1 h for all the specimens at the specified baking temperature. It is clear that significant outgassing occurred at baking temperatures above about 300 °C for all the specimens. The outgassing increased signi-

TABLE I The ratio of oxygen to carbon in a-C:H films determined by using RBS and pyrolysis (PY) techniques.

Sample	$a-C: H-S$	$a-C:H-R$	$a-C: H-10$	$a-C: H-30$
$[O]/[C]_{(RBS)}$ 10.2%		$12.1\%$	14.6%	19.7%
$[O]/[C]_{\rho y_1}$	$10.6\%$	13.2%	NA	NΑ



*Figure 4* The effect of the oxygen in the films on the outgassing fraction as a function of the baking temperature:  $(\blacksquare)$  a-C: H-30,  $(\square)$ a-C:H-10, ( $\blacktriangle$ ) a-C:H-R, and ( $\triangle$ ) a-C:H-S.



*Figure 5* The dependence of the sp<sup>2</sup> fraction of carbon on the baking temperature in:  $(\bullet)$  the a-C: H-R film, and  $(\blacktriangle)$  the a-C: H-10 film. The sp<sup>2</sup> fraction was determined by integration of the  $\pi^*$ peak on the carbon K edge in the EELS spectrum.

ficantly with the oxygen-to-carbon ratio. This result is consistent with the assumption that the oxygen in the films plays an important role in the outgassing process, and thus in the process of porosity formation. It would be interesting to determine whether the outgassing under these baking temperatures is very small for films with a very low oxygen content. However, despite considerable effort in this study, we were unable to produce films with a very low oxygen content. It seems that even very small amounts of oxygen in the discharge are preferentially incorporated into the film, presumably because of the very strong interaction between oxygen ions and carbon species.

3.4. The  $sp^2$  fraction and the plasmon-energy The dependence of the  $sp^2$  fraction in the films on the baking temperature is shown in Fig. 5 for the a-C : H-R and a-C:H-10 specimens. Both films had a similar behaviour. At baking temperatures below approximately 350 $\degree$ C, the change in the sp<sup>2</sup> fraction was relatively small. Above this temperature, however, a significant increase in the  $sp<sup>2</sup>$  fraction took place. This observation agreed with a previous result obtaine'd

using a nuclear magnetic resonance (NMR) technique [18]. This baking-temperature dependence is similar to that of the outgassing in the films; this probably indicates that a similar mechanism is responsible for all these effects. The low  $sp<sup>2</sup>$  fraction for the films baked at low temperatures implies that the carbon atoms in the films are present mainly in an aliphatic co-ordination [18]. The aliphatic structure can be due to the presence of either hydrogen or oxygen in the films. The increase in the  $sp<sup>2</sup>$  fraction for the films baked at higher temperatures indicates that the material becomes more and more aromatic during this process.

Values for the plasmon energy of the a-C : H-R and a-C:H-10 films are given in Fig. 6 as a function of the baking temperature. If we assume that the number of valence electrons per carbon atom is equal to four for the films, irrespective of the bonding configuration, these data can be used to deduce the density of the films. The low plasmon energy for films baked at temperatures about  $350-400$  °C may be interpreted as resulting from a reduction of the density due to the outgassing without significant collapse in the films. The slight increase in the plasmon energy for the films baked at  $500^{\circ}$ C may be due to two effects. Firstly, collapse may occur in the films during this baking. Secondly, the carbon-to-oxygen ratio in the films increased due to the outgassing of carbon-oxygen compounds, and each oxygen atom in the films provided fewer free electrons than each carbon atom.

#### **4. Discussion**

An active carbon model is proposed as the mechanism of the morphology reconstruction of the a-C: H films during heating in vacuum. The activation process of the film consists of the incorporation of oxygen in the a-C:H films during deposition, followed by out gassing during heating in vacuum. The picture emerging for the process is that the porosity of baked films essentially depends on the oxygen-to-carbon ratio in the as-prepared films. By varying the content of the oxygen in the as-prepared a-C: H film and the heating condition, active carbon films ean be obtained with a variety of morphologies and chemical structures. In addition, in a similar way to traditional activation



*Figure 6* The plasmon energy obtained from the EELS spectrum as a function of the baking temperature for:  $(\bullet)$  the a-C:H-R film, and  $(A)$  the a-C:H-10 film.

processes, the films may be further activated by further outgassing after oxidation of the baked material.

A comparison was made of the morphology reconstruction and properties of the film and those of conventional active carbons. Many physical properties of the film, and the processes which occur during the heat treatment, were shown to be very similar to those for conventional activated carbons. The mechanism of activation presumably involves the removal of oxygen from the film in the form of carbon-oxygen compounds.

The density of the as-deposited a-C:H film, or the raw material, used in this study was about  $1.2-1.6$  g cm<sup>-3</sup>, depending on deposition conditions [5]. The as-prepared a-C:H films consisted mainly of carbon, oxygen and hydrogen. The carbon content and the density were very close to those of soft coal or to a semi-hard coal material, which is one of the most commonly used materials in the manufacture of activated carbons [19]. This raw material shows some of the characteristics of polymer-like materials. We have shown using the electron-energy-loss technique that the as-deposited  $a-C$ : H film contained a large amount of aliphatic structures. This observation is consistent with previous i.r. and NMR spectroscopy studies [5, 18]. The heat-treated films contained a substantial amount of carbon in threefold co-ordination; this arises from the presence of aromatic structures. These aromatic structures are a characteristic of a conventional activated carbon [19].

