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Reactivity of lithium-containing amorphous carbon (a-C) films

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Abstract

The reactivity of lithium-containing amorphous carbon (a-C) films was studied by in situ photoelectron spectroscopy in both the X-ray and ultraviolet excited regimes (XPS, UPS). All preparation and measurement procedures were carried out in ultrahigh vacuum (UHV). Carbon matrices were deposited by evaporation of graphite onto substrates at temperatures from ambient to 800°C. Lithium incorporation was achieved by diffusion after deposition of lithium atoms on top of the carbon films. Changes in the films' surface composition and in their electronic structure were monitored after exposure to molecular oxygen, to energetic oxygen ions and to air. While gettering oxygen and oxygen containing species, lithium atoms segregate from the films and accumulate in a mainly oxidic layer on top of them. This process is accompanied by a decrease in the electron work-function. Exposure to air effected the formation of an additional carbonate compound. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous carbon; Lithium; Lithium oxide; Oxygen gettering; Photoelectron spectroscopy

1. Introduction

Combinations of carbon structures with metal atoms as functional components are investigated with respect to diverse applications, especially in energy research. For use, e.g., as electrodes in rechargeable lithium batteries, mainly the capacity for lithium incorporation has been of interest [1]. For an application like this, the reaction of metal atoms with oxygen containing species is detrimental and finally destroys the respective device.

In the case of first wall materials for a thermonuclear fusion vessel, the objective is a different one and the oxidation reaction is favourable with respect to the resulting gettering of impurities from the fusion plasma. While carbon in the form of graphite has long been a well-established material in fusion research, various reactive components have been studied either as constituents of the first wall's structure itself (B, Be) or as additives in a wall conditioning procedure (B, Si, Li) [2]. The next step fusion device (ITER/ITER-FEAT) will not be all carbon based [3]. However, certain regions of its vessel will probably still be covered with graphite. A more thorough knowledge of the interaction of its surface with light reactive elements and with plasma impurities is therefore required. The use of amorphous carbon (a-C) in this study on the one hand allows to model the surface of a carbon material which has been subjected to particle impact and is thus superficially amorphized [4]. The a-C's structural properties can be controlled through the choice of deposition temperature [5], thus allowing to investigate the influence of order within the carbon structure on its interaction with a reactive species.

2. Experiment

Deposition of a-C films was performed by electron beam evaporation of graphite onto boron-doped silicon (1 0 0) substrates which were kept at room temperature or heated up to 800°C. Lithium atoms were evaporated from commercially available dispensers (SAES-Getters). Preparation and in situ analysis were carried out in an ultrahigh vacuum (UHV) apparatus with a base pressure of less than 2×10^{-10} mbar. Thus the oxygen content of clean metal-containing samples was generally kept below 1.5 at.%, mostly below 1 at.%. All stages of sample

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processing including the pristine carbon films were monitored by in situ photoelectron spectroscopy with X-ray and ultraviolet excitation (XPS, UPS) in a Leybold-SPECS EA11/100MCD spectrometer. XPS was routinely performed with MgK_α-radiation of 1253.6 eV and a resolution of about 0.9 eV. UPS employed the HeI and HeII lines with energies of 21.22 and 40.82 eV, respectively. Resolution of UPS was 0.1–0.2 eV. Electron energies are referred to the Au $4f_{7/2}$-signal of a clean gold sample at 84.0 eV, and its Fermi edge, respectively. Spectra are presented as measured with neither background nor satellite subtraction.

While XPS mainly yields information about the elemental composition within the escape depth of photoelectrons, UPS probes the electronic structure of the valence band which in the case of carbon materials is closely related to the geometric structure.

For the investigation of reactivity, the clean lithium-containing samples were exposed to molecular oxygen (a few to several hundred Langmuir, one Langmuir (L) equalling 1.33×10^{-6} mbar s or 10^{-6} Torr s). For irradiation with energetic oxygen ions, an ion beam was extracted from a Penning type ion source (Leybold/Heraeus IQP 10/63) at pressures of about 4×10^{-4} mbar. A number of samples were re-investigated after storage in air for several hours to up to 10 months.