As in other traditional activation processes, outgassing or evolution of volatiles occurs from the films during heating. The amount of outgassing is also an important parameter in traditional activation processes being related to the pore volume and the pore size distribution of active carbons. An extensive thermomanometric study [17] showed that the outgassing materials in the film consist of mainly CO and of a small amount  $CO<sub>2</sub>$ . In the first stage of the heating process, the outgassing involves thermal decomposition of the carbonaceous material, eliminating non-carbon species, such as Ar. The removal of the volatiles mostly occurs [17, 20] at baking temperatures below 350 $\degree$ C. This process is very similar to the carbonization process in the manufacture of conventional active carbons. These materials can be further activated by baking at temperatures over  $350^{\circ}$ C. Heat treatment of the films at temperatures over  $350^{\circ}$ C causes significant outgassing, principally of CO. As the amount of outgassing progressively increases, the heat treatment first opens the micropores in the slightly mesoporous, or rough, raw material, and then it enlarges these micropores by burning off the walls between them; thus the number of mesopores is increased. With prolonged heating at high temperatures, further burning off occurs, resulting in the collapse of the films; this reduces the numbers of mesopores. This process of morphology reconstruction is similar to that which occurs in the manufacture of active carbons [19].

In conventional active carbons, the activation temperature is usually in the range  $400-800$  °C for chemical activation and it is in the range 800-1100 °C for physical activation. In contrast, the activation process of the a-C: H films occurs at quite low temperatures, and it arises from the carbon activation with oxygen. It is known that in the case of the traditional activation of carbon material with oxygen both the reactions

$$
C + O_2 \rightarrow CO_2 + 386 \text{ kJ}
$$
 (3)

$$
2C + O_2 \rightarrow 2CO + 225 \text{ kJ}
$$
 (4)

are exothermic and that the reaction is difficult to control. In our case, the oxygen was incorporated into the films during the deposition at room temperature. These oxygen-carbon structures which formed during deposition can be removed by heating in a vacuum at relatively low temperatures. We ruled out the possibility that the a-C: H films had been activated during the deposition process, and that other gases block up the pores in this material during exposure to air in the course of transfer from the deposition apparatus to the porosity-measurement system. We found that less than 2.0% of mass of the films arose from irreversible adsorption of air onto the films due to exposure to the atmospheric pressure of air after deposition.

There is no doubt that volatiles other than carbon-oxygen compounds also contribute to outgassing during heat treatment. We estimate, however, that about 60-70% of outgassing may directly arise from carbon-oxygen evolution. Argon and hydrogen, which were certainly observed in the previous thermomanometric study, probably account for less than half of the missing volatiles. It is clear that outgassing from the a-C:H film also depends on the history of heat treatment because chemisorption of oxygen on baked carbon materials can easily occur. Significant chemisorption of oxygen on the baked a-C: H films has also been observed [21], even in ultra high vacuum systems. The adsorbed oxygen cannot itself be outgassed, but it is emitted in the form of carbon-oxygen, and thus further mass loss occurs.

It is possible that the outgassing of the rest of the missing volatiles, approximately 20% of the total mass loss, may arise from the release of hydrocarbons. Wild and Koidl have found qualitatively [22] that effusion of hydrocarbons from glow-discharge deposited a-C:H films can occur at heating temperatures lower than  $500^{\circ}$ C if the voltage of the negatively biased substrate onto which the film is deposited is smaller than about 300 V. They claimed that the increase in the degree of cross-linking and the decrease in the pore size in the material can reduce the evolution of hydrocarbons during heating. During the heat treatment in this study, a large amount of outgassing of carbon-oxygen species may have broken down the hydrocarbon network in this material thus forming some volatile hydrocarbon species at the baking temperatures. The total outgassing quantity decreased as the oxygen content in the films was reduced. This indicates that significant outgassing of hydrocarbon species will not occur without outgassing of carbon-oxygen compounds at these baking temperatures. This secondary outgassing mechanism of hydrocarbons is consistent with the result that the ratio of the missing volatiles is approximately independent of the ratio of oxygen to carbon in the film. The outgassed hydrocarbon species may condense on the walls of the chamber without reaching the massspectrometer analyser; this perhaps explains why no obvious hydrocarbon evolution from the films was found in a previous study [17]. Further experimental work should be undertaken in order to confirm this idea. However, compared to the effect of oxygen, this secondary outgassing effect of hydrocarbons should be less important for the material studied in this work.