3. Results and discussion

3.1. Metal-containing samples

When lithium diffuses into a-C a strong interaction between metal and carbon atoms occurs. Fig. 1 shows an example for the changes in C1s spectra obtained before and after room temperature lithium addition on a-C previously deposited at 450°C. The binding energy of the respective electrons is increasing during metal addition. As is known from works on graphitic intercalation compounds (GICs), signal shifts in carbon-metal composites cannot be understood in a concept of chemical shifts alone [6]. Chemical shifts do contribute, but they have to be viewed together with the effects of the occupation of empty electronic states of carbon. For a more detailed discussion see [7]. For the understanding of metal diffusion and reactions during exposure of the lithium-containing materials to reactive gases one has to consider the structural characteristics of this material. The a-C consists to a large extent of an amorphous matrix with sp^2-hybridized carbon atoms. Clusters of likewise sp^2-hybridized carbon, but with a graphite-like arrangement of atoms [5] are embedded into the matrix. The coexistence of these environments is responsible for variations in the C1s peak's full width at half maximum (FWHM) which is largest in the least ordered material. While in room temperature deposited samples, ordered clusters of up to 2 nm were observed, their size in 800°C deposited samples is up to 20 nm [5]. Therefore, the C1s peak becomes narrower with increasing deposition temperature because the ordered regions dominate the spectra. In the following we will address all the materials as a-C although the term is not fully justified e.g., for the material deposited at 800°C.

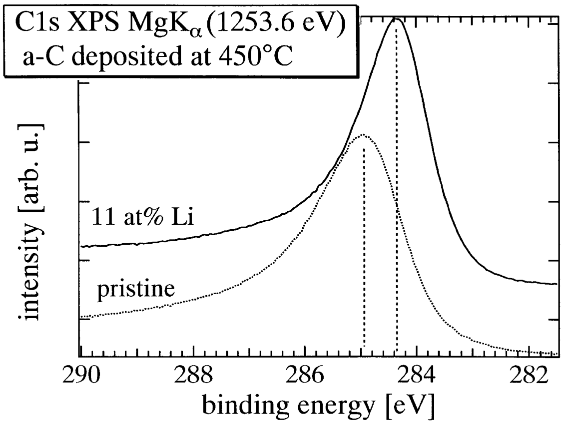

Fig. 1. Example of C1s spectra measured on a-C deposited at 450°C prior to and after lithium addition. The shift to lower binding energy is generally observed when metal atoms are added. Its value depends on the structural characteristics of the respective carbon matrix.

As a consequence of this structural diversity at least two different binding sites for guest atoms can be distinguished. On the one hand, disorder in the matrix leaves a considerable number of carbon valences unsaturated as dangling bonds. They remain available for covalent bonding, e.g., of diffusing atoms such as lithium. The graphite-like clusters are available for the intercalation of guest atoms into the graphite inter-layer spacings as is pure graphite for the formation of GICs. Just as GICs are synthetic metals, even the only partly ordered material we studied here shows metal-like characteristics after lithium incorporation, such as a decrease in work-function and the formation of a Fermi-edge. Again, the latter effect is more pronounced in the samples deposited at higher temperature [7].

3.2. Exposure to molecular oxygen

To test the chemical reactivity of the lithium-containing films, molecular oxygen was employed as a reagent with only thermal particle energies. The minimum exposure was 1 Langmuir (1.33×10^{-6} mbar s) usually followed by higher exposures to up to hundreds of Langmuirs.

The high reactivity induced strong changes in the composition of the film surface (Fig. 2) which can be followed with all three core levels (Li1s, O1s, C1s).

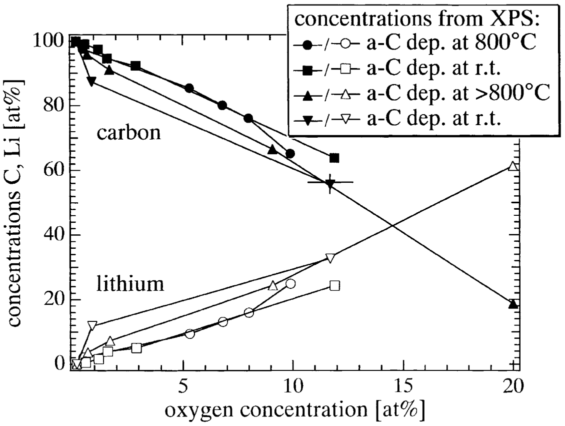

Fig. 2. Development of lithium and carbon concentrations, respectively, as a function of oxygen content in various samples. Open symbols refer to lithium concentrations, filled symbols to the ones of carbon.

Under the described experimental conditions, the oxygen uptake was accompanied by a strong increase in lithium content compared to the metal containing, oxygen-free state (Fig. 2). This is strong evidence that an overlayer of lithium oxide was formed [8]. It cannot be decided to which extent this may include a filling of voids in the surface. Evidently, the oxidation reaction at the sample surface acts as driving force for the outdiffusion of a large number of lithium atoms to the surface. This reaction-driven segregation resembles the decay of GICs with vacuum impurities [9] and is related to observations of lithium diffusion under helium ion bombardment [10]. It is likely that mainly lithium atoms from intercalate-like states accumulate in this way as intercalate-like features (e.g., Fermi edge) in valence band spectra disappear at the same time. In most cases the lithium content exceeded the one for a stoichiometric oxide Li_2O. Under these conditions certainly a number of compounds with different stoichiometries coexist. It is also possible that the overlayer is not only closed, but even inhibits the further reaction between Li and O_2 as a kind of diffusion barrier for oxygen. With respect to the supply of lithium we cannot determine which fraction of lithium atoms remains bonded within the network. Their number would set the lower limit for lithium depletion by the chemical reaction alone.

Changes in peak widths and binding energies are mainly observed with Li1s (Fig. 3(b)) and O1s (Fig. 3(c)) core levels. Binding energies of the Li1s signal decrease by up to 1eV when samples are oxidized (56.8–55.8 eV, see Fig. 3(b), top and cf. [11]). Again, this is an effect which is not correctly described by a simple point charge picture which would even predict a shift in the opposite direction. In the O1s spectra, the most striking feature is the presence of two clearly separated electronic states at about 533 and 530 eV binding energies, respectively (Fig. 3(c), top). The one at lower binding energy is known for alkali metal oxides [12,13]. As long as the samples are treated in UHV and only oxygen is applied, the signal of the oxide is the more intensive one. The peak at 533 eV is ascribed to sub-, super- and peroxides [14], hydroxides and further adsorbed oxygen species [13].

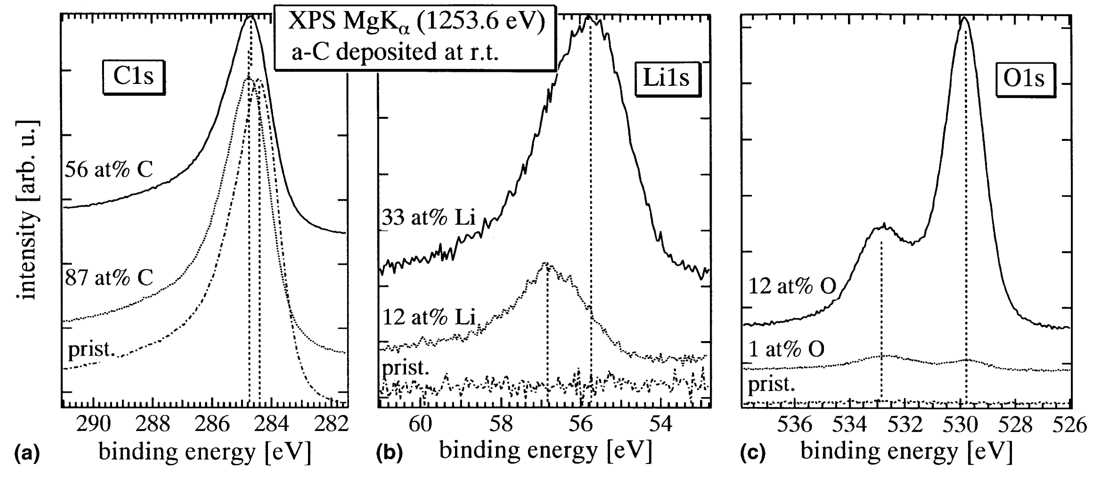

Fig. 3. (a) Example of C1s core levels measured on a-C deposited at r.t. in metal-free, clean metal-containing and oxidized states. Binding energy decreases during lithium incorporation and the shift is only minimally reversed during oxidation. (b) Li1s core levels for the same samples as in Fig. 3(a). Binding energy increases during oxidation, in this case by about 1 eV. The width of the signal is indicative of the presence of more than one lithium bonding state which is reflected in the spectra of the other elements, too. (c) O1s spectra for the same samples as in Figs. 3(a) and (b). The peak at about 530 eV is due to lithium oxidic species, while the one at about 533 eV is assigned to other oxygen-containing reaction products and adsorbates such as suboxides, hydroxides or carbon oxides.

C1s signals show a minute decrease in binding energy with the progress of oxidation. It is much less pronounced than the increase during metal addition (Fig. 3(a)), which has also been observed during oxidation of alkali metal GICs [9]. This probably means that the removal of lithium from the material is not complete and the depletion zone in the a-C begins rather deeply within the film. Experimental results rule out the formation of volatile carbon oxides as reason for this effect [8].