Commercial activated carbons (bulk materials) are excellent adsorbents. Because of their high adsorption capacity and their high degree of surface reactivity, they are used widely in applications such as purification, detoxication and catalysis. The activated carbon film studied here may also have many applications. The highly porous a-C:H film obtained in this laboratory has been used [23] as a *thermal switch* in evacuated tubular solar thermal collectors: at low temperatures it adsorbs gases and increases the level of the vacuum in the collectors, resulting in low thermal losses from the collectors; and at high temperatures it desorbs gases, resulting in an increase in the heat loss thus reducing the stagnation temperatures in the tubes. Recently, two of the authors also found [24] that this material can be prepared as an excellent molecular-sieve film, which may be used in some special circumstances. In addition, many unusual properties of activated carbons are associated with small amounts of other substances in the materials. The sputter deposition technique enables precise amounts of other substances to be incorporated into activated carbon films. Carbon films may thus be used to study further properties of activated-carbon compounds, and the modification of the surface properties of these materials.

## **5. Conclusion**

Adsorption results were presented for benzene on a-C : H films deposited by a d.c. sputtering technique. Heating the films in a vacuum resulted in a significant increase in the porosity. The pore volume and the pore size distribution was strongly dependent on the heattreatment conditions. This dependence can be understood in terms of the outgassing occurring during heating. The  $sp<sup>2</sup>$  hybridization in the films changed during baking in a similar way to the change in the mass of the outgassed material. The plasmon-energy data for the films led to estimates of the film density which are consistent with the process of the morphology reconstruction and with the composition changes which occur during the heating. The amount of outgassing is dependent on the oxygen-to-carbon ratio in the material. The mechanism of the morphology reconstruction is therefore interpreted as an activation process consisting of the incorporation of oxygen in the a-C:H film during deposition, followed by outgassing of carbon-oxygen compounds by heating in vacuum. It was shown that many of the properties of the a-C : H films are very similar to those exhibited by conventional activated carbons. We conclude that the **porous baked films are, indeed, a form of activated carbon, with the principal mechanism of activation being removal of oxygen from the films in the form of carbon-oxygen compounds.** 

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#### **References**

- 1. K. ENKE, *Mater. Sci. Forum,* 52, 53 (1989) 559.
- 2. A. BUBENZER, B. DISCHLER, G. BRANDT and P. KOIDL, *J. Appl. Phys.* 54 (1983) 4590
- 3. J.W. ZOU, K. SCHMIDL, K. REICHELT and STRIZKER, *J. Vac. Sci. Technol.* A 6 (1988) 3103.
- 4. W. DWORSCHAK, R. KLEBER, A. FUCHS, B. SCHEP-PAT, G. KELLER, K. JUNG and H. EHRHARDT, *Thin Solid Films* 189 (1990) 257.
- 5. D.R. MCKENZIE, R. C. MCPHEDRAN, N. SAVVIDES and L. C. BOTTON, *Philos. Mag. B 48* (1983) 341.
- 6. Y. YIN and R. E. COLLINS, Presented at **the First** International Conference on Surface Engineering, Adelaide, 12-14 March 1991, **unpublished.**
- 7. Y. YIN, R. E. COLLINS and B. A. PAILTHORPE, *J. Appl. Phys,* 71 (1992) 3806.
- 8. G. L. HARDING, B. WINDOW, D. MCKENZIE, A. R. COLLINS and C. M. HORWlTZ, *J. Vac. Sci. Technol* 16 (1980) 2105.
- 9. G.L. HARDING and B. WINDOW, *Solar Energy Mats. 4*  (1981) 265.
- 10. C. L. WANG, J. KRIM and M. F. TONEY, *J. Vac. Sci. Technol.* A 7 (1989) 2481.
- 11. Y. YIN and R. E. COLLINS, *Thin Solid Films,* to be published.
- 12. C. LU and A. W. CZANDERNA "Application of piezoelectric quartz crystal microbalances" (Elsevier, Amsterdam, 1984).
- 13. R.F. EGERTON; "Electron energy-loss spectroscopy in **the**  electron microscopy" (Plenum, New York, 1986).
- 14. S. D. BERGER, D. R. MCKENZIE and P. J. MARTIN, *Philos. Mag. Lett,* 57 (1988) 288.
- 15. s.J. GREGG and K. S. W. SING, "Adsorption, surface area and porosity", (Academic Press, London, 1982).
- 16. D. AVNIR and M. JARONIEC, *Langmuir* 5 (1989) 1431.
- 17. S.P. CHOW, PhD thesis, Sydney University (1984).
- 18. P.B. LUKINS, A. M. VASSALLO, D. R. MCKENZIE and J. V. HANNA, *Carbon* 31 (1993) 569.
- 19. R.C. BANSAL, J. DONNET and F. STOECKLI, "Active carbon" (Marcel Dekker, New York, 1988)
- 20. G.L. HARDING and B. WINDOW, *Solar energy Mats. 7*  (1982) 101.
- 21. Y. YIN, PhD thesis, Sydney University (1993).
- 22. CH. WILD and P. KOIDL, *Appl Phys. Lett,* 51 (1987) 1506. 23. B. A. PAILTHORPE, R. E. COLLINS and S. O'SHEA,
- *Solar Energy.* 39 (1987) 73.
- 24. Y. YIN and R. E. COLLINS, *Carbon* 31 (8) (1993) 1333.

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