3.3. Exposure to air

Following the described in situ experiments, samples were exposed to atmosphere and stored for different periods of time. Single samples were not previously oxidized in situ, but exposed to air for several hours directly after lithium incorporation. After exposure to air the most striking spectral feature can be found with the C1s core level where a new state at about 291 eV evolves (Fig. 4(a)). This state is due to the formation of a lithium carbonate species on the film surface [11,15]. Comparison with metal-free samples shows that a peak of this intensity cannot result from simply adsorbed carbon oxides. Furthermore, binding energies of the adsorbed carbon oxides are lower (cf. state at 290 eV in Fig. 4(a), top). Most probably the carbonate is formed by reaction of hydroxidic lithium compounds in the film with CO_2 or CO. The formation of the hydroxide must mainly originate from reaction with moisture in air because oxygen states assigned to hydroxides in the in situ measurements cannot account for the quantity of carbonate formed afterwards. As long as air exposure lasts only for several hours (here: 18 h), the carbonate dominates the C1s spectra and reduces the contribution of the underlying a-C's signal at 284.6 eV (Fig. 4(a), middle). After storage in air for months, the carbon adsorbates' signal at 286 eV [16] becomes the most intensive C1s feature (Fig. 4(a), top). During reaction with water and carbon oxides, the oxygen content still increases while the signals of lithium and carbon are attenuated (Fig. 4(b)). After the reaction is accomplished, adsorption of hydrocarbons makes the carbon concentration grow at the expense of both lithium and oxygen. Adsorbed unreacted carbon oxides appear at 290 eV (Fig. 4(a), top).

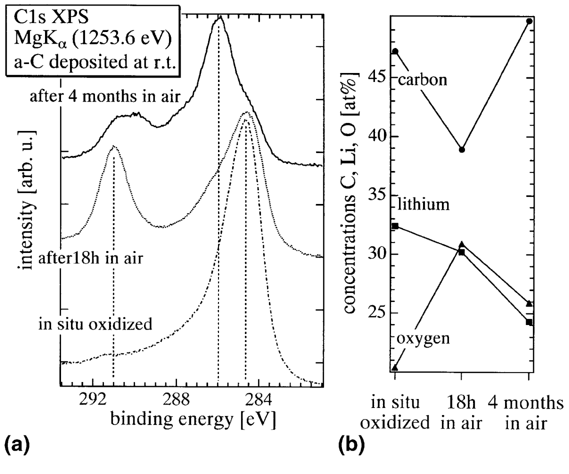

Fig. 4. (a) Comparison of in situ oxidation products and air exposure. While the in situ measurement (bottom) is dominated by the carbon state of a-C at 284.6 eV, air exposure yields additional states of carbonates (291 eV) and adsorbed hydrocarbons (286 eV) with similar intensities (middle). Long-time air exposure leads to further adsorption of hydrocarbons (top). Due to this increasing coverage of the surface, the other states are increasingly suppressed. (b) Compositions of the respective samples.

3.4. Irradiation with oxygen ions

Energetic oxygen ions (mainly O_2^+) were used for irradiation in order to combine the chemical reactivity of oxygen with particle impact. Preliminary results for lithium-free films confirm the expected amorphization of previously rather ordered carbon material already at ion energies as low as 200 eV [4]. For lithium-containing material, there is some indication that impact of energetic oxygen ions alone may suffice to form carbonates through reaction with matrix carbon atoms. For the interpretation of such effects it has to be considered that the Penning type ion source used in this case requires a base pressure of as much as 4×10^{-4} mbar of oxygen in the vacuum chamber to be ignited. Given the reactivity of the films it is evident that the ions impinge on a lithium-oxide layer rather than on lithium-containing carbon. It will have to be tested whether the formation of carbonates with matrix atoms induces erosion of carbon. This could be the case e.g., during irradiation or during annealing. After annealing, carbon was recovered for renewed use with virtually no lithium or oxygen left and no changes to its structure.

4. Conclusions

Our study of the reactivity of lithium-containing a-C showed the potential of such a compound as an oxygen getter material. Whenever an oxidation is induced by contact with oxygen-containing gaseous species, it is not only the outer surface of the getter material which is affected, but deeper regions, too. The surface reaction acts as driving force for the diffusion of lithium atoms from the bulk of the film material towards the surface where a three- to fourfold accumulation in comparison to the initial metal atom concentration is observed. a-C may be regarded as representing the disordered surface region of graphite exposed to particle impact. However, it may be possible to modify the structural characteristics of such a material in order to optimize its function as a reservoir for lithium atoms which are made available through diffusion when this is required through the progress of the surface oxidation. Under plasma conditions, lithium atoms will be dispensed from the material into the plasma due to the increased temperature and sputtering. As has been reported, the addition of lithium to the fusion plasma can be beneficial for plasma performance [17], so this may be an interesting option when control over the quantities of material is ensured which are delivered into the device. Observations including the results of oxygen exposure are in agreement with a structural model of a-C comprising amorphous and small-scale crystalline arrangements of sp^2-hybridized atoms. The latter are thought to act as the host for the intercalation of lithium atoms between carbon layers from where they can be mobilized again under the driving force of the oxidation on the sample surface.

The influence of air is characterized by the presence of moisture and carbon oxide species which form lithium carbonate on the samples. While this is a purely chemical effect there is evidence that a similar result can be obtained by irradiating the metal-containing samples with energetic ions which are able to damage the carbon network.

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